The effect of microalloying on the morphology of austenite during hot working.

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THE EFFECT OF MICROALLOYING ON THE MORPHOLOGY OF AUSTENITE DURING HOT WORKING.

By

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SYNOPSIS

Studies have been made of the effects of thermo-mechanical treatment variables on the recrystallization of austenite, the transformation of austenite and precipitation strengthening in C-Mn steel containing niobium, niobium plus vanadium, vanadium and vanadium plus nitrogen. The amounts of niobium and vanadium were varied across the stoichiometric ratio of M:C and M:N inorder to investigate the effect of stoichiometric ratio on the precipitation strengthening.

Austenite grain coarsening studies, revealed that an increase in niobium or vanadium refined the austenite grain size at a given austenitizing temperature and increased the austenite grain coarsening temperature. However, it was not possible to refine the austenite grain size indefinately at a given temperature by increasing the niobium or vanadium, because there was an equilibrium grain size beyond which grain refinement did not occur. This equilibrium austenite grain size increased with increase in the austenitizing temperature. Niobium was found to be more effective than vanadium in retarding austenite grain growth due to the increased stability and slower coarsening rate of Nb(C,N) compared with V(C,N). The austenite grain coarsening temperature was always lower than the solubility temperature of the alloy carbonitrides. An increase in the nitrogen content in vanadium steels from 0.008% to 0.02% resulted in an increased austenite grain coarsening temperature.

During thermo-mechanical treatments, recrystallization of austenite increased with decreasing the prior austenite grain size, increasing the rolling temperature and increasing the rolling reduction. Additions of niobium retarded recrystallization of austenite with increasing niobium in solution prior to deformation. The mechanisms by which niobium retarded the recrystallization of austenite include :-

(a) retardation of the nucleation of the recrystallized grains by both niobium in the solution and strain-induced Nb(C,N) precipitates, and

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Vanadium also retarded recrystallization of austenite but this was observed at lower temperatures than for niobium. Combined additions of

niobium and vanadium were found to retard recrystallization of austenite more effectively than when niobium or vanadium added seperately.

Both niobium and vanadium refined the recrystallized austenite grain size, but this was more pronounced in niobium steels than in vanadium steels. However, an increase in the nitrogen content in vanadium steels increased the effectiveness of vanadium in refining the recrystallized austenite grain size. Conditions underwhich the grain growth of the recrystallized grains can be retarded prior to the transformation have been identified and discussed.

Niobium in solution increased the hardenability of austenite, but niobium as Nb(C,N) decreased the hardenability. Any thermo-mechanical treatment which lowered the niobium in solution, lowered the hardenability of austenite. Additions of niobium to C-Mn steel refined the ferrite grain size after thermo-mechanical treatment and this effect increased with up to 0.07% Nb, but above 0.16% Nb had no further ferrite grain refining effect. The effect of various thermo-mechanical treatment variables on the ferrite grain size have been presented and discussed. In general, low reheating temperatures, low rolling temperatures, high rolling reductions and minimum holding times after rolling, all refined the ferrite grain size. Similar to niobium, vanadium also refined the ferrite grain size particularly after rolling at low temperatures. An increase in the nitrogen content in the vanadium steels, enhanced this effect of vanadium. In high nitrogen vanadium steels the refinement of the ferrite grain size occurred after holding at 950°C after rolling, which was in contrast to the effect observed in niobium steels in which the ferrite grain size increased. This has been explained on the basis of an interaction between V-N-Al in the high nitrogen steels.

The occurrence of mixed ferrite grain sizes in the controlled rolled steels results in the deterioration of toughness properties. The sources for the occurrence of mixed ferrite grain size in the controlled rolled steels have been identified and suggestions have been made to reduce or eliminate such structures.

Precipitation of Nb(C,N) in the ferrite has been shown to induce precipitation strengthening which was found to increase with an increase in

Nb:C ratio up to stoichiometry, whilst above stoichiometry the precipitation strengthening decreased. Strain induced precipitation of Nb(C,N) in austenite decreased precipitation strengthening. The kinetics for strain induced precipitation of Nb(C,N) in the austenite showed a 'C' curve, having maximum precipitation rate at 900°-950°C. Heavy deformations and holding in this temperature range, lowered the precipitation strengthening substantially. Similar to niobium, vanadium also imparted strengthening through the precipitation of V(C,N) in ferrite, and the maximum precipitation strengthening was attained at the stoichiometric ratio of V:C. Strain induced precipitation of VN in austenite occurred at a maximum rate at 900°-950°C whilst that of V_4C_3 occurred at a lower temperature of 830°-850°C. An increase up to 0.02% N increased precipitation strengthening in vanadium steels. The mechanism by which nitrogen enhances precipitation strengthening in vanadium steels have been discussed. Also in high nitrogen vanadium steels the effects of the interaction between V-N-Al on the precipitation strengthening has been discussed. It has been shown that most of the precipitation of V(C,N) occurred in the ferrite during the $\gamma \rightarrow \alpha$ transformation by an interphase mechanism, whilst a very small amount of precipitation occurred from the ferrite. Therefore, it has been suggested that to intensify the precipitation strengthening, control over the interphase precipitate size and distribution should be achieved. Comparative effects of niobium and vanadium on the precipitation strengthening have been presented and discussed. Combined additions of niobium and vanadium gave lower precipitation strengthening than the sum of that which can be achieved from niobium and vanadium added individually.

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This thesis is based on an investigation carried out at The Sheffield City Polytechnic, during the period October' 1975 to July' 1979, under the supervision of Dr. F. B. Pickering and Mr. G. Butterworth. The following conferences were attended:

1 " Controlled Processing of High Strength Low Alloy Steels", Held at University of York, 28-30 September' 1976.
2 " Low Carbon Structural Steels for the Eighties " Held at Royal Naval Engineering College, Plymouth, 9-12 March, 1977.
3 " Mini-Mills" Held at UMIST, Manchester, 21st March' 1978.
4 " The Physical Metallurgy of H.S.L.A. Steel Weldments" Held at B.S.C. , Middlesbrough, 16th March' 1978.
5 " Recrystallization in the Control of Microstructure" Held at The University of Leeds, 4-6 April' 1978.
6 " Hot Working and Forming Processes" Held at University of Sheffield, 17-20 July' 1979.

In addition the following courses of the M. Sc. at Sheffield City Polytechnic, were attended.

1 Mechanical metallurgy,
2 Heat treatment and transformation,
3 High strength steels,
4 Cost and management accountancy,
5 Numerical analysis and computing methods.

The results presented in the thesis are to the best of my knowledge, original except where reference has been made to other authors. No part of this thesis has been submitted for a degree at any other University or College.

R. K. Amin.

October' 1980.

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CHAPTER 1

THE EFFECT OF MICROALLOYING ON THE MORPHOLOGY OF AUSTENITE DURING HOT WORKING.

1.1 Introduction

Ferrite grain refinement is an established method for improving the properties of steels, and indeed is the only mechanism by which both the strength and toughness may be increased simultaneously. It is widely used in the manufacture of plates for structural purposes, in line pipe steels, in certain pressure vessels, and in steel strip for many high strength, formable applications.

Grain refinement in carbon-manganese steels is materially influenced by the hot working or thermo-mechanical treatment. The following are some of the more important factors :-

(a) The recrystallization of the austenite; decreasing the recrystallization rate, often by micro-alloying additions such as niobium, tends to promote elongated unrecrystallized austenite grains which transform to fine grained ferrite by virtue of the rapid nucleation of ferrite at the austenite grain boundaries and on deformation bands, and the impingement of the ferrite grains before they have chance to grow.

(b) The rate of nucleation of ferrite during the transformation of austenite; a high nucleation rate decreasing the ferrite grain size of the transformed structure. The nucleation rate can be increased by increasing the number of ferrite nucleation sites, which may be prior austenite grain boundaries, deformation bands, sub-structures, or second phase particles.

(c) The rate of grain growth of the austenite prior to transformation and the rate of growth of the ferrite during or subsequent to the transformation. A slow rate of grain growth of the austenite preserves a fine grained austenite and therefore results in fine grained ferrite. Similarly, a slow rate of growth of ferrite during the transformation will allow more nuclei to be activated and thus a finer ferrite grain size to be produced. A decrease in the rate of grain growth of the ferrite after transformation will tend to preserve a fine ferrite grain size. Fine carbonitrides can inhibit either austenite or ferrite grain growth by pinning the grain boundaries, whilst certain microalloying additions, such as niobium, can exert a solute drag effect on grain boundaries.

(d) The transformation temperature of the austenite-ferrite reaction; a decrease in the transformation temperature decreases the ferrite grain size. Manganese is particularly effective in this respect, as also are even small additions of the microalloying elements. Fast cooling prior to transformation is also effective in depressing the transformation temperature.

(e) The prior austenite grain size; the finer the austenite grain size the finer the transformed ferrite grain size because of the increased ferrite nucleation rate. The initial austenite grain size is controlled by the thermo-mechanical treatment parameters,the presence of second phase particles and the presence of microalloying additions.

Precipitation strengthening is used to achieve higher strength in microalloyed steels. However, such a strengthening mechanism is harmful to the toughness but this can be partly off-set if it is associated with grain refinement. Precipitation strengthening in carbon-manganese steels can be obtained by addition of the same alloying elements which are used to refine the ferrite grain size in controlled rolled steels (i.e niobium, vanadium or titanium). The intensity of precipitation strengthening is dependent on the volume fraction, size and distribution of precipitates and these are very much influenced by the following :-

(a) The amount of alloying elements in solution; a larger amount of precipitating elements in solution is required to increase the volume fraction of precipitates. This can be achieved by using a reheating temperature at which most of the elements are in solution and this depends very much on the temperature dependent solubility of the alloying element concerned. Also the maximum solubility occurs at the stoichiometric composition for a given temperature, and therefore the amount of precipitate will be a function of composition.

(b) The temperature of precipitation; precipitation at higher temperature, mainly in austenite, generally results in coarse precipitates which are not very effective in strengthening the

> matrix and hence every effort is required to minimise this form of precipitation so that more precipitation can occur at low temperature. Precipitates formed at low temperatures, particularly in ferrite are fine and semi-coherent with the matrix and thus cause strengthening. Low temperatures can also avoid coarsening of precipitates, resulting in numerous fine precipitates and therefore enhanced precipitation strengthening.

Microalloying additions such as niobium and vanadium decrease the rate of recrystallization, and their carbonitrides effectively restrict austenite and ferrite grain growth. In addition, they also impart some precipitation strengthening. The use of such additions, augmented by controlled processing, has made it possible to produce High Strength Low Alloy (H.S.L.A.) steels with yield strengths up to 750 MN/m^2 and high toughness. The control of the optimum microalloying addition is not fully understood in terms of the smallest addition which can control austenite recrystallization during thermo-mechanical treatment, with the minimum of production difficulties. The high deformations at low finishing rolling temperatures required to achieve ultra fine transformed ferrite grain sizes are limited by mill capacities. Also there have been few systematic studies in to the effect of various rolling parameters on the precipitation strengthening in microalloyed steels. It is desirable to understand the effect of various rolling variables on ferrite grain refinement and the intensity of precipitation strengthening, as the optimum combinations of these two strengthening mechanisms are required to achieve the required strength-toughness properties, in controlled rolled H.S.L.A steels.

Whilst the recrystallization of H.S.L.A steels has been extensively studied, there is a lack of quantitative data on the effect of microalloying elements such as niobium and vanadium on the kinetics of austenite recrystallization and grain growth during thermo-mechanical treatment. The effect of composition, in terms of carbonitride stoichiometry, on recrystallization during thermo-mechanical treatment are also important in controlling the final ferrite grain size, because this stoichiometry influences the temperature dependence of the solubility of the carbonitrides. It is necessary therefore to investigate systematically the effects of varying micro-alloying additions, and their stoichiometry with respect to carbon and nitrogen, on recrystallization and grain growth of austenite, and on the mechanism of nucleation and growth of the ferrite during the transformation of varying morphologies of austenite.

The precipitation strengthening by various micro-alloying additions, varies in controlled rolled steels depending on the rolling practice used. Various rolling parameters affect the volume fraction of carbonitrides precipitated in the austenite and therefore available for subsequent precipitation in ferrite. Any rolling variable which leads to an increased precipitation in austenite will reduce the precipitation strengthening. Therefore it is desirable to investigate systematically the effect of various rolling variables such as reheating temperature, rolling temperature, holding temperature and time, and deformation on the precipitation strengthening in H.S.L.A steels containing niobium and vanadium. It is well known that the temperature dependence of solubility is a maximum at the stoichiometric composition of the alloy carbonitride and hence maximum precipitation strengthening can occur at such composition. However, there is little experimental data available for H.S.L.A steels to substantiate this and therefore it is required to study the effect of metal to carbon ratio on the precipitation strengthening.

These studies are best carried out at carbon contents somewhat lower than those conventionally used in many current H.S.L.A steels i.e. in the range 0.07 / 0.09 % C, in order to allow the use of a wider range of micro-alloying contents so that variations about stoichiometry may be employed within realisable economic restraints. In addition, these lower carbon contents will benefit both toughness and ductility.

1.2 Objective of Investigation

The effect of varying micro-alloying additions such as niobium and vanadium, with respect of the ratio of the alloying element to carbon and nitrogen, has been investigated on the response of 0.07 / 0.09 % C, 0.8 / 1.0 % Mn steels to thermo-mechanical treatment. The following effects have been studied :-

(a) The austenite grain coarsening behaviour

(b) The development of the austenite grain structure with respect to deformation temperature, and strain after different initial reheating temperatures.

(c) The recrystallization kinetics of austenite after varying controlled thermo-mechanical treatments.

(d) The kinetics of grain growth of austenite after completion of recrystallization at different temperatures.

(e) The mechanisms by which micro-alloying additions may retard the austenite recrystallization.

(f) The refinement of ferrite grain size after various thermo-mechanical treatments.

(g) The development of the ferrite grain structure from different morphologies of austenite grains, and the mechanism of nucleation and growth of the ferrite grains.

(h) The effects of deformation on the isothermal transformation of austenite to ferrite.

(i) The effects of various thermo-mechanical treatments on precipitation strengthening.

The method used for thermo-mechanically treating the alloys comprised deformation mainly by rolling. The following variables were studied :-

(i) The heating temperature prior to hot working in order to vary the initial austenite grain size and the amount of alloy carbonitrides in solution.

(ii) The hot deformation temperature.

(iii) The hot deformation reduction.

(iv) The holding temperature subsequent to deformation.

(v) The holding time subsequent to deformation.

CHAPTER 2

RECRYSTALLIZATION OF METALS

2.1 Introduction

During annealing, deformed metal passes through various stages to achieve the equilibrium strain free condition. These stages have been classified as recovery, recrystallization and grain growth.

Recovery is the first change that occurs upon annealing a deformed metal, and has no incubation period, the rate decreasing as the process proceeds. During recovery annihilation of dislocations of opposite sign and the formation of walls from dislocations of the same sign occurs, also known as polygonization. As no migration of high angle grain boundaries occurs during recovery, the deformed structure retains its basic identity. This process will not be considered in detail, but its involvement during nucleation processes for recrystallization will be discussed.

Primary recrystallization is the process of nucleation and growth of strain free grains and occurs at the expense of the deformed material. The growth of strain free grains is accomplished by the migration of high angle grain boundaries. The various processes involved in recrystallization such as nucleation and migration of high angle grain boundaries will be discussed in subsequent sections.

Recovery or recrystallization can occur during deformation or after deformation, the former is known as dyanmic recovery or recrystallization and the later as static recovery or recrystallization. In f.c.c. alloys, as the separation of the partial dislocations increases (i.e decreasing stacking fault energy) the dislocations become more confined to their slip planes, rendering climb and cross-slip more difficult. Thus low stacking fault energy alloys exhibit less dynamic recovery, and in this situation dynamic recrystallization can occur if the alloy is strained beyond the stress drop in a high temperature tensile test. Recovery opposes the build-up of stored energy necessary for dynamic recrystallization.

2.2 Nucleation

2.2.1 Introduction

Nucleation of recrystallized grains in a plastically deformed matrix is the first stage in the recrystallization process. Because of the lack of direct evidence various theories of nucleation have been proposed(1-6). These are mainly;

1. Classical nucleation theory(1),
2. The subgrain growth model(2,3),
3. The subgrain coalescence model(4),
4. The strain induced boundary migration model(5).

Extensive experimental observation has led to the establishment of some basic principles for the mechanism of nucleation. These are:-

(a) Nuclei form preferentially in regions of high residual strain energy. More specifically they form in regions of large strain gradient.

(b) The larger the strain, the more nuclei are formed. The nuclei show a spectrum of nucleation potential, the more highly potential nuclei being activated at the shorter times.

(c) The most active nucleation site is the matrix grain boundary.

(d) Some deformation bands act as nucleation sites.

(e) Fine second phase dispersions inhibit both nucleation and growth while coarse dispersions aid nucleation without seriously retarding the growth of nuclei.

2.2.2 Classical nucleation theory.

First developed by Becker(1) for the nucleation of solids in supercooled liquids, the theory was extended to nucleation in solids by Burke and Turnbull(7). The critical nucleus size is determined by the condition that for the nucleus to be stable, an infinitesimal increase in size will result in zero change in free energy, because the increase in interfacial energy is just balanced by the reduction in volume internal energy. In the present case, this second term must represent the energy of dislocations destroyed, or favourably rearranged, as the nucleus grows.

The change in free energy due to the growth of the embryo is given by:-

$$\Delta F_T = 4\pi r^2\Upsilon - \frac{4}{3}\pi r^3 \Delta F_v \qquad \text{-----------------------------(1)}$$

where ΔF_T - total free energy change per unit volume,
r - the radius of the embryo,
Υ - the interfacial energy per unit area of interface,
ΔF_v - the volume free energy change per unit volume.

Differentiating the above equation with respect to'r' and equating the result to zero, will give the critical nucleus size:-

$$r_c = -\frac{2\Upsilon}{F_v} \qquad \text{----------------------------------- (2)}$$

The change in total free energy required to form the critical nucleus size ,$(\Delta F_{T(c)})$, is given by,

$$\Delta F_{T(c)} = \frac{16\pi\Upsilon^3}{3\Delta F_v{}^2} \qquad \text{--------------------------------(3)}$$

This model assumes that subcritical embryos are constantly being generated and destroyed. Occasionally, an embryo by chance exceeds the critical size and will then grow.

This model has certain advantages:-
(a) it accounts for the existance of an incubation period,
(b) as predicted the preferential nucleation sites are severely deformed regions and this is in accord with experience,
(c) it also predicts feasible values of the nucleation frequency and critical nucleus size.

Limitation of the classical nucleation theory are:-
(a) The prediction that recrystallized grains should have a low misfit with the deformed matrix in order to have low interfacial energy values. This would lead to very slow migration of such boundaries and hence slow growth of recrystallized grains. In fact the growth of such grains is fast.

(b) No effect of purity is allowed for, yet purity is probably of paramount importance in recrystallization.

2.2.3 The subgrain-growth model

Polygonization of the deformed matrix forms the strain free cells. Cahn(2) suggested that some of these strain free cells would become viable nuclei for recrystallization. The model is shown in fig. 1. A region of high strain gradient is converted into a small strain-free cell by a process of dislocation climb and rearrangement. The subgrain can grow at the expense of its immediate surroundings by two mechanisms:-

(a) Being substantially larger than any cells surrounding it, the triple-point angles with other sub-boundaries exceed 120°. The subgrain grows in an attempt to restore the equilibrium angles of 120°. This argument only applies if all the sub-boundaries have the same energy, i.e all misorientations between nearest neighbours are the same.

(b) Highly disoriented subgrains grow at the expense of their neighbours even if they are not larger than the average size(8).

Thus a highly misoriented subgrain grows freely at the expense of its neighbours. Eventually, the boundary angle approaches a critical value θ_m as shown in fig. 2(9), at which the individual dislocations on the boundary begin to lose their identity. Near this condition, the boundary ceases to incorporate dislocations from the matrix within it. The driving force for subgrain growth is assumed to be the difference between the decrease in volume free energy and the increase in surface free energy. This leads to a critical radius for growth shown by equation (2).

2.2.4 The subgrain coalescence model

This theory, developed by Hu(6) as a result of extensive studies of recrystallization in 3 %Si iron, assumes that one subgrain can merge with its neighbour not by sub-boundary motion, but by a rotation of one of the subgrains till its lattice is parallel to that of its neighbour.

Li(10) analysed the situation by considering the free energy of a sub-boundary as a function of misorientation, and showed that it is always possible to coalesce boundaries having the same dislocation structure. The driving force for the rotation of any subgrain relative to its neighbours depends on the axis of rotation and the orientations of surrounding subgrains. Calculation of this driving force showed that the sub-boundary having the largest area, smallest angle, largest free energy and a misfit axis nearest to the rotation axis in question, will possess the highest driving force. Rotation of a subgrain would therefore eliminate the sub-boundary, as shown in fig. 3. The initial structure is shown in fig. 3(a), which also shows the degree of misorientation. The common boundary CH can be eliminated by the rotation of the right hand subgrain. This is achieved by the diffusion of atoms along the boundaries, fig. 3(b). Fig, 3(c) shows the coalesced subgrain at this stage in the process. Finally the coalesced subgrain will take up the form shown in fig. 3(d) as the result of the rearrangement of the affected boundaries, BC, CD, IH and HG in order to remove the unstable re-entrant angles at C and H.

Evidence for the formation of recrystallized nuclei by subgrain-coalescence in low carbon steel has been reported by Goodenow(11).

2.2.5 Strain-induced boundary migration (SIBM)

Beck and Sperry(12) first gave a detailed description of nucleation by strain-induced boundary migration, also known as grain boundary bulging. The process consists of irregular movement of a boundary with an irregular jagged front, made up of curved sections as shown in fig. 4. Such a grain boundary moves away from its centre of curvature, preferentially into the matrix of high stored energy, the stored energy difference providing the driving force.

The mechanism is explained schematically in fig. 5. Two grains, A and B, have an appropriate misorientation so that the grain boundary can move into grain B, and it is assumed that there is a strain energy difference between the two grains. It is suggested that the growing grain has initially a coarser subgrain structure than the grain being consumed. The energy is then reduced when a small volume of the grain is consumed, due to the total area of sub-boundary destroyed being greater than the area of sub-boundary newly created by the bulge (s) because the bulge has an even coarser substructure than the subgrains in the growing grain.

Bailey and Hirsch(13) developed a model to explain this bulge nucleation. As shown in fig. 6, an original grain boundary of length 2L migrates by bowing out into spherical cap, the condition for the bulge to grow is :-

$$L > \frac{2\gamma}{\Delta E} \qquad \text{------------------------}(4)$$

where γ is specific grain boundary energy,

and ΔE is the difference in stored energy, per unit volume, across the migrating boundary.

As no separate nucleation event occurs in this mechanism the incubation period is zero. The limited evidence available suggests that SIBM declines in importance at higher deformations(14). This may be due to the requirement of a strain energy difference between the grains on either side of the relevant boundary, which is particularly prevalent at low deformations in association with local inhomogeity of deformation, or where there is a very variable matrix deformed grain size.

2.2.6 Experimental observation of nucleation in iron and steel

Although classical nucleation theory successfully accounts for the existance of an incubation period, preferential nucleation in the severely deformed regions and value of nucleation frequency, it suffers a serious drawback from the prediction that new grains should always be close in orientation to those of the matrix. Frequently the converse is observed experimentally. Since the predicted critical nucleus size is far too small to observe by the available experimental techniques, no experimental evidence against this model appears to exist. Experimentally observed evidence of nucleation in iron by subgrain growth(15,16) and by SIBM(17), in Fe-Si alloys by subgrain coalescence(6,18) and SIBM(19), and in aluminium-killed steel by SIBM(11) have however been reported.

2.3 Grain Boundary Migration

2.3.1 Introduction

During recrystallization, after the formation of a critical sized nucleus, growth of the nucleus occurs and the rate of growth will affect the final recrystallized grain size. However, grain growth after completion of recrystallization will also increase the grain size. Grain boundary migration is caused by the decrease in the energy of the system as the unrecrystallized matrix is consumed by the growing recrystallized grains, and the control of the final grain size is dependent upon the rate of migration of the boundaries of recrystallizing grains and that of the recrystallized grain boundaries themselves as grain growth occurs in the fully recrystallized structure.

It is known that the migration rate of a grain boundary is affected by both solutes and second phase particles, as will be discussed later.

2.3.2 Grain boundary structure

A grain boundary can be defined as an interface where two crystals of different orientation join each other. The structure of the grain boundary depends on the orientation of the grains and the arrangement of atoms in the interface. There are various models for the structure of the grain boundary:-

1 The dislocation model,
2 The island model,
3 The coincidence model.

2.3.2.1 The dislocation model

Read and Shockley$^{(20)}$ assumed the grain boundary to be an array of dislocations and if 'b' is the Burgers vector of the dislocations of mean spacing 'd', then:-

$$d = \frac{b}{\text{Sin}\,\Theta} \simeq \frac{b}{\Theta} \qquad \text{———————————} (5)$$

where Θ is the angle of rotation between the two grains. Increasing misorientation between the two grains causes 'd' to decrease. At a misorientation of $\sim 10^{\circ}$ the Read-Shockly concept breaks down, because the interaction of the closely adjacent dislocations changes the core structure and the boundary is no longer simple. At somewhat higher angles, $\sim 15^{\circ}$, dislocations would be so closely spaced that they would lose their identity and the dislocation model becomes of little or no value(21).

2.3.2.2 The island model

This was developed by Mott(22) who suggested that if two crystal planes are in contact, but cannot fit owing to different orientations, then the surface of contact is divided in to islands where the fit is reasonably good separated by areas where the fit is poor. He then set out to characterize the good and the bad fit in terms of the "melting" of the good fit islands, which must occur to allow boundary migration. To remove an atom from an island requires energy equivalent to the latent heat of fusion. In some respects, this model has similarities with the coincidence model.

2.3.2.3 The coincidence model

The significant feature of the coincidence boundary is that some atoms occupy sites that belong to both crystals, and there is a periodic repetition of very small units of structure. Such boundaries have low energy. Bishop and Chalmers(23) proposed a model to characterize special orientations which is entirely based on the concept of boundary coincidence. Fig. 7 shows the structure of a symmetrical tilt boundary with a rotation of 28.1° about $\langle 100 \rangle$ axis in f.c.c lattice. Any deviation from this orientation because of the disturbances in the ledge sequences in the boundary may lead to an increase in the grain boundary energy.

2.3.3 Mechanism of grain boundary migration

Turnbull(24), by assuming that the atoms are transferred singly across a migrating boundary, derived an expression for the boundary migration rate based on absolute reaction rate theory. The rate of grain boundary migration 'G' is:-

$$G = G_o e^{-Q/RT} \quad \text{------------------} \quad (6)$$

where Q is the activation energy, T the absolute temperature and R the gas constant. The value of G_o depends on :-

(a) the local boundary movement when an atom is transferred from one grain to the other,

(b) the lattice parameter,

(c) the driving force,

and (d) the temperature.

Most, although not all, of the experimental results are consistent with this relationship(25). Since it has been assumed that all the atoms at the grain boundary have the same jump probabilities and always find a free place on the adjoining grain surface, this relationship will give the maximum possible value of the migration rate.

Hofmann and Haessner(26) modified this model in the following way:-

(a) The grain boundary is assumed to be a layer a few atoms thick.

(b) The probability of an atom jumping across the boundary is different in the two jump directions.

(c) An atom can make a jump only when there is a vacant site into which it can move.

The migration rate 'G' was :-

$$G = \frac{\frac{a^6}{\delta} \cdot \nu \cdot C_\beta^2 \cdot \frac{Z_I}{C_I} \cdot \frac{\Delta E}{RT} \cdot \exp\left(-\Delta E_{II}/RT\right)}{1 + \frac{a}{\delta} \cdot C_\beta \cdot \left(\frac{1}{C_I} + \frac{1}{C_{II}}\right)} \quad \text{-----------}(7)$$

where a is the lattice parameter;

ν is the vibrational frequency;

δ is the grain boundary thickness;

C_β, C_I and C_{II} are the vacant sites/ cm^2 in boundary, grain and matrix respectively;

Z_I is the number of atoms/cm^2 at the surface of the grain, which are capable of jumping;

ΔE is the difference in free energy between the matrix and the grain;

and ΔE_{II} is the Gibbs free energy of activation per mole for the jump of one atom across the boundary.

This relationship has been simplified for the following two limiting cases:-

(a) The rate cotrolling process may be the transport of atoms through the boundary and in this case:-

$$\frac{a}{\delta} \cdot C_\beta \left(\frac{1}{C_I} + \frac{1}{C_{II}} \right) \ll 1 \qquad \text{which gives}$$

$$G = \frac{a^6 \cdot \nu \cdot C_\beta^2 \cdot \Delta E}{\delta \cdot RT} \cdot \frac{Z_I}{C_I} \cdot \exp\left(- \frac{\Delta E_{II}}{RT} \right) \text{------} (8)$$

(b) The rate controlling process may be the emission of the atoms from the unrecrystallized matrix and their incorporation in the recrystallized grain. This corresponds to the condition:-

$$\frac{a}{\delta} \cdot C_\beta \cdot \left(\frac{1}{C_I} + \frac{1}{C_{II}} \right) \gg 1 \text{ , so that}$$

$$G = \frac{a^5 \cdot \nu \cdot C_\beta \cdot \Delta E}{RT \cdot \left(\frac{1}{C_I} + \frac{1}{C_{II}} \right)} \cdot \frac{Z_I}{C_I} \cdot \exp\left(- \frac{\Delta E_{II}}{RT} \right) \text{-------} (9)$$

Mott(22) assumed that in the "island" grain boundary model, atoms are activated in groups during their transfer across the boundary and that the basic process involves the "melting" of a group of atoms belonging to one crystal followed by their re-solidification on the other crystal. This gave a similar relationship as that of Turnbull, equation (6). However, in Mott's theory 'G_o' is related to the number of atoms in the transferring group and is an exponential function of the latent heat of fusion of the metal. It has been pointed out(27) that there is no fundamental reason to suppose that the transfer of atoms during boundary migration occurs in groups rather than singly.

Li(28) suggested that the vacancy concentration in high angle boundaries increases with increasing misorientation. The movement of individual atoms in the grain boundary is suggested to be the dominant grain boundary migration mechanism when the local vacancy concentration is large; a supply of vacancies thus enhances grain boundary mobility. Talbot(29) found that thin iron films did not recrystallize at temperatures at which the bulk metal recrystallized very rapidly and this may be attributed to the removal of vacancies to the surface in thin films.

All these models do not take into account the effect of solute and second-phase particles on the migration of grain boundaries, which will be discussed later.

2.3.4 Effect of solutes on grain boundary migration

2.3.4.1 Introduction

Solutes have tendency to segregate to grain boundaries to a degree depending on temperature, type of solute and the structure of the grain boundary. Such segregation decreases the total energy of the grain boundaries probably by reducing the elastic and electronic disturbances. Segregation of solutes at grain boundaries profoundly affects the kinetics of recrystallization and grain growth. Many theoretical treatments of the effect of solutes on grain boundary migration kinetics have been proposed, and a summary of these will be presented.

2.3.4.2 Lucke and Detert theory

This theory assumes(30) that the interaction between the solute and the boundary is elastic in nature, and therefore dependent on the elastic-stress field surrounding the foreign atom. Hence, the greater the size difference between solute and solvent atoms the larger is the elastic-stress field, the larger the interaction energy, and the greater the retardation of grain boundary migration. Also it is assumed that the driving force for boundary migration is provided by the difference in the line tensions of dislocations in the grain on either side of the boundary. In the presence of solute atoms, it is suggested that there is tendency for solute atoms to be left behind as a boundary moves, but due to elastic attraction of the atoms to the boundary, the solute atoms may be able to diffuse with the boundary, provided that the boundary moves slowly enough. For a constant velocity, the driving force should be just equal to the drag of the solute atoms. The boundary velocity 'V' at high solute concentrations and low temperatures is:-

$$V = V_o \exp\left[- \left\{ \frac{Q_D + U}{k\,T} \right\} \right] \qquad \text{------------------------}(10)$$

where Q_D is the activation energy for volume diffusion;

U is the interaction energy between the boundary and a solute atom;

k is the Boltzman constant;

and T is the absolute temperature.

The exponential term represents the activation energy for growth of the recrystallized grain, ($U \ll Q_D$) and the pre-exponential term is given by:-

$$V_o = \frac{\mu\, r^2 \Lambda\, a^2\, D_o}{\sqrt{2\,kT\,C_o}} \qquad \text{------------------------}(11)$$

where μ is the shear modulus;

r is the solvent atom radius;

D_o is the pre-exponential factor for the basic volume diffusion;

Λ is the difference of the number of dislocation lines in the deformed and recrystallized grains;

C_o is the average solute concentration;

and a is the lattice parameter.

The controlling mechanism for grain boundary migration is the rate at which impurity atoms can diffuse behind the boundary. If the driving force for boundary migration is higher than the solute drag force, then the solute atom atmosphere will break away from the moving boundary. The maximum velocity of foreign atom is then :-

$$V\,\max = \frac{f_o\ D_o}{k\ T} \cdot \exp - \frac{Q_D}{k\ T} \qquad \text{------------------------}(12)$$

where f_o is the maximum possible interaction force of solute with grain boundary, and D_o, k, T, Q_D are as defined for equations (10) and (11). Fig. 8 shows the solute limited grain boundary velocity and breakaway conditions for three different compositions where $C_1 > C_2 > C_3$. The curves show that as the temperature is raised and the concentration of foreign atoms in the grain boundary decreases, a critical temperature is reached where the retarding force is less than the driving force, and hence breakaway occurs. The temperature at which breakaway occurs will be lower as the average concentration of solutes, C_o, is decreased. The dotted line represents the temperature dependence of V max - see equation (12)

2.3.4.3 Cahn's theory

This theory(31) is limited to very low solute concentrations. The boundary is represented as a planar discontinuity characterized by an interaction energy between solute atoms and the boundary. The migrating boundary is therefore pictured as a moving one dimensional potential well, in an infinite medium. By solving the diffusion equation for this problem the solute distribution across the boundary during the steady state motion is obtained. Once the composition profile across the boundary is known, the total force, 'P_i' exerted by all the impurity atoms on the boundary is given by :-

$$P_i = - N_v \int_{-\infty}^{+\infty} (C - C_o) \frac{dE}{dx} \, dx \qquad \text{--------------------} (13)$$

where N_v is the number of atoms per unit volume;
C is the boundary solute concentration;
C_o is the average solute concentration;
and $E_{(x)}$ is the interaction energy between solute and boundary.

Because of the change in the composition profile with the velocity of the boundary, the total force exerted on the boundary will also vary.

For the high velocity limit :-

$$P_i \sim \frac{C_o N_v}{k T V} \int_{-\infty}^{+\infty} E^2 D \, dx \qquad \text{--------------------} (14)$$

where D is the diffusion coefficient of solute normal to grain boundary. This equation shows that the impurity drag force P_i is proportional to D, but inversely proportional to V, the grain boundary velocity.

For the low velocity limit :-

$$P_i = 4 N_v C_o V k T \int_{-\infty}^{+\infty} \frac{\sinh^2 \left[E_{(x)} / 2kT \right]}{D_{(x)}} \, dx \qquad \text{----------} (15)$$

By comparing equation (14) and (15) it is possible to construct an approximate equationsfor the drag, which fits the high and low velocity extremes.

$$P_i = \frac{\alpha V C_o}{1 + \beta^2 V^2} \qquad \text{———————————(16)}$$

where α and β are constants which may be calculated from the interaction potential between the solute and the boundary and the diffusion coefficient of the solute as:-

$$\alpha = 4 N_v k T \int_{-\infty}^{+\infty} \frac{\text{Sinh}^2 \cdot \frac{E(x)}{2kT} \cdot dx}{D_{(x)}} \qquad \text{——————(17)}$$

$$\text{and } \frac{\alpha}{\beta^2} = \frac{N_v}{k T} \int_{-\infty}^{+\infty} \left(\frac{dE}{dx} \right)^2 \cdot D_{(x)} \cdot dx \qquad \text{——————(18)}$$

Cahn also derived a relationship for the grain boundary velocity as a function of temperature, composition and driving force. For impure material he defined an intrinsic drag Po (V) to be the difference between the actual driving force P(V,C) which gives a velocity V in a material with impurity concentration C, and the impurity drag $P_i(V,C)$. i.e :-

$$P(V,C) = Po(V) + P_i(V,C) \qquad \text{————————(19)}$$

By assuming that P_i is given by equation (16) and that $Po = \lambda V$, equation (19) becomes :-

$$P = \lambda V + \frac{\alpha C_o V}{1 + \beta^2 V^2} \qquad \text{————————(20)}$$

where λ is the intrinsic drag coefficient and is the reciprocal of the boundary mobility. Simple relationships for P, V and C_o were derived for the following limiting conditions :-

(a) For low velocity and low driving force :-

$$V = \frac{P}{\lambda + \alpha C_o} \qquad \text{————————(21)}$$

(b) For the high velocity and high driving force :-

$$V = \frac{P}{\lambda}\left(1 - \frac{\propto \lambda C_o}{\beta^2 P^2}\right) \qquad \text{------------------------}(22)$$

(c) For high velocity and low driving force :-

$$V = \frac{P}{\lambda}\left(1 - \frac{\propto C_o}{\lambda}\right) \qquad \text{------------------------}(23)$$

Fig. 9 shows the calculated driving force, P, versus velocity, V, curves for various solute concentrations. In general, no proportionality exists between the driving force and the velocity. For very high velocity where the solute atoms cannot follow the boundary, the velocity approaches the value which would be observed in the absence of any solute. For sufficiently high solute concentrations, as shown in curve 'C', a region exists (broken part of the curve) in which the velocity increases with decreasing driving force. Obviously in this region the movement is unstable.

2.3.4.4 Machlin's model

Machlin(32) proposed a model for the motion of solute atoms in association with the boundary. According to this model solute atoms can influence grain boundary migration by three alternative process, depending on the solute concentration. At low solute concentrations the controlling process is "mechanical breakaway" in which the solute atoms affect the driving force and not the grain boundary mobility. At higher solute concentrations, solute atoms are bound to the boundary and diffuse by boundary diffusion along cusps in the boundary developed at the solute atoms. In this region the velocity is controlled by its component in the direction of boundary migration at the rate at which the boundary solute atoms can diffuse. At the highest concentrations it is predicted that thermal activation will enable the boundaries to break away from the binding solute atoms.

This theory does not predict the temperature dependence of the exponent of the concentration of solute, and a number of arguments as to the validity of the theory have been raised by Lucke and Stuwe(33).

2.3.4.5 Li's theory

In this theory(21) it is assumed that the solute atoms segregate to the boundary in order to reduce the vacancy concentration at the boundary. This assumption implies that the size of solute atoms is more important than other effects (e.g. valency). The reduction in the vacancy concentration caused by the segregated solute atoms will discourage individual atomic movement, and will also increase the activation energy for grain boundary migration. Therefore, grain boundary migration will always be reduced by solute atoms. Li derived the following equation for the mobility of a boundary in a solid solution :-

$$\nu = \nu_0 \ \exp\left[- \frac{A\ (\Delta Vo - \Delta V)}{R\ T} \cdot \frac{Kc}{1 + Kc} \right] \quad \text{---------------}(24)$$

where ν_0 and Vo are the mobility and vacancy concentration of the boundary in the pure material and ν and ΔV are the corresponding values in the solid solution which has a solute concentration, C. Kc and A are constants. Kc characterizes the interaction energy between the solute atoms and the boundary.

2.3.4.6 Abrahamson et al's electron interaction theory

Abrahamson et al(34) found a correlation between the recrystallization temperature and the electronic configurations of solute and solvent atoms in dilute solutions of transition metals. It was proposed that the electrons of the solute atoms affect the bonding in the vicinity of each solute atom. Fig. 10 shows the initial rate of change of recrystallization temperature with solute atomic percent as a function of the number of outer shell electrons of the solute element in iron. This indicates that :-

(a) For solutes having a given number of S-shell electrons the rate of increase of recrystallization temperature with solute concentration is increased as the number of d-shell electrons decreases below 7.

(b) For solute atoms having a given number of d-shell electrons, the fewer the S-shell electrons, the greater the rate of increase of recrystallization temperature with solute concentration.

(c) The greater the number of electrons in an inner shell, the greater the increase in recrystallization temperature with solute concentration. For example Ti, Zr and Hf have unfilled energy levels in the 3d, 4d and 5d energy bands respectively.

Thus the experimental evidence suggest that electronic interactions between solute and solvent atoms or between solute atoms and grain boundaries have a greater influence on recrystallization than elastic interactions, at least for transition metals.

2.3.5 Effect of second-phase particles on grain boundary migration

2.3.5.1 Introduction

Many commercial alloys contain second phase particles which may be either alloy carbides, nitrides, carbonitrides or non-metallic inclusions. The presence of these particles, depending on their size, shape, distribution and amount, influences the kinetics of grain boundary migration. A migrating boundary experiences a pinning force which tends to retard its migration. Several theoretical models have been proposed by many authors:-

1. Zener's model,
2. Hillert's model,

and 3. Gladman's model.

A brief consideration of the original model by Zener will be made at this point.

2.3.5.2 Zener's model

Zener(35) was the first to calculate the interaction force between a boundary and an second phase particle. Fig. 11 shows the interaction of grain boundary with a spherical particle of radius 'r'. The retarding force 'P' exerted by the particle in the Y direction is given by:-

$$P = \pi r \gamma \sin 2\theta \qquad \text{------------------------------}(25)$$

where γ is the specific grain boundary energy per unit area, and θ is an angle which depends upon the relative position of boundary to the particle. The maximum force is exerted at $\theta = 45^\circ$ and is equal to:-

$$P\ max = \pi r \gamma \qquad \text{------------------------------}(26)$$

If N is the number of particles of radius r randomly distributed in a unit volume, then the volume fraction of these particle is $4/3\,\pi\, r^3N$. A boundary of unit area will intersect all particles within a volume 2r, i.e. 2rN particles. Hence the number 'n' of particles intersecting unit area of a boundary is given by :-

$$n = \frac{3f}{2\pi r^2} \qquad \text{------------------------------}(27)$$

So the retarding force, Pu, per unit area of boundary is n.Pmax i.e :-

$$Pu = \frac{3 f \Upsilon}{2 r} \qquad (28)$$

If the boundary is migrating under the influence of its own interfacial tension and the grain periphery has a radius of curvature Ro , then the driving force for grain growth is $\frac{2 \Upsilon}{R\ crit}$. The growth stops at a critical grain radius, R crit, when the retarding force balances the driving force. Thus Zener proposed the relation :-

$$R\ crit = \frac{4}{3} r / f \qquad (29)$$

where f is the volume fraction of second phase particles.

This relationship might apply to the pinning of growing grains during recrystallization, providing that an increased driving force is assumed due to the overall decrease in energy of the system as recrystallization occurs. Thus during recrystallization, a finer particle size or a larger volume fraction of particles is required to inhibit boundary migration (equation 28), than is the case for simple grain growth.

Consideration of the Gladman and Hillert models will be made under the heading of grain growth.

CHAPTER 3

GRAIN GROWTH

3.1 Introduction

Recrystallization and grain growth both occur by the migration of grain boundaries. The mobility, M, of such boundaries is defined as:-

$$V = M F \qquad \text{------------------} (30)$$

where V is the rate of migration and F is the driving force. In recrystallization driving force derives from stored energy whilst grain growth is the result of the need to minimise the grain boundary energy.

Grain growth has been classified as of two types :-

(a) "Normal" or "Continuous" grain growth. This is characterized by maintenance of an equiaxed grain structure, in which the distribution of grain size retains a constant form, and the distribution of grain shapes is constant.

(b) "Abnormal" or "Discontinuous" grain growth. This is also known as secondary recrystallization. In this, the differences in the individual sizes of grains increases by some of the grains growing rapidly. When they have consumed all the other grains, the resulting grains may again be of a relatively uniform size.

3.2 Kinetics of Grain Growth

Beck et.al(36,37) were the first to formulate an empirical equation to relate the grain size during normal grain growth to the isothermal annealing time :-

$$D_g = K t^n \qquad \text{--------------------------} (31)$$

where D_g is the average grain diameter, at any instant during grain growth, t is the annealing time, and K and n are constants which depend on the alloy composition and on the annealing temperature, but which are independent of the grain size. This relationship applies best if the initial (pre-growth) grain size is small compared with the grain size which is being measured during growth. Since this is often not the case, especially in the early stages of growth, Beck et al established that the relationship should normally be expressed in the following more general form :-

$$D_g^{1/n} - D_{g(o)}^{1/n} = C\ t \qquad \text{-----------------------(32)}$$

where $D_{g(o)}$ is the initial pre-growth average grain diameter, and C is a constant which contains a temperature dependent mobility term and the grain boundary energy. This relationship has been found experimentally for extremely pure metals. The presence of solute atoms and second - phase particles can obstruct grain boundary migration, and this hindrance to normal grain growth can be so pronounced that the boundaries can only migrate at a few places, which will lead to abnormal grain growth.

Hillert(38) and Gladman(39) have developed theories of the role of second-phase particles in relation to the growth of individual grains within a polycrystalline microstructure.

3.3 Hillert's Theory

Hillert's(38) analysis is based on the following assumptions :-

(a) The velocity of grain boundary movement is proportional to the pressure difference caused by its curvature.

(b) The rate of grain growth is proportional to the rate of grain boundary migration.

(c) There is a critical grain size for grain growth to occur, such that grains larger than this size will grow and grains smaller than this size will be eliminated.

(d) The size of each grain can be expressed by the radius R of an equivalent circle or sphere having the same areaor volume respectively.

Using these assumption, an expression for the rate of grain growth, $\frac{dR}{dT}$ was developed :-

$$\frac{dR}{dT} = \alpha . M . \sigma . \left(\frac{1}{R_{cr}} - \frac{1}{R} \right) \qquad \text{-----------------------(33)}$$

where α is a dimensionless constant, M is the grain boundary mobility, σ is the grain boundary specific interfacial energy, R is the radius of a growing grain and R_{cr} is the critical grain radius for growth to occur.

Taking second phase particles in-to account, and considering the hypothetical pinning stress, $S = \frac{3f\sigma}{4\,r}$, or $S = \sigma . Z$, Hillert expressed the rate of grain growth in the presence of second phase particles as :-

$$\frac{dR}{dT} = \alpha . M . \sigma . \left(\frac{1}{R_{cr}} - \frac{1}{R} \pm \frac{Z}{\alpha} \right) \qquad \text{------------------(34)}$$

where $Z = \frac{3\,f}{4\,r}$, f is the volume fraction of second phase particles and r is particle radius. The sign must be chosen in each case such that the pinning stress, S, is acting against the movement of the grain boundary. The negative sign holds when $1/R < 1/R_{cr} - Z/\alpha$ and the positive sign when $1/R > 1/R_{cr} + Z/\alpha$. Between these two limits $\frac{dR}{dT} = 0$.

3.4 Gladman's Theory

Gladman's analysis$^{(39)}$ of the effect of precipitate particles on grain growth in metals is primarily concerned with the release of grain boundaries from the pinning effects of the dispersed particles. For this to occur, the energy has to be supplied from some other source, e.g. from the energy release resulting from grain growth. It has been shown by Gladman that the energy provided by grain growth, E_n is given by :-

$$E_n = \frac{\sigma_b}{\bar{R}_o} \left(\frac{2}{Z} - \frac{3}{2} \right) \qquad \text{------------------------(35)}$$

where E_n is the energy released per unit area of the advancing grain boundary,

σ_b is the grain boundary energy,

R_o is the matrix grain radius,

and Z is the ratio of the radii of the growing grain to the matrix grains.

According to this equation, energy is released only when $Z > 4/3$, and this is in accord with the many experimental observations that grain growth is cannibalistic, large grains growing at the expense of smaller grains. In metals containing second phase particles the energy release per particle due to grain growth, E_1, is :-

$$E_1 = \frac{E_n}{2\, r\, n_v} \tag{36}$$

where, r is the radius of the pinning particle and n_v is the number of particles per unit volume.

$$\text{or} \quad E_1 = \frac{2\, S \pi\, r^2 \gamma}{3\, R_o\, f} \left(\frac{2}{Z} - \frac{3}{2} \right) \tag{37}$$

where S is the displacement from the diametral plane of the particle,
γ is the grain boundary interfacial energy,
and f is the volume fraction of particle.

Thus the total energy change associated with the unpinning of a single particle, E_T is :-

$$E_T = E_p + E_1 \tag{38}$$

where E_p is the pinning energy.

It has been mentioned that unless the rate of decrease in energy due to grain growth exceeds the maximum rate of increase in energy due to pinning, an energy barrier will occur in the total energy change accompanying grain boundary movement, and the magnitude of such an energy barrier is a function of particle size and volume fraction of particles. This leads to the concept of a critical particle radius for unpinning, which is the minimum particle radius for which the activation energy barrier involved in the unpinning process is reduced to a level at which thermally initiated grain boundary release can occur. This radius, r_{crt}, can be calculated from the associated energy changes, per particle, and is given by :-

$$r_{crt} = \frac{6\, R_o\, f}{\pi} \left(\frac{3}{2} - \frac{2}{Z} \right)^{-1} \tag{39}$$

CHAPTER 4

GRAIN REFINED FERRITE-PEARLITE STRUCTURAL STEELS

4.1 Development

The development of the grain refined ferrite-pearlite structural steels is mainly because of the requirement for a lower transition temperature coupled with higher strength, increased ductility, weldability and formability, for gas and oil line pipe steels. Ferrite grain refinement in addition to decreasing the impact transition temperature, increases the yield strength and therefore ferrite grain refinement is the most important strengthening mechanism. There are two relationships on which the structure property relationships are based :-

(a) Hall-Petch equation(40,41):

$$\sigma_y = \sigma_o + K_y d^{-1/2} \qquad \text{--------------------(40)}$$

(b) Petch equation(42):

$$T_c = f(\sigma_o) - K d^{-1/2} \qquad \text{--------------------(41)}$$

where σ_y is the yield stress,
d is the grain size of the polygonal ferrite,
T_c is the impact transition temperature,
and σ_o, K_y & K are constants.

The introduction of aluminium-killed fine grain steels was one of the first steps in the development of grain refined high strength steels, and grain refinement was achieved by normalising, which also ensured uniformity of structure. This increased the yield stress from 225 to 300 MN/ m^2 and lowered the impact transition temperature to below 0°C. Later, a further increase in yield strength were achieved by precipitation strengthening, and to achieve this niobium, vanadium and titanium were added. However, precipitation strengthening increased the impact transition temperature, and so to offset this further ferrite grain refinement was achieved by the use of low finishing temperatures during rolling(43). The yield strengths achieved increased to 450-525 MN/m^2 with impact transition temperatures as low as -80°C.

The advent of welding to replace rivetting and bolting led to the requirement of improved weldability and this was achieved by lowering the carbon content. The lower carbon content, led to some loss in strength, and to compensate this precipitation strengthening was increased. An improvement in the weldability of ferrite-pearlite steels due to a decrease in the carbon content is due to decrease in heat affected zone hydrogen induced cracking with decreasing carbon equivalent, which is basically an expression combining the effect of composition on both hardenability and M_s-temperature. Carbon equivalents can be derived by the follwing formula :-

$$C.E = C + \frac{Mn}{6} + \frac{Mo + Cr + V}{5} + \frac{Ni}{15} \qquad \text{------------------(42)}$$

The need for improved formability led to the production of steels with low carbon content, low and uniform dispersed, equiaxed, non-metallic inclusions, low sulphur content, and shape control of the inclusions. In order to prevent elongation of manganese sulphide inclusions during rolling, which is detrimental to toughness and ductility particularly in the through thickness direction, an addition of zirconium, cerium or calcium may be made, as such additions modify the sulphide inclusions by decreasing their deformability, and thus preventing their elongation during rolling.

Various processing techniques have been introduced, involving lower finishing temperatures and/or heavier reductions during the final rolling passes to achieve substructure and texture strengthening in high strength low alloy steels. The use of micro-alloying additions such as niobium, vanadium and titanium, augmented by controlled processing, has made it possible to produce high strength low alloy steels with yield strengths up to 750 MN/m^2 and high toughness.

4.2 The Strengthening Mechanisms

4.2.1 Grain size

Refinement of the ferrite grain size increases the yield strength and decreases the impact transition temperature, and is the only strengthening mechanism by which both the strength and toughness may be increased simultaneously. In current industrial rolling practice it is possible to achieve ferrite grain sizes of the order of ∼5 μm in plates and 3-4 μm in strip(44), and this can contribute up to 250 MN/m^2 to the yield strength. Irvine et al(45) showed that in low C-Mn steel for a 1 MN/m^2 increase in yield strength produced by grain refinement, the impact transition temperature decreases by approximately 0.64°C.

4.2.2 Solid solution strengthening

The effect of various alloying elements on yield strength and transition temperature are as follows :-

Element	Change in Y.S MN/m^2/wt%	Change in I.T.T°C/wt %
C	+4600	-
N_{free}	+4600	+700*
P	+670	+400
Sn	+140	+150
Si	+85	+44
Cu	+39	-
Mn	+32	-30
Mo	+11	-
Ni	0	-13
Cr ≠	-30	-
Al	0	+75 $\not-$

* Not linear

$\not-$ Al in solid solution only

≠ Negative, possibly due to removal of interstitial solutes.

Although carbon and free nitrogen greatly increase the yield strength, they are of limited use because of their adverse effect on the impact transition temperature, formability and weldability. Phosphorus and tin, because of their embrittling effect, are kept to a minimum. Manganese is beneficial as it increases the strength without adversely affecting the impact transition temperature, due to it depressing the transformation temperature and consequently refining the ferrite grain size. However, manganese is usually limited to 1.5/1.7 %, to avoid too much depression of the transformation temperature and thus bainite formation, which can lead to embrittlement(44). Higher manganese can be accommodated with lower carbon contents, as this avoids formation of bainite or grain boundary cementite(46). Although silicon is very effective as a solid solution strengthening element, it is usually limited to $\sim$0.4 % in H.S.L.A steels, because it increases the impact transition temperature by raising the transformation temperature, thus producing coarse ferrite grains. Copper increases the yield strength but it causes hot shortness and increases the impact transition temperature. However, hot shortness can be avoided by addition of nickel but as can be seen from the foregoing table nickel does not contribute to solid solution strengthening but does improve toughness. Nickel however is expensive. Molybdenum has some solid solution strengthening but also is expensive. Aluminium, by removing the free nitrogen by forming AlN, improves the impact transition temperature, but any further increase in aluminium than that required to form AlN is harmful as aluminium in solid solution increases the impact transition temperature. Hence Al is usually limited to about 0.04 % .

By taking into account the effects of various alloying elements on strength and impact transition temperature, it can be seen that a low carbon, aluminium killed high manganese grain refined steel will offer an optimum combination of strength and toughness.

4.2.3 Precipitation strengthening

One of the most important methods of achieving high strength is by an addition of carbide and nitride forming elements such as niobium, vanadium and titanium. In addition these elements refine the ferrite grain size, thus decreasing the impact transition temperature and increasing the strength. It is often stated that precipitates reduce the notch toughness, although this generalization has been qualified(47). The volume fraction of precipitates formed during cooling depends on the solubility of the carbo-nitride and on the stoichiometric ratio of the alloying element with respect to carbon and nitrogen. The maximum temperature dependence of solubility of carbides or nitrides occurs along the stoichiometric line, and compositions on this line have the maximum in steel, by forcing screw dislocations to cross-slip, increase the rate of dislocation multiplication. Generation of dislocations at precipitates also increases the dislocation density. The cell and subgrain sizes are also a function of the dispersion spacing(53,54).

Dislocation strengthening can be achieved by rolling the steel in the $(\alpha+\gamma)$ or α temperature ranges, and as shown in fig.13 the dislocation strengthening increases with decreasing finish rolling temperature. Work by Bramfit et al(55) on very low C-Mn steel shows a strengthening effect of 9.02 $MN/m^2/mm^{-1/2}$ in steel rolled by 30 % in the temperature range 670-750°C. Another method of increasing the dislocation density is by decreasing the transformation temperature, either by alloying or by increasing the cooling rate, and this can increase the yield stress by about 50 MN/m^2(57).

Although dislocation strengthening offers an increase in strength, its use is not widely accepted in grain refined H.S.L.A steels due to its adverse effect on impact transition temperature and processing difficulties. However, it has been reported(58) that the adverse effect on toughness can be eliminated by the formation of a fine polygonized substructure, and the development of cube-on-corner crystallographic textures by a continuum rolling practice(55).

4.2.5 Texture strengthening

Estimates of the texture strengthening indicate an increment over randomly oriented material of about 5 % in the longitudinal and 10 % in the transverse direction for steel rolled at 710°C(59). In spite of the small effect on strength, the [111] ⟨110⟩ texture can lower the transition temperature, and improve the plastic strain ratio and the deep drawing characteristics. Bramfit et al(55) showed by continuum rolling of C-Mn steel that the transition temperature can be related to a texture parameter, C, based on the product of intensities of [111] in the rolling plane and [110] in the transverse plane, fig.14. This can be written as:-

$$T_{cv\ 20^{\circ}C} = 75 - 13\,d^{-1/2} + 0.63\,C \qquad \text{-----------------}(45)$$

where T_{cv} is the temperature for 20J absorbed energy

d is the ferrite grain size

and C is the texture parameter

$$\text{i.e.} \quad C = \left(I_{111} \right)_{R.P} \cdot \left(I_{110} \right)_{T.P}^{-1}$$

It can be seen that the transition temperature decreases with an increase in the texture parameter.

CHAPTER 5

SOLUBILITY RELATIONSHIPS FOR MICRO-ALLOYING ELEMENTS IN AUSTENITE

5.1 Introduction

The concentrations of various types of micro-alloying elements in equilibrium with carbon and nitrogen at various temperatures are important because of their ultimate effects on recovery and recrystallization processes in deformed austenite, and on the intensity of precipitation strengthening. Because of the decrease in the solubility of the carbo-nitrides of niobium, vanadium and titanium with decreasing temperature, precipitation of these phases occurs when the steel is cooled. From the solubility relationships for such carbo-nitrides it is possible to calculate the approximate amount of micro-alloying element in solution and as precipitate. In view of the importance of niobium, vanadium, titanium, and aluminium in micro-alloyed steels, the solubility product relationships have been established either by experiment or by thermodynamic calculations. These solubility products will be discussed in the following sections.

5.2 Niobium

Niobium forms either carbides or carbo-nitrides. Various authors have assumed the compositions of the carbides and carbo-nitrides to establish the solubility product. However, the assumed compositions of the carbides/carbo-nitrides varies, and therefore varying solubility relationships appear in the literature. Irvine et al$^{(45)}$ considered the nitrogen content in terms of an equivalent carbon content i.e carbon equivalent = $C + \frac{12}{14} N$, and established the solubility relationship in C-Mn steel as :-

$$\log [Nb]\left[C + \frac{12}{14} N\right] = \frac{-6770}{T} + 2.26 \qquad \text{------------------}(46)$$

where the elements are in weight percent and T is the absolute temperature.

A critical review by Nordberg et al$^{(60)}$ reinterpreted the available experimental results, and assuming the composition of niobium carbide to be $NbC_{0.87}$, suggested the solubility of niobium carbide in austenite to be :-

$$\log [\mathrm{Nb}][\mathrm{C}]^{0.87} = \frac{-7700}{T} + 3.18 \tag{47}$$

Mori et al$^{(61)}$ checked the compositions of the carbonitrides and established the solubility products for $\mathrm{NbC}_{0.87}$ and $\mathrm{Nb(C_{0.24}N_{0.65})}$ in austenite as :-

$$\log [\mathrm{Nb}]\ [\mathrm{C}]^{0.87} = \frac{-7700}{T} + 3.18 \tag{48}$$

$$\log [\mathrm{Nb}]\ [\mathrm{C}]^{0.24}\ [\mathrm{N}]^{0.65} = \frac{-10,000}{T} + 4.09 \tag{49}$$

5.3 Vanadium

Vanadium forms both carbide and nitride, the nitride being the more stable. The composition of the vanadium carbide is V_4C_3, and its solubility in austenite has been expressed by Bungardt et al$^{(62)}$ as :-

$$\log [\mathrm{V}]^{4/3}\ [\mathrm{C}] = \frac{-10,800}{T} + 7.06 \tag{50}$$

Frohenberg et al$^{(63)}$ determined the solubility of vanadium nitride in high purity austenite as :-

$$\log [\mathrm{V}]\ [\mathrm{N}] = \frac{-7070}{T} + 2.27 \tag{51}$$

Irvine et al$^{(45)}$ determined the solubility relationship for commercial C-Mn steel by chemical methods :-

$$\log [\mathrm{V}]\ [\mathrm{N}] = \frac{-8330}{T} + 3.46 \tag{52}$$

This relationship gives similar values of solubility product to those of Frohenberg. The same authors also found an increase in the solubility of vanadium nitride with an increase in manganese content :-

$$\log [\mathrm{V}]\ [\mathrm{N}] = \frac{-8330}{T} + 3.46 + 0.12(\%\ \mathrm{Mn}) \tag{53}$$

The increase in solubility of vanadium nitride with increase in manganese is a result of the decrease in activity coeffecient of nitrogen in austenite by manganese.

5.4 Titanium

Irvine et al(45) found that TiN is virtually insoluble in austenite at temperatures up to 1350°C. However, the solubility product of TiC was determined as :-

$$\log [Ti][C] = \frac{-7000}{T} + 2.75 \qquad \text{------------------------}(54)$$

Roberts(64) calculated the solubility of titanium nitride, assuming that titanium in iron obeys Henry's low. Using the standard free energy of Fe_2Ti to compute the titanium activity together with established information on the solubility of nitrogen in austenite, he obtained the following solubility product :-

$$\log [Ti][N] = \frac{-14,400}{T} + 5.0 \qquad \text{------------------------}(55)$$

5.5 Aluminium

There is no evidence that aluminium carbide can form in steel, but aluminium nitride is readily formed. The solubility of aluminium nitride has been established by Darken et al(65) in C-Mn steel over the temperature range 1050-1350°C :-

$$\log [Al][N] = \frac{-7400}{T} + 1.95 \qquad \text{------------------------}(56)$$

Wiester et al(66) showed that this relationship can be used down to 900°C. Irvine et al(45) studied the solubility relationship over the temperature range 950-1350°C in which nitrogen in the form of AlN was determined by the ester-halogen method and expressed their results as :-

$$\log [Al][N] = \frac{-6770}{T} + 1.03 \qquad \text{------------------------}(57)$$

This is in close agreement with data reported previously on commercial steels(67-69).

CHAPTER 6

GRAIN COARSENING OF AUSTENITE

6.1 The Effect of Niobium

Additions of niobium to steel affect the austenite grain coarsening behaviour, mainly by pinning the austenite grain boundaries by Nb(C,N) precipitates. The effectiveness of the pinning depends on the size, volume fraction, interparticle spacing and the coarsening behaviour of Nb(C,N) precipitates. In general, a uniform distribution of fine Nb(C,N) precipitates in the matrix retards grain growth very effectively. However, increased temperature, or time above a certain temperature, usually leads to the coarsening of precipitates which in turn increases the interparticle spacing and the size of precipitates, hence resulting in abnormal grain growth.

In steels containing niobium, above a certain temperature abnormal grain growth leads to the formation of a coarser austenite grain size than in plain carbon steel, which contains no niobium, because in the plain carbon steel there are no precipitates and therefore grain growth occurs normally, producing a uniform grain size(70).

The grain coarsening temperature has been found to increase with increasing niobium content because of the increase in volume fraction of precipitates(71-73). Gladman and Pickering(73) showed that increased volume fraction of fine Nb(C,N) precipitated during thermo-mechanical treatment were most effective in increasing the grain coarsening temperature. However, they suggested that in addition to this, the large insoluble particles exert some influence on the grain coarsening temperature. The holding time at different temperatures will also affect the grain coarsening temperature(74) because the coarsening of precipitates is time dependent.

The grain growth kinetics of Si-Mn and niobium containing steels have been shown(75) to follow Miller's equation :-

$$D_g = K t^n \qquad \text{------------------------------(58)}$$

where t is time, K is a constant at a given temperature and n is the time exponent. Si-Mn steel, which showed normal grain growth, gave a value of n $\sim$ 0.20 but niobium steel gave a very small value of n i.e 0.04 at 1050°C.

Fig. 15 shows typical curves for change in austenite grain size with reheating temperature in C-Mn, C-Mn-V and C-Mn-Nb steels. This shows the two plateaux around 900°C and about 1150°C. In these regions the austenite grain size is uniform but in the regions which show a progressive increase in grain size with temperature, there is a mixture of small and coarse grains. It has been suggested(39,73) that the plateau temperature range depends on the number of precipitates, and can also be affected by the time at the reheating temperature i.e increased time can lower the plateau temperature range.

The effect of strain induced Nb(C,N) precipitates on austenite grain growth have been demonstrated by LeBon et al(77) and Ouchi et al(75). LeBon showed that after complete dynamic recrystallization of austenite, initially grain growth was parabolic in the niobium steel, fig. 16 but after about 5 sec. or less, a marked retardation of grain growth was observed due to the simultaneous nucleation of Nb(C,N) precipitates. Grain growth in the niobium free steel showed no such retardation. Ouchi on the other hand, showed the effectiveness of strain induced Nb(C,N) on the retardation of grain growth. It was observed that isothermal holding at different temperatures after deformation, led to much slower growth of recrystallized grains and therefore a finer austenite grain size at a given temperature than was obtained by reheating, as shown in fig. 17. This was suggested to be due to the precipitation of Nb(C,N) induced by deformation.

6.2 The Effect of Vanadium

Vanadium retards austenite grain growth by pinning the grain boundaries by V_4C_3 , VN or V(C,N). Of these precipitates, VN is the most stable at high temperature and therefore is the most important phase in retarding the grain growth of austenite.

The grain coarsening temperature has been found to increase with increasing vanadium content(78). Erasmus(78) associated the variation of the 'initial' and 'final' grain coarsening temperature with increasing vanadium content to the solution temperature of V_4C_3 and VN in the austenite, fig. 18. It was observed that :-

(a) the 'initial' grain coarsening temperature was well below the solubility of V_4C_3 and VN in austenite,

(b) the 'final' grain coarsening temperature closely followed the VN solution temperature curve at all vanadium contents.

It was suggested that the 'initial' grain coarsening, which occurs before the solution of precipitates is due to the coarsening of VN. From fig. 18 it can also be seen that, at higher vanadium contents the 'initial' coarsening results considerably depart from the VN solution curve than at low vanadium contents. This was suggested to be due to very large particle sizes which were developed at increasing volume fractions of precipitate, even at lower temperature. Also the inhomogeneous distribution of the undissolved particles at higher vanadium contents can lead to the coarsening of austenite grains at much lower temperature than the solution temperature of VN.

Webster and Allen(79) studied austenite grain growth in steels containing ~0.4 % C and 0.1 % V, and showed that abnormal grain growth can be prevented by :-

(a) rapid heating to the austenitizing temperature;

and (b) austenitizing below the solubility temperature for carbides, particularly within critical range.

6.3 The Effect of Titanium

In steels containing titanium, austenite grain growth is inhibited by the pinning effects of TiN and TiC, and such effects increase with increasing titanium content(80).

George and Irani(81) showed that the highest grain coarsening temperature was achieved in a steel when all the titanium was combined as TiN, but when there was an excess of titanium the grain coarsening temperature was lowered. The reason for this observation is not clear. It was however concluded that TiN was responsible for the high grain coarsening temperature, and that titanium should be added in the proper proportions relative to nitrogen in order to form a high volume fraction of TiN. TiN is much more stable than TiC at high temperature.

Increased holding time, tends to lower the austenite grain coarsening temperature(81,82), but increased heating rate generally decreases the growth of the austenite grains and therefore results in a finer austenite grain size(82).

6.4 Comparative Effects of Niobium, Vanadium and Titanium on Austenite Grain Growth

It is clear that the grain coarsening temperature is dependent on :-

(a) the temperature dependence [illegible] solubility of the carbides and nitrides of the alloying elements: A decrease in the solubility of alloy carbides and nitrides, increases the grain coarsening temperature due to the stability of precipitates to occur at higher temperature. The solubility of carbides and nitrides of niobium, vanadium and titanium increases in the order of V_4C_3 , VN, TiC, Nb(C,N) and TiN. From this it can be seen that TiN is the most stable phase and therefore titanium addition in the steel should give the highest austenite grain coarsening temperature, followed by niobium and vanadium in decreasing order. This has been confirmed by many investigators(72,74-76).

(b) the coarsening rate of precipitates at various temperatures: Precipitates which coarsen rapidly give lower grain coarsening temperatures compared to those which coarsen slowly. The coarsening rate of different phases in decreasing order is V_4C_3 , VN, TiC, Nb(C,N) and TiN. The effect of temperature on the particle size of Nb(C,N)(73) and TiN(81) are shown in fig. 19, from which it can be seen that TiN is very stable even at temperatures as high as 1300°C. Also TiN has a lower coarsening rate than Nb(C,N), which results in a finer particle size at any given temperature compared with Nb(C,N). Therefore, titanium additions raise the austenite grain coarsening temperature significantly compared with niobium.

(c) the particle size and distribution: A uniform distribution of fine particles is necessary to achieve an optimum effect for a given volume fraction of precipitates in retarding grain growth. There is an optimum size for precipitates which can give a maximum pinning effect at the grain boundary. The size and distribution of particles are affected by the history of the steel, the type of heat treatment and the thermo-mechanical treatment. Strain-induced precipitates, which are usually fine and uniformly distributed, retard austenite grain growth very effectively.

CHAPTER 7

CONTROLLED ROLLING

7.1 Introduction

The main purpose of controlled rolling is to refine the ferrite grain size which is produced by the transformation of the "conditioned" austenite, as there exists a relationship between the austenite grain morphology and the ferrite grain size. In general very fine recrystallized austenite, or thin elongated unrecrystallized austenite, is preferred, as such morphologies offer maximum nucleation for ferrite and therefore the finest possible ferrite grain size. However, controlled rolling is also used to optimize various strengthening mechanisms such as precipitation strengthening and texture strengthening, without adversely affecting toughness. The various processing parameters involved during controlled rolling are :-

- Reheating temperature,
- Finishing temperature,
- Amount of deformation,
- Holding temperature and time,
- Cooling rate,

and - Coiling temperature in coiled products.

These parameters are used mainly to achieve the austenite grain morphology which can transform to a uniform fine ferrite grain size, and to prevent the ferrite grain growth after transformation. The austenite grain morphology can be varied by means of the recrystallization of austenite and this is also dependent upon the alloy composition. For example additions of alloying elements such as niobium and vanadium retard the recrystallization of austenite thus giving thin elongated grains at low rolling temperatures, whilst at higher rolling temperatures strain induced precipitation can give finer recrystallized grain sizes than can be achieved in plain carbon steel for similar rolling conditions.

In order to control the recrystallization kinetics and grain growth of austenite, additions of niobium, vanadium or titanium are made to the plain carbon steel either singly or in combination.

7.2 Effect of Thermo-Mechanical Variables on the Ferrite Grain Size and Mechanical Properties of Micro-Alloyed Steels.

7.2.1 Reheating temperature

Reheating temperature affects the initial austenite grain size and the amount of micro-alloying carbides, nitrides or carbonitrides dissolved in the austenite. Such changes can lead to variations in the final properties obtained in steel through their effect on the final ferrite grain size and precipitation strengthening.

The effect of reheating temperature has been studied either using a single deformation(83) or multiple deformations(84,85). Using a single deformation, a decrease in reheating temperature refines the ferrite grain size, and the intensity of such ferrite grain refinement was found to be composition dependent. Additions of alloying elements such as niobium, vanadium and titanium form carbonitrides, and the presence of these precipitates retards the grain growth of austenite leading to further grain refinement compared with plain carbon steels, as discussed previously.

A similar effect of reheating temperature on the ferrite grain size has also been observed after multipass rolling of plain carbon and micro-alloyed steels(86). However, Priestner et al(86) found no effect of reheating temperature on the ferrite grain size after multipass rolling, because the earlier passes refine the austenite grain size and so create a condition not entirely developed by the reheating temperature.

Particularly in micro-alloyed steels a decrease in the reheating temperature will reduce the amount of alloy carbonitrides in solution, and therefore will reduce the potential precipitation strengthening. Such a reduction in precipitation strengthening will improve the toughness. Also it has been claimed that a decrease in transition temperature with decrease in reheating temperature is due to the refinement of the ferrite grain size. Such an effect has been observed(85) in plain carbon steel after multipass rolling, so that the decreased transition temperature cannot be only be due to a reduction of precipitation strengthening.

7.2.2 Finishing rolling temperature

The finishing rolling temperature can be divided in to three temperature ranges :-

- Rolling in the austenitic range (Above Ar_3 temperature)
- Rolling in the austenite plus ferrite range(Between Ar_1 and Ar_3 temperatures)
- Rolling in the ferritic range (Below Ar_1 temperature)

Decreasing the finishing rolling temperature in general, refines the ferrite size, due to an increase in ferrite nucleation because of the increased austenite grain boundary area per unit volume, which results from the formation of either fine recrystallized austenite grain sizes, if rolled above the recrystallization temperature or elongated unrecrystallized austenite grains containing deformation bands when rolling is performed below the recrystallization temperature. Partially recrystallized austenite can transform to mixed ferrite grain sizes(87), and such a structure is known to be detrimental to toughness.

Rolling in the austenitic range leads to the formation of polygonal ferrite and maximum ferrite grain refinement can be achieved by giving heavy deformations just above the Ar_3 temperature. The degree of ferrite grain refinement decreases as the finishing rolling temperature is lowered in the austenite plus ferrite range(58), whilst mainly ferrite grain elongation occurs when steel is deformed in the ferritic range.

The degree of ferrite grain refinement due to a decrease in the finishing rolling temperature can be enhanced by proper control of alloy composition. It has been frequently shown that additions of niobium, vanadium or titanium either singly or in combination enhances ferrite grain refinement. On many occasions niobium has been proved more efficient in this respect than vanadium when added singly, but if niobium and vanadium are added in combination, further refinement of the ferrite grain size occurs compared with single additions of niobium or vanadium for a similar finishing rolling temperature(88,89). It has been shown(90) that an increase in carbon content from 0.1 to 0.25 mass % in 0.1 mass % V steel refined the ferrite grain size even when rolled at similar finishing temperatures. Irvine et al(83) also found a similar effect of carbon in plain carbon and niobium micro-alloyed steels. The effect of vanadium on ferrite grain refinement has been found to increase with an increase in nitrogen content from 0.006 to 0.02 mass % .

The composition of the steel affects the intensity of the ferrite grain refinement and therefore also affects the mechanical properties related to ferrite grain size. Rolling in the austenite plus ferrite range results in the deformation of proeutectoid ferrite and so, this offers additional strengthening due to the increase in dislocation density. However, such strengthening increases the transition temperature(83,91-93), when rolling is continued in austenite plus ferrite range. A decrease in transformation temperature by an addition of an alloying element such as manganese can allow a further decrease in rolling temperature without impairing the impact transition temperature, as the deformation of ferrite can be avoided due to decrease in the transformation temperature(83).

A rolling procedure called "continuum" rolling has been developed(58) in which rolling is continued down to temperatures as low as 400°C and, such a procedure has been found to increase the yield strength without adversely affecting toughness; in fact there is an improvement of toughness. The improvement in toughness inspite of the increase in yield strength after "continuum" rolling is attributed to the grain refinement, sub-grain formation and cube-on-corner texture formation.

7.2.3 Amount of deformation

An increase in deformation above the recrystallization temperature refines the recrystallized austenite grain size. Also an increase in deformation below the recrystallization temperature increases the austenite grain boundary area per unit volume by elongating the grains and increasing the density of deformation bands(94). Thus, irrespective of the finishing rolling temperature, an increase in deformation increases the austenite grain boundary area per unit volume, and therefore refines the ferrite grain size.

Because of the refinement of the ferrite grain size with increased deformation, the yield strength and impact transition temperature will improve, and such an effect can be enhanced by lowering the deformation temperature as mentioned previously. Increasing the deformation in a high hardenability steel, i.e. 1.5 % Mn, was found(83) to eliminate bainite formation, and so led to an improvement in toughness. However, it has been reported(76) that in niobium steels, an increase in deformation decreased the ductile fracture energy whilst the reverse was observed in plain carbon steel. The reason for this is suggested to be due to pinning of dislocations by precipitates in niobium steel, which inhibited their glide. McPherson(95) has also suggested that a high unpinned dislocation density in the absence of any marked precipitation can lead to improvement in toughness, although the reasons quoted for this effect seen rather speculative.

Additions of micro-alloying elements allow a wider temperature range for rolling below the recrystallization temperature because they raise the recrystallization temperature. Thus it is possible to increase the amount of deformation below the recrystallization temperature by increasing the number of rolling passes whilst still maintaining a high rolling temperature.

7.2.4 Holding temperature and time

The main purpose of holding is to achieve a low finishing temperature after reheating the steel at high temperatures. Although low reheating temperatures can lead to low finishing temperatures without holding, this would be at the expense of precipitation strengthening particularly in niobium and titanium micro-alloyed steels due to the temperature dependent solubility of alloy carbides and nitrides. Such processing methods can lead to production difficulties. Low finishing temperatures can be achieved by starting with a thicker section but this will require longer rolling times to reach the final section size, and therefore such a process would not be economical.

During controlled rolling, slab can be held either prior to the start of rolling or at an intermediate stage during rolling. Holding prior to rolling is only economically viable where as much solubility of the carbo-nitrides as possible is essential.

Intermediate holding can lead to the following, depending on the state of the austenite, the holding temperature, the holding time, the amount of stored energy and the composition of the steel :-

- If the austenite is recrystallized, grain growth will occur but this can be minimized by solute drag or pinning the austenite grains by second phase particles.
- If the austenite is partially recrystallized, a further recrystallization will occur by either, growth of the recrystallized austenite grains in the unrecrystallized matrix and/or the formation of new recrystallization nuclei. The former tends to coarsen the austenite grain size whilst the latter refines the austenite grain size.
- If the austenite is completely unrecrystallized, recovery or recrystallization will occur.

Irvine et al(83) showed that holding plain C-Mn and C-Mn-Nb steels for 5 minutes at 800°C led to coarsening of the ferrite grains in plain-carbon steels whilst niobium steel showed little evidence of such coarsening. This is because niobium retards recrystallization and grain growth to times in excess of 5 minutes at 800°C. However, it was suggested that holding at a higher temperature for a niobium steel, where recrystallization could occur more rapidly, caused detrimental effects similar to those shown for plain carbon steels.

Holding at high temperatures results in coarse ferrite grain sizes and therefore will decrease the yield strength and increase the transition temperature. Chapman(96) studied the effect of the holding start temperature and the holding finish temperature on the transition temperature in niobium containing ship plate steel. A decrease in both the start and finish holding temperatures led to a progressive improvement in the charpy values. This was attributed to microstructural refinement in the austenite. In industrial processing however, there is an inter-relationship between the finishing rolling temperature and temperature at the end of the holding period.

Heavy deformations after an intermediate holding are necessary to ensure either fine recrystallized austenite or very thin elongated austenite grains, to transform to a fine ferrite grain size.

7.2.5 Cooling rate

Cooling rate, also known as "controlled cooling", can be used to achieve optimum mechanical properties through its effect on the $\gamma \rightarrow \alpha$ transformation temperature, grain growth of the austenite and ferrite, and precipitation strengthening. Higher cooling rates between rolling passes can also be used to achieve low finishing temperatures, and hence to eliminate holding during rolling. The effects of cooling rate on the microstructure and hence the mechanical properties of controlled rolled steels depends very much so on the way such cooling has been applied. The important variables in controlled cooling are :-

- cooling rate,
- the starting temperature for cooling,

and - the finishing temperature for cooling.

It is well known that a fast cooling rate depresses the transformation temperature and minimises grain growth of the austenite. Both of these will increase ferrite nucleation and therefore will result in a fine ferrite grain size. Accelerated cooling by water sprays on the mill run-out table are used mainly to produce strip$^{(43)}$. The cooling rate should not be so high that it leads to the formation of acicular transformation products, and thus to a deterioration in toughness. Slow cooling rates on the other hand lead to formation of coarse ferrite grains and can also, lead to mixed ferrite grain sizes$^{(89)}$, both of which have a tendency to increase the impact transition temperature and decrease the yield strength. Figure 20$^{(90)}$ shows the effect of cooling rate on the ferrite grain size for several plain carbon and low alloy steels having the same finishing temperature of 926°C and a final reduction of 20 %. For these steels, the cooling rate predominates over the composition (Nb or V content) with respect to control of the ferrite grain size.

The starting temperature for cooling is important particularly when the advantage of a high cooling rate on retarded austenite grain growth and the depression of the transformation temperature has to be utilized. The best results are obtained by cooling directly from the finishing rolling temperature with minimum delay(97). A minimum delay ensures minimum austenite grain growth prior to transformation and hence results in a fine ferrite grain size. A fast cooling rate from above Ar_3 gives maximum refinement of the ferrite grains and hence the maximum increment of strength and decrease in transition temperature. On the other hand, ferrite grain refinement is less pronounced with a lowering of the starting temperature below Ar_3, for a given cooling rate(98).

It is important(99) to complete the transformation of austenite on the strip run-out table prior to coiling, in order to avoid any transformation occurring during very slow cooling after coiling, because this results in the formation of coarse ferrite grains. Also the finishing cooling.temperature should be as low as possible to achieve the lowest coiling temperature which can give minimum ferrite grain growth, coupled with optimum precipitation strengthening.

7.2.6 Coiling temperature

It is possible to obtain a range of mechanical properties in coiled strip products by varying the coiling temperature. This is because of the control of the ferrite grain size and precipitation strengthening during cooling from the coiling temperature.

Too high a coiling temperature leads to transformation of austenite at very slow cooling rates after coiling, and thus would result in formation of coarse ferrite. High coiling temperature can also give rise to ferrite grain growth after transformation, and a decrease in yield strength and deterioration in toughness.

Another important strengthening mechanism affected by the coiling temperature is precipitation strengthening. Too high a coiling temperature can allow overageing whilst very low coiling temperatures may suppress the precipitation due to high cooling rates required to achieve the low coiling temperature. It has been shown(96) that a high coiling temperature increases the grain boundary carbide thickness and this has deleterious effect on toughness.

CHAPTER 8

RECRYSTALLIZATION OF AUSTENITE

8.1 Introduction

An understanding of austenite recrystallization during controlled rolling is important to achieve the austenite grain morphology which can transform to very fine uniform ferrite grain sizes. Plain C-Mn steel recrystallizes very rapidly even at 800°C, and therefore it is difficult to "condition" the austenite prior to transformation, as only a small temperature range is available for controlled rolling. It is possible to raise the austenite recrystallization temperature by elements such as niobium and vanadium; so that the temperature range in which controlled rolling can be carried out is increased.

Studies of the effect of microalloying additions on the dynamic and static recrystallization of austenite after various thermo-mechanical treatments have been made by many investigators. The recrystallization behaviour has been studied after deformation by rolling(76,83,86,94, 98,100-111), compression(112-116), tension(117-124) or torsion(77,125,126); and the recrystallization kinetics have been evaluated by either quantitative metallography or by the decrease in the yield stress of the recrystallizing austenite.

Additions of niobium and vanadium retard the recrystallization of austenite and to understand this phenomenon it is necessary to consider the effects of these elements on the various recrystallization processes namely :-

- Nucleation
- Growth of the recrystallized grain, and
- Grain growth after completion of recrystallization.

8.2 Nucleation

Prior austenite grain boundaries are the major nucleation sites for recrystallization. However, in addition to this, nucleation can occur at non-coherent twin boundaries, grain boundaries, triple points(105), deformation bands, and at interfaces between recrystallized and unrecrystallized grains(109,127). Some parts of the prior austenite grain boundaries do not function as effective nucleation sites, which may be due to high coincidence with the neighbouring grain, and therefore nucleation at prior austenite grain boundaries is not always uniform. There is no evidence for homogeneous nucleation for recrystallization.

Nucleation occurs mainly by subgrain growth or subgrain coalescence mechanisms(107), but nucleation by strain induced grain boundary migration (S.I.B.M)(76,128) and bulge nucleation has also been observed. Kozasu et al(105) observed boundary serrations after hot deformation and suggested that this might be related to nucleation. Tanaka et al (129-130) noticed S.I.B.M for less than 8 % deformation whilst Roberts(128) observed S.I.B.M during dynamic recrystallization of austenite when a very large deformation was given at high temperatures.

There is an incubation period before a viable nuclei can form and grow, and an increased incubation period denotes retarded nucleation. Precipitation of Nb(C,N) and V(C,N) on substructures in deformed austenite have been observed by many investigators, and such an effect has been shown to retard recrystallization, although whether this actually increases the incubation period is not always clearly stated. Jonas(131), discussing the results of LeBon et al(77,125,126), suggested that niobium retards static recrystallization due to the effect of precipitation of Nb(C,N) on the nucleation process, rather than on the growth of the recrystallizing grains. Roberts(109) also suggested that the presence of niobium increases the incubation time for nucleation.

Another mechanism by which niobium or vanadium can retard nucleation is by preventing dislocation movement by solute-dislocation interaction. Coldas et al(132) after studying the temperature dependence of the time exponent 'n' in Avarmi's equation, for plain carbon and niobium steels, suggested that the main influence of niobium is on the static recrystallization incubation time and not on the kinetics of recrystallization after incubation. It was shown that niobium retarded nucleation by a solute effect which was supported by the absence of observable precipitation of Nb(C,N) particles during the incubation period. White et al(115) also noted a similar effect of niobium and vanadium solute atoms on the incubation time. However, they found that on a mass percent basis niobium was more effective than vanadium in increasing the nucleation incubation time. Roberts(114) studied dynamic recrystallization in vanadium steel and showed that vanadium in solution retarded dynamic recrystallization by increasing the nucleation incubation time .

Regardless of the mechanism by which niobium and vanadium increase the nucleation incubation time i.e by pinning of dislocations by precipitates or solute atoms, it is clear that additions of these elements retard nucleation and therefore recrystallization. The mechanism by which they retard nucleation is still not very clear and no satisfactory model is available to predict quantitatively the effects of precipitates or solutes on nucleation for recrystallization.

8.3 Growth of the Recrystallized Grains

Any retardation in growth of the recrystallized grains into the unrecrystallized matrix can also result in a retardation of recrystallization and, after the nucleation process, this may be the rate controlling process.

Growth of recrystallized grains will leave behind a region with a much lower dislocation density. The major driving force for the growth of recrystallized grains is the difference in dislocation density between the deformed and recrystallized regions. The rate of growth of the recrystallized grains increases with an increase in deformation. On the other hand an increase in deformation would also increase the nucleation rate and the net result would be a refinement of recrystallized grain size.

The growth rate of the recrystallized grains can be retarded by the presence of second-phase particles, and for this to occur very fine distributions are required. In the initial stages, when the recrystallizing grains are fine, only very fine particles can retard growth of the recrystallizing grains. Although solute has been shown to retard grain growth after completion of recrystallization in dilute solid solutions, it may not be effective in retarding growth of recrystallizing grains due to the very high driving force available for recrystallizing grains to grow. Thus it seems probable that second-phase particles can only inhibit grain growth of recrystallized grains.

Many investigators have attributed the effect of niobium on the retardation of recrystallization, to the inhibited grain boundary migration of recrystallizing grains by Nb(C,N) precipitates(109,123). Such an effect can also occur in vanadium microalloyed steels but due to the higher solubility in austenite of V(C,N) compared with Nb(C,N), it would be expected that vanadium would be effective at lower temperatures than niobium.

There is no theoretical treatment available to describe the growth of recrystallizing grains into the unrecrystallized matrix. Also much of the published work on the recrystallization of austenite in microalloyed steels has considered the overall recrystallization kinetics rather than the separate effects of nucleation and growth of the nuclei into the unrecrystallized matrix.

8.4 Recrystallization Kinetics of Austenite

8.4.1 Niobium steel

8.4.1.1 Effect of reheating temperature

A higher critical reduction for recrystallization has been observed to be necessary as the reheating temperature increases, in both plain-carbon and niobium steels. It has therefore been suggested (76,94) that an increase in the austenite grain size is responsible for increasing the critical reduction for recrystallization. However, in niobium steels, an increase in reheating temperature also increases the niobium in solution and it has been shown by many investigators(76,111,133) that increased niobium in solution retards austenite recrystallization either by solute drag(133) or by precipitates(94,111). In general, therefore an increase in reheating temperature leads to retardation of austenite recrystallization more in niobium steels compared with plain-carbon steels. To utilize the effect of niobium on the retardation of austenite recrystallization it is desirable to dissolve the niobium in austenite prior to deformation.

8.4.1.2 Effect of rolling temperature

In accordance with the general principles of recrystallization, the critical reduction for complete recrystallization decreases with an increase in rolling temperature. As shown in fig.21, the influence of initial austenite grain size and deformation temperature is small in plain-carbon steel, but in niobium steel the effect of both these variables is extremely large. The critical amount of deformation required for completion of recrystallization increases rapidly with decreasing deformation temperature in niobium steels. Thus the addition of niobium increases the dependence of the critical strain for recrystallization on the initial austenite grain size and deformation temperature. In niobium steels, recrystallization is completely suppressed below about 950°C(76). On the other hand plain carbon steels recrystallize in a few seconds, even at 800°C.

8.4.1.3 Effect of deformation

An increase in deformation will increase the driving force for recrystallization. However, a critical amount of deformation is required to initiate recrystallization, and this has been found to increase with niobium additions to plain-carbon steel(76,94). Particularly in niobium steels, the critical amount of deformation is very much dependent on the rolling temperature and the initial austenite grain size, fig.21. The critical amount of deformation required for the recrystallization of austenite decreases with a reduction in initial austenite grain size and an increase in rolling temperature.

8.4.1.4 Effect of holding temperature and time

Because of the importance of holding temperature and time in the controlled rolling of microalloyed steels for plate or strip, many studies have been made of the effect of holding temperature and time on the recrystallization kinetics of austenite. Such studies have been made using varying techniques, many alloy compositions and using different thermomechanical treatments(102,109,115,116,126,134-136). In general the addition of niobium to plain-carbon steels retards austenite recrystallization, and this effect increases with decreasing rolling and holding temperature.

The practical significance in industry of time-temperature-recrystallization data such as that illustrated in fig.22, can be important if such information is associated with other variables such as deformation and rolling temperature because it governs the recrystallization kinetics. Kozasu et al(94) represented such information for a 0.03 % Nb steel reheated to 1250°C for 20 min. and rolled in one pass as illustrated in fig. 23, which shows the state of recrystallization, including the change in recrystallized grain size, at various rolling temperatures, after different reductions. Such data is valuable in designing controlled rolling schedules.

8.4.1.5 Effect of strain rate

The effect of strain rate has been studied mainly on dynamic recrystallization. Wray(137) studied the effect of strain rate on the strain to recrystallize in 0.93 % C steel, and observed an increase in strain rate from 10^{-5} to 10^{-2} at various deformation temperatures to increase the strain to recrystallize. He also suggested that the high strain rate used in hot rolling may require greater than 30 % strain to initiate dynamic recrystallization. LeBon et al(126) investigated the effect of niobium on dynamic recrystallization using various strain rates in torsion. They found that the strain needed to initiate dynamic recrystallization was higher for the niobium steel compared with the niobium free steel. It may be concluded that for the very high strain rates used in the hot rolling of niobium microalloyed steel, greater than 30 % strain may be desirable to initiate dynamic recrystallization. Thus dynamic recrystallization in hot rolled niobium steels may not occur under many industrial conditions.

LeBon et al(126) showed that an increase in strain rate increased the work-hardening of austenite, more in a niobium steel than in a niobium free steel. On the other hand, Kozasu et al(94) suggested that lowering the strain rate from 25 to 5 per sec. was not sufficient to change the critical deformation for dynamic recrystallization.

Petković et al(116) and Weiss et al(138) studied the softening behaviours of plain-carbon and niobium microalloyed steel after deformation at 930°C at various strain rates (8 x 10^{-2} and 8 x 10^{-3} s^{-1}), and it was shown that an increase in the strain rate of one order of magnitude for the plain-carbon steel increased the rate of softening also by about an order of magnitude. On the other hand, in the niobium modified steel, a two order of magnitude change in strain rate produced much less change in the rate of softening. The increase in the rates of both recovery and recrystallization in both steels, were attributed to the increase in retained dislocation density, and therefore in the driving force for softening, which accompanies the increase in strain rate.

In conclusion, the effect of niobium is to increase the strain to initiate dynamic recrystallization and this increases with an increase in strain rate. The effect is greater in niobium steel than in plain-carbon steel. However, once dynamic recrystallization is initiated the rate of recrystallization is faster in niobium steel compared with niobium-free steel.

8.4.1.6 Effect of composition

Studies (94,139) on the effect of increasing the amount of niobium up to ∿ 0.13 % on austenite recrystallization has shown an increased retardation of recrystallization as the niobium increases, fig. 24. It has been suggested(139) that increasing niobium up to 0.06 % is very effective in retarding static recrystallization. A similar effect of niobium content has also been observed on dynamic recrystallization, as shown in fig. 24.

Petković et al(116) observed that the softening, after an identical treatment, was retarded more in 0.68 % C steel than in 0.42 % C steel. Other studies(111,112) showed that an increase in Nb : C also resulted in a retardation of austenite recrystallization. However, the independent effects of carbon and niobium are by no means clear.

The effect of manganese on austenite recrystallization in niobium steel is not known, but large additions of manganese (∿ 5.2 %) in a 0.05 % C steel retarded the recrystallization of austenite(137). This effect of manganese was suggested to be due to an increase in the stacking fault energy of austenite.

Lamberigts et al(120) investigated the effect of 0.018 % Nb and 0.018 % Nb + 0.065 % V on austenite recrystallization at various temperatures. They observed that the presence of as little vanadium as 0.065 % caused more marked retardation of recrystallization below 950°C. On the other hand, it has recently been shown(115) that in a Nb-V-N steel containing 0.03 % Nb, less than 0.2 % V has no influence on the rate of work hardening but if the vanadium content is raised to 0.2 %, the effects due to niobium and vanadium tend to be additive.

The effect of aluminium on static austenite recrystallization after various thermomechanical treatments is reported to be insignificant(83,86), but in contrast to this Kozasu et al(105) observed an acceleration of recrystallization in plain-carbon steel on increasing the aluminium content from 0.002 % to 0.049 %, at 0.017 % N. It was suggested that aluminium in solution seems to promote nucleation and accelerate grain boundary migration, and therefore acceleratedrecrystallization. However, it was also mentioned that such an effect of aluminium was not large. A similar effect of aluminium on the acceleration of austenite recrystallization was also observed by Roberts(109) in niobium microalloyed steel. Although Roberts observed acceleration of static recrystallization in the presence of aluminium, he also noticed more retardation of dynamic recrystallization by niobium when in additions aluminium were present. Such contrasting effects of aluminium on static and dynamic recrystallization are not fully understood(109).

8.4.2 Vanadium steels

8.4.2.1 Effect of reheating temperature

In contrast to niobium, vanadium can be dissolved at low reheating temperatures and therefore very high reheating temperatures are not needed. However, the temperature for complete solution of vanadium carbonitride is dependent on the composition, and therefore the reheating temperature required to dissolve the vanadium carbonitride will vary with composition. Thus the effect of reheating temperature on austenite recrystallization in vanadium microalloyed steel will mainly be due to the variation in the initial austenite grain size rather than due to vanadium, provided the reheating temperature is above the solubility temperature of V(C,N). A lower reheating temperature may give finer austenite grain sizes prior to rolling, and therefore may accelerate recrystallization.

8.4.2.2 Effect of rolling temperature

The effect of vanadium on the retardation of static austenite recrystallization has on many occasions been related to the precipitation of V(C,N) in austenite after deformation. Thus only rolling at temperatures which can precipitate strain induced V(C,N) in austenite will affect the recrystallization of austenite. In agreement with this, it has been reported that vanadium retards austenite recrystallization during rolling below 950°C(105,107,114,140,141), and such an effect increases with a decrease in rolling temperature.

8.4.2.3 Effect of holding temperature and time

The effects of holding temperature and time on the progress of recrystallization of austenite in vanadium steels have been studied by many investigators(109,114,120). Below 900°C vanadium retards recrystallization very effectively and the effect increases as the holding temperature decreases; recrystallization being completly suppressed at or below 800°C.

8.4.2.4 Effect of strain rate

Roberts(114) studied the recrystallization kinetics of 0.09 % V steel at various temperature after deformation at strain rates of 0.05 s^{-1} and 1.0 s^{-1} , using compression. He noted that at 850°C, the same kinetics were found even when the strain rate during predeformation was increased by a factor of 20. This result is in agreement with observations made by Ahlblom(127) in 18/9 austenitic steel. It should be noted that these results are in contrast to those discussed in section 8.4.1.5 for plain-carbon and niobium microalloyed steels.

8.4.2.5 Effect of composition

It is generally believed that vanadium retards austenite recrystallization due to strain induced precipitation of V(C,N). It is also well established that VN precipitates at higher temperatures than VC. Therefore an increase in nitrogen content will increase the volume fraction of VN, and enhance the retardation of austenite recrystallization at higher temperatures. However, such an effect of nitrogen in vanadium steel has not been investigated in detail.

8.4.3 Titanium steels

Titanium, due to its high reactivity with oxygen, nitrogen and sulphur, is difficult to control during the production of steel, and this has prevented the wider use of titanium in the C-Mn steel. Therefore, very little work has been done on the effect of titanium on the recrystallization of austenite. However, some of the work does show that the presence of titanium in the C-Mn steel retards recrystallization of austenite(99,151), and this has been suggested to be due to TiC precipitates(151). Korchynsky(99) showed that titanium retards austenite recrystallization more effectively than does either niobium or vanadium.

Titanium, in fact raises the austenite grain coarsening temperature markedly, mainly due to low coarsening rate of TiN and TiC, hence after austenite recrystallization the presence of TiN and TiC will prevent the coarsening of austenite grains. Thus titanium will refine the austenite grain size.

8.5 Comparison of the Effect of Niobium and Vanadium on Austenite Recrystallization

Many investigators(83,105,106,111,114,115,119,121,135,142) have compared the effects of niobium and vanadium on the static recrystallization of austenite. Such comparisons have been made either on the basis of their effect on the temperature of recrystallization(105,114,119) or on the basis of unit weight percent or atomic percent(108,115,121).

In general there is agreement that vanadium does retard the recrystallization of austenite compared with plain-carbon steels. When such effect of vanadium is compared with that of niobium it has been shown that vanadium has less effect in retarding recrystallization of austenite than does niobium. However, it would be desirable to explain the comparitive effects of niobium and vanadium in temperature ranges where both retard recrystallization of austenite.

There seems to be general agreement that niobium retards recrystallization at higher temperatures than vanadium. In fact it has been noted that vanadium retards recrystallization only below 900°C(105,107,114,140,141) and is not very effective above 900°C. If the effect of vanadium is compared with niobium above 900°C, vanadium does have a smaller effect on retardation of austenite recrystallization, as has been noted by many investigators.

However, if the effect of niobium and vanadium are compared at temperatures below which both of these elements retard recrystallization of austenite then, as has been shown in fig. 25 and discussed by Roberts(114), the suppression of recrystallization due to vanadium is very marked at 800°C compared with niobium. On the other hand at ∼ 900°C niobium is a more effective inhibiter of recrystallization than is vanadium, in terms of the degree of inhibition per unit concentration.

It is well known that an addition of niobium(150) or vanadium(110,113,114,121,122) to plain-carbon austenite retards dynamic recrystallization. However, it has been shown on many occasions(83,94,123,142) that retardation of dynamic recrystallization is greater when niobium is added instead of vanadium. In contrast to these observations Roberts(114) has shown that the effect of vanadium on the retardation of dynamic recrystallization is atleast equivalent to that of niobium on a unit concentration (wt %) basis, but in terms of atomic percent, the effect of niobium is somewhat stronger.

8.6 Mechanism of Recrystallization of Austenite

The following summarizes the major differences of opinion:-

(a) Niobium in solution increases the incubation period for nucleation and thereby retards the recrystallization of austenite. Such an increase in incubation time for viable nuclei to form has been attributed to solute-dislocation interaction and therefore to the formation of recrystallized nuclei by subgrain growth or by subgrain coalescence mechanisms.

(b) Nb(C,N) precipitates, particularly strain-induced, which are finer than ~ 100 Å retard recrystallization of austenite, perhaps by increasing the incubation period for nucleation or by retardation of recrystallized grain boundary migration after the formation of a viable nucleus.

Similar suggestions have been made for the effect of vanadium.

Many investigators have attributed the effect of niobium on the retardation of austenite recrystallization to solute drag due to niobium in solution pinning the dislocations(103,110,125,132,133,143-145). For example LeBon et al(77) and Cordea et al(121) showed that, when niobium in solution was reduced either by a low reheating temperature or by pre-precipitation prior to deformation, the retarding effect of niobium on recrystallization decreased. They suggested that recrystallization was retarded only when niobium was in solution. Coldas et al(132) studied the effect of niobium on the variables in Avarmi's equation(which states the dependence of the recrystallized volume fraction on the time elapsed from the start of recrystallization) and after comparing the effects in plain-carbon steel and niobium bearing steel they concluded that delayed recrystallization of austenite in the niobium bearing steel was due to niobium in solution. Jonas and Weiss(146) superimposed the curves for precipitation kinetics of Nb(C,N) and recrystallization kinetics, as shown in fig. 26, and they showed that niobium retarded recrystallization of austenite even before precipitation of Nb(C,N) started and therefore they suggested that niobium in solution does retard recrystallization. Such an interpretation may be questionable because of the doubtful accuracy of the precipitation kinetics. Also the results of LeBon et al(77) and Cordea et al(121) support the solution theory, but have been questioned on the grounds that a reduction in dissolved niobium will decrease the niobium available for strain induced precipitation and this may decrease the retarding effect on recrystallization.

On the other hand, many investigators have suggested that retardation of recrystallization by niobium(102,103,105,111,119,120,142,143,147-149) or vanadium(107,115,140,141) is due to strain induced precipitation pinning the dislocations and substructure produced by deformation. In most of the investigations, precipitation on dislocations and substructure have been observed after deformation and this has been shown to retard the recrystallization of austenite. Sekine and Marayama(108) compared the fraction recrystallized with niobium precipitated and niobium in solution and observed better correspondence with the amount of niobium as Nb(C,N) precipitated in the austenite matrix. A similar treatment has been made by LeBon et al(126) and Jonas(131) and their results also showed a better agreement of retardation of recrystallization with the niobium as strain induced Nb(C,N). In fact they showed that the maximum rate of precipitation coincides with the most effective recrystallization inhibition. LeBon et al(126) suggested that strain induced precipitation of Nb(C,N) existing before deformation does have an inhibiting effect on static recrystallization at temperatures below ~ 900°C, but that this inhibition is not so strong as in the case of strain induced precipitation occurring during the incubation period of an isothermal deformation and recrystallization treatment. Davenport et al(144) indicated that the important factor in optimizing the precipitate retardation effect is not only one of volume fraction, but also that the particle size should not exceed a critical size. From their experimental results they found the critical precipitate size to be ~100 Å. White et al(115) found an inhibition of recrystallization when precipitation commenced,and therefore concluded that the same particles were responsible for the two events. These precipitates would be ~100 Å diameter. Although Davenport et al showed that the retardation of recrystallization to be due to the pinning of the deformation substructure by strain induced precipitates of Nb(C,N) and they also suggested that these observations do not provide unequivocal proof of the precipitate pinning mechanism, as it is possible that the fundamental retardation process involves some form of substitutional solute-dislocation interaction and that the Nb(C,N) precipitation effect is merely a secondary process which can occur as a result of the initial stabilization of the substructure.

CHAPTER 9

TRANSFORMATION OF AUSTENITE TO FERRITE IN MICROALLOYED STEELS

9.1 Introduction

Because the transformation of austenite to ferrite occurs during cooling and because the austenite morphology prior to transformation affects the ferrite grain size produced, it has been possible to obtain finer ferrite grain sizes, mainly through the control of the austenite grain morphology. However, there are other factors which, if associated with the conditioning of the austenite, can enhance the ferrite grain refinement. These are mainly transformation temperature, cooling rate after transformation, coiling temperature in coiled products, and the composition of the steel.

To achieve optimum ferrite grain refinement it is necessary to have a maximum ferrite nucleation rate coupled with a minimum grain growth rate of the ferrite during and after transformation. Thus the conditioning of austenite is generally aimed at achieving a maximum ferrite nucleation rate through the control of the composition, second phase particle distribution, and cooling rate, and minimum growth of ferrite grains during transformation.

9.2 The Mechanism of Ferrite Nucleation

Austenite grain boundaries are the principal nucleation sites and therefore austenite grain size plays an important role in the transformation to ferrite. However, in thermo-mechanically worked austenite, not only is the austenite grain boundary area increased by grain elongation or serrated (bulged) grain boundaries, but also nucleation occurs within the austenite grains, thereby increasing the nucleation rate and refining the subsequent ferrite grain size.

On many occasions it has been noted that deformation not only leads to intragranular nucleation but also enhances nucleation at the austenite grain boundaries(94,114,126,152). Priestner(153) for example showed that the frequency of ferrite nucleation on austenite grain boundaries did not increase with rolling strain of up to 35 % in a niobium steel but that the grain refinement obtained was due to increased intragranular nucleation. The various intragranular nucleation sites for ferrite were observed to be dislocations and dislocation substructures(94,153,154), deformation bands(75,94,154,155), second phase particles(139,154) such as carbides and nitrides, and austenite twins(154).

With regard to nucleation on substructures, Priestner and de los Rios(156) postulated that the substructure should be unrecovered, as recovery prior to transformation removes the ferrite nucleating ability of the substructure, although a substructure of dislocation cells can enhance nucleation and yet is produced by a recovery process.

Kozasu et al(94) showed that deformation bands are important as nucleation sites for ferrite grains but suggested that not all deformation bands have the same ferrite nucleation potential.

Although Walker and Honeycombe(154) showed evidence for nucleation of ferrite grains on second-phase particles, Roberts et al(128) suggested that the evidence for such an effect is unconvincing. It is frequently observed that ferrite can nucleate at certain non-metallic inclusions, particularly MnS.

It has also been suggested(126) that ferrite can nucleate at the ferrite-unrecrystallized austenite interface. LeBon et al identified such a mechanism as "cascade" nucleation whilst Walker and Honeycombe(154) identified it as sympathatic nucleation on pre-existing ferrite.

9.3 Effect of Niobium and Vanadium on the Transformation of Austenite

It is well known that niobium is very effective in refining the ferrite grain size in controlled rolled steel and there have been many studies of the effect of niobium on the transformation process of austenite to ferrite-pearlite(70,94,110,139,157-159). In general dissolved niobium depresses the transformation temperature, i.e Ar_3 temperature of undeformed austenite, but an early investigation of Fletcher et al(71), on the effect of niobium on the hardenability of 0.33 % C-0.65 % Mn-0.2 % Si after various reheating temperatures, showed that at high reheating temperatures i.e above the austenite grain coarsening temperature, the hardenability increased with an increase in niobium content. They suggested that this is related to the coarser austenite grain size. Gray$^{(159)}$ on the other hand showed that 0.05 % Nb can depress the austenite-ferrite transformation temperature by $\sim 55^{\circ}C$ in a steel cooled at $\sim 5^{\circ}C/sec$, and that such an effect is equivalent to the benefit gained from 1.0 % additional alloying with either chromium or manganese.

Transformation start temperatures are also dependent on the austenite grain size. An increase in austenite grain size depresses the Ar_3 temperature$^{(110)}$, as shown in fig. 27, which also shows that 0.03 % Nb depresses the transformation temperature compared with plain-carbon steel, particularly at the coarser austenite grain sizes. When the austenite grain size is fine, niobium does not depress the Ar_3 because such fine austenite grain sizes are the result of low reheating temperatures and therefore very low amounts of dissolved niobium. Meyer et al$^{(139)}$ studied the effect of up to 0.12 % Nb after reheating at 900, 1100 and 1250°C, and showed that at high reheating temperatures increasing dissolved niobium retarded transformation. At low reheating temperatures the transformation was accelerated due to ferrite nucleation on undissolved carbides, a low dissolved niobium and a fine austenite grain size. They concluded that niobium was similar to molybdenium in its effect on hardenability and the formation of acicular structures during cooling. Fisher and Geils$^{(158)}$, in fact compared the retarding effect of niobium on transformation with a similar effect observed for boron and suggested that these elements retard ferrite nucleation by either lowering the rate of diffusion of carbon away from the ferrite nuclei or by affecting ΔF_0, the free energy of nucleation.

Like niobium, vanadium also increases the hardenability of plain-carbon steels$^{(160-162)}$. However, the effect of vanadium on hardenability is low compared with that of niobium.

9.4 Effect of Thermo-Mechanical Treatment on the Transformation of Austenite

9.4.1 Effect of reheating temperature

Increasing reheating temperature coarsens the austenite grain size and also increases the alloying elements in solution. The latter effect is particularly important for niobium steels. Both effects decrease the Ar_3 temperature(70,94,110,139,157-159). It is particularly important that V(C,N) dissolves at much lower temperatures than Nb(C,N).

It has been suggested(130) that if initial reheating leads to mixed austenite grain sizes these are not easily removed by controlled rolling; and therefore result in mixed ferrite grain sizes which are deleterious to toughness. There is some doubt as to the effect of heavy reductions on the recrystallization of initially mixed austenite grain sizes.

9.4.2 Effect of rolling temperature

Depending on the amount of deformation, the rolling temperature will affect the austenite grain morphology and therefore alter the transformation characteristics. Three temperature ranges can be identified according to their effect on the austenite grain morphology.

(i) Rolling in the temperature range where complete recrystallization occurs:
This refines the austenite grain size and increases the Ar_3 temperature. However, such effects can be observed only if there is no substantial grain growth of the austenite prior to transformation. Additions of alloying elements such as niobium and vanadium can affect the refinement of the austenite due to their effects on recrystallization and grain growth. Recrystallization produced uniform austenite which leads to a uniform ferrite grain size. Such structures have been shown to have improved toughness.

(ii) Rolling in the temperature range where partial recrystallization occurs:
Partial recrystallization of austenite results in a non-uniform ferrite nucleation rate leading to mixed ferrite grain sizes(89,103,163-165). Mixed ferrite grain size structure are deleterious to toughness.

(iii) Rolling in the temperature range where there is no recrystallization:
This increases the Ar_3 temperature(130,157), due to an increased nucleation rate at the austenite grain boundaries, and

also due to intragranular nucleation. Deformation in this temperature range leads to a high nucleation rate and therefore refines the ferrite grain size despite the higher transformation temperature. Additions of niobium and vanadium also retard ferrite grain growth and thus help to maintain the fine ferrite structure even after completion of transformation.

9.4.3 Effect of deformation

As outlined previously, the effects of deformation on the transformation of austenite will be very dependent on the temperature range in which deformation occurs. It has been shown(157) that if increased deformation leads to recrystallization of austenite then the transformation of austenite is retarded. However, increased deformation below the recrystallization temperature increases the Ar_3 temperature and accelerates transformation(75,94,157,166-168) due to increased ferrite nucleation, fig. 28. Thus an increase in deformation below the recrystallization temperature increases the effective austenite grain boundary area, which enhances nucleation and therefore refines the ferrite grain size, figure 29(94). The density of deformation bands increases with increasing deformation, and this leads to an increase in the ferrite nucleation rate. It has been shown(94) that the density of deformation bands depends primarily on the amount of deformation and is little affected by temperature and strain rate.

9.4.4 Effect of cooling rate

It is well established that an increase of the cooling rate lowers the Ar_3 temperature and thus increases the nucleation rate of ferrite(90,99). Many investigators(83,90) have observed ferrite grain refinement due to an increased cooling rate and a lower Ar_3 temperature. To maintain a fine ferrite grain size, it is desirable in hot rolled strip to coil after the completion of transformation, as coiling after partial transformation may lead to ferrite coarsening due to the very slow cooling rate after coiling.

9.5 Effect of Austenite Grain Size on the Ferrite Grain Size

It is well known that the ferrite grain size depends on the austenite grain size because austenite grain boundaries are the principal nucleation sites. Because of this relationship it has been possible to refine the ferrite grain size by refining the austenite grain size, for example in normalizing. In order to achieve increased refinement of austenite, use of second-phase particles such as AlN has been made to restrict grain growth during reheating and soaking treatments. Similarly additions of niobium were also made to refine the ferrite grain size of normalized carbon steel.

Webster and Woodhead(70) studied the effect of austenite grain size on the ferrite grain size after reheating at various temperatures in plain-carbon steel which was closely related to the austenite grain size. On the other hand, in the niobium steel the ferrite grain size increased with austenitizing temperature but was rather finer than for the plain-carbon steel even when the latter had the finer austenite grain size. They(70) suggested that in niobium steels undissolved particles at the austenitizing temperature exerted a direct refining effect on ferrite grain size, independent of any effect they may have on the austenite grain size. A similar effect of additional ferrite grain refinement due to niobium and vanadium additions even at identical austenite grain size has been observed by Sekine and Maruyama(108). Kozasu et al(94) determined the ratio of the linear-intercept grain diameter of ferrite to that of austenite, which was 2.3, and suggested that this is in agreement with the results of Maruyama et al(169).

It has been noted(94) that deformation refines the ferrite grain size although the austenite grain boundary area per unit volume does not change. High deformation leads to the formation of deformation bands, and their density increases with increasing deformation. Deformation bands are also known to nucleate ferrite, therefore Kozasu et al(94) included deformation bands in their calculation of the effective austenite interface area (S_v), which was ultimately related to the ferrite grain size. They found that for a fixed S_v, deformation below the recrystallization temperature refined the ferrite more effectively. Roberts and Ahlblom(128), however, suggested that the relationship between S_v and nucleation frequency for ferrite is not linear when S_v becomes very large, and therefore it would not be possible to reduce the austenite grain size indefinitely and expect to obtain ever finer ferrite.

CHAPTER 10

PRECIPITATION IN MICROALLOYED STEELS

10.1 Niobium Steels

Niobium is added to C-Mn steels mainly to refine the ferrite grain size and also to impart some precipitation strengthening due to formation of semi-coherent Nb(C,N) precipitates in ferrite. Niobium is known(170) to form an isomorphous series of solid solutions between its carbide and its nitride, and Nb(C,N) has a f.c.c. structure with a lattice parameter intermediate(110) between that of NbN(0.442 nm) and NbC(0.447 nm). Gauthier and LeBon(171) suggested that Nb(C,N) is carbon rich and very close to the carbide NbC. However, Hoogendoorn et al(172) observed an increase of nitrogen in Nb(C,N) with increasing precipitation temperature. Also the composition of Nb(C,N) depends on the composition of the alloy(173).

Precipitation of Nb(C,N) occurs in austenite, during the transformation of austenite to ferrite, and in the ferrite. The preferential nucleation sites for Nb(C,N) are dislocations(125), existing nuclei(45,174), subgrain and grain boundaries(103,125).

10.1.1 Precipitation in austenite

It is well known(83,175) that precipitation of Nb(C,N) in austenite occurs as coarse particles which do not contribute to strengthening and will reduce the subsequent precipitation strengthening which can otherwise be achieved.

Due to the small number of lattice defects in undeformed austenite, precipitation of Nb(C,N) occurs very slowly(77,139) and the amount of such precipitation is very small. The amount precipitated depends on the cooling rate(110,176), and fast cooling lowers the amount of Nb(C,N) precipitated in austenite. However, deformation of the austenite accelerates the precipitation of Nb(C,N)(103,177) which is attributed to the increase in lattice defects and the diffusion coefficients(177). After deformation, nucleation of Nb(C,N) occurs primarily on the sub-grains(103,125).

The precipitation kinetics of Nb(C,N) in undeformed and deformed austenite have shown(178,181) that the progress of precipitation is characterized by C-curve behaviour with a nose temperature around about 950°C. This is due to the both changes in the degree of supersaturation and diffusivity of niobium in austenite, associated with temperature. Deformation of austenite reduces the incubation time for precipitation and therefore moves the C-curve to shorter times(75,110,126,181). LeBon et al(126) showed that strain induced precipitates have mean sizes in the range of 30-50 Å diameter, in contrast with 1000-3000 Å diameter particles obtained after isothermal holding of undeformed austenite.

Watanabe(180) studied the effect of molybdenum, nitrogen and aluminium additions on the kinetics of precipitation of Nb(C,N) in austenite, and found that an addition of molybdenum (0.29%) moved the C-curve to lower temperatures and shorter times. However, in deformed austenite, 30% reduction, molybdenum decreased the precipitation rate at 925°C. An increase in nitrogen from 0.006% to 0.010% increased the precipitation rate in the temperature range 870°-925°C. On the other hand an increase in aluminium from 0.025% to 0.047% did not affect the precipitation kinetics of Nb(C,N) significantly.

The precipitation strengthening contribution due to Nb(C,N) therefore varies in controlled rolled steels, depending on the rolling schedule used. Morrison et al(182) have pointed out that only about half the maximum hardening effect of Nb(C,N) precipitation is obtained in controlled steels.

10.1.2 Precipitation during the austenite → ferrite transformation

Precipitation of Nb(C,N) also occurs during the austenite → ferrite transformation(175,183,184), and is characterized by interphase precipitation. Precipitates formed during transformation are in the size range 50-100 Å(175), and do not impart the maximum strengthening which can be obtained from precipitation of Nb(C,N). The intensity of precipitation strengthening depends on the size, interparticle spacing and volume fraction of precipitates, and these tend to vary with transformation temperature(175) and cooling rate(175,186). A fast cooling rate decrease the amount of niobium precipitated(186) and lowers the transformation temperature, resulting(175) in a closer spacing of precipitates and a decrease in precipitate size.

10.1.3 Precipitation in ferrite

The remnant niobium in solution after transformation will precipitate in the ferrite. The preferential nucleation sites for such precipitation are dislocations in the ferrite. There is an orientation relationship between Nb(C,N) and ferrite matrix(176);

$$\{100\} \quad // \quad \{100\}_{Nb(C,N)}$$

$$\langle 011\rangle \quad // \quad \langle 010\rangle_{Nb(C,N)} .$$

It is generally accepted that a significant strengthening effect is obtained when Nb(C,N) precipitates semi-coherently in the ferrite. Also the size of the Nb(C,N) precipitates are extremely fine (< 50 Å), and thus are very effective strengtheners.

Hoogendoorn et al(110) studied the effect of the addition of vanadium to 0.03% Nb steel on the precipitation of Nb(C,N) in ferrite during cooling, and found that vanadium increases the amount of precipitation, possibly due to a complete series of solid solutions existing between Nb(C,N) and V(C,N) (201).

10.1.4 Precipitation strengthening

Because of the higher precipitation temperature of Nb(C,N), much of it tends to precipitate in austenite, particularly during controlled rolling, and therefore very small amounts of niobium remain in solid solution to precipitate in ferrite. The amount of niobium precipitated in ferrite, and hence the precipitation strengthening, is greatly influenced by solution temperature, thermo-mechanical treatment and transformation temperature. In order to achieve optimum precipitation strengthening from Nb(C,N) it is desirable:-

(a) to soak the steel at temperature where complete solution of Nb(C,N) can occur(133,161),

(b) to suppress the precipitation of Nb(C,N) in austenite so that more niobium is available to precipitate in ferrite,(103,175)

(c) to control the transformation temperature so as to control the size and volume fraction of precipitate formed in ferrite,(187)

and (d) to control the coiling temperature of strip products to prevent the overaging of precipitates.

Decreasing the soaking temperature from 1300°C to 1200°C decreased the yield strength increment due to 0.036% Nb from 115 MPa to 55 MPa(133,161). At high finishing temperature i.e. $> 1050^{\circ}$C, very little precipitation of Nb(C,N) occurs in austenite and therefore finishing at high temperature leads to maximum precipitation strengthening in niobium steel(103,175). Irvine et al(83) investigated the effect of holding at 800°C and 900°C after 50% deformation on the change in precipitation strengthening in 0.03% Nb steel, and found that a holding period of 15 min. at 900°C lowered the precipitation strengthening contribution due to Nb(C,N) by at least 75 MPa.

Gray(187) suggested that the size of the precipitate formed in ferrite decreases with decreasing transformation temperature. However, he noted that there is an optimum transformation temperature for strengthening, as at higher temperatures the precipitates are too coarse whilst at lower temperatures precipitation of Nb(C,N) is incomplete.

10.2 Vanadium Steels

Vanadium, due to its relatively low solution temperature compared with niobium, does not precipitate in austenite to the same extent as niobium and hence imparts significant precipitation strengthening. Vanadium forms both carbides and nitrides but there are different opinions as to whether these form continuous solid solutions in steel. However, it is known(188,189) that vanadium carbides and nitrides are mutually soluble and therefore it is appropriate to consider the vanadium compound as V(C,N), with varying carbon and nitrogen content depending on the composition of the steel. Due to the variation of carbon and nitrogen in V(C,N), the lattice parameter is likely to vary, and it has been suggested(190) that the lattice parameter decreases with increasing nitrogen content.

10.2.1 Precipitation in austenite

Because of the high solubility, precipitation of V(C,N) generally does not occur in undeformed austenite(175,191). However, it should be noted that this will be dependent on the composition of the alloy(189,192,193), high vanadium and nitrogen leading to precipitation of V(C,N) in austenite. It has been suggested(135,142) that V(C,N) does not precipitate in austenite during hot rolling. Jones and Burton(192) indicated that precipitation of vanadium is likely to occur at the lower end of the austenite temperature range, whilst Baker(194) showed that the rate of V(C,N) precipitation during controlled rolling of 0.05-0.1% V, 0.01% N steel in the temperature range 800-950°C is too slow for the theoretical volume fraction to be formed. However, much evidence for strain induced precipitation of V(C,N) in austenite during rolling at low temperatures has been obtained(83,140). Inspite of this it should be noted that the amount of V(C,N) precipitated in austenite is low compared with Nb(C,N), and therefore most of the vanadium should be available for precipitation during the transformation or in the ferrite. The strain induced precipitation of V(C,N) has been observed only when the nitrogen contents are higher than normally used in structural steels.

10.2.2 Precipitation during the austenite → ferrite transformation

Vanadium precipitates faster during the austenite → ferrite transformation than in either austenite or ferrite. Opinions about the mechanism of nucleation for interphase precipitation are divided, and many workers have suggested(175,195-197) that nucleation occurs at the austenite → ferrite interface due to the lower solubility of V(C,N) in ferrite than in austenite. Others(198) suggest that nuclei are not formed until the austenite → ferrite interface has moved forward into the receding austenite, thus resulting in homogeneous nucleation in ferrite. On the other hand, Suzuki and Tanino(199) proposed that the dislocations produced by the transformation nucleate vanadium precipitates heterogeneously, and this is more likely than homogeneous precipitation.

Batte and Honeycombe(200) examined the size and dispersion of V(C,N) in a series of Fe-V-C alloys after isothermal transformation at 600°-800°C. They showed that the particle size distribution and the inter-band spacing increases with increasing transformation temperature. In identical transformation conditions they also found that the dispersion became coarser as the concentration of (V+C) decreased i.e. as the volume fraction of vanadium carbide was reduced. An increase in cooling rate has been found to produce a finer dispersion of precipitates. Such an effect of cooling rate(114,202) has been attributed to the decrease in transformation temperature. For an identical cooling rate, Roberts(114) found finer precipitates in hot-rolled steel than in normalized steel and suggested that the reason for this is not understood. Bucher and Grozier(202) also found similar results in hot-rolled and normalized steels. However, too fast a cooling rate can suppress interphase precipitation, and thereby increase the subsequent precipitation in ferrite either during cooling or during tempering.

Additions of alloying elements such as manganese, chromium and nickel displace the T.T.T. curve to longer times and therefore lead to a coarser dispersion for a given isothermal temperature because of the slower reaction which allows more time for diffusion to occur(203). On the other hand, additions of silicon and aluminium, which raise the T.T.T. curve and by virtue of austenite grain refinement displace it to shorter times, can accelerate the interphase reaction with a refinement of the precipitates(204). However, during continuous cooling, manganese has been found(139) to refine V(C,N) precipitates and this effect has been attributed to the low transformation temperature when manganese is present.

10.2.3 Precipitation in ferrite

It is generally believed(120,175,191,205) that most of the vanadium precipitates during the austenite → ferrite transformation and therefore little or no precipitation occurs in ferrite. It is possible that a fast cooling rate may prevent precipitation during transformation, hence allowing it to occur in ferrite after the transformation. For example Stephenson et al(206) showed the existence of very fine particles of V(C,N) in ferrite. They suggested that these precipitates were coherent with the matrix and hence were precipitated in the ferrite. On the other hand, Heikkinen and Boyd(140) suggested that precipitation of V(C,N) in ferrite proceeds mainly by the growth of existing nuclei.

10.2.4 Precipitation strengthening

Although it has been suggested that vanadium can precipitate as V(C,N) on many occasions precipitation strengthening derived from vanadium has been differentiated in terms of that due to VN and that due to VC. In a recent review Morrison et al(182) have noted that strengthening which can be achieved by precipitating VC is 1000 MPa/%V whilst that due to VN is 3000 MPa/%V. The higher contribution to the yield strength from VN compared with VC is due to the difference in the strain fields developed around VN(207).

To achieve the high volume fraction of VN and therefore high increment in strength, the amount of nitrogen in vanadium steels has been increased. Stephenson et al(206) observed an increase in yield strength by about 105 MPa in as rolled 9 mm. plate when combined additions of 0.05%V and 0.014%N were made. They noted that this increment in strength was greater than that produced by the sum of the single additions. Many other workers have also shown the benifit of an increase in nitrogen on the yield strength in vanadium steels(99,115,135). Undissolved aluminium nitrides, which can lower the amount of nitrogen available for vanadium nitride precipitation tend to lower the strength(135,208). On the other hand, additions of manganese have been shown to increase the solubility of vanadium nitrides in austenite(45,209) and therefore produce a higher volume fraction of VN in the ferrite and an increase in yield strength. Manganese however, lowers the Ar_3 temperature and this can lead to finer precipitation and thereby an increase in the intensity of precipitation strengthening. Meyer et al(209) observed an increased precipitation strengthening due to additions of silicon, and suggested that this may be due to an increase in the solubility of VN/VC in austenite, or a decrease in the solubility in ferrite. Suzuki et al(210) found the effect of manganese and nickel on precipitation strengthening was surprisingly large when additions of manganese or nickel were made. They suggested that the manganese addition suppresses the growth of precipitates by lowering the Ar_3 temperature and hence results in finer precipitation. Nickel on the other hand, markedly accelerates the nucleation, but retards the growth of VC by increasing the degree of supersaturation of VC in ferrite as well as by lowering Ar_3 temperature.

Fukuda et al(89) showed that a high finish rolling temperature in a vanadium steel leads to remarkable strengthening, and indicated that this is due to precipitation at low temperatures. They mentioned that such precipitation strengthening was associated with severe embrittlement. On the other hand, at low finish rolling temperatures (700 to 800°C) at which precipitation of V(C,N) occurs at high temperature, provides significant strengthening without loss of toughness. They suggested that such practice gave virtually no harmful effects of vanadium. On the other hand, Chapman and Philips(211), and Irani et al(212) also observed an improvement in the toughness properties due to low finishing temperatures, but they attributed this effect to the refinement of the ferrite grain size rather then to precipitation at high temperatures. Cooling rate can affect the intensity of precipitation strengthening; too slow cooling leading to the formation of coarse precipitates whilst too fast cooling rate leads to the suppression of precipitation. Both effects reduce precipitation strengthening. Because the distribution of precipitates is dependent on the cooling rate, it is necessary to optimise this in order to achieve maximum precipitation strengthening(213). Particularly in coiled strip products, suppressed precipitation due to fast cooling prior to coiling can result in subsequent precipitation in the ferrite at low temperatures in the coil. The size and distribution of precipitates is governed by the coiling temperature; too high a coiling temperatures resulting in overaging whilst too a low coiling temperature leads to incomplete precipitation(208).

CHAPTER 11

EXPERIMENTAL TECHNIQUES

11.1 Manufacture of Experimental Steels

Three series of steels, to a base composition of 0.07/0.09% C, 0.8/1.0% Mn, 0.2/0.4% Si, 0.02/0.05% Al, were made with varying additions of niobium or vanadium. The niobium steels were made with nominally low nitrogen contents of 0.006/0.009%, whilst the vanadium steels were made at both the low nitrogen content and at a higher nitrogen content of 0.015/0.02%. In addition, two steels containing additions of 0.03/0.05% Nb with 0.10/0.12% V were made at both nitrogen levels. Finally a very low carbon-nitrogen steel was made containing 0.25/0.30 % Nb in order specifically to investigate the effect of niobium in solution on the recrystallization of austenite. The analyses of these experimental steels are given in Table 1.

Each melt weighed about 15 Kg, and was poured into one ingot of dimensions 77 mm x 77 mm x 450 mm. In order to maintain a constant base composition to which the various microalloying additions were made, the following standardised steel making procedure was developed. The base materials were Swedish iron of very low residual content, high carbon ferro-manganese, ferro-silicon and aluminium. The appropriate carbon content was achieved by adding the required amounts of high and low carbon ferro-manganese. All the alloys, except that containing very low carbon and nitrogen with niobium, were air melted in an induction furnace, using the following standard technique:-

(a) Melt Swedish iron and slag off.
(b) Deoxidise with aluminium, repeating slag off.
(c) Add ferro-manganese and ferro-silicon.
(d) Adjust temperature to 1570/ 1600°C.
(e) Add microalloying addition as appropriate ferro-alloy to ensure effective solution.
(f) Sample for chemical analysis.
(g) Teem into ingot mould.

The microalloying additions were allowed 3 minutes to dissolve before teeming at a temperature of about 1570°C, which resulted in a high and reproducible recovery. In order to minimise piping in the ingot, an exothermic anti-piping compound was used. Inclusion assessments revealed an adequate level of steel cleanness.

11.2 Initial Rolling prior to Experimental Deformation Programme.

In order to remove the ingot pipe, 60mm was cut from the top of each ingot, and the ingot surfaces were scalped to provide a clean, defect-free surface for further processing. The ingots were then rolled to either 20mm square or 20mm diameter stock material. For the rolling experiments these sections were further reduced in section to 10mm and 6.5mm thick which respectively were used for the experimental reductions of 50% and 20% in one pass. This allowed a final thickness of 5mm after the experimental rolling schedules, thus allowing a constant cooling rate to be achieved after rolling.

11.3 Experimental Programme of Thermo-Mechanical Treatments.

Prior to the experimental thermo-mechanical treatments, all the steels were solution treated for 15min at 1300°C, using an argon protective atmosphere. It was ascertained that this produced virtually no decarburization. During homogenization at 1300°C, much of the carbo-nitride in the niobium steels dissolved but was reprecipitated during air cooling to give a fine uniform distribution of particles. Every specimen thus gave a uniform initial microstructure. In some of the high niobium steels, coarse carbo-nitrides remained undissolved; but in the low nitrogen-vanadium steels all the carbo-nitrides were expected to be dissolved on the basis of published solubility data. In the high nitrogen- high vanadium steels however, there was some undissolved vanadium nitride due to the lower solubility of vanadium nitride compared with vanadium carbide.

11.3.1 Austenite grain coarsening studies

For austenite grain coarsening studies, 5mm thick slices were cut from the initial stock material after solution treatment for 30min at 1300°C.

The temperatures used for grain coarsening studies were 1000°C, 1050°C, 1150°C, 1250°C and 1300°C. The specimens were soaked for 30min at the reheating temperature under an argon protective atmosphere, after which the specimens were transfered to another furnace maintained in the temperature range 900-920°C and held for 5min followed by quenching in water. Holding at 900-920°C for 5min prior to quenching led to either segregation of impurities or precipitation of alloying carbo-nitrides at the austenite grain boundaries, which clearly revealed the grain boundaries on etching. It was confirmed that holding at 900-920°C for 5min did not change the austenite grain size.

11.3.2 Experimental hot rolling programme.

A flow chart of the hot rolling experiments is shown in Fig.30, illustrating the different variables which were investigated. The reheating temperatures for rolling were 1300°C, 1150°C and 1000°C, argon atmospheres being used to minimise oxidation and decarburization. A constant reheating time of 30min was used. Rolling was carried out in three temperature ranges, namely 1200/1250°C, 900/950°C and 700/750°C. Reheating at 1300°C allowed all three rolling temperature ranges to be used, but only the two lower temperature ranges were possible with reheating temperatures of 1150°C and 1000°C. Prior to rolling, the temperature of each slab was stabilised in a furnace held at the appropriate rolling temperature. Rolling reductions of either 20% or 50% in thickness were carried out in one pass at each rolling temperature, and immediately after rolling a specimen was hot sheared and quenched into iced brine to reveal the austenite grain structure. The remainder of the slab was then held for 100s or 1000s at temperatures of 1200/1250°C, 900/950°C or 700/750°C according to the rolling temperature used:-

Rolling Temperature	Holding Temperatures
1200/1250°C	1200/1250°C; 900/950°C; 700/750°C
900/ 950°C	900/950°C; 700/750°C
700/ 750°C	700/750°C.

After the appropriate holding time, the slab was hot sheared into two pieces, one being iced brine quenched to reveal the austenite grain structure whilst the other was cooled in a sand bed to allow transformation of the austenite to occur at a cooling rate of approximately 400°C/min; i.e. equivalent to air cooling a plate about 12mm thick. The shearing affected a region about 2mm from the sheared edge and as the specimens were 30mm long x 20mm x 5mm; this did not materially affect the structure of the bulk of the specimen. Initial experiments showed that the shearing could be accomplished in less than 20s., so that very little loss of temperature occurred.

The rolling mill used for this experimental work was a two high mill of roll diameter 260mm. The rolling speed was maintained at 10 r.p.m. throughout the experimental programme, which gave a strain rate of 3.7/s estimated from rolling theory with sticking friction(214) as:-

$$\dot{\varepsilon} = \frac{V}{\left[R(h_o - h_f)\right]^{1/2}} \cdot \ln\frac{h_o}{h_f} \qquad \text{-----------------------} \quad (59)$$

where $\dot{\varepsilon}$ = Strain rate,

V = Peripheral speed of rolls,

R = Roll radius,

h_o = Initial slab thickness,

and h_f = Final slab thickness.

This strain rate was similar to that for plate rolling but rather low compared with modern hot-strip rolling. However, it was necessary to use such a low strain rate to allow the handling of the small samples used. Also, it minimised adiabatic heating during rolling.

11.3.3 Experimental press forging programme

The effect of deformation on the austenite to ferrite transformation in the base steel and 0.07% Nb and 0.14% V steels containing low and high nitrogen, was studied. The deformation was carried out by press forging at a equivalent strain rate to that used in the rolling experiments. The plattens of the forging press were heated to about 500°C to minimise chilling of the extremities of the specimen. The specimens used in this experiment were machined from the solution treated initial stock material to a size of 15mm diameter x 20mm high. Each specimen was heated at only the one reheating temperature of 1150°C for 30min. After 50% deformation by thickness, specimens were held in a salt bath maintained at 700°C for periods of 5s, 10s, 50s or 100s and then quenched into iced brine. In order to make a comparative study of the effect of deformation on the isothermal transformation with that of undeformed specimens, isothermal transformation under similar conditions without deformation was also carried out.

11.4 Metallographic Techniques

For austenite grain coarsening studies, specimens were cut in two transversely and the new surface used for metallographic examination. On the other hand, longitudinal sections were used for recrystallization and transformation studies in the rolled specimens. All the specimens were mounted in cold setting resin and polished by standard methods. The austenite grain boundaries in the quenched specimens were revealed by etching in:-

(a) 2% Nital; or

(b) a saturated solution of picric acid in alcohol containing a small addition of the wetting agent "Teepol" ; or

(c) a saturated aqueous solution of picric acid containing 2% ammonium persulphate and 6 drops of "Teepol" per 100 cm^3.

The ferrite grain structure in the sand cooled specimens and partially transformed specimens was revealed by etching in 2% Nital.

Quantitative metallographic methods were used to determine the austenite and ferrite grain sizes. The mean linear intercept method for grain size was used, where the mean linear intercept, $\bar{d}$, is given by :-

$$\bar{d} = \frac{L}{N} = \frac{1}{N_L} \qquad \text{------------------------------------}(60)$$

where N = the number of grain boundaries or grains intersecting in a linear traverse of length, L

and N_L = the number of grain boundaries or grains intersecting unit length of linear traverse.

Some 250 grains were measured to give $\bar{d}$ values with a relative error of ± 5 % with 95 % confidence. In the case of unrecrystallized austenite, which showed an elongated morphology, measurements were made parallel and perpendicular to the rolling direction in order to minimise the error due to anisotropy.

The determination of the percent recrystallization of the austenite in quenched specimens was carried out by point counting. The number of points falling in recrystallized austenite, P_R , was determined using a total number of points laid down of $P \simeq 600$. This led to a relative error of between ± 1 % and ± 6 % depending on the actual value of the percent recrystallization, which is given by :-

$$\% \text{ Recrystallized} = \frac{P_R}{P} \times 100. \qquad \text{------------------------}(61)$$

A similar method was used to determine the percent transformation in isothermal transformation studies of austenite to ferrite. In this case the number of points falling in the ferrite grains, P_F , or martensite, P_M , were determined using a total number of points laid down of $P \simeq 600$. This will give a relative error in the of ± 1 % to ± 6 % depending on the percent transformation. The percent transformation was given by :-

$$\% \text{ Transformation} = \frac{P_F}{P} \times 100 \qquad \text{------------------------}(62)$$

$$\text{or} \qquad = 100 - \left(\frac{P_M}{P} \times 100 \right) \qquad \text{--------------------}(63)$$

11.5 Hardness Measurements

Standard Vickers hardness tests were carried out on specimens which were sand cooled and comprised ferrite-pearlite, acicular ferrite or bainitic microstructures. In addition, the hardness of phases in selected specimens was investigated by means of microhardness techniques.

11.6 Electron Microscopy

Electron microscopical examination was carried out only on a limited selection of specimens. Carbon extraction replicas and thin foils were used. In order to extract fine precipitates, a light etch in 2 % Nital coupled with a thin carbon coating was found to give satisfactory results. Replicas were extracted by final etching in 6 % Nital. To prepare thin foils 3mm diameter rods were machined out of the specimens and then sliced, ground to about 0.25mm thickness and polished in a solution of 5 % perchloric acid in methanol at – 40°C by using a Struers automatic polishing equipment.

CHAPTER 12

EXPERIMENTAL RESULTS

12.1 Austenite Grain Coarsening

12.1.1 The effect of niobium

The variation of austenite grain size with temperature is listed in Table 2 and these results are presented graphically in Fig. 31. All the niobium steels had consistently finer grain size than the base steel below 1200°C. However, at 1300°C, the 0.07% Nb and 1.03% Nb steels showed coarser grain sizes than the base steel. This was due to abnormal grain growth in the 0.07% Nb and 1.03% Nb steels. Such an effect however was found to decrease as the niobium content was increased from 0.16% Nb to 0.73% Nb, i.e. up to the stoichiometric ratio.

Fig. 32 shows that additions of niobium refined the austenite grain size. Up to 1050°C, niobium contents as low as 0.07% refined the austenite grain size to about 10 μm, and any further increase in niobium did not cause any further refinement of the grain size. In the temperature range of 1150°C to 1200°C there was progressive grain refinement with increasing niobium contents up to about 0.46% but higher niobium contents did not further refine grain size.

Fig. 33 shows the effect of niobium on the austenite grain coarsening temperature. It can be seen that the austenite coarsening temperature increased up to 1200°C when the niobium content was increased to 0.46%.Nb contents higher than 0.46% decreased the austenite grain coarsening temperature.

12.1.2 The effect of vanadium

The effects of reheating temperature on the austenite grain size are listed in Table 3, and are presented in graphical form in Fig. 34. It can be seen that for all vanadium contents the austenite grain size was finer than for the base steel when the reheating temperature was lower than 1050°C. At temperatures of 1050-1150°C the 0.11% and 0.14% V steels had grain sizes similar to that of the base steel, whilst the higher vanadium content steels had finer austenite grain sizes than the base steel. However, except for the 0.98% V steel, all the vanadium steels studied gave coarser austenite grain size at 1300°C than did the base steel.

Fig. 35 shows the effect of vanadium content on the austenite grain size at various temperatures. It can be seen that as the reheating temperature increased above 1050°C the effect of vanadium content, even as high as 0.98%, on the austenite grain size disappeared. This effect is very clearly demonstrated in Fig. 35 for the temperature range of 1150-1200°C.

Fig. 36 shows the effect of vanadium content on the austenite grain coarsening temperature, and it can be seen that above 1050°C all the vanadium alloys coarsened. However, this coarsening temperature was higher than the austenite grain coarsening temperature of the base steel. In fact increasing the vanadium content up to 0.22% increased the coarsening temperature up to 1050°C and thereafter vanadium did not have any further effect.

12.1.3 The effect of vanadium plus nitrogen

The effect of temperature on the austenite grain size in vanadium plus nitrogen (V-N) steels is listed in Table 4, and presented in graphical form in Fig. 37. At 1000°C, all the vanadium steels had finer austenite grain sizes than the base steel but the grain coarsening effect varied with vanadium content so that at 1050°C only vanadium contents greater than 0.14% had grain sizes less than that of the base steel. At 1150°C, only the 0.46% V and 0.98% V steels had finer grain sizes than the base steel, whilst at 1200°C there was little effect of vanadium on the austenite grain size. At 1300°C, all the vanadium steels had coarser austenite grain sizes than the base steel, due to abnormal grain growth.

Fig. 38 shows the effect of vanadium in the high nitrogen steels on the austenite grain size. It can be seen that at 1000°C and 1050°C the austenite grain size became finer with an increase in vanadium content up to about 0.10% for 1000°C and about 0.40% for 1050°C. At reheating temperatures of 1150°C and 1200°C there was little or no effect of vanadium on the austenite grain size.

The austenite grain coarsening behaviour in V-N steels is shown in Fig. 39, there being an increased austenite grain coarsening temperature with increasing vanadium contents up to 0.40%.

12.1.4 The effect of niobium plus vanadium

The austenite grain sizes of the low and high nitrogen Nb+V steels at various temperatures are presented in Fig. 40. It can be seen that an increase in nitrogen from 0.009% to 0.019% in the Nb+V steel studied had little or no effect on the austenite grain size up to about 1200°C. However, at 1300°C, the high nitrogen Nb+V steel gave a finer austenite grain size compared with the low nitrogen Nb+V steel, but both of these alloys had coarser grain sizes than the base steel. The austenite grain coarsening temperature were more or less the same in both the Nb+V steels.

12.2 Effect of Thermo-Mechanical Treatments on the Recrystallization and Grain Growth of Austenite.

12.2.1 Niobium and niobium plus vanadium (Nb+V) steels

12.2.1.1 Recrystallization of austenite

12.2.1.1.1 1300°C reheating temperature, 1250°C rolling temperature and 1250°C holding temperature.

In order to avoid strain induced precipitation of Nb(C,N) in austenite during rolling, and therefore to study the effect of niobium in solution on the recrystallization of austenite, the steels were rolled at 1250°C after reheating at 1300°C. The progress of recrystallization in the various alloys during holding at 1250°C after rolling at 1250°C to either 20% or 50% reduction in one pass, are listed in Table 5, and are presented in Fig. 41. After both 20% and 50% reduction at 1250°C there was complete recrystallization of the austenite in the base steel immediately after rolling. On the other hand in the 0.07% Nb and 0.16%

Nb steels there was partial recrystallization after 20% deformation, but complete recrystallization in the 0.07% Nb steel and nearly complete recrystallization in the 0.16% Nb steel after 50% deformation. However, niobium contents higher than 0.16% led to less recrystallization even after 50% deformation at 1250°C, and in fact holding at 1250°C of the 0.46% Nb, 0.73% Nb and 1.03% Nb steels resulted in very slow recrystallization. Even when these steels were held at 1250°C for 1000s, complete recrystallization did not occur. Fig. 42 shows typical partially recrystallized structures in the 0.46% Nb and 0.73% Nb steels after holding 100s at 1250°C. The effect of niobium content on the percent recrystallization is shown in Fig. 43, which reveals the effectiveness of niobium in retarding the recrystallization of austenite even at temperatures as high as 1250°C. It can be seen that niobium contents up to about 0.16% were not effective in retarding recrystallization but above 0.16% Nb the retardation of austenite recrystallization increased up to about 0.46% Nb and thereafter the effect was found to decrease.

In the case of Nb+V steels, both the low and high nitrogen Nb+V steel showed complete recrystallization of the austenite immediately after rolling to 50% reduction at 1250°C.

12.2.1.1.2 1300°C reheating temperature, 1250°C rolling temperature and 950°C holding temperature.

The effects of precipitation of Nb(C,N) from the austenite after rolling, on the recrystallization of austenite, were studied by holding the steels at 950°C after rolling at 1250°C to either 20% or 50% reduction after reheating at 1300°C. The results, given in Table 6 and presented in Fig. 44, show the same general effects as holding at 1250°C in that with increasing niobium content the amount of recrystallization decreased. The progress of recrystallization in the 0.46% Nb and 0.73% Nb steels at 950°C was also similar to when they were held at 1250°C, which can be shown by comparing Figs. 41 and 44. However, the 1.03% Nb steel showed increased recrystallization of austenite when held at 950°C for 100s instead of at 1250°C, and this effect was substantiated by the finer austenite grain size obtained after holding at 950°C for 100s, due to the increased recrystallization rate.

12.2.1.1.3 1300°C reheating temperature, 950°C rolling temperature and 950°C holding temperature.

To investigate the effect of strain induced precipitation in austenite on the recrystallization of austenite, a lower rolling temperature than 1250°C, such as 950°C, was used. Table 7 and Fig. 45 shows the progress of recrystallization and the austenite grain size of various Nb and Nb+V steels during holding at 950°C after reheating at 1300°C and rolling at 950°C by either 20% or 50% reduction. It can be seen that after 20% reduction, the base steel was partially recrystallized immediately after rolling and that the amount of recrystallization increased during holding at 950°C from 13% to 23% after 1000s. On the other hand, in the 0.07% Nb and 0.16% Nb steels recrystallization did not even start after 1000s holding at 950°C. 50% deformation at 950°C however, led to the start of recrystallization in the 0.07% Nb and 0.16% Nb steels after 100s holding at 950°C, larger amounts of recrystallization occurring in the 0.07% Nb steel than in the 0.16% Nb steel. In the base steel, however, the austenite was partially recrystallized immediately after rolling i.e about 44%, but complete recrystallization occurred after about 100s holding time.

Both the low and high nitrogen Nb+V steels did not even begin to recrystallize after 1000s holding . It is interesting to note that these Nb+V steels had lower niobium contents than the 0.07% Nb steel, and yet they did not show any evidence of recrystallization, which is in contrast to the results obtained on the 0.07% Nb steel which did begin to recrystallize when held for more than 100s. Such an enhanced effect of niobium on retardation of recrystallization can only be attributed to the presence of vanadium.

12.2.1.1.4. 1150°C reheating temperature, 950°C rolling temperature and 950°C holding temperature.

The effect of a finer initial austenite grain size and decreased niobium in solution on the recrystallization of austenite was investigated by reheating the experimental steels at lower temperatures than 1300°C i.e 1150°C. Thereafter the steels were rolled at 950°C and then held at 950°C for various times. The results on the progress of recrystallization and changes in austenite grain size are listed in Table 8 and presented graphically in Fig. 46. In the base steel, the austenite was much less recrystallized immediately after 20% deformation compared with 50% deformation, but the amounts recrystallized were the same after about 100s holding at 950°C. The 0.07% Nb and 0.16% Nb steels, on the other hand, had about the same amount of recrystallization immediately after rolling when deformed by either 20% or 50%; also the progress of recrystallization during holding these alloys was not affected by the amount of deformation. In all the niobium alloys after 50% deformation, the amount of austenite recrystallization was less than in the base steel, the greatest differences being immediately after rolling but such difference decreasing during holding at 950°C.

In the low and high nitrogen Nb+V steels, the amount of austenite recrystallized immediately after rolling was similar to that obtained in the niobium steels, but the progress of recrystallization during holding at 950°C was much slower in both the Nb+V steels compared with the niobium steels. Among the low and high nitrogen Nb+V steels, recrystallization progressed faster in the high nitrogen steel than in the low nitrogen steel. In all the niobium and Nb+V steels, recrystallization of the austenite was incomplete after 1000s holding at 950°C, but was complete in the base steel under these conditions.

The effect of reheating temperature i.e 1300°C compared with 1150°C, on the recrystallization of austenite after similar rolling conditions can be studied by comparing Figs. 45 and 46. The steels were rolled at 950°C by either 20% or 50% reduction in one pass. The recrystallization kinetics of the base steel after 20% deformation shows very slow recrystallization during holding at 950°C when the reheating temperature was 1300°C, but the recrystallization rate was very fast during the first 100s holding when the reheating temperature was 1150°C, and in fact recrystallization was complete after 1000s holding. On the other hand, the percent recrystallized did not increase beyond 23% during 1000s holding when the reheating temperature was 1300°C. In contrast to the base steel, the niobium steels did not even begin to recrystallize after 1000s holding when the reheating temperature was 1300°C. However, after 1150°C reheating, the austenite did recrystallize during holding and the rate of recrystallization was very fast during the first 100s i.e from completely unrecrystallized to about 82% recrystallization in 100s at 950°C.

After 50% deformation, the base steel showed less recrystallization when the reheating temperature was 1300°C compared with 1150°C. However, after 100s holding at 950°C, recrystallization was nearly complete for both the reheating conditions i.e 1300°C and 1150°C. The niobium steels were completely unrecrystallized up to about 100s holding when the reheating temperature was 1300°C, but during this period when the reheating temperature was 1150°C the recrystallization was initiated and proceeded at a very high rate. Nb+V steels did not show any sign of beginning to recrystallize even after 1000s holding after 1300°C reheating, but recrystallization did start immediately after rolling and progressed gradualy during holding at 950°C when the reheating temperature was 1150°C.

12.2.1.2 Mechanism of recrystallization

Studies of the microstructures and austenite grain morphology after various thermo-mechanical treatments revealed the following nucleation sites for recrystallized grains:-

(i) Austenite grain boundaries: These were the preferential nucleation sites. Nucleation was found to initiate first at the triple junctions of austenite grain boundaries.

(ii) Interfaces of recrystallized austenite grains with unrecrystallized grains: Such nucleation was not observed in the base alloy and therefore it was restricted only to the niobium alloys. The evidence for such nucleation is shown in Figs. 47 (a), (b) and (c).

(iii) Deformation bands: Occasionally nucleation of recrystallized grains on the deformation bands was observed. Such nucleation was generally found to occur at a junction between a recrystallized grain boundary and the deformation band, as shown in Fig.48. Recrystallized grains nucleated at the deformation bands tended to grow along the deformation band.

Homogeneous nucleation of recrystallized grains was not observed.

After nucleation, recrystallization progressed by growth of the various nuclei into the unrecrystallized grains. The growth of recrystallized nuclei was found to be very much dependent on the composition of the alloy. Qualitative observations suggested that the growth of nuclei into unrecrystallized grain was slow in niobium alloys compared with the base steel.

12.2.1.3 Recrystallized grain size and its growth.

The effect of niobium content on the recrystallized austenite grain size were investigated by rolling the steel at 1250°C to 50% reduction after reheating at 1300°C. Lower rolling temperatures and percent reductions resulted in partially recrystallized austenite in niobium steels and therefore after such rolling conditions it was not possible to study the effect of niobium on the recrystallized austenite grain size. It can be seen from Fig. 49 that the presence of niobium in the C-Mn steel refined the recrystallized austenite grain size and this effect increased significantly up to about 0.16% Nb. Thereafter the extent of the grain refinement of the recrystallized austenite grain size decreased.

The effect of holding at 1250°C and 950°C on the grain growth of recrystallized austenite in the plain C-Mn and niobium steels is shown in Figs. 50 (a) and (b). Fig. 50 (a) shows that at 1250°C during the first 100s holding there was little or no grain growth of the recrystallized grains in all the steels investigated after 50% reduction at 1250°C. On the other hand, in the base steel after 20% deformation, the austenite grains coarsened during 100s holding and this growth continued up to 1000s holding. In the base and 0.07% Nb steels, recrystallized austenite grains coarsened when held at 1250°C for more than 100s, but in steels containing 0.16% Nb the austenite grains did not coarsen even when held for 1000s.

Holding at 950°C resulted in only slight grain growth of the recrystallized austenite in the base steel as well as in the niobium steels, as shown in Fig. 50 (b).

12.2.2 Vanadium and vanadium plus nitrogen (V-N) steels

12.2.2.1 Recrystallization of austenite

In order to study the comparative effects of vanadium and niobium on the recrystallization of austenite, it was necessary to use the same rolling conditions for the vanadium steels as those used for the niobium steels.

12.2.2.1.1 1300°C reheating temperature, 1250°C rolling temperature and 1250°C holding temperature.

The results on the recrystallization of austenite after 20% and 50% deformation at 1250°C are listed in Table 9, and it can be seen that all the steels were completely recrystallized after 20% as well as after 50% deformation at 1250°C. Holding at 1250°C simply led to growth of the recrystallized grains.

12.2.2.1.2 1300°C reheating temperature, 950°C rolling temperature and 950°C holding temperature.

Table 10 and Fig. 51 shows the effect of holding at 950°C on the recrystallization of austenite in various steels after 20% and 50% deformation at 950°C. It can be seen that after 20% deformation, Fig. 51 (c), there was 13% recrystallization immediatly after rolling in the base steel and this increased to about 23% in 100s at 950°C, and thereafter there was no further increase. All the vanadium alloys, i.e 0.14% V, 0.22% V and 0.55% V, were completely unrecrystallized even up to 100s at 950°C, and only about 5% recrystallization occurred during holding up to 1000s. Thus the addition of vanadium to C-Mn steel retarded the recrystallization of austenite.

After 50% deformation, the base steel was about 44% recrystallized compared to 13% recrystallized after 20% deformation, when quenched immediately after rolling. Complete recrystallization of austenite occurred in 100s at 950°C when 50% deformation was given, but only partial recrystallization occurred even after 1000s holding at 950°C when 20% deformation was given. Vanadium alloys on the other hand were completely unrecrystallized immediately after rolling, as shown in Figs. 52 (a) and (b). However, recrystallization occurred during holding at 950°C as shown in Figs. 51 (a) and 52 (c). The amount of recrystallization decreased with increasing vanadium content from 0.14% V to 0.55% V. Comparison of Figs. 51 (a) and (c) indicate that an increase in deformation from 20% to 50% increased the recrystallization in all the vanadium steels. Complete recrystallization of the austenite in vanadium steels did not occur even after 1000s holding at 950°C.

V-N steels were also completely unrecrystallized immediately after 50% deformation at 950°C. However, during holding at 950°C, as shown in Fig. 51 (b), recrystallization commenced and continued but did not reach completion even after holding for 1000s. Compared with vanadium steels, the V-N steels recrystallized faster during the first 100s at 950°C, but after this time the progress of recrystallization was slower than in the vanadium steels. The percent recrystallized was lower in the 0.14% V-N steel than in the 0.14% V steel after 1000s holding, but this was about the same as in the 0.22% V and 0.25% V-N, and the 0.55% V and 0.46% V-N steels. Addition of vanadium, or vanadium plus nitrogen, to the C-Mn steel was found to retard the recrystallization of austenite, and the effect increased with increasing vanadium content in both low and high nitrogen C-Mn steels, as shown in Fig. 53.

12.2.2.1.3 1150°C reheating temperature, 950°C rolling temperature and 950°C holding temperature.

The effect of low reheating temperature on the recrystallization in the vanadium and V-N steels was investigated by using the lower reheating temperature of 1150°C. The results on the progress of recrystallization and changes in the average austenite grain size during holding at 950°C after rolling 20% or 50% reduction at 950°C are listed in Table-11 and presented graphically in Fig. 54.

Fig. 54 (c) shows the progress of recrystallization after 20% deformation in the base steel and the, 0.14% V, 0.22% V and 0.55% V steels. The base steel was only about 11% recrystallized immediately after rolling, but this increased rapidly during first 100s holding at 950°C and thereafter further recrystallization occurred very slowly. However, complete recrystallization of the austenite had occurred after 1000s at 950°C. All the vanadium steels were completely unrecrystallized after rolling, but recrystallization occurred during holding at 950°C. In the 0.14% V steel the progress of recrystallization was similar to that which occurred in base steel, i.e. faster during the first 100s holding and slower thereafter, but complete recrystallization in this steel did not occur even after 1000s holding, compared with the complete recrystallization which occurred in the base steel. On the other hand, in the 0.22% V and 0.55% V steels recrystallization occurred at an increasing rate, and there was no difference between these two steels, during holding up to 1000s at 950°C. Similarly to 0.14% V steel, these steels did not recrystallize completely after 1000s holding. All the vanadium steels showed a lower percentage recrystallization than the base steel for a given holding time. When these results are compared with those obtained after reheating at 1300°C but with the same rolling conditions, i.e compare Fig. 54 (c) with 51 (c), it can be seen that decreasing the reheating temperature from 1300°C to 1150°C led to an increased amount of recrystallization in the base steel as well as in the vanadium steels. In the base steel, recrystallization proceeded very rapidly when the reheating temperature was 1150°C, and was complete after 1000s, whilst after reheating at 1300°C the austenite did not recrystallize more than 23% during 1000s holding at 950°C.

After 50% deformation, as shown in Fig. 54 (a), the base steel showed more recrystallization than after 20% deformation, immediately after rolling. During holding at 950°C, recrystallization in the base steel was almost complete after 100s. The vanadium steels were only slightly recrystallized, i.e up to about 5%, immediately after rolling. The progress of recrystallization and the amount recrystallized were nearly the same in all the vanadium steels at any given time during holding at 950°C. The progress of recrystallization was very rapid during the first 100s holding from 5% immediately after rolling to about 95% after 100s. In all the vanadium steels, complete recrystallization of austenite did not occur during 1000s holding at 950°C. A comparison of Figs. 54 (a) and (c), indicates that an increase in deformation from 20% to 50% increased the extent of recrystallization during holding at 950°C in all the vanadium steels.

The effect of a lower reheating temperature on the recrystallization of austenite after 50% deformation at 950°C can be shown by comparing Figs. 51 (a) and 54 (a). After reheating at 1150°C the amount of recrystallization immediately after rolling in base steel was higher than after reheating at 1300°C. However, recrystallization was nearly complete in about 100s after both reheating conditions. From the same figures, it can be seen that reheating at 1300°C led to very slow recrystallization in all the vanadium steels during holding at 950°C, compared with reheating at 1150°C. In general, the effect of reheating temperature on the recrystallization of austenite after rolling and during holding at 950°C was more pronounced in the vanadium steels than in the base steel. After reheating at 1300°C retardation of recrystallization increased with increasing vanadium content but, on the other hand, after reheating at 1150°C all the vanadium steels showed similar effects of holding on the progress of recrystallization.

Fig. 54 (b) shows the progress of recrystallization during holding at 950°C after 50% deformation at the same temperature, in the base and various V-N steels. An increase in vanadium content in the V-N steels from 0.14% to 0.25%, increased the retardation of recrystallization, but from 0.25% to 0.46% V did not alter the progress of recrystallization during holding at 950°C. All the V-N steels showed less recrystallization than the base steel. High nitrogen in the 0.25% V and 0.46% V steels increased the retardation of recrystallization, whilst in the 0.14% V steel nitrogen had a much less effect on the retardation of recrystallization, compared with the 0.25% V and 0.46% V steels. From Figs. 51 (b) and 54 (b) it can be seen that lowering the reheating temperature from 1300°C to 1150°C prior to rolling increased the amount of recrystallization of austenite during holding at 950°C.

12.2.2.2 Mechanism of recrystallization

As for the niobium steels, in both the low and high nitrogen vanadium steels, the preferential nucleation sites for recrystallization were prior austenite grain boundaries. However, nucleation on the deformation bands was also observed, Fig. 55, but the frequency for such nucleation was low compared with that occurring at the austenite grain boundaries. In V-N steels the deformed austenite grain boundaries became serrated when held at 950°C, as shown in Fig. 56. Such serrations of austenite grain boundaries were not observed in the low nitrogen vanadium steels. Homogeneous nucleation of recrystallized grains was not observed.

The progress of recrystallization occurred mainly by an increase in the nucleation of recrystallized grains until most of the nucleation sites were saturated. Thereafter growth of recrystallized nuclei occurred.

12.2.2.3 The recrystallized grain size and its growth.

The effect of vanadium on the recrystallized austenite grain size in low and high nitrogen C-Mn steels is shown in Fig. 57. The steels were reheated to 1300°C, and rolled at 1250°C to 50% reduction. It can be seen that increasing the vanadium content in both low and high nitrogen C-Mn steels refined the recrystallized grain size, and it should be noted that for similar vanadium contents the amount of such grain refinement was more pronounced in steels containing high nitrogen.

Grain growth of the recrystallized grains in the base steel and in the vanadium steels at 950°C and 1250°C, after 50% deformation at 1250°C, is shown in Fig. 58. At 950°C there was very slight grain growth in the base steel and the 0.22% V steel, and no grain growth in the 0.55% V and 0.98% V steels when held for 1000s. On the other hand at 1250°C there was significant grain growth on holding for up to 1000s. The base steel and the 0.98% V steel showed much slower rates of grain-growth than the 0.22% V and 0.55% V steels. An increase in vanadium content slowed down the growth of recrystallized austenite grains at holding temperatures of both 950°C and 1250°C. In the base steel, compared with the 0.22% V and 0.55% V steels, austenite grain growth was slower and therefore the base steel had the finer austenite grain size. A similar effect on austenite grain coarsening at higher temperatures was observed in the vanadium steels, see section 12.1.2.

Austenite grain growth during holding at 950°C and 1250°C after 20% deformation at 1250°C in the base steel and the vanadium steels is shown in Fig. 59. Compared with 50% deformation at the same temperature, all the steels had larger recrystallized austenite grain sizes immediately after rolling, and this remained the case during holding at 950°C.

At 1250°C, during the first 100s, the 0.14% V and 0.22% V steels showed slower grain growth rates than the base steel, but after 100s all these steels had similar grain growth rates. Even at 1250°C, the 0.55% V steel showed much less growth of the austenite grains compared with the other steels.

12.3 Effect of Thermo-Mechanical Treatments on the Transformation of Austenite and the Ferrite Grain Size.

The transformation of thermo-mechanically treated austenite will be influenced by the nucleation and growth, particularly, of the polygonal ferrite. This is controlled by:-

(i) the composition of the austenite prior to transformation, which depends on the type of alloying elements present in the steel, temperature dependent solubility effects of alloy compounds, and the effect of thermo-mechanical treatment on the precipitation of the alloy compounds.

(ii) the state of austenite prior to transformation which will be influenced by the alloying elements in the steel and the thermo-mechanical treatment used prior to transformation.

(iii) the size and distribution of second phase particles which will be affected by the types of precipitate which form in the austenite prior to or during transformation, and thermo-mechanical treatment used.

Maximum ferrite grain refinement is achieved by a maximum nucleation rate for ferrite grains coupled with a minimum growth rate during and after transformation. The maximum nucleation rate is achieved by increasing the number of nucleation sites such as austenite grain boundaries, deformation bands, sub-structural effects and second-phase particles. A uniform distribution of very fine precipitates in the austenite minimizes the growth of ferrite grains during, as well as after transformation.

Niobium and vanadium are the most widely used elements in H.S.L.A. steels for the purpose of ferrite grain refinement and therefore in the present studies the effects of niobium and vanadium contents after various thermo-mechanical treatments have been investigated.

12.3.1 Reheated at 1300°C.

12.3.1.1 The effect of niobium.

Due to the high reheating temperature at which much of the niobium was dissolved, Table 12, rolling to 20% and 50% reduction at 1250°C produced little ferrite in any of the steels when cooled at the rate of approximately 400°C/ min; (i.e. equivalent to air cooling a plate of about 12mm thickness) and the amount of ferrite decreased rapidly with increasing niobium in spite of the refined recrystallized austenite grain size which was observed with up to 0.46% Nb when deformed by 50%, Table 5. Steels containing more than 0.46% Nb contained partially recrystallized austenite. All the niobium steels transformed mainly to bainite, which decreased in carbon content with increasing niobium due to carbon tied up with undissolved Nb(C,N). Similar effects were observed on holding at 950°C after rolling at 1250°C, the amount of precipitated Nb(C,N) being insufficient to lower the hardenability to the extent that large amounts of ferrite were formed. In fact above 0.16% Nb the formation of polygonal ferrite was completely suppressed. With increasing niobium, the bainite formed became finer, indicating again the effect of niobium on the hardenability and the consequent depression of the transformation temperature on cooling. Decreasing the holding temperature to 750°C which was within the critical range, allowed the recrystallized austenite to transform to ferrite, but only up to 0.16% Nb after holding for 100s. Holding for 1000s at 750°C however allowed measurable amounts of ferrite to form up to 0.73% Nb, due not only to the increased time but also to the precipitation of some Nb(C,N) which thereby decreased the niobium in solution. A typical structure showing nucleation of ferrite at the prior austenite grain boundaries is shown in Fig. 60 (a), the remaining austenite transforming to bainite. The ferrite grain size as a function of niobium is shown in Fig. 61 after holding at 750°C for 1000s. It can be seen that the ferrite grain size was coarse and varied very little with niobium content, mainly due to low rate of nucleation.

Decreasing the rolling temperature to 950°C revealed that holding at 950°C for 100s or 1000s produced large amounts of ferrite up to 0.73% Nb, Fig. 60 (b). This illustrates the effect of precipitation of Nb(C,N) in austenite during rolling at 950°C, and unrecrystallized austenite on the transformation of austenite. Precipitation of Nb(C.N) in austenite decreased the niobium in solution, and in fact also nucleated for ferrite. Above 0.73% Nb, the structure was mainly bainitic, but it was observed that the amount of ferrite increased with increasing holding time at 950°C, indicating further precipitation of Nb(C,N). The effect of niobium on the ferrite grain size is shown in Fig. 62, from which it can be seen that:-

(i) The grain size decreased with increasing niobium up to 0.11% and thereafter remained constant.

(ii) The grain size was much finer during rolling at 950°C compared with rolling at 1250°C.

(iii) Increasing the holding time at 950°C caused a slight but consistent increase in grain size, probably due to increased precipitation of Nb(C,N) during holding which decreased the niobium in solution and thereby the hardenability. Such an effect produced a coarser ferrite grain size on transforming during continuous cooling. The recovery of deformed austenite decreases the nucleation rate for ferrite and therefore the ferrite grain size coarsened.

(iv) Increasing the reduction during rolling from 20% to 50% caused a pronounced decrease in the ferrite grain size, due to the smaller austenite grain boundary area at low deformation which decreased the number of ferrite nuclei and thus allowed the ferrite grains to be coarse. This was further substantiated by the fact that large amounts of bainite occurred above 0.16% Nb, thus preventing the measurement of ferrite grain size.

A further commentary on the microstructures was that with increasing niobium content the amount of pearlite decreased due to the effective carbon being decreased by the undissolved NbC. Using the same rolling temperature, but holding at 750°C, i.e. within the critical range, the precipitation of Nb(C,N) was much slower than during holding at 950°C, as will be shown later. Consequently there was more niobium in solution and an increased hardenability, so that bainite was formed at lower niobium contents, Fig. 60 (c), thus preventing the ferrite grain size from being determined, Fig. 63. It can be seen that:-

(i) There was little or no effect of increasing the holding time, which confirmed the less extent of Nb(C,N) precipitation at this temperature.

(ii) The ferrite grain sizes were rather coarser than those produced after holding at 950°C because the ferrite largely formed at 750°C during holding, but at rather lower temperatures during cooling from 950°C. Also, there was less effect of niobium on the grain size due to the fact that the ferrite virtually formed isothermally.

(iii) The lower deformation of 20% gave a coarser ferrite grain size for the reasons discussed earlier.

Decreasing the rolling temperature to 750°C followed by holding at 750°C for 100s or 1000s caused both deformation and holding to be carried out in the critical range. In the steels containing less than 0.16% Nb, ferrite formed at the deformed austenite grain boundaries, and was itself deformed, Fig. 64 (a). In this structure, the austenite had transformed during the quench to ferrite and martensite. Holding for 100s at 750°C allowed the deformed ferrite to recrystallize to very fine grains outlining the deformed austenite grains, which themselves had transformed on cooling to rather coarse ferrite-pearlite, Fig. 64(b). The result was a very heterogeneous grain size, but the recrystallized ferrite grain size decreased with increasing niobium up to 0.16%. However, with increasing niobium, the transformation to ferrite was retarded and this was augmented by the fact that even strain induced Nb(C,N) precipitation during rolling was very slow at 750°C. Consequently less ferrite formed at the deformed austenite grain boundaries, but during holding or cooling from the holding temperature multiple nucleation of very fine ferrite grains occurred at the boundaries of the deformed austenite, Fig. 64 (c), in the niobium steels. This will be discussed later, but such a structure should be clearly differentiated from that produced by recrystallization of the deformed ferrite formed during low temperature rolling. Whilst the effects which have been described were for 50% rolling reduction, similar features were observed after 20% deformation, but in this case some unrecrystallized ferrite was observed indicating insufficient deformation to cause the ferrite to recrystallize. The effect of niobium content on the ferrite grain size is shown in Fig. 65, from which it can be seen that the range of niobium contents over which ferrite was observed was limited by the hardenability of the steel. The hardenability effect of niobium was not diminished due to lack of strain- induced Nb(C,N) precipitation at this temperature. In general, the effects of niobium, holding time and deformation on the ferrite grain size were similar to those described earlier, but the amount of ferrite in the structures increased with increased holding time, as expected. Using 20% rather than 50% rolling deformation, caused less ferrite to be formed, probably due to a smaller driving force for ferrite formation during deformation, and less precipitation of Nb(C,N) to decrease the hardenability.

12.3.1.2 The effect of niobium plus vanadium.

Reheating at 1300°C caused all the niobium and vanadium to be dissolved. Rolling 50% at 1250°C led to complete recrystallization of the austenite immediately after rolling. Holding at 1250°C for 100s or 1000s followed by sand cooling resulted in ferrite formation at the austenite grain boundaries and bainite within the austenite grains . The formation of bainite was, infact, due to the combined effect of niobium and vanadium in solution and a coarse recrystallized austenite grain size, both of which increases the hardenability. Holding at 950°C instead of 1250°C led to increased transformation of austenite to ferrite because of less niobium and vanadium in solution due to precipitation of Nb(C,N) and VN or V_4C_3 in the austenite, and the finer austenite grain size prior to transformation. A qualitative comparison of the microstructures of the transformed specimens revealed that both the (Nb+V) steels showed a larger amount of transformation to ferrite than in the 0.07% Nb steel. In the (Nb+V) steels, the high nitrogen (Nb+V) steel showed more transformation to ferrite than the low nitrogen (Nb+V) steel. Thus the effect of vanadium in a niobium steel was to increase the amount of transformation of austenite to ferrite, and the effect was enhanced by high nitrogen. The grain sizes of both the (Nb+V) steels are compared with the grain size of 0.07% Nb steel in Table 13. It can be seen that holding for 100s at 950°C after rolling at 1250°C, caused the niobium steel to have a finer ferrite grain size than the low nitrogen (Nb+V) steel but a slightly coarser grain size than in the high nitrogen (Nb+V) steel. High nitrogen (Nb+V) steels had finer ferrite grain sizes than low nitrogen (Nb+V) steels. An increased holding time of 1000s at 950°C led to a refinement of the ferrite grain size in both the (Nb+V) steels, but opposite effects in the niobium steel. Comparison of the ferrite grain sizes obtained after this treatment indicated that maximum ferrite grain refinement occurred in high nitrogen (Nb+V) steels, and it should be noted that such ferrite grain refinement occurred inspite of lower niobium content, i.e 0.03% in (Nb+V) steel compared with 0.07% in niobium steel.

A decreased rolling temperature of 950°C, but holding at 950°C, led to a refinement of the ferrite grain size in all the niobium and (Nb+V) steels when compared to rolling at 1250°C, Table 13. The reasons for refinement of ferrite grain size due to decreased rolling temperature have already been discussed. From the table it can be seen that after 100s holding at 950°C, both the niobium and high nitrogen (Nb+V) steels showed the same ferrite grain size, which was infact finer than in the low nitrogen (Nb+V) steel. As after rolling at 1250°C, the high nitrogen (Nb+V) steel had a finer ferrite grain size than its counterpart containing low nitrogen. Increase in the holding time at 950°C to 1000s led to coarsening of the ferrite grain size in the niobium steel which still maintained a finer grain size than in low nitrogen (Nb+V) steel, but on the other hand, such a treatment refined the ferrite grain size in high nitrogen (Nb+V) steel, whilst maintaining constant ferrite grain size in low nitrogen (Nb+V) steel. The end result was the finest ferrite grain size in high nitrogen (Nb+V) steel followed by the 0.07% Nb steel and the low nitrogen (Nb+V) steel. The refinement of the ferrite grain size due to holding for 1000s at 950°C, particularly in the high nitrogen (Nb+V) steel, was a very unusual effect. However, a similar effect has been observed in high nitrogen vanadium steels as will be presented later. It seems therefore that refinement of the ferrite grain size may be due to an interaction of vanadium, aluminium and nitrogen. This will be discussed later.

12.3.1.3 The effect of vanadium

From Figs. 66 and 67 it can be seen that at 1300°C all the carbides and nitrides of vanadium were in solution. Rolling 20% and 50% at 1250°C led to complete recrystallization of the austenite and holding at 1250°C prior to transformation simply resulted in grain coarsening of the recrystallized austenite. Due to the coarse austenite grain size, ferrite formed only at the austenite grain boundaries whilst bainite formed within the austenite grains. Holding at 950°C instead of 1250°C prevented austenite grain growth, and therefore maintained a finer recrystallized grain size. The net result was an increased amount of transformation of austenite to ferrite. Again such transformation was found to increase with an increase from 20% to 50% deformation. This was due to the finer recrystallized austenite grain size after the higher deformation. After 50% deformation it was noticed that transformation of austenite to ferrite increased with an increase in vanadium content. Holding for 1000s at 950°C did not alter the austenite grain size significantly, and therefore increased holding time had very little effect on the transformation. The ferrite grain sizes after 100s and 1000s at 950°C are given in Table 14, and it can be seen that steels containing vanadium had finer ferrite grain sizes than the base steel. However, there was no relationship between the ferrite grain size and the vanadium contents, in contrast to the observations in niobium steels. An increased holding time of 1000s resulted in a coarser ferrite grain size in all the steels, which was more pronounced in the base steel than in the vanadium steels. Holding at the lowest temperature of 750°C led to isothermal transformation of austenite and, as shown in Fig. 68, nucleation of ferrite occurred mainly at austenite grain boundaries. These nuclei grew during holding at 750°C. From the same figure it can also be seen that the amount of ferrite increased with an increase in vanadium content. However, the amounts of ferrite formed were not enough to determine the ferrite grain size.

Rolling and holding at 950°C for 100s or 1000s resulted in significant transformation to ferrite and pearlite. However, after 20% deformation the amount of ferrite formed was insufficient to determine the ferrite grain sizes but it was enough in the case of 50% deformation. The ferrite grain sizes obtained after 50% deformation are given in Table 14, and it can be seen that after 100s at 950°C the ferrite grain size was about the same in both the base steel and the vanadium steels. Holding for 100s resulted in an increase in the ferrite grain size for all the steels but this was more pronounced in the base steel than in the vanadium steels. The net result was a slightly finer ferrite grain size in the vanadium steels than in base steel. Again there was no relationship between ferrite grain size and vanadium content. Holding at 750°C led to isothermal transformation of the austenite. After both 20% and 50% deformation all the vanadium steels were completely unrecrystallized and nucleation of ferrite occurred at the austenite grain boundaries as well as within the grains, Fig. 69. From Fig. 69 (c) it can be seen that within the unrecrystallized austenite grains, nucleation occurred mainly at deformation bands and at second phase particles. After 20% deformation and 100s holding, some bainite formed in 0.11% V and 0.14% V steels. However, after a longer holding time of 1000s all the austenite transformed to ferrite and pearlite. A higher deformation of 50% also eliminated the formation of bainite after both 100s and 1000s holding at 750°C. After 50% deformation all the vanadium steels had mixed ferrite grain sizes. The average ferrite grain sizes obtained after such rolling conditions are given in Table 14, and it can be seen that after both 100s and 1000s holding all the vanadium steels had finer ferrite grain sizes than the base steel.

Rolling at the lowest temperature of 750°C led to the deformation of proeutectoid ferrite formed at the prior austenite grain boundaries prior to rolling, and also of the untransformed austenite. During holding at 750°C in all the vanadium steels except that containing 0.98% V, two features were observed:-

(i) The deformed proeutectoid ferrite recrystallized in all the vanadium steels giving outlinement of the prior austenite grain boundaries by very fine recrystallized ferrite grains, Fig. 70. This effect is similar to that occurring in the base steel, Fig. 64 (a).

(ii) The deformed austenite transformed to ferrite and pearlite.

It should be noted that the deformed ferrite in the niobium steels did not recrystallize even after the longest holding time of 1000s. In contrast to this, in all the vanadium steels the deformed ferrite recrystallized after the shortest holding time of 100s, as also occurred in the base steel. From Table 14 it can be seen that an increase in deformation refined the ferrite grain size in all the vanadium steels. Surprisingly, after this rolling condition the base steel had a finer ferrite grain size than the vanadium steels, and there was no systematic variation of ferrite grain size with vanadium content.

12.3.1.4 The effect of vanadium plus nitrogen (V-N).

From Fig. 67 it can be seen that at 1300°C, in all the vanadium steels, all the VN was in solution. Rolling 50% at 1250°C led to complete recrystallization of austenite and holding at 1250°C simply resulted in growth of the recrystallized grains. Hence during sand cooling ferrite formed only at austenite grain boundaries whilst bainite formed within the austenite grains. The structure of all the steels were mainly bainitic.

Holding at 950°C after rolling at 1250°C maintained a fine recrystallized austenite grain size. Due to the many nucleation sites, all the V-N steels transformed mainly to ferrite and pearlite. After 100s hold at 950°C and sand cooling, some bainite formed in the 0.14% V-N steel, but no ferrite formed in the 0.25% and 0.46% V-N steels. This was probably due to the coarser austenite grain size in 0.14% V-N steel compared to the other V-N steels, Table 9. The ferrite grain sizes obtained in the base steel and V-N steels are given in Table 15 and it can be seen that after holding 100s and 1000s all the V-N steels had finer ferrite grain sizes than the base steel. There was no systematic relationship of ferrite grain size to vanadium content. Increased holding time at 950°C led to the refinement of the ferrite grain size in all the steels, except the 0.46% V-N steel, and it should be noted that such refinement of the ferrite grain size due to increased holding time did not occur in low nitrogen vanadium steels. Holding at a still lower temperature of 750°C, which was within the critical range, led to isothermal transformation of austenite in all the steels. The ferrite formed mainly at the austenite grain boundaries. Holding for 100s was not enough to complete the transformation of austenite to ferrite, and during sand cooling the remaining austenite transformed to bainite. Increased holding of 1000s led to more transformation of austenite to ferrite and therefore very little bainite was formed. From Table 15 it can be seen that all the V-N steels had similar ferrite grain sizes, and were finer than the base steel. It can also be seen that isothermal transformation of austenite occurred to form coarser ferrite grain sizes than when transformation occurred during cooling after holding at 950°C.

Rolling 50% at 950°C gave completly unrecrystallized austenite in the V-N steels immediately after rolling, but recrystallization started during holding at 950°C, as shown in Fig. 51 (b). Therefore after such a thermo-mechanical treatment, transformation occurred from partialy recrystallized austenite. In all the steels transformation occurred mainly to ferrite and pearlite. Holding up to 100s followed by sand cooling resulted in mixed ferrite grain sizes in all the V-N steels, but the ferrite grain size was uniform in the base steel. However, an increased holding time of 1000s reduced the occurrence of mixed ferrite grain sizes. The ferrite grain sizes determined after such a thermomechanical treatment showed (Table. 15) that after both 100s and 1000s holding all the V-N steels had finer ferrite grain sizes than the base steel. It can also be seen that increased holding at 950°C led to the formation of a coarser ferrite grain size in the base steel, but surprisingly finer ferrite grain sizes in all the V-N steels. Holding at an even lower temperature of 750°C transformed the austenite isothermally, and therefore the ferrite grain size in all the steels was coarser than obtained after holding at 950°C, in which case austenite transformed during cooling. In all the V-N steels the austenite transformed to mixed ferrite grain sizes. From Table 15 it can be seen that all the V-N steels had finer ferrite grain sizes than the base steel. Increased holding time at 750°C did not alter the ferrite grain size significantly in the base steel and 0.14% V-N steel, but refined the ferrite grain size in the 0.25% and 0.46% V-N steels.

Rolling at the lowest temperature of 750°C led to the deformation of the proeutectoid ferrite and the austenite. However, the 0.46% V-N steel mostly transformed to ferrite prior to rolling and therefore in this steel there was very little or no deformed austenite. Holding at 750°C led to the isothermal transformation of any deformed austenite to very fine ferrite grains, but the amount of such ferrite was very small. In all the V-N steels, the deformed ferrite did not recrystallize during holding at 750°C and it should be noted that such an effect is in contrast to the observation made in the base and low N-V steels where ferrite recrystallized during holding at 750°C, but is similar to that observed in steels containing niobium. As the amount of polygonal ferrite was so small in all the V-N steels, the ferrite grain size could not be determined.

12.3.2 Reheated at 1150°C

12.3.2.1 The effect of niobium

There was much less niobium in solution at 1150°C than at 1300°C, Table 12. Rolling 50% reduction at 950°C and holding at 950°C produced ferrite over a wide range of niobium contents, because the hardenability was much decreased due to the low dissolved niobium and the fine austenite grain size. The microstructures of steels containing up to 0.16% Nb, rolled to 50% reduction were of a mixed ferrite grain size due to the variable austenite grain size prior to rolling, and because there was partial recrystallization of the austenite. This occurrence of mixed ferrite grain sizes was observed up to 0.73% Nb in steel reheated at 1300°C as all the steels had variable austenite grain sizes prior to rolling and also were partially recrystallized. Above 0.73% Nb, even with the lower reheating temperature of 1150°C, the hardenability was sufficient to prevent large amounts of ferrite being formed. Decreasing the rolling reduction to 20% however, produced a uniform ferrite grain size, even in the lower niobium steels inspite of the variable austenite grain size prior to rolling and the partial recrystallization of the austenite prior to transformation. The grain size of the ferrite was, however, coarser as shown in Fig. 71 for the reasons outlined earlier in section 12.3.1.1. The effects shown in Fig.71 were very similar to those described earlier in terms of the effect of niobium, deformation and holding time. However the grain sizes were rather finer than those obtained for equivalent thermo-mechanical treatments after reheating at 1300°C. This was because of the absence of austenite recrystallization and the coarser prior austenite grains after reheating at 1300°C, which produced rather coarser ferrite grain sizes than did the partially recrystallized austenite resulting from the lower reheating temperature.

Using 50% reduction at the same rolling temperature of 950°C, but a holding temperature of 750°C, i.e. within the critical range, resulted in complete transformation to ferrite and pearlite in steels containing up to 0.16% Nb. The higher niobium steels contained less pearlite due to the presence of undissolved Nb(C,N), which decreased the effective carbon, see Table 12. In the highest niobium steel the structure comprised only ferrite. Similar structures were observed to those in specimens held at 950°C, but as shown by comparing Fig.72 with Fig. 71, the ferrite grain sizes were rather finer. In steels containing up to 0.16% Nb, there were regions of coarse ferrite grains, Fig. 73(a), resulting from the presence of coarse unrecrystallized austenite which derived from the variable austenite grain size prior to rolling, shown in Fig. 73(b).

At higher niobium contents there was a more uniform ferrite grain size, Fig. 73(c), resulting from the partially recrystallized austenite formed from fine uniform austenite grains as shown in Fig. 73(d). A similar uniform, but coarser ferrite grain size was observed after 20% reduction. As can be seen in Fig. 72, the general effects of niobium, holding temperature, holding time and reduction during rolling were similar to those described earlier, section 12.3.1.1.

Decreasing the rolling temperature to 750°C and holding at 750°C, which is within the critical range, caused some formation and deformation of ferrite during rolling to 50% reduction in all the steels. In fact steels containing more than 0.46% Nb were completly transformed to ferrite prior to rolling and so the structure comprised only deformed ferrite, Fig. 74(a). But steels containing less than 0.16% Nb were only partially transformed to ferrite prior to rolling and therefore after rolling the structure comprised deformed ferrite and deformed austenite; the austenite transforming to ferrite and pearlite as shown in Fig. 74(b). It was not possible to obtain realistic ferrite grain size measurements from these structures, particularly as most of the deformed ferrite had not recrystallized, possibly due to the inhibiting effect of niobium in solution.

12.3.2.2 The effect of niobium plus vanadium (Nb+V).

Both the (Nb+V) steels had uniform ferrite-pearlite structures after rolling at 950°C to 50% reduction, followed by holding at 950°C and sand cooling. This was due to finer austenite grain size prior to rolling after reheating at 1150°C compared with 1300°C, and the low niobium contents of both steels. The ferrite grain sizes of the (Nb+V) steels, obtained after such thermo-mechanical treatment are given in Table 13, and are compared with those of the 0.07% Nb steel, i.e. the steel containing the lowest niobium in the present investigation. It can be seen that among the (Nb+V) steels, that containing high nitrogen had the finer ferrite grain size after both holding times of 100s and 1000s at 950°C. In both the steels, an increased holding time of 1000s led to the formation of coarse ferrite grains. It can also be seen that the Nb-V-N steels had the same ferrite grain size as the niobium steels, inspite of the very low niobium contents in Nb-V-N steels compared to the niobium steels. However, the low nitrogen (Nb+V) steel had a coarser ferrite grain size than the niobium steel after holding for 100s hold. Thus the effect of nitrogen in (Nb+V) steel after this rolling condition was to enhance the refinement of the ferrite grain size. After 1000s holding, both the (Nb+V) steels and niobium steels had the same ferrite grain size. Therefore increased holding time resulted in a much coarser ferrite grains in niobium steels than in (Nb+V) steels.

Holding at 750°C after rolling at 950°C resulted in isothermal transformation of the austenite. The austenite was of variable grain size prior to rolling, and also after rolling due to the presence of unrecrystallized grains. Isothermal transformation of such a variable austenite morphology gave a mixed ferrite grain size; fine ferrite grains forming from the fine unrecrystallized austenite and coarse ferrite from the coarse unrecrystallized austenite grains, Fig. 75. It should be noted that such a mixed ferrite grain size did not form after holding at 950°C. The reason for the difference between holding at 950°C and 750°C seems to be associated with intragranular nucleation of ferrite in the austenite grains during transformation, i.e. isothermal transformation of unrecrystallized austenite minimises intragranular nucleation of ferrite and promotes transformation of austenite mainly by growth of ferrite grains nucleated at the deformed austenite grain boundaries, resulting in coarse ferrite grain islands, Fig. 75, however when transformation occurs during continuously cooling, due to the increased nucleation rate of ferrite grains within the unrecrystallized austenite grains, fine ferrite grains form even in coarse unrecrystallized austenite and hence a uniform ferrite grain size is produced as shown in Fig. 75(c) and (d). The average ferrite grain sizes obtained are given in Table 13, from which it can be seen that in the (Nb+V) steels, the one containing high nitrogen had a coarser ferrite grain size than its counterpart containing low nitrogen. It should be noted that this is in contrast to the effect observed after holding at 950°C. Compared to the 0.07% Nb steel, both the (Nb+V) steels had coarser ferrite grain sizes after holding 100s and 1000s at 750°C.

Rolling at 750°C, which is within the critical range, led to the deformation of the proeutectoid ferrite and the remaining austenite. During holding at 750°C deformed austenite transformed to ferrite and pearlite.

The deformed ferrite did not recrystallize during holding, and so the final structure was deformed ferrite and islands of ferrite-pearlite.

12.3.2.3 The effect of vanadium

At 1150°C all the V_4C_3 was dissolved in the austenite in all the steels, as also was all the VN except in the steel containing 0.98% V. Rolling the alloys at 950°C to 20% reduction, and holding for 100s at 950°C followed by sand cooling, resulted in mainly ferrite-pearlite structures, but some bainite formed particularly in the 0.11% V and 0.14% V steels. Bainite however was absent in the 0.55% V steel. An increased deformation of 50% reduced the amount of bainite significantly and therefore the structure was mainly ferrite-pearlite in all the steels containing up to 0.55% V. The amount of pearlite decreased above 0.14% V due to the strain induced precipitation of V_4C_3 during rolling and also V_4C_3 precipitation during holding at 950°C. There was virtually no pearlite in the 0.98% V steel, the structure being ferrite with copious V_4C_3 (and VN) precipitates. From Table 14 it can be seen that after 20% deformation and 100s holding time at 950°C, all the vanadium steels had slightly finer ferrite grain sizes than the base steel. Increased deformation of 50% refined the ferrite grain size of all the steels, and it can be seen that all the vanadium steels except that containing 0.98% V had finer ferrite grain sizes than the base steel after both holding for 100s, and 1000s at 950°C. Among the vanadium steels, there was no systematic relationship between ferrite grain size and vanadium content. However, after 50% deformation the steels containing more than 0.14% V had coarser ferrite grain sizes than the steels containing less than 0.14% V. Using the same rolling temperature of 950°C, but holding for 100s at 750°C after 20% deformation, followed by sand cooling, showed that up to 0.55% V the structures comprised ferrite and pearlite. However, increasing the deformation to 50% resulted in ferrite-pearlite structures only up to 0.22% V, whilst the 0.55% V steel had a completly ferritic structure. The absence of pearlite in the 0.55% V steel after increased deformation may be due to increased strain induced precipitation of V_4C_3 in austenite. The 0.06% V steel had a uniform ferrite grain size after 100s holding at 750°C, but steels containing more than 0.06% V had mixed ferrite grain sizes and these mixed grain sizes increased with - vanadium content up to 0.22%. The coarse ferrite grains formed isothermally at the grain boundaries of unrecrystallized austenite grains, as mentioned earlier. A longer holding time of 1000s at 750°C led to still more transformation of austenite to ferrite and as discussed earlier, tended to form increased amounts of mixed ferrite grain sizes from the coarse unrecrystallized austenite, as shown in Figs. 76(a) and (b). The steels containing 0.55% V and 0.98% V showed unusual structures after rolling at 950°C and holding at 750°C, comprising decreasing amounts of what appeared to be deformed ferrite in a matrix of low carbon martensite or bainite. A possible interpretation of these structures is that in these high vanadium steels there was delta ferrite present at 950°C so that rolling occurred in a duplex structure. This is in fact indicated by the Fe-V equilibrium diagram(215), especially as the effective carbon will have been lowered by strain induced V_4C_3 precipitation. This delta ferrite then acted as nuclei for further precipitation of ferrite during holding at 750°C, but with increasing vanadium, the amount of ferrite formed isothermally at 750°C decreased because of the retarded transformation, thus giving less overall ferrite content in the 0.98% V steel compared with the 0.55% V steel, Figs. 77(a) and (b). The reason why this deformed delta ferrite was not observed during holding at 950°C was due to it recrystallizing at that temperature, but the strain induced precipitation of V_4C_3 prevented its growth and thus no very coarse ferrite grains were observed. Holding at 750°C also allowed partitioning of carbon to occur to the residual austenite, which would thus contain higher carbon and an increased hardenability, resulting in bainite or martensite during cooling. This effect was only observed after holding at 750°C, due to the isothermal ferrite formation leading to less austenite which therefore contained a higher carbon content. From Table 14 it can be seen that after 50% deformation, all the vanadium steels had slightly finer or about the same ferrite grain size as the base steel. Among the vanadium steels there was little difference in ferrite grain size produced by holding at 750°C, compared with holding at 950°C.

With the same reheating temperature of 1150°C, but rolling at 750°C followed by holding at 750°C and sand cooling, the structures clearly showed the presence of unrecrystallized austenite even at as low a vanadium content as 0.06%. During holding at 750°C, deformed proeutectoid ferrite recrystallized to very fine ferrite grains, and deformed austenite transformed to ferrite-pearlite structures. The ferrite formed through transformation of the austenite was coarser than that formed by recrystallization of ferrite. The result was mixed ferrite grain sizes. After 50% deformation in steels containing 0.55% and 0.98% V, the structure comprised wholly of deformed ferrite with carbide precipitates, due to the rolling temperature for these steels being within the wholly ferritic region(215). This supported the contention that there was delta ferrite at the highest vanadium contents. The deformed ferrite had not apparently recrystallized, possibly due to the copious fine carbide-nitride precipitates. From Table 14 it can be seen that all the vanadium steels had finer ferrite grain sizes than the base steel. On the other hand, after 50% deformation all the vanadium steels showed the same ferrite grain size as the base steel. Rolling at 750°C produced finer ferrite grain sizes than rolling at 950°C.

12.3.2.4 The effect of vanadium plus nitrogen (V-N)

In these steels, similar to the low nitrogen-vanadium steels, the vanadium contents varied across the stoichiometric ratio. It should be noted that for the stoichiomatric V:N ratio a small amount of vanadium is required due to the low nitrogen content of the steel but the opposite is the case for the V:C stoichiometric ratio, see figures 66 and 67. At 1150°C all the V_4C_3 in all the V-N steels will be in solution, but this is not the case with respect to VN, as steels containing more than ~ 0.28% V will contain undissolved VN, the amount of which increases with increasing vanadium content at constant nitrogen level. The effects of thermo-mechanical treatment on transformation was studied in steels containing 0.14%, 0.25% and 0.46% V.

Rolling and holding at 950°C after 50% deformation gave ferrite-pearlite structures in all the steels. The ferrite grain size in the 0.14% V steel was uniform but in the 0.25% V and 0.46% V steels it was mixed, and in fact it was much more mixed in the 0.46% V steel than in the 0.25% V steel. An increased holding time of 1000s at 950°C prior to transformation led to the formation of mixed ferrite grain sizes in all the steels. The reason for mixed ferrite grain size in high V-N steels after 100s holding condition seems to be due to presence of coarse unrecrystallized austenite grains, originating from a mixed initial austenite grain size. Increased holding time led to the growth of recrystallized grains and also resulted in recovery in the unrecrystallized grains. Both of these effects led to slow ferrite nucleation within the austenite grains, and therefore such conditions will transform austenite to mixed ferrite grain sizes. From Table 15, it is evident that after holding for both 100s and 1000s at 950°C, all the vanadium steels had finer ferrite grain sizes than the base steel. Among vanadium steels there was no systematic variation of ferrite grain size due to an increase in vanadium content. It should be noted that increasing the holding time from 100s to 1000s at 950°C led to the refinement of the ferrite grain size in all the vanadium steels but the opposite was the case in the base steel. Similar phenomena was also observed after reheating at 1300°C but with the same rolling conditions. Ferrite grain refinement in the 0.46% V steel was less than in the 0.14% V and 0.25% V steels. The refinement of the ferrite grain size due to increased holding time only in these high nitrogen steels containing vanadium, is due to the competition of vanadium and aluminium to combine with nitrogen. This will be discussed later. Holding at 750°C after rolling at 950°C, increased the tendency for transformation of austenite to mixed ferrite grain sizes, especially from austenite morphologies which contained coarse unrecrystallized austenite in either a completely unrecrystallized matrix or a partially recrystallized matrix. Therefore there was a mixed ferrite grain size in all the steels after holding for both 100s and 1000s at 750°C. The ferrite grain sizes in all the steels containing vanadium were finer than those in the base steel, Table 15. In the 0.25% V and 0.46% V steels, ferrite grain refinement occurred with an increased holding time, but the reverse was the case in the 0.14% V steel.

Rolling at 750°C which was within the critical temperature range, led to the deformation of both the proeutectoid ferrite and untransformed austenite. The deformed austenite transformed to a very fine ferrite-pearlite structure in the 0.14% V and 0.25% V steels. On the other hand, in the 0.46% V steel, the structure comprised only deformed ferrite. Deformed ferrite did not recrystallize during holding at 750°C.

12.3.3 Reheated at 1000°C

12.3.3.1 The effect of niobium

At this lowest reheating temperature, the initial austenite grain size was fine and the niobium in solution was small, Table. 12. Rolling and holding at 950°C produced a uniform ferrite grain size in steels containing up to 0.73% Nb after both 20% and 50% reduction. The ferrite grain sizes were not however much different from those produced by the same thermo-mechanical treatments, but using a higher reheating temperature of 1150°C, c.f. Figs. 71 and 78. Generally the effects of niobium, holding temperature and rolling reduction were similar to those described for other thermo-mechanical treatments, but the ferrite grain size tended to coarsen at 0.73% Nb. It is suggested that this was due to the large amount of undissolved Nb(C,N) in the high niobium steels, on to which Nb(C,N) precipitates during the transformation. Also the amount of niobium precipitated as fine precipitates was small in steels which had Nb:C ratios greater than stoichiometry. Consequently there were few fine precipitates to prevent growth of the ferrite during and after transformation, with a consequent coarser ferrite grain size. Using the same rolling temperature of 950°C, but decreasing the holding temperature to 750°C, gave the results shown in Fig. 79. Again the effects of niobium, rolling reduction and holding time were similar to those described earlier, but the ferrite grain sizes were rather smaller than after holding at 950°C, and it should be noted that such an effect was consistent with that observed after reheating at 1150°C. The holding temperature of 750°C was within the critical range, and the isothermal transformation which had occurred gave fine and uniform ferrite structures, in the higher niobium steels, Figs. 80(a) and (b).

Decreasing the rolling temperature to 750°C and holding at 750°C, which was within the critical range, produced structures in which the austenite was deformed and ferrite precipitated during the deformation so that it also was deformed, but did not recrystallize even after the longest holding time. The remnant deformed austenite transformed during holding to a very fine ferrite-pearlite structure. These effects are illustrated for the niobium free steel in Figs. 80(c) and (d). The resulting structures in the niobium steels were not capable of giving realistic grain size measurements due to elongated morphology of the grains, Fig. 80 (e).

12.3.3.2 The effect of niobium plus vanadium (Nb+V).

Because of the fine austenite grain size and small amount of niobium and vanadium in solution at 1000°C, both the (Nb+V) steels, transformed to ferrite-pearlite structures after rolling at 950°C to 50% reduction. The ferrite grain sizes were fairly uniform after holding at both 100s and 1000s at 950°C. The ferrite grain sizes in the (Nb+V) and 0.07% Nb steels, after such thermo-mechanical treatments are given in Table 13. It can be seen that:-

(a) after 100s holding at 950°C, the high nitrogen (Nb+V) steel had the coarser ferrite grain size.

(b) Both the (Nb+V) steels had coarser ferrite grain sizes than the 0.07% Nb steel.

(c) After 1000s holding at 950°C, both the (Nb+V) steels had similar ferrite grain sizes, which were finer than that of the 0.07% Nb steel.

(d) Increasing the holding time from 100s to 1000s refined the ferrite grain size in the high nitrogen (Nb+V) steel, but did not change it in the low nitrogen steel. The ferrite grain size coarsened in the 0.07% Nb steel.

It should be noted that the low nitrogen (Nb+V) steel showed no effect of increased holding time at 950°C after rolling at 950°C irrespective of reheating temperature, see Table 13. On the other hand, in the high nitrogen (Nb+V) steel the ferrite grain size became finer with increased holding time after reheating at 1300°C and 1000°C, and rolling at 950°C, whilst it coarsened after reheating at 1150°C. Thus the effect of holding time on the ferrite grain size was not consistent with the different thermo-mechanical treatments in the high nitrogen (Nb+V) steels.

Holding at 750°C after rolling at 950°C led to isothermal transformation of the austenite. The low nitrogen (Nb+V) steel transformed to fine uniform ferrite-pearlite structures after holding for both 100s and 1000s. On the other hand, the high nitrogen (Nb+V) steel showed some islands of coarse ferrite grains and thus a mixed ferrite grain size after holding for 100s and 1000s. It should be noted that the occurrence of mixed ferrite grain sizes was not observed during holding at 950°C, Fig. 81(a). The reason for the occurrence of mixed ferrite grain sizes after holding at 750°C, Fig. 81(b), and its absence after holding at 950°C were similar to those given earlier. The ferrite grain sizes in both the (Nb+V) steels were similar after both 100s and 1000s holding, see Table 13, and the ferrite grain sizes of these steels were very comparable to thoseobtained in the 0.07% Nb steel. Increasing the holding time from 100s to 1000s did not affect the ferrite grain size in these steels. Transformation at 750°C immediately after rolling at 950°C, gave a finer ferrite grain size in both the (Nb+V) steels than after holding at 950°C followed by transformation. Such an effect was also observed in the niobium steels.

Rolling at 750°C, which is within the critical range, led to deformation of the ferrite and the austenite. Reheating at 1000°C gave a much finer initial austenite grain size than after reheating at either 1300°C or 1150°C, and therefore, more transformation to ferrite occurred at 750°C prior to rolling. This resulted in mainly deformed ferritic structures. Deformed ferrite did not recrystallize during holding at 750°C up to 1000s.

12.3.3.3 The effect of vanadium

At 1000°C all the V_4C_3 was in solution in the austenite in steels containing up to 0.50% V, but VN was in solution only up to ~ 0.13% V. Rolling to 20% or 50% reduction at 950°C and holding at 950°C for 100s followed by sand cooling, produced structures very similar to those observed using the higher reheating temperature of 1150°C, and the ferrite grain sizes were identical, see Table 14. At the highest vanadium content, delta ferrite was present. An increase in holding time up to 1000s at 950°C, after 50% reduction, resulted in a somewhat coarser ferrite grain size in the base and 0.11% V steels, but there was no change in ferrite grain size in the 0.14% and 0.55% V steels. Austenite grain growth was inhibited by VN in steels containing more than 0.14% V, which therefore showed no change in ferrite grain size due to increased holding time.

Holding at 750°C for 100s after rolling at 950°C showed a marked decrease in the pearlite content above 0.14% V, and the presence of delta ferrite was very evident in the 0.55% and 0.98% V steels, Fig. 82, for reasons which have been discussed earlier. After 20% reduction, the 0.14% V steel showed a mixed ferrite grain size whilst other steels had uniform ferrite grain sizes. It should be noted that holding at 950°C for 100s did not produce a mixed ferrite grain size in the 0.14% V steel. After 50% reduction, all the steels transformed to uniform ferrite grain sizes. An increase in holding time up to 1000s at 750°C, after 50% reduction at 950°C, led to the occurrence of mixed ferrite grain sizes in the 0.11% V and 0.14% V steels, Fig. 83, due to the original austenite having a mixed grain morphology. Holding at 750°C instead of 950°C, slightly refined the ferrite grain size in steels containing more than 0.14% V. Progressive refinement of the ferrite grain size occurred as the vanadium content increased when held at 750°C. This was in contrast to the observation made after holding at 950°C, see Table. 14.

Rolling at 750°C, which was within the critical range, led to deformation of both ferrite and austenite. Neither the deformed ferrite nor austenite was recrystallized at this low rolling and holding temperature. The structures of the 0.06% and 0.11% V steels were identical after both 20% and 50% reduction at 750°C, but the 0.14% V steel showed a much finer deformed austenite grain structure due to the increased vanadium which resulted in VN being undissolved at the reheating temperature, Fig. 67. A similar feature was observed, with even finer unrecrystallized austenite, in the 0.22% V steel in which there was even more undissolved VN at 1000°C. The 0.55% and 0.98% V steels showed only deformed ferrite, as these steels were in the ferritic condition at 750°C.

12.3.3.4 The effect of vanadium plus nitrogen

After reheating at 1000°C, similar to the low nitrogen vanadium steels, the austenite grain size was fine but not all the VN was in solution. Considering the presence of the high nitrogen, from Fig. 67 it can be seen that at about 0.018% N, steels containing more than ~ 0.06% V contained undissolved VN at 1000°C and the amount of this increased with increasing vanadium content .

Rolling and holding at 950°C for 100s or 1000s after 50% reduction, transformed the austenite to a fine uniform ferrite grain size in all the high nitrogen-vanadium steels. From Fig. 84 it can be seen that all these steels had finer ferrite grain sizes than the base steel, and increasing the vanadium content from 0.14% to 0.46% increased the refinement of ferrite grain size. It should be noted that such ferrite grain refinement due to vanadium was not observed when the nitrogen content of the steel was low, after similar rolling conditions, see Tables 14 and 15. Increasing the holding time at 950°C, resulted in a coarser ferrite grain size in the base steel but refined the ferrite grain size in the 0.14% and 0.25% V high nitrogen steels, see Fig. 84. Such refinement of the ferrite grain size in the vanadium steels due to increased holding time at 950°C has also been observed after similar rolling conditions but higher reheating temperatures.

Holding at 750°C for 100s after 50% reduction at 950°C transformed the austenite to a uniform ferrite grain size in the high nitrogen 0.25% and 0.46% V steels. A similar rolling condition gave mixed ferrite grain size in the high nitrogen 0.14% V steel. Except the 0.14% V steel, all the other high nitrogen steels showed finer ferrite grain sizes than base steel, Fig. 85. An increase in holding time to 1000s at 750°C, gave similar transformation structures to those after 100s holding. However, refinement of the ferrite grain size occurred with increased holding times in all the high nitrogen steels and also the ferrite grain sizes were finer than in base steel. It should be noted that the high nitrogen steels containing 0.25% and 0.46% V transformed to the finest ferrite grain sizes after this rolling condition, see Table 15, and the presence of nitrogen led to substantial grain refinement in the vanadium steels.

Rolling at 750°C, led to deformation of the ferrite and the austenite. The deformed ferrite transformed to a fine ferrite grain size but the amount of such polygonal ferrite grains was small and their proportion decreased with increasing vanadium contents. During holding at 750°C, this deformed ferrite did not recrystallize.

12.3.4 Isothermal transformation of austenite

The effect of niobium and vanadium on the isothermal transformation of austenite at 700°C were studied at two austenite grain sizes. The austenite grain size of the steels was changed by 50% reduction at the reheating temperature of 1150°C, using press forging. The austenite grain sizes after reheating at 1150°C are given in Table 16. Although this deformation refined the austenite grain size, the effect was variable in the different steel compositions. As deformation was performed at the reheating temperature, it is likely that the alloying elements in solution were the same as at the reheating temperature. Therefore, for a given steel it was possible to study the effect of austenite grain size on the kinetics of transformation at 700°C.

The effect of austenite grain size on the transformation after different transformation times in the base steel, 0.07% Nb, 0.14% V low nitrogen and 0.14% V high nitrogen steels, are shown in Fig. 86. It can be seen that the transformation at a given time increased with refinement of the austenite grain size, in all the steels.

The kinetics of transformation of austenite to ferrite in the various steels are shown in Fig. 87. It can be seen that transformation proceeded slowly in all the steels when they were not deformed. On the other hand, 50% deformation at 1150°C, which refined the austenite grain size, accelerated the transformation of austenite in all the steels.

The progress of transformation after reheating at 1150°C showed a significant effect of niobium in retarding the transformation of austenite to ferrite. Of the steels considered, the rate of transformation decreased with the alloying additions, in the order:- 0.14% V low nitrogen, 0.14% V high nitrogen and 0.07% Nb. However, after 50% reduction at 1150°C, it can be seen that the transformation curves for all the steels approached nearer to the transformation curve of base steel, see Fig. 87, and the kinetics of transformation were but little dependent on the composition of the steel.

12.4 Effects of Thermo-Mechanical Treatments and Composition Variables on the Precipitation Strengthening.

The intensity of precipitation strengthening, after various thermo-mechanical treatments, in the predominantly ferrite-pearlite structures produced, was evaluated from hardness measurements. The hardness values were compensated for variations in the ferrite grain size by obtaining the relationship between the ferrite grain size and hardness for the base steel, subjected to various thermo-mechanical treatments.

Fig. 88 shows the relationship between hardness and grain size, $(d^{-\frac{1}{2}})$,:-

$$H = 100 + 3.2\, d^{-\frac{1}{2}} \qquad \text{------------------}(64)$$

This is in excellent agreement with an equation recently developed to describe the hardness of heavily spheroidised carbon steels$^{(216)}$:-

$$H = 113(\pm 6) + 3.43(\pm 0.2)\, d^{-\frac{1}{2}} \qquad \text{----------}(65)$$

The hardness values of all the specimens were then compared with the hardness which would have been obtained from the appropriate grain size in the absence of precipitation strengthening, the difference between the two values, $(\Delta H)_p$, being due to precipitation strengthening by precipitates. Any further correction due to variations in the base composition of the alloy series was negligible.

12.4.1 The effect of reheating temperature on $(\Delta H)_p$.

12.4.1.1 Niobium steels.

Increasing the reheating temperature increased the precipitation strengthening irrespective of the rolling temperature, the rolling reduction and the holding conditions after rolling. This is shown by typical curves for the 0.07% Nb, 0.11% Nb and 0.16% Nb steels, after rolling at 950°C and holding at 950°C, Fig. 89. This diagram also shows that the intensity of precipitation strengthening, $(\Delta H)_p$, increased with increasing niobium content up to 0.16%. $(\Delta H)_p$ was also greater after rolling at 750°C than after rolling at 950°C.

12.4.1.2 Vanadium steels.

The effects of reheating temperature on the precipitation strengthening in vanadium steels is shown in Fig. 90. The steels were rolled to 50% reduction at 950°C and held at this temperature for either 100s or 1000s prior to sand cooling. In steels containing up to 0.14% V, there was little or no effect of reheating temperature on $(\Delta H)_p$, however, the 0.55% V steel did show an increment in $(\Delta H)_p$ with increase in reheating temperature from 1000°C to 1300°C, and it should be noted that such an effect was more marked after 1000s. holding than after 100s holding. The $(\Delta H)_p$ value increased with increasing vanadium content from 0.06% to 0.55%.

12.4.1.3 Vanadium plus nitrogen steels

Fig. 91 shows the effect of reheating temperature on $(\Delta H)_p$ in vanadium steels containing a higher nitrogen content (~0.02%) than was used in the plain vanadium steels (i.e. 0.008%) after similar thermo-mechanical treatment. An increase in reheating temperature from 1000°C to 1300°C:-

(i) did not alter $(\Delta H)_p$ in the 0.14% V-N steel.

(ii) slightly increased $(\Delta H)_p$ in 0.25% V-N steel when the reheating temperature was increased from 1000°C to 1150°C but little or no change in $(\Delta H)_p$ was observed at higher reheating temperatures.

(iii) increased $(\Delta H)_p$ at an increasing rate in the 0.46% V-N steel after 100s holding at 950°C. On the other hand, after 1000s holding condition, $(\Delta H)_p$ increased when the reheating temperature was increased from 1000°C to 1150°C but thereafter, no change in $(\Delta H)_p$ occurred. A significant increase in $(\Delta H)_p$ occurred in the 0.46% V-N steel between 1000°C and 1150°C reheating temperatures, when the holding time at 950°C was 1000s instead of 100s. The increase in $(\Delta H)_p$ due to increasing holding time up to 1000s was more marked after 1150°C reheating than after 1000°C, see Fig. 91(b).

12.4.1.4 Niobium plus vanadium steels

From Fig. 92 it can be seen that the steel containing low nitrogen showed a slight increase in $(\Delta H)_p$ with increasing reheating temperature. On the other hand, there were rather complex effects of reheating temperature on $(\Delta H)_p$ in the high nitrogen (Nb+V) steel. After 100s holding at 950°C, $(\Delta H)_p$ was lowest for the 1150°C reheating temperature compared with that obtained after reheating at both 1000°C and 1300°C, see Fig. 92, whilst after 1000s holding at 950°C, there was no change in $(\Delta H)_p$ with reheating temperature.

12.4.2 The effect of rolling temperature on $(\Delta H)_p$.

12.4.2.1 Niobium steels.

Fig. 93 shows the effect of rolling temperature, on $(\Delta H)_p$ for 0.07% and 0.11% Nb steels, after different reheating temperatures, and holding for 100s or 1000s at 750°C before cooling. The results which are for a constant single pass rolling reduction of 50%, show that:-

(i) Rolling at 1250°C and 750°C after reheating at 1300°C, produced a much larger $(\Delta H)_p$ value than rolling at 950°C. This gave a 'C' curve for $(\Delta H)_p$, the nose giving minimum $(\Delta H)_p$ during rolling at 950°C.

(ii) Lowering the reheating temperature to 1150°C showed a similar effect, although the $(\Delta H)_p$ value was lower because of the lower initial solubility of the Nb(C,N).

(iii) Increasing the niobium content from 0.07% to 0.11% also showed a similar effect to (i), but the value of $(\Delta H)_p$ at any given rolling temperature was increased. This was due to increased temperature dependence of the solubility of Nb(C,N) as the niobium content increased towards the stoichiometric ratio.

(iv) Increasing the holding time at 750°C from 100s to 1000s decreased $(\Delta H)_p$ at any given rolling temperature, whilst still maintaining a typical effect of rolling temperature on $(\Delta H)_p$.

12.4.2.2 Vanadium steels.

The results obtained on the effect of rolling temperature on precipitation strengthening in vanadium steels are shown in Fig. 94. It should be noted that the effects of rolling temperature on $(\Delta H)_p$ in these steels were very similar to that obtained in niobium steels. It can be seen that rolling at 1250°C and 750°C led to much larger precipitation strengthening than rolling at 950°C. This effect of rolling temperature is consistent in all the steels containing a range of vanadium contents, and irrespective of reheating temperature. However, an increase in vanadium content increased $(\Delta H)_p$, as shown in Fig. 94.

From the Fig. 94 it should be noted that in the 0.22% and 0.55% V steels, rolling at 750°C resulted in somewhat lower precipitation strengthening than after rolling at 1250°C, but still higher than that obtained after rolling at 950°C. It is also evident that the 'C' curve for $(\Delta H)_p$ tended to show that $(\Delta H)_p$ became less dependent on rolling temperature as the vanadium contents decreased from 0.22% to 0.06%.

12.4.2.3 Vanadium plus nitrogen steels.

A similar effect of rolling temperature on $(\Delta H)_p$ was observed to that seen in niobium and vanadium steels, Fig. 95.

12.4.2.4 Niobium plus vanadium steels.

Limited data for the steels containing both niobium and vanadium in low and high nitrogen C-Mn steels, on the effect of rolling temperature on $(\Delta H)_p$, suggests that these steels show exactly the same effect of rolling temperature on $(\Delta H)_p$ as observed in niobium, vanadium and V-N steels, see Table. 17.

12.4.3 The effect of holding temperature and time on $(\Delta H)_p$

12.4.3.1 Niobium steels.

Increasing the holding time at both 950°C and 750°C decreased the intensity of precipitation strengthening, see Table. 18. However, holding at 950°C after rolling at 950°C gave a relatively small decrease in $(\Delta H)_p$, but rolling at 750°C and holding at 750°C produced a much greater decrease in $(\Delta H)_p$.

In general, the decrease in $(\Delta H)_p$ with increasing holding time at both 950°C and 750°C became less pronounced with decreasing reheating temperature prior to rolling, Table. 18. The effect of increasing the niobium content from 0.07% to 0.11% was slightly to increase the value of $(\Delta H)_p$ for all the rolling and holding temperatures.

12.4.3.2 Vanadium steels.

The effect of holding temperature on $(\Delta H)_p$, after various rolling conditions is shown in Fig. 96. Decreasing the holding temperature from 950°C to 750°C, decreased the value of $(\Delta H)_p$ in all the steels. However, the decrease in $(\Delta H)_p$ depended on :-

(i) Composition: For a given rolling condition, an increase in vanadium from 0.06% to 0.55% showed more decrease in $(\Delta H)_p$.

(ii) Rolling temperature : A decrease in rolling temperature from 1250°C to 950°C after reheating at 1300°C showed a rapid decrease in $(\Delta H)_p$ after holding at 750°C for 100s in 0.22% V and 0.55% V steels. This effect was much more pronounced in the 0.55% V steel than in the 0.22% V steel.

(iii) Holding time: An increase in holding time up to 1000s led to a rapid decrease in $(\Delta H)_p$.

The effects of holding time on $(\Delta H)_p$ at 950°C or 750°C after various thermo-mechanical treatments are shown in Fig. 97. The results presented are for a 50% rolling reduction. It is evident that the effect of holding time on $(\Delta H)_p$ was affected by the holding temperature. In general, an increase in holding time from 100s to 1000s led to a decrease in $(\Delta H)_p$, in all the steels. However, this decrease in $(\Delta H)_p$ was lower after holding at 950°C where $(\Delta H)_p$ decreased slightly with increasing holding time.

12.4.3.3 Vanadium plus nitrogen steels.

The effects of holding temperature are presented in Fig. 98. A decrease in holding temperature from 950°C to 750°C decreased $(\Delta H)_p$ after most of the rolling conditions, irrespective of composition and reheating temperature. The only exception to this trend was after reheating at 1300°C followed by rolling at 950°C, as there was no change in $(\Delta H)_p$ due to a decrease in holding temperature in the 0.14% V-N and 0.25% V-N steels after 100s. But, there was a decrease in $(\Delta H)_p$ after 1000s holding. On the other hand, in the 0.46% V-N steel, there was a decrease in $(\Delta H)_p$ after holding for both 100s and 1000s, similar to that observed after most of the rolling conditions.

The effects of increased holding time from 100s to 1000s at holding temperatures of 950°C and 750°C on $(\Delta H)_p$, Fig. 99, were:-

(i) a decreased $(\Delta H)_p$ at both holding temperatures of 950°C and 750°C after rolling at 1250°C to 50% reduction.

(ii) an increased $(\Delta H)_p$ after rolling at 950°C and holding at 950°C, irrespective of reheating temperature. It should be noted that such an increase in $(\Delta H)_p$ due to increased holding time did not occur in the niobium and vanadium steels.

(iii) a decreased $(\Delta H)_p$ after holding at 750°C after all the rolling conditions.

12.4.3.4 Niobium plus vanadium steels.

The data on the effect of holding temperature and time on $(\Delta H)_p$ in the two (Nb+V) steels are given in Table. 19. Lowering the holding temperature from 950°C to 750°C, decreased $(\Delta H)_p$ after all the rolling conditions, and it should be noted that this effect was similar to that observed in the niobium and vanadium steels. However, in the 0.03% Nb-0.12% V-N steel, $(\Delta H)_p$ increased when the holding temperature was lowered after reheating at 1150°C, rolling at 950°C and holding for 100s.

An increase in holding time from 100s to 1000s at both the holding temperatures of 950°C and 750°C, lowered $(\Delta H)_p$, particularly for reheating temperatures of 1300°C or 1150°C.

12.4.4 The effect of rolling reduction on $(\Delta H)_p$

12.4.4.1 Niobium steels

The effects of increasing the rolling reduction were complex, and depended upon the reheating temperature, Fig. 100. Reheating at 1300°C followed by rolling at 950°C and holding either at 950°C or 750°C caused the precipitation strengthening to decrease with increasing rolling reduction. On the other hand, after reheating at 1150°C and 1000°C, rolling at 950°C and holding at either 950°C or 750°C, caused the precipitation strengthening to increase with increasing rolling reduction. These effects will be discussed later.

12.4.4.2 Vanadium steels.

The effect of increasing the rolling reduction from 20% to 50% on $(\Delta H)_p$ are shown in Fig. 101. In the 0.11% V and 0.14% V steels, there was either no change in $(\Delta H)_p$ or a slight decrease, due to increasing deformation. On the other hand, the 0.55% V steel showed a decrease in $(\Delta H)_p$ due to increasing rolling reduction after most of the rolling conditions, see Fig. 101, except after rolling at 950°C and holding at 750°C for 100s in which case $(\Delta H)_p$ increased slightly due to the increase in rolling reduction.

12.4.5 The effect of metal to carbon ratio on $(\Delta H)_p$

12.4.5.1 Niobium steels.

A carbon equivalent (i.e. C+N) has been used to calculate the Nb:C ratio, due to the fact that carbon and nitrogen are interchangeable in Nb(C,N). However, because of the low nitrogen content present in the steel, the nitrogen makes very little difference to the ratio.

The effect of Nb:C_{Eq} ratio on the precipitation strengthening is shown in Fig. 102, for varying conditions of thermo-mechanical treatment. It can be seen that, for all the conditions of treatment for which data was available, the intensity of precipitation strengthening increased with increasing Nb:C_{Eq} ratio up to the stoichiometric ratio of about 8. The evidence also shows that the value of $(\Delta H)_p$ decreased above the stoichiometric ratio. However, Fig. 102 clearly shows that the precipitation strengthening was dependent on the thermo-mechanical processing conditions. The maximum precipitation strengthening observed occurred with the highest reheating temperature of 1300°C, and using the highest rolling temperature of 1250°C. With these rolling condition, increasing the holding time from 100s to 1000s at 750°C, Fig. 102, markedly decreased $(\Delta H)_p$. It can also be seen that the greater the initial value of $(\Delta H)_p$ after 100s holding at 750°C, the greater was the decrease in $(\Delta H)_p$ on increasing the holding time to 1000s.

Using the same reheating temperature of 1300°C, but rolling at 950°C, resulted in an even more marked decrease in $(\Delta H)_p$, and $(\Delta H)_p$ decreased further with increasing holding time at 950°C.

12.4.5.2 Vanadium steels.

These steels contained very low nitrogen and therefore it was probable that the precipitating phase was mainly carbide rather nitride. The effect of V:C ratio on $(\Delta H)_p$ after various thermo-mechanical treatments is shown in Fig. 103. It can be seen that, for all the rolling conditions investigated, the intensity of precipitation strengthening increased with increasing V:C ratio up to the stoichiometric ratio of about 5.65 and above the stoichiometric ratio the value of $(\Delta H)_p$ decreased.

The precipitation strengthening was dependent on the thermo-mechanical treatment, i.e:-

(i) Reheating at 1300°C, rolling at 1250°C and holding at 950°C for 100s gave maximum precipitation strengthening.

(ii) Decreasing the holding temperature from 950°C to 750°C decreased $(\Delta H)_p$ in all the steels, and this effect was found to increase with increasing V:C ratio.

(iii) Rolling and holding at 750°C gave minimum $(\Delta H)_p$ values.

12.4.5.3 Vanadium plus nitrogen steels.

The influence of nitrogen contents up to 0.02% in vanadium steels, on the effect of V:C ratio on $(\Delta H)_p$ were studied after various thermo-mechanical treatments. The vanadium contents in these steels were varied so as to achieve V:N ratios across stoichiometry, whilst only up to stoichiometry with respect to the V:C ratio. Table. 20 shows the V:C, V:N and V:(C+N) ratios for V-N steels. The stoichiometric ratio for V:C is $\sim$ 5.65 and for V:N it is $\sim$ 3.63. Therefore, the steel containing 0.46% V whose V:C ratio is 6.13 is nearest to VC stoichiometry and the steel containing 0.06% V with V:N ratio of 3.75 is nearer to VN stoichiometry.

The results obtained on the increment in hardness due to precipitation of vanadium compounds with respect to ratios of V:C, V:N and V:(C+N) are presented in Fig. 104. It can be seen that there is a continuous increase in $(\Delta H)_p$ with an increase in the various ratios considered. It should be noted that there is increase in $(\Delta H)_p$ above the stoichiometric ratio for V:N, see Fig. 104(b). These effects will also be discussed later.

CHAPTER 13

DISCUSSION

13.1 Austenite Grain Coarsening.

13.1.1 Niobium steels.

The variation of austenite grain size with temperature, Fig. 31, suggests that grain growth was dependent on the niobium content of the steel. An increase in niobium generally refined the austenite grain size, see Fig. 32, because of increased volume fraction of undissolved Nb(C,N). However, it should be noted that the austenite grain size can not be refined indefinitely by increasing niobium content. Under normal reheating conditions there is an equilibrium austenite grain size related to a particular reheating temperature, and further grain refinement above this value can not be achieved, Fig. 32. Considering the constant austenite grain size as the equilibrium grain size the equilibrium austenite grain size increased with increasing temperature and also the critical amount of undissolved precipitates required to achieve the equilibrium austenite grain size increased with temperature.

For a given carbon and nitrogen content in the steel, an increase in niobium will increase the amount of undissolved Nb(C,N), but the precipitate particle size will depend on the previous heat treatment. For instance the precipitates which remain undissolved at the highest reheating temperature are coarse but those which have formed during cooling are fine. The niobium is in the following forms depending on the composition and reheating temperature:-

(i) Nb as fine precipitates,
(ii) Nb as coarse undissolved precipitates, and
(iii) Nb in solution.

An illustration of this for the 1.03% Nb steel is shown in Fig. 105. A theoretical consideration suggest that only fine precipitates are effective in retarding the grain growth of austenite(39). Fig. 106 shows the variation of austenite grain size with %Nb as fine precipitates. It can be seen that an increase in niobium as fine precipitates refines the grain size.

Fig. 106 also shows that for a given niobium as precipitates, the austenite grain size was finer at 1000°C than at 1150°C. This was due to coarsening of Nb(C,N) precipitates at higher temperature which in turn increases particle size and reduces the number of particles. Unfortunately, the Nb(C,N) precipitates size has not been determined but plotting the results on the graph(217) showing the effect of particle size and volume fraction of precipitates on austenite grain size, Fig. 107, clearly illustrates the point.

Inspite of an increase in the amount of niobium as Nb(C,N) precipitates with increasing niobium contents up to 1.03%, the austenite grain coarsening temperature with increase of niobium did not increase continuously, Fig. 33. Instead it increased only up to ~ 0.5% Nb and then at higher niobium contents it decreased. This can be explained by taking in to account only the niobium as fine precipitates. Fine precipitates are more effective in raising the austenite grain coarsening temperature. From Fig. 108 it can be seen that the amount of niobium as fine precipitates increased up to ~ 0.7% Nb and then at high niobium contents it decreased. This shows the role of fine precipitates in raising the austenite grain coarsening temperature. A graph of the variation in austenite grain coarsening temperature against the niobium as fine precipitates showed a continuous increase in austenite grain coarsening temperature, see Fig. 109. A similar effect has been demonstrated for the effect of aluminium content on the grain coarsening temperature by Gladman and Pickering(73).

13.1.2 Vanadium steels.

In these steels, vanadium precipitated as both carbide and nitride. Carbides being less stable than nitride, dissolved at low temperature leaving mainly nitride for retarding grain growth. Steels containing up to 0.55% V have all their carbides in solution at 1000°C which is the lowest reheating temperature used in the present investigation, see Fig. 66. On the other hand, steels containing more than ~ 0.12% V, contain some undissolved nitride at 1000°C, see Fig. 67. However, the amount of nitride in all the steels was limited to a small quantity due to low nitrogen contents of the steels.

In view of the above, it is apparent that austenite will coarsen at or above 1000°C in steels containing less than 0.14% V, see Fig. 34, but steels containing more than 0.14% V will show some retardation of austenite grain growth up to ~1150°C. Thus the experimental results are in agreement with the prediction made from the solubility relationship for VN.

The effect of vanadium content on the austenite grain size at various temperatures is shown in Fig. 35. The results can be explained by using the temperature dependent solubility of VN. Vanadium contents up to ~ 0.22% refined the austenite grain size down to ~10 μm at reheating temperatures of 1000°-1050°C and further increases in vanadium content caused no further grain refinement. It should be noted that the low solubility of VN at 1000°C gave consistently finer austenite grain sizes up to 0.22% V. Reheating at 1150°C and 1250°C, where all the VN is in solution for the vanadium contents up to 0.55%, did not show any refinement of the austenite grain size because of the absence of pinning by second phase particles. In the 0.98% V steel, despite the presence of some VN precipitates, there was no grain refinement. This was due to coarsening of the precipitates at this temperature.

The austenite grain coarsening temperature increased with increasing vanadium content up to 1050°C and then remained constant, Fig. 36. This is not surprising because there was not much VN above 1050°C even in steels containing more than 0.22% V. The results are therefore in agreement with those obtained by Erasmus(78) for vanadium steels containing some what higher carbon contents than the present steels.

Fig. 110 shows the relationship between the solubility temperature of VN and the austenite grain coarsening temperature. For steels containing less than 0.20% V there is a good correlation between the grain coarsening temperature and the VN solubility temperature, but it should be noted that the grain coarsening temperature was always slightly lower than the solution temperature of VN. Erasmus(78) also observed a similar effect and suggested that because of the coarsening of precipitates, the grain coarsening temperature was lower than the solution temperature. However, it should also be realized that an increase in temperature, in addition to coarsening the precipitates, also dissolved some of the VN and hence will decrease the volume fraction of particles, which also has a tendency to lower the grain coarsening temperature. At higher vanadium contents the difference between the solution temperature of VN and the grain coarsening temperature increased with vanadium content, Fig. 110. This was mainly due to excessive coarsening of precipitates at high temperatures, but there will also be some contribution from a decreased volume fraction of precipitates.

13.1.3 Vanadium plus nitrogen steels.

It is clear from the above discussion that in vanadium steels, VN retards grain growth of austenite. An addition of nitrogen in these steels would be expected to increase the volume fraction of VN and therefore a retardation of austenite grain growth. However, the results did not show this increased retardation of grain growth when the nitrogen content was increased from ~0.008% to ~ 0.018%, compare Figs. 34 and 37, and also Fig. 35 and 38. This is also shown by the microstructures in Fig. 111, for high nitrogen 0.46% V, and for low nitrogen 0.55% V and 0.98% V steels. It is suggested that the increased volume fraction of VN in the present steels was not sufficient to further inhibit grain growth compared with the low nitrogen vanadium steels. This will be explained later. Also the austenite grain size was somewhat coarser in 0.25% V high nitrogen steel compared with its counterpart containing 0.22% V with low nitrogen, after reheating at 1050°C. White et al(115) also observed no effect of nitrogen on the retardation of austenite grain growth in steels containing ~0.10% V. The present results confirms this for nitrogen contents up to ~ 0.018%, and for vanadium contents higher than 0.10%.

The austenite grain coarsening temperature increased with increasing vanadium content as observed in steels containing low nitrogen, see Figs. 36 and 39. Again the effect of nitrogen on the austenite grain coarsening temperature was not very significant.

The following table shows the calculated amount of vanadium as VN at 1000°C in both low and high nitrogen vanadium steels;-

% Vanadium in steel	% Vanadium as VN		Total increase in vanadium as VN
	Low N	High N	
0.14	0.01	0.04	0.03
0.22	0.02		0.00
0.25		0.05	0.03
0.55	0.03		0.00
0.46		0.07	0.04

It can be seen that an increase in nitrogen increases the vanadium as VN in the range ~ 0.03 to 0.04%, which is a very small amount. Thus there was little or no effect on the austenite grain growth. At higher temperature however, some VN does exist in steels containing high nitrogen and vanadium, but again the total amount of vanadium present as VN (for example at 1150°C) was less than ~ 0.03%. Such a small amount of VN together with the high coarsening rate of VN at high temperatures, produced no effect of nitrogen on austenite grain growth. Therefore, it is not surprising that increased nitrogen contents in vanadium steels did not markedly retard austenite grain growth.

13.1.4 Niobium plus vanadium steels.

Steels containing ~0.11% to 0.14% V in both low and high nitrogen steels showed coarser austenite grain sizes at 1050°C than the (Nb+V) steels containing low and high nitrogen, see Figs. 34, 37 and 40. Therefore, the temperature dependent austenite grain growth in (Nb+V) steels was mainly controlled by Nb(C,N) precipitates rather than VN. Because of low niobium present in these steels, the austenite grain coarsening temperature was ~1000°C, but the austenite grain size remained finer than in the base steel up to ~1060°C in the high nitrogen steel and up to ~1150°C in the low nitrogen steel. The finer austenite grain size in the low nitrogen steel than in the high nitrogen steel was due to the high niobium content in the low nitrogen steel, i.e. 0.05% Nb in the low nitrogen steel compared with 0.03% Nb in the high nitrogen steel.

13.1.5 Comparison of the effect of niobium and vanadium.

The effectiveness of alloying elements on the retardation of grain growth depends on the temperature dependent solubility of their precipitates and its coarsening rate. For a given size and distribution of precipitates Nb(C,N), being more stable than VN or V_4C_3 will be more effective in retarding grain growth of austenite than VN or V_4C_3. Consequently niobium will give the high grain coarsening temperature. This is consistent with the observations made in the present investigation. Also Nb(C,N) coarsens more slowly than either VN or V_4C_3 and this further increases the effectiveness of Nb(C,N) in retarding austenite grain growth.

A comparative effect of niobium and vanadium on austenite grain refinement at temperature as high as 1200°C is shown in Fig. 112. It should be noted that all three steels contained similar quantities of either niobium or vanadium and that for a given weight percent of element, niobium was much more effective in retarding austenite grain growth than vanadium.

13.2 Recrystallization of Austenite.

13.2.1 Niobium steels.

13.2.1.1 Effects of thermo-mechanical treatment.

The mechanism and kinetics of austenite recrystallization during thermo-mechanical treatment control the subsequent transformation of the austenite by influencing the austenite grain size and morphology.

By varying the reheating temperature prior to rolling, varying amounts of niobium in solution and as undissolved Nb(C,N) can be achieved. The solubility of Nb(C,N) in austenite is shown in Fig. 113(45), together with the composition of the steels used and the stoichiometric line. At 1300°C, most of the niobium will be in solution in the lower niobium steels, but with more than about 0.12% Nb at a carbon content of ~0.08%, there will be increasing amounts of undissolved Nb(C,N) which will increase with decreasing reheating temperature. The presence of coarse undissolved Nb(C,N) does not retard recrystallization, and indeed can actually nucleate for recrystallized grains. The effect of reheating temperature on the percent recrystallization immediately after rolling 20% and 50%

reduction at 950°C in one pass, in the base steel and 0.073% Nb steels are shown in Fig. 114, which as expected shows an increased recrystallization with decreasing reheating temperature. Lowering the reheating temperature refines the austenite grain size in both the base and niobium steels, and by doing so increases the number of nucleation sites for recrystallization. However, it should be noted that the niobium steel did not begin to recrystallize on lowering the reheating temperature from 1300°C to 1150°C, thus showing the effect of niobium in retarding the recrystallization. When the reheating temperature was lowered below 1150°C, the niobium steels showed a progressive increase in recrystallization but still gave less recrystallization than in the base steel. At the lowest reheating temperature of 1000°C the percent recrystallization in the base and niobium steels was nearly complete. A much reduced retardation of recrystallization by niobium at 1000°C was due to the very fine initial austenite grain size and the small amount of dissolved niobium.

The effect of rolling temperature on recrystallization after reheating at 1300°C is shown in Fig. 115. A decrease in rolling temperature decreased recrystallization in all the steels, but the effect was more pronounced in the niobium steels. It is known that a decrease in temperature increases the incubation time for nucleation and at the same time decreases the grain growth of recrystallized grains. In niobium steels, the initiation and progress of recrystallization will be retarded further due to the fact that a decrease in rolling temperature increases the volume fraction of fine Nb(C,N) which is known to retard both nucleation(109,131) and growth of the recrystallized grains(109,123).

The effect of increasing rolling reduction at 1250°C and 950°C after reheating at 1300°C is shown in Fig. 116. Rolling at 1250°C by 20% led to complete recrystallization in the base steel which therefore showed no effect of deformation. However, rolling at 950°C showed an increased recrystallization with increasing deformation. On the other hand, there was partial recrystallization in the niobium steels after 20% reduction at 1250°C and hence recrystallization increased with increasing deformation. An increase in deformation increases the stored energy and thus the driving force for recrystallization. It should be noted that niobium steels did not recrystallize even after 50% reduction at 950°C, showing a strong effect of niobium in retarding recrystallization.

In summary, the present work shows that the recrystallization of austenite increases with decreasing prior austenite grain size, increasing rolling temperature and increasing deformation.

13.2.1.2 Effect of niobium content.

It has been shown, Fig. 42, that the amount of recrystallization even at such a high rolling temperature as 1250°C is dependent on the niobium in solution. There continues to be controversy as to whether the major effect of niobium is due to solute drag or to the precipitation of fine Nb(C,N) during rolling. The results shown in Fig. 42, which are for rolling at 1250°C, clearly indicate a major effect due to solute drag, i.e. niobium in solution, because it has been shown that precipitation during rolling at 1250°C is very slow and moreover any such precipitates would readily coarsen to sizes which promote rather than inhibit recrystallization(2.218.219). In fact, the minimum amount of recrystallization in the steel containing 0.46% Nb, which at 1250°C contains ∼0.135% Nb in solution, can be related to the niobium in solution, whilst the greater amounts of recrystallization in the higher niobium steels, despite increased niobium in solution, are due to the nucleating effects for recrystallization produced by increasing volume fractions of coarser undissolved Nb(C,N) particles, coupled with the finer prior austenite grain sizes.

The fact that ∼0.08% Nb in solution does not produce any unrecrystallized austenite at 1250°C possibly reflects the high temperature and the relatively high reduction employed. Holding at 1250°C allows more recrystallization to occur, Fig. 42, which may be due to a simple effect of increasing time, or to niobium precipitated from the austenite; this latter effect would be expected to be slow. The results however, are not unequivocal, because if it is assumed that there is strain induced precipitation at 1250°C, which can inhibit recrystallization, it can be shown, Fig. 117, that there is a relationship between the maximum amount of niobium precipitated as Nb(C,N) and the amount of recrystallization. If the assumption is correct, which may be doubted for reasons given earlier, then increasing amounts of strain induced Nb(C,N) precipitation retard recrystallization. At high temperatures, however, all the indications are that solute drag plays a major role in retarding recrystallization.

To resolve the controversy and to quantify the effect of niobium in solution on recrystallization, a steel was made containing less than 0.008% total (C+N) with 0.29% Nb, in which, because of very low (C+N) all the niobium will remain in solution above 1100°C. Therefore it would be possible to avoid undissolved Nb(C,N) and also strain induced precipitates. The results obtained from this will be presented and discussed in the next section.

A similar effect of niobium on the retardation of recrystallization was observed after rolling at lower temperature, i.e. 950°C, Table 7. However, at lower rolling temperatures, the presence of fine strain induced Nb(C,N) precipitates may retard recrystallization by inhibiting sub-grain boundary migration.

An increasing effect of niobium on the retardation of recrystallization with increasing niobium contents has been demonstrated in Fig. 118.

13.2.1.3 Mechanism of recrystallization.

13.2.1.3.1 Nucleation.

In the present work, the observed microstructures indicate that the main nucleation site for recrystallization was the deformed austenite grain boundaries. The amount of deformation is important as this can influence the strain energy gradient near the grain boundary and thus affect the rate of nucleation. Austenite grain boundaries nucleate for recrystallization by sub-grain growth(9) or sub-grain coalescence(6,10,11).

After low deformations, on many occasions serrated grain boundaries were observed which suggest that nucleation also occurred by strain-induced grain boundary migration, (S.I.B.M.). The major requirement for nucleation by S.I.B.M. is local strain energy difference on either side of the grain boundary(14) and this can best be produced by using low deformations. At high deformation where the deformation of the matrix tends to be more homogeneous, nucleation by S.I.B.M. is not so prevalent, and this is in agreement with the present results.

Nucleation at interfaces between recrystallized and unrecrystallized austenite grains was observed in the niobium steels, Fig. 47. Nucleation at such sites is not documented in the literature, but has been observed by Roberts(109) and Ahlblom(127). This type of nucleation raises questions such as, why the recrystallized grain did not grow in to the unrecrystallized grain rather then nucleating a new one, and how the nucleation actually occurs. Recrystallization occurs by the nucleation of recrystallized grains which grow in to the unrecrystallized matrix. The presence of second-phase particles can inhibit growth of the recrystallised grains, but it should be appreciated that the recrystallised grains are fine and therefore only fine and uniform distributions of Nb(C,N) precipitates can inhibit their growth. The driving force for recrystallized grain growth is high compared with that for abnormal grain growth(219), so that very strong grain boundary pinning by Nb(C,N) precipitates is needed to inhibit it. The strain induced Nb(C,N) precipitates which are fine and uniformly distributed can thus inhibit recrystallized grain growth, and under these circumstances stable nucleation sites can operate. A moving grain boundary is unlikely to act as a nucleation site, and hence it is a prerequisite to have a stable grain boundary structure to nucleate for recrystallized grains. Strain gradients at the recrystallized - unrecrystallized grain interfaces can be expected, particularly at high deformations, to nucleate new grains, but it is possible that these strain gradients may be smaller than at the original deformed austenite grain boundaries. Nucleation at recrystallized- unrecrystallized grain interfaces was not observed in the base steel indicating the importance of second phase precipitates in promoting nucleation at such interfaces.

It has been reported(220) that nucleation can occur on deformation bands.

Such an effect has been observed in the present work, Fig. 48, but it should be noted that not all the deformation bands act in this way probably due to variations in the strain energy associated with them. Dillamore (221) has developed a model for nucleation at deformation bands. Due to low potential for nucleation at the deformation bands it is unlikely to be important in the kinetics of recrystallization, compared with nucleation at the austenite grain boundaries.

The progress of recrystallization after nucleation has occurred is by the growth of recrystallized grains. However, such growth was inhibited in the niobium steels by strain induced Nb(C,N) precipitates, and this forced new grains to form. On the other hand, in the base steel the nuclei grew in to the unrecrystallized grains without any inhibition, because of the absence of second phase particles.

13.2.1.3.2 Effect of undissolved precipitates.

It has been suggested, (13.2.1.2), that undissolved precipitates of Nb(C,N) in steels containing more than 0.46% Nb, accelerated recrystallization of austenite. Second phase particles, depending on their size, can either accelerate or retard recrystallization. Cahn(2) shows that a coarse precipitate can nucleate recrystallized grains if its size is greater than the critical nucleus size. However, the critical nucleus size decreases with increase in strain and therefore small particles can become potential nucleation sites for recrystallized grains at high strains(222). The smallest particles at which nucleation of recrystallized grains have been observed in iron alloys are $\sim 0.8\,\mu m$(223). On the other hand, Gladman et al(224) observed nucleation of recrystallized ferrite on particles as small as $0.5\,\mu m$; recently Gladman(217) has suggested that particles directly responsible for nucleation of recrystallized grains are generally in excess of 1-2 μm diameter. Both strain gradients developed at the particle and its interfacial energy favour nucleation of recrystallized grains.

The particle size distribution of undissolved Nb(C,N) for sizes $>0.10\,\mu m$ after reheating at 1300°C, in 0.46% and 0.73% Nb steels, are shown in Fig. 119 (a) and (b). In the 0.46% Nb steel, Fig. 119(a), about 80% of precipitates were in the size range 0.10-0.30 μm, whilst in 0.73% Nb steel, although there were more precipitates in the size range 0.20-0.30 μm, there were many more precipitates $>$ 0.30 μm than in the 0.46% Nb steel. It would be expected therefore, that the number of precipitates $>$0.50 μm will be higher in 1.03% Nb steel than in 0.73% Nb steel. Hence considering the fact that only particles of sizes above 0.50 μm can accelerate recrystallization, the steels containing more than 0.46% Nb will show acceleration of recrystallization, which is in agreement with the present observations, Fig. 42.

However, all the studies on the effect of particle size in nucleating recrystallized grains have been done only after cold deformation and annealing treatment, rather than after hot deformation, so that the above interpretation may be questioned. Neverthless, decreased strain induced precipitation in steels containing $>$0.46% Nb cannot account for the acceleration of recrystallization as strain induced precipitation at 1250°C will not affect recrystallization due to the high particle coarsening rate. Therefore, the acceleration of recrystallization in high niobium steels can only be attributed to the presence of coarse undissolved precipitates.

13.2.1.3.3 Mechanism of retardation of recrystallization by niobium.

The mechanism by which niobium retards the recrystallization of austenite is not well understood, see section 8.6. In the present investigation an attempt has been made to study whether niobium in solution or as precipitates retard the recrystallization. Discussion of the effect of niobium content on the recrystallization of austenite, section 13.2.1.2, could offer no conclusive evidence for the mechanism involved, but did show that niobium in solution retarded the recrystallization.

From Fig. 42 it is evident that $>$ 0.46% Nb gave maximum retardation of recrystallization, i.e. when $\sim$0.27% Nb was undissolved, $\sim$ 0.05% Nb was strain induced as Nb(C,N) and 0.14% Nb was in solution. In this steel the undissolved precipitates were mainly in the size range 0.10-0.30 μm, Fig. 119(a), and as discussed earlier this sizes of precipitates cannot nucleate recrystallized grains. However, it can retard the growth of recrystallized grains and therby retard the recrystallization rate. Strain induced precipitates will coarsen rapidly at 1250°C and the volume fraction will be too low to be effective in retarding recrystallization. Niobium in solution can retard recrystallization by either retarding nucleation or the growth of recrystallized grains.

The effect of niobium in solution on the recrystallization has been investigated by using a 0.29% Nb steel containing less than 0.008% total (C+N). In this steel all the Nb(C,N) was in solution above 1100°C. Rolling 50% reduction at 1250°C after reheating at 1300°C gave ~50% recrystallization of austenite, Fig. 120 , compared with 100% recrystallization in the base steel. This provides positive evidence that niobium in solution retards recrystallization of austenite. To identify the individual effects of niobium in solution on the nucleation and the growth of recrystallized grains, the steel was held after rolling at 1250°C for 100s and 1000s. After 100s holding the austenite was completly recrystallized and further increase in holding time simply coarsened the austenite grain size. This suggest that niobium in solution did not retard the growth of recrystallized grains, and therefore it can be concluded that niobium in solution retarded the recrystallization by retarding the nucleation of recrystallized grains. This was further confirmed by press forging experiments.

Niobium in solution retards the nucleation of recrystallized grains by retarding the movement of dislocations by:-

(i) Solute-vacancy interaction: This lowers the tendency for dislocation climb and therefore the formation of the sub-grains necessary for nucleation by either sub-grain growth or sub-grain coalescence mechanisms.

(ii) Segregation of niobium and carbon atoms around dislocations: Such segregation of niobium and carbon atoms is known to retard the movement of dislocations and thereby retards the nucleation of recrystallized grains by the above mechanisms. It should be noted that the segregation of niobium and carbon atoms at dislocations is a first step towards precipitation on dislocations.

The present work provides unequivocal evidence for the retardation of nucleation by niobium in solution. Although a similar effect of niobium in solution on nucleation has been reported by Roberts(109) during dynamic recrystallization and by Coldas et al(132) during static recrystallization, these authors did not provide direct evidence.

The above discussion stressed the effect of niobium in solution on the retardation of nucleation, but there exists another mechanism by which niobium can retard nucleation, and this is by strain induced precipitation of Nb(C,N) on dislocations(126,131). These precipitates are very fine and hence can pin the dislocations. Strain induced precipitation of Nb(C,N) on sub-grain boundaries in the 0.11% Nb steel are shown in Fig. 121.

Also the effect of holding temperature on recrystallization after 50% reduction at 1250°C was investigated to ascertain whether the influence of niobium in solution on recrystallization is dependent on temperature. The holding temperatures used were 1250°C, 1150°C, 1050°C and 950°C for 100s and 1000s. There was ~50% recrystallization after rolling at 1250°C, but complete recrystallization occurred during holding at 1250°C, 1150°C and 1050°C. On the other hand, holding at 950°C did not lead to complete recrystallization of austenite. This evidence suggests that niobium in solution did not retard growth of the recrystallized grains into unrecrystallized grain, nor would it be expected to do so even at lower temperatures than 1050°C. The reason for retardation of recrystallization during holding at 950°C is mainly associated with the inhibition of growth of recrystallized grains, by freshly precipitated Nb(C,N). It should be noted that such precipitation in austenite can occur even at this low interstitial content below ~1100°C. The amount of Nb(C,N) precipitated at 1050°C was not sufficient however to retard the recrystallization.

It can therefore be concluded that although niobium in solution retards recrystallization of austenite by decreasing the nucleation rate, the presence of a fine, uniform distribution of Nb(C,N) is needed to enhance this effect.

13.2.1.4 The effect of niobium on the austenite grain size.

The presence of niobium up to ~0.16% refined the recrystallized austenite grain size, Fig. 49, immediately after rolling. Steels containing >0.16% Nb contained unrecrystallized austenite immediately after rolling, but the extent of recrystallization increased during holding at 1250°C. After 1000s hold, it was possible to determine the recrystallized grain size in all the steels, Fig. 49, and niobium up to ~0.73% refined the recrystallized grain size but higher niobium contents caused the recrystallized austenite grain size to coarsen. The effect of niobium in refining recrystallized austenite grain size has also been observed by other worker(225), and secondary recrystallization in niobium treated steels(226) has also been reported.

At a given starting austenite grain size, fine recrystallized grains can form only when there is a high nucleation rate and a low growth rate of the recrystallized grains. An increase in deformation and decreasing deformation temperature increases the nucleation rate and can refine the austenite grain size. However, in niobium steels increasing deformation increases the incubation time for nucleation of recrystallized grains, and hence this decreases the nucleation rate, so that it may be argued that niobium should not refine austenite grain sizes. On the other hand, it has also been shown that strain induced precipitates of Nb(C,N) retard recrystallized grain growth, and therefore promote intragranular and interfacial nucleation for recrystallized grains. Thus it is not surprising to have finer recrystallized austenite grain size in niobium treated steels than in niobium free steels.

An increase in niobium increases the volume fraction of strain induced precipitate which, by retarding the growth of recrystallized grains, increases the refinement of recrystallized grains as shown in Fig. 49.

At the highest niobium content of 1.03% the recrystallized grains coarsened due to the fact that in this steel the amount of strain - induced Nb(C,N) was very low and also the undissolved precipitates were too coarse to be effective in pinning the grain boundaries. It can be concluded that an optimum amount of niobium would be that which gives maximum amount of strain induced Nb(C,N) and minium undissolved Nb(C,N).

The maintenance of a fine austenite grain size, which leads to a fine transformed ferrite grain size is also conditional on the inhibition of austenite grain growth. The effect of holding time at 1250°C and 950°C on the grain growth of austenite is shown in Figs. 50(a) and (b). It can be seen that at 1250°C there was no significant grain growth in steels containing $>$ 0.07% Nb for holding up to 100s, but grain growth occurred in the base and the 0.07% Nb steel. The growth of recrystallized grains was slightly slower in the niobium steel than in base steel due to Nb(C,N) precipitates pinning the grain boundaries. At 1250°C in the 0.07% Nb steel, the amount of Nb(C,N) precipitates was small and grain growth was not retarded effectively. On the other hand in the 0.16% Nb steel, where the amount of Nb(C,N) precipitates was large, there was no grain coarsening at 1250°C up to 1000s holding time.

The time dependent growth of recrystallized grains in the base steel was different after 50% and 20% rolling reduction, Fig. 50, there being faster growth after 20% reduction than after 50% reduction. Such an effect has also been shown by Sellars and Whiteman(227), who suggested that low deformations in the finishing passes for the purposes of attaining the required thickness, can be dangerous as they promote the formation of coarse austenite grains; hence coarse ferrite grain sizes. The faster grain coarsening after low deformation can be associated with low nucleation rates and inhomogeneous grain sizes.

At 950°C, progressive grain growth occurred in the base steel, but in the 0.07% Nb steel grain growth only occurred after 1000s holding. There was no grain growth in the 0.16% Nb steel. It is suggested that austenite grain growth was retarded mainly by Nb(C,N) precipitated during rolling or subsequent holding. It has been shown in earlier discussion that niobium in solution does not retard the growth of recrystallized grains into the unrecrystallized matrix. The driving force for normal or abnormal grain growth is not so high as that for the growth of recrystallized grains into an unrecrystallized matrix. The effect of dissolved niobium on the grain growth of completely recrystallized austenite is not known. In steels which contain, undissolved Nb(C,N), Nb(C,N) precipitated in austenite and niobium in solution, a relative effect of these different forms of niobium on the austenite grain growth is difficult to distinguish. However, the results summarised in Table 21 enable it to be concluded that :-

(i) 0.07% Nb in solution does not inhibit grain growth, although it inhibits recrystallization; and

(ii) 0.08% Nb as undissolved and precipitated Nb(C,N) in austenite does inhibit grain growth.

13.2.2 Niobium plus vanadium steels.

After 50% reduction at 1250°C, the austenite was completly recrystallized. Therefore it was not possible to study the relative effect of niobium and (Nb+V) on the recrystallization kinetics. However, after rolling and holding at 950°C, as shown in Figs. 45 and 46, it is clear that the addition of vanadium to niobium steel enhances the retardation of recrystallization of austenite. A similar effect of additions of both niobium and vanadium together, on the recrystallization kinetics was also shown by Lamberigts et al(120).

The reason for retardation of recrystallization when niobium and vanadium are added together has not been explained in the literature. Although, combined additions of niobium and vanadium have been suggested for optimum strength and toughness in controlled rolled strip or plate, little information is available on their effect on recrystallization and precipitation strengthening.

Nb(C,N) and V(C,N) are known(228,229) to form a series of solid solutions. Therefore, when niobium and vanadium are added together it is likely that niobium and vanadium may not precipitate as their individual carbides and nitrides. Because Nb(C,N) and V(C,N) are completly soluble, niobium and vanadium can substitute for each other in carbides, nitrides or carbo-nitrides. Thus when both niobium and vanadium are present in the steel, NbV(C,N) could form. It would be expected that the solubility of NbV(C,N) will be intermediate between that of Nb(C,N) and V(C,N), and will also be governed by the relative proportion of niobium and vanadium in the carbo-nitride.

If the above interpretation is correct, it can explain why additions of vanadium to niobium steels enhances the retardation of recrystallization over and above that which can be achieved by niobium alone. The vanadium addition is likely to increase the volume fraction of precipitates which can be strain induced during deformation. This will undoubtedly increase the retardation of recrystallization.

A similar concept of the formation of NbV(C,N) in (Nb+V) steels, also explains the results obtained on precipitation strengthening in these steels. This will be discussed latter under a separate heading.

13.2.3 Vanadium and vanadium plus nitrogen steels.

13.2.3.1 The effect of thermo-mechanical treatment.

The effects of reheating and rolling temperatures in the base steel, 0.14% V in low nitrogen and 0.14% V in high nitrogen steels are shown in Figs. 122 and 123 respectively. The effect of various thermo-mechanical treatment variables on recrystallization has already been discussed, and there is the general trend of increasing recrystallization with decreasing reheating temperature or increasing rolling temperature. From Figs. 122 and 123 it is evident that vanadium retards the recrystallization of austenite.

V(C,N), due to its greater solubility compared with Nb(C,N) in austenite, dissolves at lower reheating temperatures. Hence less recrystallization occurs with reheating temperatures above 1150°C, due to the coarsening of the initial austenite grains.

13.2.3.2 The effect of vanadium content.

An increase in vanadium content in low and high nitrogen steels, increased the retardation of recrystallization, Fig. 54. The retardation of recrystallization increased significantly when vanadium was increased up to $\sim$0.15- 0.20% whilst a further increase in vanadium had relatively minor effects.

An increase in vanadium will increase the amount of both carbides and nitrides, but at 950°C the carbide will be entirely in solution up to 0.35% V, Fig. 66. On the other hand, some VN will be undissolved in steels containing $> 0.05\%$ V with low nitrogen, and $> 0.03\%$ V with high nitrogen, see Fig. 67. It was shown in niobium steels that dissolved niobium retarded the nucleation of recrystallized grains but did not retard their growth into an unrecrystallized matrix. Assuming that a similar effect applies for vanadium steels then it is possible to associate an increased retardation of recrystallization by vanadium to the strain induced precipitates of VN or V(C,N) which are rich in nitrogen. These are very fine and precipitate on the substructure, as shown in Fig. 124(a). Also during holding precipitation occurs on the austenite grain boundaries, Fig. 124(b), but these precipitates are relatively coarse compared with the strain induced precipitates, Fig. 124(a). However, both types of precipitates can retard the growth of recrystallized grains into the matrix and thereby retard recrystallization.

The optimum vanadium content which produces sufficient precipitate to retard the growth of recrystallized grains into unrecrystallized matrix will give maximum retardation of recrystallization, whilst further increases in vanadium simply stabilize the recrystallized grain boundaries. In this situation, further recrystallization occurs by the formation of new recrystallized nuclei and their growth.

From Fig. 54 it can be seen that, there was no acceleration of recrystallization above a certain vanadium content. In niobium steels acceleration of recrystallization above $\sim 0.46\%$ Nb was attributed to the undissolved Nb(C,N) precipitates nucleating recrystallized grains. In vanadium steels, even for the highest vanadium content used in the low nitrogen steels, all the VN was in solution at 1300°C, Fig. 67, whilst in the high nitrogen-vanadium steels very small amounts of VN were undissolved and were thus ineffective in accelerating recrystallization.

13.2.3.3 The effect of nitrogen in vanadium steels.

Immediately after rolling, vanadium was found to retard the recrystallization even at high rolling temperature, see Fig. 123. The progress of recrystallization was very rapid at these high temperatures, due to the fact that there was insufficient V(C,N) precipitated in the austenite to retard the growth of the recrystallized grains into the unrecrystallized matrix; thus recrystallization was complete in very short holding times. On the other hand at low rolling temperatures when a significant quantity of V(C,N) precipitates were present, the progress of recrystallization was retarded or inhibited completly, see Fig. 51, as shown by other workers(121,141).

It has been suggested that the growth of recrystallized grains into the unrecrystallized matrix is also retarded by solute drag(109,121) due to segregating vanadium at the grain boundaries. However, the results discussed for niobium strongly suggest that solute drag cannot retard the growth of the recrystallized grains.

It is therefore the precipitates which are important in the retardation of recrystallization, and any increase in their volume fraction would accentuate the retardation of recrystallization. An increase in nitrogen content will increase the volume fraction of VN at a given vanadium content, and hence will retard recrystallization during holding, see Figs. 51 and 53.

13.2.3.4 Mechanism of recrystallization.

The nucleation sites for recrystallization, observed in these vanadium steels containing both low and high nitrogen, were same as those observed in niobium steels, and hence do not need any further discussion.

After nucleation, recrystallization progressed by the growth of these nuclei. In vanadium steels, growth of the recrystallized grains was retarded by V(C,N) precipitates, particularly at low temperature as V(C,N) generally does not precipitate at high temperature due to its high solubility in austenite. Therefore, vanadium does not retard recrystallization at high temperature. It has been suggested(105,107,114,140,141) that vanadium retards the recrystallization only below ~900°C. However, an increased volume fraction of precipitates, due to increasing vanadium content, can increase the temperature where vanadium can retard recrysta-

-llization, but such an effect is likely to be small, due to the limitation on the amount of V(C,N) which can be precipitated at higher temperatures.

13.2.3.5 The effect of vanadium on the austenite grain size.

Vanadium in both low and high nitrogen C-Mn steels was found to refine the recrystallized austenite grain size observed immediately after rolling, Fig. 57. This refinement of the recrystallized grain size was also observed in steels containing niobium, and is due to an increased nucleation rate of the recrystallized grains coupled with slow growth of these grains. The slow growth of recrystallized grains was due to the pinning effect by strain induced Nb(C,N) precipitates. Whether a similar concept can be applied to vanadium steels to explain the refinement of recrystallized grains by vanadium must be considered.

During rolling at 1250°C, all the V_4C_3 and VN was in solution in both low and high nitrogen steels. Therefore, there was no strain induced precipitation of V(C,N) at 1250°C. This indicates that the growth of recrystallized grains was not inhibited by strain induced precipitates of V(C,N). However, very little time was available after rolling at 1250°C for the growth of recrystallized grains to occur, indicating less importance of strain induced precipitates in refining the recrystallized grain size, when the grain size was measured immediately after rolling. Another factor by which vanadium can refine the recrystallized grains is by increasing their nucleation rate. In niobium steels, it was shown that new grains nucleated intragranularly and at interfaces of recrystallized grains with the unrecrystallized matrix, which in turn increased the number of nucleation sites, and produced a fine recrystallized grain size. In vanadium steels, on the other hand, nucleation at such sites may not occur due to the fact that there were no precipitates to inhibit the growth of recrystallized grains into the unrecrystallized matrix, which is a requirement for such nucleation to occur. Vanadium in solution however, does not retard the nucleation as much as does niobium and therefore in vanadium steels the nucleation rate can increase with an increase in the number of nucleation sites or stored energy. Vanadium can increase the stored energy prior to recrystallization due to retardation of recovery, and thereby, will increase the rate of nucleation, leading to the refinement of the recrystallized grain size.

An increase in vanadium in both the low and high nitrogen steels, refined the recrystallized grain size. This may be due to the increased stored energy at a given deformation condition with increasing vanadium contents.

The presence of high nitrogen in vanadium steels, tended to increase the refinement of the recrystallized austenite grain size, for a given vanadium content and thermo-mechanical treatment, Fig. 57. All the VN was in solution at 1250°C and therefore enhanced refinement of the grain size due to increased nitrogen, cannot be attributed to the increased volume fraction of precipitates. A possible reason for the enhanced nucleation of recrystallized grains in the presence of high nitrogen may be a further increase in stored energy when high nitrogen is present. Such a further increase in stored energy when nitrogen is present in vanadium steels, can be due to:-

(i) V-N interactions around dislocations: This can retard the movement of dislocations and hence will increase the stored energy. V-N interaction is likely to be stronger than V-C interaction due to higher affinity of vanadium for nitrogen than for carbon.

(ii) Segregation of nitrogen atoms to dislocations: This is a well known phenomena, in which nitrogen locks the dislocations and therefore as mentioned above would be expected to increase the stored energy, but is not likely to be operative at the high temperature involved.

The time dependent growth of recrystallized grains at 1250°C and 950°C in vanadium steels is shown in Figs. 58 and 59, and it can be seen that grain growth occurred at 1250°C but was inhibited at 950°C. At 1250°C all the V_4C_3 and VN was in solution and hence there was no inhibition of grain growth, but at 950°C sufficient precipitation in austenite occurred to inhibit the grain growth.

13.2.4 Comparison of the effect of niobium and vanadium.

From the above discussions it is possible to summarise the factors which can retard recrystallization. The basic processes which retard recrystallization are:-

(i) The retardation of nucleation of recrystallized grains; and

(ii) The retardation of the growth of nuclei into the unrecrystallized matrix.

The retardation of nucleation has been shown to occur when the movement of the dislocations is inhibited either by solute-vacancy interaction, by segregation of solute atoms at dislocations or by precipitate formation at dislocations. Both, the solute-vacancy interaction and segregation of solute atoms are likely to be more pronounced when the solute atom has a greater atomic size difference with the iron. It is thus possible to explain the effect of niobium and vanadium as solutes on the nucleation process for recrystallization, i.e. niobium which is the larger atom is more likely to retard nucleation than vanadium. This is in agreement with the observations. With regard to precipitation on the dislocations, the Nb(C,N) is much less soluble in austenite than V(C,N) and again it will be the Nb(C,N) which will precipitate in preference to V(C,N). Therefore, niobium is most likely to retard nucleation at much higher temperature than will vanadium.

After nucleation, recrystallization proceeds by the growth of the recrystallized grains into unrecrystallized matrix. Niobium in solution does not retard this process. Calculations on the solute drag effects exerted by niobium in solution on the moving grain boundary(230), also suggest that niobium in solution cannot retard the growth of recrystallized grains, nor will vanadium.

On the other hand, strain induced precipitates of Nb(C,N) or VN are very fine and hence can retard the growth of recrystallized grains into unrecrystallized matrix. Nb(C,N) will precipitate at higher temperature than V(C,N) and therefore niobium additions will retard the growth of recrystallized grains at much higher temperature than vanadium. To inhibit the growth of recrystallized grains into the unrecrystallized matrix over a longer time, it would be necessary to keep the size of the precipitates small. However, the precipitates tends to coarsen during holding, which inturn decreases their number and increases their size, thus giving less effective pinning of grain boundaries, and leading to an increased rate of recrystallization. At a given temperature, the coarsening rate of V(C,N) is much faster than that of Nb(C,N), suggesting that vanadium will not be able to retard recrystallization so effectively as niobium.

13.3 Effect of Thermo-Mechanical Treatment on the Transformation of Austenite and Ferrite Grain Size.

13.3.1 Niobium steels

13.3.1.1 Effect of niobium on the transformation of austenite

Niobium in solution increased the hardenability, i.e. decreased the nucleation rate for ferrite during the transformation of austenite. This was particularly marked for niobium contents >0.16%. Due to the solubility effects, increasing the reheating temperature increased the amount of dissolved niobium, and thereby the hardenability, which was further increased by the coarse austenite grain sizes produced by high temperature deformation. Rolling at 950°C caused precipitation of strain induced Nb(C,N), and the hardenability decreased. The hardenability influenced the transformed structure in that the ferrite mainly nucleated at the austenite grain boundaries and if the hardenability was high, the rest of the austenite grain transformed to bainite. Generally a high hardenability resulted in a lower transformation temperature on cooling, which if the ferrite nucleation rate is sufficiently high, will give a very fine ferrite grain size.

Alloying elements decrease the rate of nucleation of ferrite, and low niobium contents seem particularly effective in this respect, possibly due to niobium segregating to austenite grain boundaries, lowering their surface energy, and decreasing the rate of ferrite nucleation. Some authors(139) have suggested that niobium is similar, whilst the others(158) have compared it with boron. Niobium undoubtedly decreases the diffusion rate and increases the activation energy for carbon diffusion, which will also decrease the rate of ferrite nucleation and the ferrite growth rate.

13.3.1.2 Effect of niobium on the ferrite grain size.

The effect of niobium in refining the ferrite grain size under given cooling conditions was marked, but did not increase above ~0.07% Nb, possibly due to increasing amounts of niobium decreasing the ferrite nucleation rate, so that each nucleus grew into a larger grain. Also undissolved Nb(C,N) are sites for precipitation of further Nb(C,N) so that there are fewer fine grain boundary pinning particles which do not restrict the ferrite grain growth. Whilst the nucleation rate of ferrite was decreased by increasing niobium, and thus might be expected to lead to a coarser ferrite grain size, this was not the case because the transformation period was extended, thus allowing more nuclei to form. Moreover, the growth of the ferrite was retarded by niobium thus allowing advantage to be taken of the many nuclei to produce a fine ferrite grain size. Once the ferrite grains impinge, subsequent growth is inhibited by niobium.

13.3.1.3 Effect of thermo-mechanical treatments on ferrite grain size.

The results presented in sections 12.3, show the effects of reheating temperature, rolling temperature and reduction, and holding temperature and time on the ferrite grain size produced by the transformation of thermo-mechanically treated austenite.

The effect of reheating temperature is shown in Fig.125. If the niobium free base steel is omitted, it can be seen that the ferrite grain size decreased as the reheating temperature decreased, the effect being more pronounced at the lower holding temperature of 750°C. The scatter in the bands shown encompasses the effect of niobium content. The effect shown was due to the smaller initial austenite grain size with decreasing reheating temperature giving a smaller austenite grain size irrespective of whether it was recrystallized or unrecrystallized, which increased the rate of nucleation for ferrite and thus gave a smaller ferrite grain size. In addition lower reheating temperatures resulted in less dissolved niobium, and more undissolved Nb(C,N) which acted as ferrite nuclei, and a finer austenite grain size due to grain boundary pinning. These effects all accentuated the refinement of the ferrite structure.

The effect of rolling temperature is shown in Fig. 126. Decreasing the rolling temperature produced a marked refinement of the ferrite grain size, the scatter band encompassing the effect of niobium content. Refinement of the ferrite grain size was also most apparent on decreasing the rolling temperature from 950°C to 750°C, because lower rolling temperature resulted in a finer recrystallized austenite grain size or more elongated unrecrystallized austenite grains, both of which effects increases the ferrite nucleation rate. In addition, in unrecrystallized austenite grains, the deformation bands or the polygonisation associated with recovery, produces an increased nucleation rate and a finer ferrite grain size.

The effect of rolling reduction on the ferrite grain size is shown in Fig. 127. Increasing the rolling reduction decreased appreciably the ferrite grain size. The effect seemed to be rather more pronounced in the niobium steels than in the base steel, due to reasons already discussed. More deformation also produced more strain induced Nb(C,N), less niobium in solution and thus a greater ferrite nucleation rate and a finer ferrite grain size.

The effect of holding temperature on ferrite grain size is shown in Fig. 128, and the effects were complex. The effect of holding temperature was influenced by reheating temperature, i.e. by the amount of dissolved niobium prior to rolling. Using a high reheating temperature of 1300°C, then irrespective of the rolling temperature the ferrite grain size tended to coarsen as the holding temperature decreased from 950°C to 750°C. Reheating at 1150°C caused the ferrite grain size to remain more or less constant at low niobium contents but to be refined at higher niobium contents as the holding temperature decreased from 950°C to 750°C. After reheating at 1000°C however, decreasing the holding temperature from 950°C to 750°C caused a refinement of the ferrite grain size. Only speculative explanations for these complex effects can be attempted at present, and more work is required to investigate the effect of thermo-mechanical treatments on the nucleation and growth of the ferrite during transformation. However, it should be noted that holding at 750°C was within the critical range and thus a variable amount of transformation can take place isothermally depending on the austenite grain size, the amount of niobium in solution and the amount and distribution of the

Nb(C,N) precipitates. The fact that the effects outlined occur in the base steel as well as in the niobium steels suggests that it is the austenite grain size which is most responsible for the effect of holding temperature on the ferrite grain size.

The effect of holding time however was more consistent in that Figs. 61, 62, 63, 65, 71, 72, 78, and 79 show that increasing the holding time at both 950°C and 750°C coarsened the ferrite grain size. This was probably due to continued growth of recrystallized austenite grains, especially if grain boundary pinning was not very effective, in which case some growth of the actual ferrite grains can also occur after impingement. Holding at 950°C particularly, caused precipitation in the austenite. There was therefore less dissolved niobium and less precipitation in the ferrite, so that prevention of the growth of the ferrite by interphase precipitation was less marked. Holding at 750°C, within the critical range, can lead to growth of the ferrite grains during transformation, due to the decreased nucleation rate of ferrite grains.

13.3.2.1 Effect of (Nb+V) on the transformation of austenite.

In the previous section it was shown that niobium in solution increases the hardenability and therefore, retards ferrite transformation. It has also been suggested(160-162) that vanadium increases the hardenability but the effect was small compared with that of niobium. Combined additions of niobium and vanadium, therefore might lead to a further increase in hardenability than can be achieved by niobium alone.

After most of the thermo-mechanical treatments, (Nb+V) steels showed more transformation to ferrite than steels containing 0.07% Nb. In both the (Nb+V) steels the amount of niobium was >0.07%, hence more transformation to ferrite might be expected in (Nb+V) steels. This suggests that although vanadium increased the hardenability, the effect was small compared with that of niobium. This is in agreement with the observations made in steels containing varying amounts of vanadium, as discussed later.

13.3.2.2 Effect of (Nb+V) on the ferrite grain size.

A general comparison of the ferrite grain size in 0.07% Nb and (Nb+V) steels, Table. 13, indicates that a combined addition of niobium and vanadium does not enhance ferrite grain refinement compared with that which can be achieved by niobium alone. It should be noted that the niobium content in both (Nb+V) steels was $<0.07\%$, and yet there was an equivalent ferrite grain size to that of the 0.07% Nb steel. From Figs. 62, 63, 65, 71, 72, 78 and 79, it is clear that an increase in niobium content up to 0.07% refined the ferrite grain size, and so it is possible that an increase in niobium content in (Nb+V) steels upto 0.07% would have given finer ferrite grain sizes than the 0.07% Nb steel. Due to the dissimilarity in composition, a direct comparison of ferrite grain size with composition, cannot be made. The only published work on this aspect(85) however showed that a combined additions of niobium and vanadium refined the ferrite grain size more than that which can be achieved by niobium alone.

An enhanced refinement of ferrite grain size when vanadium is added to niobium steel may be explained by considering the recrystallization of austenite. Combined additions of niobium and vanadium retard recrystallization more than does niobium alone, which will assist in increasing the nucleation rate of ferrite during transformation and hence refine the ferrite grain size. To maintain the fine ferrite grain size, it is necessary to inhibit the growth of ferrite by fine second phase particles. As suggested earlier, vanadium additions to niobium steels will increase the volume fraction of precipitates, and therefore help to refine the ferrite grain size. Such an interpretation again strengthens the view that when niobium and vanadium are added together NbV(C,N) precipitates are formed rather than Nb(C,N) and V(C,N) separately.

13.3.2.3 Effect of nitrogen in (Nb+V) steels on the ferrite grain size.

The results obtained for the (Nb+V) steels, containing low and high nitrogen are given in Table 13. It can be seen that the effect of nitrogen is rather complex, but can be summarised as follows, after holding condition at 950°C:-

(i) After reheating at 1300°C and 1150°C prior to rolling, the high nitrogen steel transformed to a finer ferrite grain size than the low nitrogen steel, irrespective of the rolling temperature.

(ii) For the lowest reheating temperature of 1000°C, there was no significant effect of nitrogen on the ferrite grain size.

An increase in nitrogen in the (Nb+V) steels, increased the volume fraction of precipitates precipitated in austenite either during cooling or deformation. The volume fraction of such precipitates will however be dependent on the initial reheating temperature. At the highest reheating temperature used the largest amount of precipitates will form in the austenite, which will lead to the transformation of austenite to finer ferrite grain sizes in the high nitrogen (Nb+V) steel. At the lowest reheating temperature of 1000°C, the initial austenite grain size was small, and small amounts of precipitate will form in austenite in both the (Nb+V) steels due to low solubility and supersaturation at the rolling temperature, and therefore nitrogen will have little effect on the ferrite grain size.

13.3.2.4 Effect of thermo-mechanical treatments on the ferrite grain size.

A decrease in reheating temperature and rolling temperature refined the ferrite grain size in both (Nb+V) steels, for the reasons discussed earlier. The effect of reheating temperature on the ferrite grain size is shown in Fig. 129.

The effect of holding temperature on the ferrite grain size after 50% reduction at 950°C is shown in Fig. 130. The variation of ferrite grain size with decreasing holding temperature from 950°C to 750°C was dependent on the initial reheating temperature employed. After reheating at 1300°C the austenite transformed to coarser ferrite grain sizes when the holding temperature was lowered to 750°C, whilst after reheating at 1150°C a decreased holding temperature to 750°C led to the formation of finer ferrite grains in the base steel but coarser ones in the high nitrogen (Nb+V) steel, but had no affect in the low nitrogen (Nb+V) steel. On the other hand, after 1000°C reheating condition, decreasing the holding temperature from 950°C to 750°C resulted in the refinement of ferrite grain size in all the steels. It should be noted that in both the (Nb+V) steels, the variation of ferrite grain size with holding temperature was generally similar to that in base steel. This observation has also been made for the niobium steels, and therefore does not require further discussion.

There was no significant change in ferrite grain size when the holding time was increased from 100s to 1000s, as can be seen from Table 13. On the other hand, Table 13 shows that in the 0.07% Nb steel, increased holding time led to coarser ferrite grain sizes. Therefore, it is suggested that the addition of vanadium to a niobium steel, tends to maintain a fine ferrite grain size even if there is a prolonged holding at 950°C or 750°C. Such an effect of vanadium in a niobium steel, can be useful in controlled rolling, by increasing flexibility in the rolling procedure without affecting the ferrite grain size. The reason for no effect of holding time on the ferrite grain size in (Nb+V) steels, can be due to the increased volume fraction of NbV(C,N) precipitates, and also, as shown earlier, to increased retardation of recrystallization of austenite.

13.3.3 Vanadium steels.

13.3.3.1 Effect of vanadium on the transformation of austenite.

A general observation of the transformed structures after various thermo-mechanical treatments, suggests that vanadium in solution increases the hardenability of austenite. A similar effect has also been observed by other workers(160-162,231).

In Fig. 68, it was shown that increasing vanadium contents from 0.14% to 0.55% increased the transformation to ferrite at 750°C. However, all the vanadium steels showed less transformation to ferrite than the base steel due to the low hardenability of base steel. As vanadium increases the hardenability, there should have been less transformation to ferrite with increasing vanadium content. On the other hand, Andrews(232) has shown an increase in the Ac_3 temperature by 104°C/wt % V. Assuming a similar effect of vanadium on the Ar_3 temperature, there would be increased transformation to ferrite when vanadium was present. Although this explains the observations in Fig. 68, it entirely neglects the fact that vanadium increases the hardenability.

The effect of vanadium on hardenability is complex due to its carbide and nitride forming tendencies. It should be noted that only vanadium in solution increases the hardenability. On the other hand, vanadium can lower the hardenability by the following effects:-

(i) Presence of V_4C_3 or VN: This can lower the amount of vanadium in solution and hence the hardenability.

(ii) Nucleating ferrite at precipitates.

(iii) Refining the austenite grain size: V_4C_3 and VN can retard the growth of austenite grains which inturn lowers the hardenability.

(iv) Decreasing the amount of carbon in solution: Formation of V_4C_3 in austenite or incomplete solution of V_4C_3 will lower the carbon content of austenite and raise both Ac_3 and Ar_3 temperatures.

A complex effect of vanadium on the hardenability of austenite is not therefore surprising. An increasing vanadium content will certainly increase the Ac_3 temperature as suggested by Andrews(232), because vanadium is a ferrite stabiliser and can decrease the carbon content of austenite due to undissolved V_4C_3 at low austenitising temperatures. A high reheating temperature, on the other hand, will increase the amount of vanadium and carbon in solution and thereby increase the hardenability, as observed in the present investigation.

Increased transformation to ferrite with increasing vanadium content, Fig. 68, seems to be associated with the finer austenite grain size with increasing vanadium content, and also to ferrite nucleating at undissolved precipitates. The transformation kinetics in the base steel and the 0.14% V steel for a similar austenite grain size, Fig. 131, clearly shows retarded transformation in the vanadium steels, indicating increased hardenability due to vanadium.

13.3.3.2 Effect of vanadium on the ferrite grain size.

Refinement of the ferrite grain size through the transformation of austenite, depends on the nucleation and growth rates of ferrite grains.

Alloying additions such as vanadium affect the nucleation and growth of ferrite by affecting the recrystallization behaviour of austenite and precipitation of carbides and nitrides in austenite prior to transformation. It has already been shown that vanadium in solution does not significantly retard the recrystallization of austenite nor retard the growth of austenite grains. Therefore, when vanadium is not precipitated in austenite during thermo-mechanical treatment, which is most likely at high rolling temperatures, it will not refine the ferrite grain size. This is in agreement with the observations made in the present investigation.

An increase in dissolved vanadium will not therefore affect the transformation behaviour of austenite significantly, and in the present investigation there was no systematic relationship between vanadium content and ferrite grain size.

Vanadium however, did refine the ferrite grain size when rolling was carried out at low temperature i.e. 750°C, but there was still no systematic relationship between ferrite grain size and vanadium content. At low rolling temperature vanadium retards the recrystallization of austenite and results in strain induced precipitation of V_4C_3 and VN in austenite, both of which tends to refine the ferrite grain size. The effectiveness of vanadium on ferrite grain refinement can be enhanced by increasing the nitrogen content which will give more precipitates in the austenite at higher temperatures, i.e. VN.

13.3.3.3 Effect of thermo-mechanical treatments on the ferrite grain size.

The effect of reheating temperature, on the ferrite grain size after various thermo-mechanical treatments is shown in Fig. 132. Reheating temperature did not affect the ferrite grain size when the steels were rolled to 50% reduction and held at 950°C prior to transformation, Fig. 132(a) and (b). On the other hand, rolling at the same temperature of 950°C but holding at 750°C, caused refinement of the ferrite grain size with decreasing reheating temperature, Fig. 132(c) and (d), and this effect was pronounced after holding for 1000s at 750°C. A similar effect of reheating temperature on the ferrite grain size was also observed after 20% reduction at 950°C, Fig. 132(e).

Holding at 750°C rather than 950°C, produces a refinement of the ferrite grain size which is particularly marked at the lowest reheating temperature of 1000°C. It should be noted that there was no significant change in ferrite grain size when held at either 750°C or 950°C.

A decrease in rolling temperature from 1250°C to 750°C refined the ferrite grain size, irrespective of the amount of deformation, Fig. 133. Maximum ferrite grain refinement was achieved by rolling at the lowest temperature of 750°C, for the reasons outlined earlier.

An increase in deformation refined the ferrite grain size in all the steels, Fig. 134. This effect was greatest after rolling at 750°C. Rolling at 950°C refined the ferrite grain size with increasing deformation, but holding at 950°C prior to transformation lowered the advantage of high deformation in refining the ferrite grain size. Thus holding at high temperatures after heavy deformation should be avoided in order to achieve maximum advantage of high deformations on ferrite grain refinement.

From Fig. 134, it can also be seen that the degree of ferrite grain refinement due to the increase in deformation from 20% to 50%, gradually decreased with decreasing reheating temperature from 1300°C to 1000°C. An increase in deformation refined the ferrite grain size mainly because of an increased number of nucleation sites. When the reheating temperature was high, i.e. a coarse austenite grain size, an increase in deformation increased the number of nucleation sites compared with the increase in the number of nucleation sites with increasing deformation when the austenite grain size was finer after low reheating temperature. Therefore, the degree of ferrite grain refinement brought about by increased deformation will be more pronounced in steels which have been reheated at high temperature than after reheating at low temperature.

Decreasing the holding temperature from 950°C to 750°C, after rolling at 950°C, did not affect the ferrite grain size after reheating at 1300°C and 1150°C, Table 14. On the other hand, reheating at 1000°C, and decreasing the holding temperature from 950°C to 750°C, resulted in a finer ferrite grain size. Holding at 750°C, which was within the critical range, led to isothermal transformation of austenite to ferrite, which formed rather coarser ferrite grains than would have been achieved by continuous cooling immediately after rolling. Examination of the quenched specimens, immediately after holding for 100s at 750°C, showed increasing amount of austenite transforming to ferrite with decreasing reheating temperature, and there was almost complete transformation of austenite to ferrite after reheating at 1000°C. Therefore it can be concluded that after reheating at 1000°C, no isothermal transformation of austenite occurred at 750°C as it was almost complete during cooling from 950°C to 750°C, which in turn refined the ferrite grain size. Holding at 950°C, led to more recrystallization of austenite and also to a coarser austenite grain size which resulted in somewhat coarser ferrite grains than would have been achieved by cooling without holding at 950°C.

An increase in holding time from 100s to 1000s at both 950°C and 750°C did not affect the ferrite grain size significantly in the vanadium steels, but consistently caused a coarser ferrite grain size in the base steel. This suggests that vanadium prevents the coarsening of the ferrite grains produced by holding after rolling.

13.3.4 Vanadium plus nitrogen steels.

13.3.4.1 Effect of nitrogen in vanadium steels on the transformation of austenite.

Little is known of the effect of nitrogen in vanadium steels on the transformation of austenite. However, a review(233) on the effect of nitrogen on hardenability indicates that nitrogen in hypereutectoid steel increases the hardenability, and it has also been noted that such effect can occur in hypoeutectoid steel. As discussed earlier, the effect of vanadium on the hardenability, in the presence of high nitrogen ($\sim$0.02%), is likely to be complex, because VN is much more stable than V_4C_3 at high temperature, and thus more difficult to dissolve. Therefore, a fairly high reheating temperature will be necessary to dissolve all the VN.

In the present investigation, studies on the transformed structures of V-N steels, after various thermo-mechanical treatments, did not show any significant effect on austenite transformation, of increasing the nitrogen content from $\sim 0.008\%$ to $\sim 0.02\%$. Therefore, any effect of nitrogen on hardenability, seems to be small. This was confirmed by isothermal transformation studies in the 0.14% V steel containing both low and high nitrogen at 700°C, Fig. 87 and 131, which showed less transformation in steels containing high nitrogen.

13.3.4.2 Effect of nitrogen in vanadium steels on the ferrite grain size.

A comparison of the ferrite grain size obtained in vanadium steels containing low and high nitrogen, suggested that $\sim 0.02\%$ N enhanced the grain refining potential of vanadium, irrespective of the thermo-mechanical treatment used. This has been shown for the 0.14% V steels in Table.22. This is in agreement with observations made by other investigators.

The enhanced ferrite grain refinement due to vanadium, in the presence of high nitrogen, is associated with increased retardation of recrystallization of austenite and strain induced precipitation of VN in austenite.

Again as observed in low nitrogen vanadium steels, no systematic variation of ferrite grain size with vanadium content was observed.

13.3.4.3 Effect of thermo-mechanical treatment on the ferrite grain size.

The effect of reheating temperature on the ferrite grain size after various thermo-mechanical treatment is shown in Fig. 135. A decrease in reheating temperature from 1300°C to 1000°C refined the ferrite grain size for a given rolling condition and this was more pronounced after holding 750°C compared with 950°C, prior to transformation. It can also be seen that increased holding time at 950°C, refined the ferrite grain size in all the vanadium steels. There was a general trend for ferrite grain refinement with decreasing reheating temperature. This effect of holding temperature will be discussed later. A comparison of the effect of reheating temperature on the ferrite grain size, in low and high nitrogen vanadium steels, Figs. 132 and 135, showed that in high nitrogen steels even holding at 950°C (after 50% reduction at 950°C) led to smaller ferrite grains with decreasing reheating temperature, whilst this was not the case for low nitrogen vanadium steels where the ferrite grain size did not vary with reheating temperature. The refinement of ferrite grain size in high nitrogen vanadium steels was due to increased retardation of recrystallization and growth of austenite grains after rolling at 950°C, by strain-induced precipitates.

Decreasing the rolling temperature refined the ferrite grain size, as observed in low nitrogen vanadium steels. However, the ferrite grain size in the high nitrogen steels was consistently finer than in the low nitrogen steels.

The effect of holding temperature on the ferrite grain size, after rolling at 950°C to 50% reduction is shown in Fig. 136. A decrease in holding temperature from 950°C to 750°C coarsened the ferrite grain size after reheating at 1300°C, but refined the ferrite grain size after reheating at 1150°C and 1000°C. This effect is similar to that observed in niobium steels and also in low nitrogen vanadium steels.

The effect of holding time on the ferrite grain size is shown in Fig. 137. Increasing the holding time from 100s to 1000s at both 950°C and 750°C, refined the ferrite grain size and the effect was more pronounced after holding at 950°C rather than 750°C. It should be noted that in the niobium steels and low nitrogen vanadium steels, increasing the holding time led to the formation of coarser ferrite grains. The reason for the refinement of the ferrite grain size with increasing holding time, can be explained by a complex interaction of V-Al-N during thermo-mechanical treatment. During rolling VN precipitation was strain-induced in the austenite in preference to AlN, because AlN is known to be slow to precipitate during cooling in austenite(68). The reason for this is associated with the high misfit of AlN in austenite compared with VN, and a consequent increase in surface energy. But during the more extended holding at 950°C, the increased thermodynamic stability of AlN allowed it to form as fine, uniformly distributed particles when it is precipitated in unrecrystallized austenite, leading to transformation of austenite to very fine ferrite grains. Such an interaction of V-Al-N is unique in the sense that aluminium can be used as a potential grain refiner when in association with vanadium, and as an agent to free vanadium from VN precipitated in austenite, so that it precipitates in ferrite and causes precipitation strengthening. The influence of aluminium on precipitation strengthening in vanadium steels will be discussed later.

13.3.5 The mechanism of ferrite formation.

13.3.5.1 Nucleation.

The following sites for ferrite nucleation, during the transformation of various morphologies of austenite, was observed:-

(i) The austenite grain boundaries: This was the prominant nucleation site . However, ferrite did not form uniformly at the recrystallized austenite grain boundaries, but rather at triple junctions and selected places on the grain boundaries, as shown in Figs. 60(a) and 68. Triple junctions provides extra surface energy for nucleation and hence promote preferential nucleation. The energy of austenite grain boundaries, varies from place to place, and its value depends on the local orientation difference between the two grains being large when the matching is poor. Hence the places where matching is poor provide preferential nucleation sites. At places where there is close matching, higher energy is required for nucleation and hence ferrite does not nucleate easily. On the other hand, deformation promotes more uniform ferrite nucleation at the austenite grain boundaries, see Figs. 60(c) and 69(c). This seems to be due to increased mismatch at grain boundaries after deformation. However, Roberts et al(234) showed that deformation leads to the formation of locally sharp curvature (bulges) on the grain boundary, which increase the nucleation area for ferrite, and suggested that these can be potential nucleation sites. In the present investigation, the formation of bulges or serrated grain boundaries were observed only when the deformation was low i.e. ~ 20% or after holding in the austenitic range after heavy deformation i.e. ~ 50%, see Fig. 56. Therefore, when serrated grain boundaries were not observed the increased ferrite nucleation is attributed to increased local mismatch at the grain boundary.

(ii) Deformation bands: Although nucleation at deformation bands was observed, Fig. 69(c), it should be noted that not all deformation bands had acted as nuclei. This was due to the variation of energy associated with deformation bands; a high energy deformation bands which nucleates ferrite, generally is formed only when larger deformations are given prior to transformation.

(iii) Second phase particles: Nucleation of ferrite on second phase particles is shown in Fig. 138.

(iv) Sub-structure or polygonised sub-grain boundary: It was very difficult to find direct evidence for this type of nucleation but intragranular nucleation in the absence of second-phase particles or deformation bands, has been interpreted as nucleation occurring on sub-grain boundaries. Such nucleation was found to increase with cooling rate as will be shown later. A typical example is shown in Fig. 139, for the 0.22% V steel. In this steel all the carbides were in solution at 950°C but some strain-induced VN occurred at 950°C. It can be seen that in the grains which do not contain deformation bands, ferrite nucleation seems to have occurred on sub-grain boundaries within the austenite grains.

(v) Twin boundaries: Non coherent twin boundaries can act as ferrite nucleation sites as it can provide some surface energy. The example for this has been shown in Fig. 139.

13.3.5.2 Mechanism for the formation of mixed ferrite grain size.

The formation of mixed ferrite grain sizes is known to be deleterious to toughness. It is essential therefore, to understand how mixed grain sizes form, so that a method can be devised to prevent them. The main reason for the formation of mixed ferrite grain size has been suggested to be due to partial recrystallization of austenite prior to transformation. However, the present work shows that although this may be the case, it is not the only mechanism in controlled rolled steels. Very little information is available on the prevention of mixed ferrite grain sizes during controlled rolling.

A comparison of the various morphologies of austenite grains and the resulting transformation structures after various thermo-mechanical treatments, suggests that the following may be responsible for the formation of a mixed ferrite grain size:-

(i) A mixed austenite grain size prior to rolling: An example of this has been shown in Fig. 73. The mixed austenite grain size prior to the finishing passes will generally result in either mixed unrecrystallized or partially recrystallized austenite, which tends to transform to a mixed ferrite grain size.

(ii) Partially recrystallized austenite: This can occur even if the austenite grain size was uniform at the reheating temperature, due to recrystallization of austenite prior to transformation. There are many reasons for the formation of partially recrystallized austenite:-

  (a) Non uniform austenite grain sizes prior to finish rolling: Fine grains recrystallizes in preference to coarse ones.

  (b) A partially recrystallized structure in the initial stages of rolling may be carried over to the following rolling passes. It is known(94) that, it is difficult to remove partially recrystallized austenite in the later passes.

  (c) If deformation in each pass is not sufficient to recrystallize the austenite completely before entering the next rolling pass, partial recrystallization will occur between rolling passes, and this will be carried over to the finishing passes.

(iii) The occurrence of multiple nucleation: Multiple nucleation of ferrite, Fig. 64(c), results in very fine ferrite grains at the deformed austenite grain boundaries, whilst coarse ferrite forms within the austenite grains. This has been termed 'cascade' nucleation(126), and leads to a very heterogeneous ferrite grain size. It must not be supposed that these fine ferrite grains are sequentially nucleated at their interfaces. Instead it is suggested that this is due to the formation of sub-grains in the austenite near to the grain boundaries because of the high strain gradient developed after large deformations. A schematic representation of the mechanism of multiple nucleation of ferrite is shown in Fig. 140. Ferrite nucleates on the sub-boundaries near to the austenite grain boundaries. It is thus a rather special form of grain boundary nucleation, giving locally very high rates of ferrite nucleation. A most beneficial structure would be the result if the whole specimen transforming by this mechanism.

(iv) Rolling in the critical range: When rolling occurs in the critical range, ferrite forms at the austenite grain boundaries, which are often deformed and unrecrystallized due to the low rolling temperature. During holding the deformed ferrite recrystallizes to a mass of very fine ferrite grains, Figs. 64(a), (b) and 70. The presence of precipitates can then prevent growth of these fine grains, and the residual austenite transforms to a coarser ferrite structure. This structure should not be confused with that produced by the transformation of the austenite, i.e. 'multiple nucleation', rather it is simply a recrystallization effect in deformed ferrite. It should be noted that deformed ferrite did not recrystallize during holding in niobium steels due to the niobium retarding recrystallization of the ferrite(235). However, in the base steel and the vanadium containing steels, ferrite did recrystallize during holding, and therefore, structures associated with recovered deformed ferrite were only observed in these steels.

It is generally believed that partially recrystallized austenite transforms to a mixed ferrite grain size. To overcome such a mixed ferrite grain size, it has often been suggested that a rolling practice is required which can give uniform recrystallized austenite prior to transformation. It should be noted that this would be difficult to achieve considering the requirement for strict control over the variables which leads to the formation of partially recrystallized austenite. Therefore, an alternative should consider a method for transforming the partially recrystallized austenite to a uniform ferrite grain size.

Studies on the transformation of austenite after various thermo-mechanical treatments suggest that, to a certain extent, the formation of mixed ferrite grain sizes can be retarded or inhibited by controlling the transformation conditions, after finish rolling. The formation of coarse ferrite grains, seems to be the main cause for the transformation of partially recrystallized austenite to mixed ferrite grain sizes.

If by some mechanism an increased nucleation of ferrite can be achieved within such coarse unrecrystallized austenite, the occurrence of mixed ferrite grain size would be minimised.

It has been shown that intragranular nucleation of ferrite occurs on the deformation bands and on sub-structural boundaries. It should be noted that these nucleation sites are not very effective due to their low energy. Hence it is necessary to activate more of these nucleation sites by increasing deformation in the finishing passes, to produce a more defective structure within the austenite grains, and by fast cooling immediately after finish rolling. Fast cooling minimises the growth of ferrite and also increases the nucleation rate within the austenite grains. This has been clearly demonstrated in the present investigation, see Figs. 75, 76, 81 and 83, which showed the transformation of austenite to mixed ferrite grain size when isothermal transformation occurs at 750°C, but when transformation occurs during continuous cooling uniform ferrite grains are formed. Isothermal transformation also represents the slow transformation which can occur during slow cooling. In conclusion, it is suggested that if sufficient deformation is given in the finishing passes, followed by fast cooling (but not so fast that transformation to acicular products occurs), the occurrence of mixed ferrite grain sizes can be minimised or prevented.

An another mechanism which leads to the formation of a mixed ferrite grain size is through non-uniform strain introduced in the through thickness direction during rolling. It is known that maximum deformation occurs just below the surface and decreases towards the mid-thickness of a steel plate. Such strain variations are likely to be more prominent in thick sections rather than in thin flat-rolled products. In the present investigation such a variation of strain was observed, as shown in Fig. 141, and resulted in a fine ferrite grain size just below the surface whilst some what coarser ferrite grains occurred at the mid-thickness.

13.3.6 A comparative effect of niobium and vanadium on the transformation of austenite, and the ferrite grain size.

Both niobium and vanadium in solution increased the hardenability of austenite, and this was particularly marked for niobium than for vanadium. However, both elements forms carbides and nitrides, thus making their effect on hardenability complex, as discussed earlier. Niobium is a strongercarbide and nitride former than vanadium and therefore it is difficult to utilise to the full the strong effect of niobium on hardenability.

The reason why niobium is more effective than vanadium may be associated with its larger atomic diameter which will cause it to segregate more positively to the austenite grain boundaries, and also to its greater affinity for carbon which will cause it to decrease the diffusion rate of carbon.

After various thermo-mechanical treatments it has been shown that additions of either niobium or vanadium refined the ferrite grain size. Vanadium refined the ferrite grain size particularly when the nitrogen content was high i.e. $\sim 0.02\%$. A general comparison of the ferrite grain size obtained suggests that niobium refined the ferrite grain over a much more wider range of thermo-mechanical treatments than did vanadium. On the other hand, vanadium refined the ferrite grain size at low rolling temperature, due to its effect on recrystallization. Therefore, a comparison of the effectiveness of niobium and vanadium on the ferrite grain refinement should be carried out at conditions giving optimum refinement for each element, rather than at the same rolling conditions. It should be noted that only a small amount of niobium or vanadium is needed to obtain the optimum ferrite grain refinement. The present results suggest that both niobium and vanadium are comparable in terms of their effect on ferrite grain refinement but the rolling practice to achieve optimum ferrite grain refinement is different for niobium and vanadium micro-alloyed steels. A possible rolling practice for niobium and vanadium steels to obtain optimum ferrite refinement, will be discussed later.

13.4 Effect of Thermo-mechanical Treatments and Composition Variables on the Precipitation Strengthening.

13.4.1 Niobium steels.

Niobium additions to plain carbon steels are used to refine the ferrite grain size and also to impart precipitation strengthening(185). Precipitation strengthening is due to the precipitation of Nb(C,N) in ferrite formed from the transformation of austenite present at the finish rolling temperature. However, precipitation of Nb(C,N) in the austenite, which can occur due to strain inducement during thermo-mechanical treatment, does not produce strengthening. Instead, by decreasing the amount of Nb(C,N) available for subsequent precipitation in the ferrite, precipitation in austenite actually decreases the precipitation strengthening which is observed(83,175). Strain induced precipitation during thermo-mechanical treatment depends on the strain, strain rate, time and temperature parameters involved, and any treatment which leads to such precipitation will reduce the general strength level observed, but there has been little systematic work to investigate this. It is also well known that the maximum precipitation strengthening occurs at the stoichiometric Nb:(C+N) ratio(44,236), because at stoichiometry the temperature dependence of the solubility of Nb(C,N) is a maximum. Again, however there is little systematic work to illustrate this effect.

The precipitation strengthening, $(\Delta H)_p$, is used as a measure of precipitation occurring in the austenite, the smaller $(\Delta H)_p$ the more precipitation having occurred in austenite.

13.4.1.1 The effect of thermo-mechanical treatments.

Precipitation strengthening increased with increasing reheating temperature, Fig. 89, due to the increased solubility of Nb(C,N). Because the lower niobium steels have less than the stoichiometric Nb:(C+N) ratio, see Fig. 113, the amount of Nb(C,N) precipitated will be controlled by the niobium dissolved in the austenite. It can be seen from Fig. 142 that for a given rolling condition, $(\Delta H)_p$ was a function of the amount of niobium dissolved in the austenite at the reheating temperature. There was also a tendency for the increase in $(\Delta H)_p$ with increasing reheating temperature to be greater as the Nb:(C+N) ratio increased up to the stoichiometric ratio.

It was apparent from Figs. 89 and 142 that the rolling temperature influenced $(\Delta H)_p$. Rolling at 1250°C and at 750°C produced a much larger $(\Delta H)_p$ value than rolling at 950°C, see Fig. 93. This was due to there being a maximum rate of strain induced precipitation of Nb(C,N) at 950°C, which therefore, precipitated more Nb(C,N) in the austenite and consequently gave less precipitation in the ferrite and a lower value of $(\Delta H)_p$. At rolling temperatures higher than 950°C, although the controlling diffusion rates were faster, the degree of supersaturation was lower, and it was the latter which resulted in the smaller strain-induced precipitation. At lower rolling temperatures than 950°C, the slow diffusion rates were responsible for the slower strain-induced precipitation. Consequently, the precipitation kinetics for strain-induced Nb(C,N) showed a 'C' curve with the maximum rate of precipitation at about 950°C. A similar effect has been observed by other workers (75,178-181). Such 'C' curve kinetics for strain induced precipitation of Nb(C,N) were observed irrespective of the prior reheating temperature and the niobium present in the steel.

Increasing the holding time at 950°C or 750°C, decreased the precipitation strengthening, Table 18. However, holding at 950°C after rolling at 950°C gave a relatively small decrease in $(\Delta H)_p$ because much of available precipitation had already been strain-induced in the austenite during rolling. On the other hand, rolling at 750°C and holding at 750°C produced a much greater decrease in $(\Delta H)_p$, because rolling at 750°C, to 50% reduction in one pass, produced rather less strain induced precipitation of Nb(C,N), and consequently more available for subsequent precipitation. The decrease in $(\Delta H)_p$ on increasing the holding time from 100s to 1000s was the result of two processes:-

(i) The continued precipitation of Nb(C,N) with increasing time in the deformed and unrecrystallized austenite, and

(ii) The growth of the Nb(C,N) already precipitated in the ferrite which had been formed either towards the end of rolling at 750°C or during the initial holding period of 100s at 750°C. This led to over-ageing of the Nb(C,N) and a decrease in $(\Delta H)_p$.

The decrease in $(\Delta H)_p$ with increasing holding time at 950°C or 750°C became less pronounced with decreasing reheating temperature prior to rolling. Again this was due to the lower supersaturation consequent upon the lower reheating temperature. An interesting effect which was observed was that after rolling at 1250°C, during which process the austenite recrystallized completly, subsequent holding at 950°C caused no effect on the intensity of precipitation strengthening. This was because there was no strain inducement of Nb(C,N) precipitation in recrystallized austenite, due to a very slow precipitation rate(110, 126,180,181). Finally, the effect of increasing the niobium content from 0.07% to 0.11% was to slightly increase $(\Delta H)_p$ for all rolling and holding temperatures, because the alloy was nearer to the stoichiometric Nb:(C+N) ratio and thus showed a greater degree of supersaturation, Table 18. It can therefore, be concluded that the degree of supersaturation, as well as the condition of the austenite, influences the degree of strain induced precipitation and thereby the precipitation strengthening.

The effect of rolling reduction on $(\Delta H)_p$, depended upon the reheating temperature, see Fig. 100. Reheating at 1300°C followed by rolling at 950°C and holding either at 950°C or 750°C caused the precipitation strengthening to decrease with increasing rolling reduction. This was because the austenite was not recrystallized, due to the retardation of recrystallization by dissolved niobium, the strain-induced Nb(C,N), the coarse initial austenite grain size and the absence of many undissolved Nb(C,N) particles which could nucleate recrystallization. Consequently, an increase in rolling deformation in the unrecrystallized austenite increased the amount of strain induced Nb(C,N) and thereby caused less Nb(C,N) to be available for precipitation strengthening of the ferrite. On the other hand, after reheating at 1150°C and 1000°C, rolling at 950°C and holding at either 950°C or 750°C, caused the precipitation strengthening to increase with increasing rolling reduction. This was because there was an increasing amount of recrystallization of the austenite with increasing rolling reduction after using these lower reheating temperatures. The reasons for this are the interaction between initial austenite grain size, the undissolved Nb(C,N) particles, the niobium in solution and the strain induced precipitation of Nb(C,N) on the recrystallization kinetics of the austenite. Because of the finer initial austenite grain size, the more undissolved Nb(C,N), the less dissolved niobium and the less strain induced Nb(C,N) consequent upon the lower supersaturation at these lower reheating temperatures, austenite recrystallization was less retarded. Hence, the amount of austenite recrystallization increased with increasing rolling deformation, being partially recrystallized after 20% reduction and completely recrystallized after 50% reduction. As the precipitation of Nb(C,N) is slow in recrystallized austenite, increasing deformation paradoxically led to less strain-induced precipitation of Nb(C,N) and consequently to an increased $(\Delta H)_p$ with increasing reduction during rolling. It is necessary therefore, always to consider the occurrence of strain induced Nb(C,N), and the consequent amount of precipitation strengthening, in context with the degree of recrystallization of the austenite.

13.4.1.2 Effect of the Nb:(C+N) ratio on $(\Delta H)_p$

An increase in Nb:(C+N) ratio up to stoichiometry, increased precipitation strengthening whilst above the stoichiometric ratio the precipitation strengthening decreased, Fig. 102. This effect is well known, the stoichiometric ratio giving the maximum supersaturation and the maximum potential for precipitation.

However, precipitation strengthening was dependent on the thermomechanical processing conditions. Consequently the effect of the Nb:(C+N) ratio must always be considered with respect to the processing conditions which may lead to strain induced precipitation of Nb(C,N) in the austenite. For example, maximum precipitation strengthening was observed with the highest reheating temperature of 1300°C, and using the highest rolling temperature of 1250°C at which virtually no strain induced precipitation occurred and in which, after rolling, the austenite was completely recrystallized. Under these conditions, increasing the holding time from 100s to 1000s at 750°C, Fig. 102, markedly decreased the precipitation strengthening. This was not due to a continued strain inducement of precipitation but rather to the growth and overageing of the Nb(C,N) precipitated in the ferrite. It can be seen that the greater the initial value of $(\Delta H)_p$ after 100s at 750°C, the greater was the decrease in $(\Delta H)_p$ on increasing the holding time to 1000s. This is believed to be a direct consequence of the effect of the Nb:(C+N) ratio on the supersaturation. The greater the number and the finer the Nb(C,N) precipitates originally present in the ferrite, the greater is the tendency for overageing and softening to occur during an increased holding time.

Using the same reheating temperature of 1300°C, but rolling at 950°C where strain induced precipitation of Nb(C,N) was most rapid, resulted in an even more marked decrease in $(\Delta H)_p$, and $(\Delta H)_p$ decreased further with increasing holding time at 950°C. This was due to strain induced precipitation decreasing the potential for subsequent precipitation strengthening, and the increased amount of strain induced precipitation formed by increasing holding time at 950°C. It was not due to overageing of the Nb(C,N) precipitated in the ferrite. It can also be seen that the detrimental effect of strain induced precipitation in the austenite became more pronounced as the Nb:(C+N) ratio approached the stoichiometric ratio, and this has been discussed previously.

The effect of the Nb:(C+N) ratio on the amount of niobium in solution at 1300°C, and therefore, available for precipitation strengthening after rolling at 1250°C and holding at 750°C, has been calculated from published solubility data, and related to the $(\Delta H)_p$ actually observed, Fig. 143. It can be seen that $(\Delta H)_p$ increased with increasing niobium in solution, but that above about 0.2% Nb in solution the value of $(\Delta H)_p$ remained virtually constant. It is suggested that this effect was due to the large amount of undissolved Nb(C,N) in those alloys which contained the largest amount of dissolved niobium. Some of the Nb(C,N) which would normally contribute to $(\Delta H)_p$ precipitated on the undissolved Nb(C,N) and thus did not add to the precipitation strengthening, with the effect shown in Fig. 143.

13.4.2 Vanadium steels.

Vanadium additions are widely used in H.S.L.A. steels to achieve both ferrite grain refinement and precipitation strengthening, but any precipitation of V(C,N) in austenite prior to its transformation to ferrite will inevitably decrease the amount of subsequent V(C,N) precipitation in the ferrite and thereby the precipitation strengthening. Such an effect has clearly been shown to exist for Nb(C,N) precipitation, but due to the greater solubility of V(C,N), it does not precipitate so extensively as Nb(C,N) in the austenite.

Whilst it is known that V(C,N) largely precipitates as an interphase precipitate during the transformation of austenite to ferrite, the extent to which it can precipitate directly from the ferrite after transformation is complete, has not been clearly established.

13.4.2.1 The effect of thermo-mechanical treatment on $(\Delta H)_p$ in low nitrogen-vanadium steels.

From published solubility data(62) vanadium carbide would be completely soluble in the austenite at 1000°C for vanadium contents up to 0.55%. On the other hand, due to the lower solubility of vanadium nitride in austenite(45), steels containing >0.11% V should contain undissolved vanadium nitride at 1000°C, but at 1150°C all the vanadium nitride should be in solution up to 0.50% V. It is not surprising therefore, that there was no effect of varying the reheating temperature from 1000°C to 1300°C on the intensity of precipitation strengthening, after rolling at 950°C or 750°C and holding at 950°C for 100s or 1000s in steels containing less than 0.22% V, Fig.90. However, the 0.55% V steel showed an increase in $(\Delta H)_p$ with an increase in reheating temperature from 1000°C to 1300°C, and this increase became more pronounced with longer holding time at 950°C. In this steel all the vanadium carbide and vanadium nitride would be dissolved at reheating temperatures of 1150°C and above. Consequently, simple solubility effects cannot explain why $(\Delta H)_p$ increased on increasing the reheating temperature from 1150°C to 1300°C. The steel however was aluminium killed, and an investigation has been made into any effect of aluminium on the solubility of vanadium nitride. It has been reported that aluminium does not affect the solubility of vanadium nitride nor vanadium of aluminium nitride(237). Nevertheless calculations assuming that aluminium nitride would be formed in preference to vanadium nitride because of its lower solubility$^{(45)}$, indicated that even so, all the vanadium-nitride would in fact be dissolved at 1000°C and above because of the decreased dissolved nitrogen content consequent on the presence of undissolved aluminium nitride. Hence, the aluminium cannot be the cause of the increase in $(\Delta H)_p$ with increasing reheating temperature. It is suggested that the effect observed is a kinetic effect, the lower temperatures of 1000°C and 1150°C not allowing complete solution of V(C,N) in the reheating time used, i.e. 30min. Hence, the higher the reheating temperature the more rapid the solution of V(C,N) and the nearer was the observed solubility to equilibrium. This could explain the increase in $(\Delta H)_p$ with increasing reheating temperature.

The greater dependence of $(\Delta H)_p$ on reheating temperature after 1000s holding at 950°C compared with 100s, in the 0.55% V steel, Fig. 90, is however a result of the aluminium present. During rolling at 950°C, vanadium nitride was strain induced in the austenite in preference to aluminium nitride because aluminium nitride is well known to be slow to precipitate during cooling austenite$^{(68)}$. The reason for this is associated with the high misfit of aluminium nitride in austenite compared with vanadium nitride, and a consequent increase in surface energy. But during the more extended holding at 950°C, the increased thermodynamic stability of aluminium nitride allows it to form, with a consequent solution of the strain induced vanadium nitride, which thereby increased the vanadium dissolved in the austenite and increased the amount of V(C,N) precipitation strengthening. The reason for the dependence of $(\Delta H)_p$ on reheating temperature being more pronounced with increasing holding time is due to greater supersaturation at the higher reheating temperature, and thus more strain inducement of vanadium nitride, together with the coarser initial austenite grain size leading to less recrystallization during rolling and hence more strain induced vanadium nitride. This effect of recrystallization was confirmed by the fact that the steel was only 32% recrystallized after 1000s at 950°C when reheated at 1300°C, compared with 96% recrystallized after reheating at 1150°C.

The effect of rolling temperature on $(\Delta H)_p$, Fig. 94, clearly showed that maximum strain induced precipitation of vanadium nitride occurred at 950°C. The effect was largely due to vanadium nitride or carbonitride as most of the vanadium carbide was readily soluble at this temperature. It is interesting to note that the maximum rate of vanadium nitride precipitation occurred at 950°C, i.e. about the same temperature as for Nb(C,N). In the 0.22% and 0.55% V steels, the value of $(\Delta H)_p$ was much less after rolling at 750°C than after rolling at 1250°C. This clearly shows that strain induced precipitation of V(C,N) occurred in austenite at 750°C. It can also be seen that the differential $(\Delta H)_p$ value between rolling at 1250°C and 750°C increased with increasing vanadium, indicating increased strain induced precipitation in austenite as the supersaturation increased. Hence, there was a difference between the vanadium and niobium steels in that the amount of strain induced precipitation, was much greater at temperatures below 950°C and down to 750°C in the vanadium steels compared with the niobium steels. The results indicate that, due to the solubility of vanadium carbide being much lower at 750°C than at 950°C, a considerable proportion of the strain induced precipitation at 750°C was vanadium carbide. Hence it is concluded that vanadium carbide was strain induced in austenite at temperatures of ~750°/ 800°C, whereas vanadium nitride was the precipitating phase at higher temperatures of ~950°C.

As indicated earlier in the discussion, the amount of strain induced precipitation in the austenite was very dependent upon the state of recrystallization of the austenite. If austenite is unrecrystallized, strain induced precipitation of V(C,N) is much more rapid and pronounced than if the austenite is fully recrystallized. This has a marked effect on the influence of holding temperature and time, which allows much more V(C,N) to be precipitated if the austenite is unrecrystallized. This is shown by, for example, the fact that rolling at 1250°C allowed complete recrystallization of austenite and there was, therefore, no strain induced precipitation and hence a high $(\Delta H)_p$ value. On the other hand, the partially recrystallized austenite during rolling at 950°C allowed considerable strain induced precipitation and thus a much lower $(\Delta H)_p$ value, Figs. 96 and 97. It can also be seen, Fig. 97, that with full solution of V(C,N) and aluminium nitride at 1300°C, followed by rolling at 1250°C, which produced complete recrystallization, increasing the holding time at 950°C caused much less strain induced precipitation than the same increase in holding time at 750°C. This was due to the greater strain inducement of V(C,N) at the lower temperature.

An increase in rolling reduction in all the steels tended to decrease $(\Delta H)_p$, the effect being more pronounced with increasing vanadium content, Fig. 101. This effect was due to increased amounts of precipitation in the austenite during rolling with the higher deformations, and to the higher supersaturation with increased vanadium content. Some variation in $(\Delta H)_p$ with varying reduction could be attributed to the more rapid precipitation in unrecrystallized austenite compared with recrystallized austenite. This effect could be either accentuated or decreased by increasing the holding time, depending on the interaction between precipitation and recrystallization.

13.4.2.2 The effect of thermo-mechanical treatment on $(\Delta H)_p$ in high-nitrogen vanadium steels.

As expected from the solubility data, in the 0.14% V steel there was no effect of reheating temperature on $(\Delta H)_p$, all the vanadium carbide and vanadium nitride being dissolved above 1000°C, Fig. 91. The 0.25% V steel is also consistent with the solubility data, showing a slight increase in $(\Delta H)_p$ with increasing reheating temperature to 1150°C and no further effect at 1300°C. In the case of the 0.46% V steel the effects are more complex. At first sight it seems that the values for $(\Delta H)_p$ after reheating at different temperatures, rolling at 950°C and holding at that temperature for 100s follow solubility predictions, i.e. all the vanadium carbide and vanadium nitride being dissolved above 1150°C, Fig. 91(a). But $(\Delta H)_p$ after reheating at 1150°C is rather small after holding for 100 s at 950°C compared with holding for 1000s. Part of the reason for this effect could be the kinetics of solution of vanadium nitride, mentioned previously, but it must also be appreciated that rolling at 950°C can strain induce vanadium nitride and so decrease $(\Delta H)_p$. But strain induced vanadium nitride cannot explain the large increase in $(\Delta H)_p$ after holding for 1000s at 950°C, as the reheating temperature changes from 1000°C to 1150°C, and the absence of any further increase in $(\Delta H)_p$ when the reheating temperature is raised further to 1300°C. A possible explanation to this effect lies in the aluminium content of the steel. Reheating at 1150°C leaves aluminium nitride undissolved, so that on holding at 950°C it may nucleate for further precipitation of aluminium nitride with a result that vanadium-nitride which had been strain induced during rolling redissolves, freeing more vanadium to take part in strengthening precipitation, i.e. increasing $(\Delta H)_p$, Fig. 91(b). On the other hand, reheating at 1300°C dissolved all the aluminium nitride, so that subsequent aluminium nitride precipitation was inhibited and thus full solution of the strain induced vanadium nitride (at 950°C) did not occur. Hence there was no continuing increase in $(\Delta H)_p$ as the reheating temperature increased to 1300°C, and it is significant that with this reheating temperature (1300°C) there was no effect of holding time on $(\Delta H)_p$. It is suggested that had the holding been increased beyond 1000s, then $(\Delta H)_p$ would have increased as aluminium nitride precipitated and the strain induced vanadium nitride dissolved.

As in the low nitrogen steels, rolling at 950°C produced maximum strain-induced precipitation in the austenite, and therefore minimum precipitation strengthening. The effects, Fig. 95, were similar to those observed in Fig. 94 for the low nitrogen steels, and the intensity of $(\Delta H)_p$ increased with increasing vanadium content, because $(\Delta H)_p$ was rather more dependent on carbon than on nitrogen. However, there was a difference between the low and high nitrogen steels in that there was not such a low relative value of $(\Delta H)_p$ after rolling at 750°C. This was interpreted as indicating that there was less strain induced precipitation in the austenite at 750°C in high nitrogen steels compared with the low nitrogen steels, which implies that vanadium nitride tends to precipitate in austenite predominantly at 950°C and above. On the other hand, vanadium carbide tends to precipitate in austenite at temperatures of 950°C and below. An interesting feature was shown by comparing the curves of $(\Delta H)_p$ against rolling temperature for high and low nitrogen contents at equivalent vanadium contents, Fig. 144, which shows that the cross over of the curves which indicates the temperature of change over from vanadium nitride to vanadium carbide strain induced precipitation, occurs at the same temperature i.e. 830/850°C, for both 0.14% and 0.22/0.25% V steels. The indications therefore are that vanadium nitride is precipitated by strain inducement in the austenite above 830/850°C whilst vanadium carbide forms strain induced precipitates in austenite below 830/850°C. It is interesting to note that a similar effect to that observed in the high nitrogen-vanadium steels was also observed in niobium steels, and that the solubility of vanadium nitride in austenite is not very different from that of niobium carbide(45), Fig. 145.

In general, decreasing the holding temperature from 950°C to 750°C decreased $(\Delta H)_p$, as was observed also for low nitrogen-vanadium steels, Fig. 98. There were, however, results which did not conform with this general trend. For example after reheating at 1300°C and rolling at 950°C, there was no change in $(\Delta H)_p$ for the 0.14% and 0.25% V steels on decreasing the holding temperature from 950°C to 750°C. This was due to the fact that there was no strain induced precipitation on rolling at 1250°C and so the increased supersaturation at 750°C gave more precipitation than during holding at 950°C, and hence lower $(\Delta H)_p$, Fig. 98. However, rolling at 950°C, caused marked strain induced precipitation which produced a lower $(\Delta H)_p$ and little effect of decreasing the holding temperature to 750°C. The effect was therefore, largely one of a lower degree of supersaturation consequent upon strain induced precipitation.

Increasing the holding time after reheating at 1300°C and rolling at 1250°C, caused a decrease in $(\Delta H)_p$, which was more pronounced on holding at 750°C than at 950°C, Fig. 99, for the reasons outlined earlier. On the other hand, reheating at 1300°C, but rolling at 950°C caused much strain induced precipitation, Fig. 95, and consequently no further precipitation occurred on holding at either 950°C or 750°C, so that $(\Delta H)_p$ remained constant, Fig.99. Decreasing the reheating temperature to either 1150°C or 1000°C gave undissolved vanadium-nitride. The maximum precipitation rate for vanadium nitride in austenite was at 950°C so that $(\Delta H)_p$ was relatively small, and because of aluminium nitride precipitation at this temperature with increasing holding time, vanadium was released to combine with carbon and thus increase $(\Delta H)_p$, Fig. 99. Generally, increasing the vanadium content increased $(\Delta H)_p$ for any given thermo-mechanical treatment conditions.

13.4.2.3 The effect of stoichiometry.

It has been demonstrated by Wadsworth, Keown and Woodhead(238) that the temperature dependence of solubility of MX carbo-nitrides in austenite shows a very sharp maximum at the stoichiometric metal:carbon or nitrogen ratio.

In the low nitrogen vanadium steels, Fig. 103 clearly shows that precipitation strengthening is a maximum at a stoichiometric ratio. Considering the work of Wadsworth et al, and using the data in Fig. 103 which lies on either side of stoichiometry, it is concluded that the stoichiometric ratio for these low nitrogen steels is $\sim$5.6. This value is much closer to the stoichiometry of V_4C_3 than of VC, which has a V:C ratio of 4.25. This suggests an interstitial defect lattice. It can also be seen that apart from the major effect of V:C ratio on $(\Delta H)_p$, the thermo-mechanical treatment also had a major effect. Any treatment which precipitated the V_4C_3 in the austenite, decreased $(\Delta H)_p$, whilst still retaining the influence of the stoichiometric ratio. However, it is always observed that, because of the maximisation of supersaturation at the stoichiometric ratio, any strain induced precipitation was always more pronounced at the stoichiometric composition.

In the high nitrogen steels, with increasing V:C, V:N or V:(C+N) ratios the value of $(\Delta H)_p$ progressively increased, Fig. 104, and there was no data for hyper-stoichiometric alloys. However, it can be seen that if $(\Delta H)_p$ is a function of the V:C ratio,it is possible that there is a maximum near to the stoichiometry for V_4C_3. The curve for $(\Delta H)_p$ as a function of V:N ratio however, clearly shows that the results do not indicate VN as the precipitate responsible for strengthening, as the V:N ratios are far in excess of stoichiometry,(3.63), and yet the $(\Delta H)_p$ increases with increasing V:N ratio. It is known however, that V(C,N) can be formed and if it is assumed that the C:N ratio in the carbonitride is the same as that in the steel, maximum $(\Delta H)_p$ values should be obtained at a ratio $\sim$4.10, if the carbo-nitride approximates to V(C,N) rather than $V_4(CN)_3$. Whilst the results are not definitive, it appears that the stoichiometric ratio is somewhat between 4.10 and 5.65, but nearer to the upper value. Again the stoichiometry indicated $V_4(CN)_3$, but it is tentatively suggested that the nitrogen can fill some of the interstitial vaccancies in the V_4C_3 lattice. A similar effect has been observed in the case of niobium carbide containing nitrogen in austenitic steel(239). Again however, any strain induced precipitation is always more pronounced as the composition moves towards the stoichiometric ratio.

13.4.2.4 The precipitation of vanadium carbide from ferrite.

Two forms of precipitation may contribute to strengthening, namely the formation of interphase precipitation at the γ/α interface during the transformation(200,240), and the precipitation of the carbide from supersaturated solid solution in the ferrite after transformation(206,240). The intensity of interphase precipitation is largely controlled by the composition of the bulk steel with respect to the stoichiometric ratio. On the other hand, precipitation from the ferrite after transformation often occurs on dislocations introduced into the ferrite by the transformation strains. This latter type of precipitate would be expected to occur at the stoichiometric ratio for the vanadium and carbon dissolved in the ferrite itself. Specimens which had been reheated at 1300°C, rolled at 950°C and held at 950°C for 100s prior to sand cooling, were then tempered at 650°C for 30min. A further increase in hardness was observed due to precipitation from the ferrite. It can be seen, Fig. 146, that if this further increase in hardness is plotted against the V:C ratio in the bulk steel, a maximum is observed, but at a V:C ratio in the bulk steel much less than the stoichiometric ratio. The reason for this is that it is the V:C in the ferrite itself which is important, and because pearlite had formed, the effective carbon dissolved in the ferrite was much less than that in the austenite at 950°C. Hence the true V:C ratio in the ferrite was higher than that indicated by the bulk composition of steel. If it is assumed that the vanadium dissolved in the austenite when transformation occurred at ~750°C was inherited in the ferrite; and that the maximum precipitation strengthening after tempering occurred at the correct stoichiometric ratio of 5.65 in the ferrite, then it can be calculated that the carbon dissolved in the ferrite was ~0.003%, whilst the vanadium dissolved in the ferrite was ~ 0.018%. Thus the solubility product of vanadium carbide was about 1000 times smaller in ferrite than in austenite. It can also be seen that vanadium decreased the solubility of carbon in ferrite by a factor of ~10.

It is worth pointing out however, that because the majority of the strengthening is the result of interphase precipitation in most continuously cooled steels, control over the interphase precipitation is essential to control the strength. Yet few studies have been made on interphase precipitation during continuous cooling.

13.4.2.5 The effect of nitrogen in vanadium steels.

The precipitation strengthening in the high nitrogen vanadium steel was consistently smaller at any given vanadium content than in the low nitrogen steel, Fig. 147. This also was observed at all V:C ratios, even though the maximum precipitation strengthening in both low and high nitrogen steels occurred at the stoichiometric ratio of ~5.65, Fig. 148.

This effect is opposite to that sometimes suggested in the literature (99,115,206), although differing opinions of the effect of high nitrogen in precipitation strengthening in vanadium steels have been proposed. The mechanism by which nitrogen may increase precipitation strengthening is not well understood, but has been attributed to an increase in coherency strains for vanadium nitride compared with vanadium carbide(207). On the other hand, it has been suggested that by strain induced precipitation of vanadium nitride in austenite at 800-900°C, the higher nitrogen content decreases precipitation strengthening(140). This latter suggestion is in agreement with the present work. An examination of the conditions under which high nitrogen increases precipitation strengthening suggests that it occurs when:-

(i) the steel contains aluminium: This precipitates aluminium-nitride in austenite and causes vanadium nitride to dissolve and produce more vanadium in solution for subsequent precipitation. This is precisely the case in the present work.

(ii) aluminium nitride is precipitated in ferrite by slow cooling after coiling: This can give more enhanced precipitation strengthening because the vanadium carbide thus formed occurs in the ferrite directly, and is finer than interphase precipitation.

(iii) heavy deformation occurs prior to transformation so that strain-induced precipitation of aluminium nitride takes place in the austenite.

(iv) the amount of vanadium is low so as to minimise the strain induced vanadium nitride precipitation in the austenite, in the absence of aluminium.

It may be concluded therefore, that high nitrogen only increases precipitation strengthening in aluminium steels where no strain induced vanadium nitride precipitation occurs in austenite, and in the present work the decrease in precipitation strengthening in the high nitrogen steels was due to the fact that aluminium nitride precipitation was incomplete under the thermo-mechanical treatment conditions used, so that full re-solution of vanadium nitride did not occur.

The suggestion reported earlier(207) that nitrogen increases the coherency strains is not in agreement with the fact that nitrogen decreases the lattice parameter of V(C,N) and thereby decreases the misfit with ferrite(190). Hence higher nitrogen should not increase precipitation strengthening by this mechanism but it is possible that the increased precipitation strengthening is due to:-

(i) the higher volume fraction of precipitates consequent upon the decreased solubility of vanadium nitride compared with vanadium-carbide(241).

(ii) the fact that vanadium nitride remains coherent longer than vanadium carbide(242), because it does not loose coherency due to its smaller misfit with ferrite.

(iii) a refinement in the interband spacing and size of interphase precipitates due to nitrogen(242).

13.4.3. Niobium plus vanadium steels.

It is generally believed that a combined additions of niobium and vanadium in controlled rolled steels can offer both grain refinement from niobium and precipitation strengthening from vanadium. It remains to be seen whether the combined additions of these alloying elements behave similar to their effects when added seperately, i.e. niobium acting as a grain refiner whilst vanadium acts to precipitation strengthen. It also needs to be established whether the grain refining and precipitation strengthening from these elements are additive. It has been shown earlier, section 13.3.2.2, that (Nb+V) steels produced finer ferrite grain sizes than could be achieved by niobium or vanadium when they were added individually. Studies on the effect of combined additions of niobium and vanadium on the precipitation strengthening in controlled rolled steels, should provide useful information for the optimisation of properties in (Nb+V) steels.

The effect of reheating temperature on the precipitation strengthening is shown in Fig. 92. When niobium and vanadium are added together it was concluded that the precipitating phase would be NbV(C,N) and the temperature dependent solubility may lie inbetween that of Nb(C,N) and V(C,N). As no information is available on the solubility data for NbV(C,N), it is difficult to test this hypothesis. An increase in reheating temperature increased the precipitation strengthening in low nitrogen (Nb+V) steel, but the effect was complex in high nitrogen (Nb+V) steel, see Fig. 92.

The effects of rolling temperature, holding temperature and time on the precipitation strengthening were similar to those observed in niobium and vanadium steels, and can be explained on a similar basis to that for niobium and vanadium steels.

13.4.4. Comparative effect of niobium and vanadium.

Fig. 149 shows the relative effects of niobium and vanadium on precipitation strengthening. It can be seen that:-

(i) providing all the Nb(C,N) is dissolved, (which implies much higher temperatures due to the lower solubility of Nb(C,N) than of V(C,N)), and that little or no strain induced Nb(C,N) occurs in the austenite, then niobium can produce higher precipitation strengthening than vanadium, at low total alloy contents, Fig. 149(a) and (c). The reason for this is the large lattice parameter of Nb(C,N) compared with V(C,N)(190) which produces more coherency strains, and the lower solubility of Nb(C,N) than V(C,N) in ferrite which increases the volume fraction of precipitates.

(ii) if the thermo-mechanical treatments are such as to lead to heavy strain induced precipitation of Nb(C,N), (which can more readily occur than for V(C,N) due to its lower solubility), then the intensity of precipitation strengthening is much reduced and is much less for Nb(C,N) than for V(C,N) at a constant alloy content, Fig. 149(b).

(iii) the precipitation strengthening by Nb(C,N) is much more sensitive to reheating temperature than is that due to V(C,N), Fig. 149 (d) and (c), so that with lower reheating temperatures vanadium produces much more precipitation strengthening than does niobium, at all alloy contents.

(iv) the amount of precipitation strengthening increases continuously with increasing vanadium content, but quickly reaches a maximum with increasing niobium content. At higher alloy levels, vanadium gives more precipitation strengthening than does niobium, and it is possible to exert more control over the intensity of precipitation strengthening by changing the composition in vanadium steels than in niobium steels.

Precipitation strengthening obtained in low nitrogen (Nb+V) steel is compared with a calculated $(\Delta H)_p$ for an equivalent amount of niobium and vanadium when they are present seperately, Table 23. Such comparisons have not been made for high nitrogen (Nb+V) steel because of complexities involved due to interaction of nitrogen in this steel with niobium, vanadium and aluminium. From Table 23, it can be seen that:-

(i) the $(\Delta H)_p$ value of (Nb+V) steel was consistently lower than the sum of $(\Delta H)_p$ for niobium and vanadium when they are added seperately. The $(\Delta H)_p$ value of (Nb+V) steel was about half or less than the calculated $(\Delta H)_p$ value, Table 23.

(ii) there was no direct relationship between $(\Delta H)_p$ for (Nb+V) steel and the calculated $(\Delta H)_p$ value for niobium or vanadium when they are added separately.

(iii) the $(\Delta H)_p$ value for (Nb+V) steels was somewhat higher than the calculated value for vanadium, depending on the thermo-mechanical treatment used.

(iv) the $(\Delta H)_p$ value for (Nb+V) steel was higher than the calculated $(\Delta H)_p$ for niobium when the thermo-mechanical treatment resulted in complete solution of Nb(C,N) and minimum strain induced precipitation of Nb(C,N) in austenite, see Table 23, coditions 1 to 3. On the other hand, when complete solution of Nb(C,N) did not occur due to too low a reheating temperature, and when the strain induced precipitation of Nb(C,N) occurred in austenite, the $(\Delta H)_p$ for (Nb+V) steels was higher than the calculated $(\Delta H)_p$ for niobium. The additional precipitation strengthening in (Nb+V) steel was due to vanadium.

Therefore, it can be concluded that the precipitation strengthening due to niobium and vanadium when added together would be lower than the sum of that which can be achieved from niobium and vanadium added individually.

CHAPTER 14

CONCLUSIONS.

Austenite Grain Coarsening.

(1) Increasing niobium refined the austenite grain size, but not indefinitely, as there exists an equilibrium grain size for each reheating temperature, and further grain refinement does not occur with increasing niobium. This equilibrium grain size increased with reheating temperature, and larger amounts of Nb(C,N) were required to achieve the equilibrium austenite grain size with increasing temperature.

(2) The austenite grain coarsening temperature was related to the fine precipitates of Nb(C,N) (calculated from the temperature dependent solubility of Nb(C,N)), increasing with niobium content up to the Nb:(C+N) stoichiometric ratio. A further increase in niobium above stoichiometry lowered the austenite grain coarsening temperature.

(3) Vanadium refined the austenite grain size mainly by the more stable VN precipitates rather than by V_4C_3 precipitates which dissolved at low temperature. As with niobium steels, there was an equilibrium austenite grain size in vanadium steels beyond which no further grain refinement was possible.

(4) Vanadium was very effective in retarding austenite grain coarsening at temperatures less than 1050°C.

(5) Increasing vanadium raised the austenite grain coarsening temperature to about 1050°C at $\sim$0.20% V, but it remained constant at higher vanadium contents.

(6) The austenite grain coarsening temperature was always lower than the solubility temperature for VN, due to coarsening of the VN precipitates and the decreased volume fraction.

(7) Increasing nitrogen to $\sim$0.02% in vanadium steels had a similar effect on the austenite grain growth, to that observed for the low nitrogen vanadium steels except that it raised the austenite grain coarsening temperature to $\sim$1100°C compared with $\sim$1050°C obtained in low nitrogen vanadium steels.

(8) In (Nb+V) steels, austenite grain coarsening was controlled by Nb(C,N) precipitates and therefore the niobium content of the steel.

(9) Niobium was more effective than vanadium in retarding austenite grain growth and in raising the austenite grain coarsening temperature. This was associated with greater stability of Nb(C,N), and slower coarsening rate of Nb(C,N) than of VN or V_4C_3.

Austenite Recrystallization.

(1) Niobium in the steel retarded the recrystallization of austenite.

(2) The recrystallization of austenite increased with decreasing prior austenite grain size, increasing rolling temperature and increasing rolling reduction.

(3) Increasing amounts of undissolved Nb(C,N) particles increased recrystallization by acting as nuclei for recrystallization.

(4) The retardation of austenite recrystallization increased with increasing niobium provided that the amount of undissolved Nb(C,N) was low.

(5) Niobium retarded the recrystallization by retarding both the nucleation and the growth of recrystallized grains.

(6) Dissolved niobium retarded the nucleation of recrystallized grains but did not retard their growth even at temperatures as low as 950°C. On the other hand, strain induced Nb(C,N) retarded both nucleation and growth of the recrystallized grains.

(7) The nucleation sites for recrystallization were deformed austenite grain boundaries, deformation bands, the interfaces between recrystallized and unrecrystallized austenite grains and second-phase particles.

(8) Nucleation at interfaces between recrystallized and unrecrystallized austenite grains occurred only when the growth of recrystallized grains was inhibited by very fine precipitates, such as strain induced Nb(C,N).

(9) The mechanism of nucleation of recrystallized grains was either by sub-grain growth or by strain induced grain boundary migration, the former being predominant at high deformations whilst the later was dominant at low deformations.

(10) In controlled rolling it is essential to retard recrystallization of austenite for a sufficient time so as to increase the flexibility of the rolling process and this can only be achieved through strain induced Nb(C,N) and not by niobium in solution, which retards recrystallization only for a very short time.

(11) Increasing niobium up to 0.46% refined the recrystallized austenite grain size, but higher niobium contents caused the recrystallized grain size to coarsen.

(12) The growth of recrystallized grains immediately after rolling was not significant up to holding times of 1000s, even at temperatures as high as 1250°C, when the steel contained >0.07% Nb. At 950°C the growth of recrystallized grains was completely inhibited in niobium containing steels.

(13) The growth of recrystallized grains was rapid in steels which had undergone 20% deformation rather than 50% deformation. This was due to an inhomogeneous grain size after 20% deformation.

(14) Combined additions of niobium and vanadium led to more retardation of recrystallization than when niobium or vanadium were added seperately.

(15) The effects of thermo-mechanical treatment variables on the recrystallization kinetics in low and high nitrogen vanadium steels were similar to those observed in niobium steels. Vanadium retarded the recrystallization at temperatures lower than 950°C.

(16) An increase in vanadium content in both low and high nitrogen steels, increased the retardation of recrystallization.

(17) Vanadium retarded recrystallization by strain induced V(C,N) precipitates. Therefore, an increase in nitrogen which increased the volume fraction of VN or V(C,N) at high temperatures, tended to enhance the retardation of recrystallization.

(18) Vanadium in both low and high nitrogen steels refined the recrystallized austenite grain size immediately after rolling. However, to maintain this fine grain size for prolonged times, it was necessary to have fine strain induced precipitates in the matrix; hence the refinement of the recrystallized grain size by vanadium was apparent at low temperatures due to V(C,N) being strain induced at such low temperature.

(19) The presence of high nitrogen in vanadium steels, tended to decrease

the recrystallized austenite grain size for a given vanadium content and thermo-mechanical treatment.

(20) The mechanism involved in the refinement of the recrystallized austenite grain size by niobium and vanadium, was associated with an increased nucleation rate and retardation of growth of the recrystallized grains, by strain induced precipitates of Nb(C,N) or V(C,N).

(21) The grain growth of recrystallized grains during holding, in both low and high nitrogen vanadium steels occurred at 1250°C, but was inhibited at 950°C.

(22) Both the niobium and vanadium retarded recrystallization but niobium did so at much higher temperatures than vanadium.

Transformation

(A) Niobium Steels.

(1) Niobium in solution increased the hardenability. Increasing the austenite grain size also increased the hardenability, but to a less extent than niobium in solution over the austenite grain size range examined.

(2) Undissolved Nb(C,N) decreased the hardenability, as also did thermo-mechanical treatments which lowered the niobium in solution, i.e. low reheating temperatures or rolling to high reductions at 950°C.

(3) Increasing the niobium to ~0.07% markedly refined the ferrite grain size, but increasing niobium above 0.16% had no further ferrite grain refining effect.

(4) Low reheating temperatures, low rolling temperatures and high rolling reductions all refined the ferrite grain size.

(5) The effect of holding temperature on the ferrite grain size was complex. Decreasing the holding temperature increased the ferrite grain size after high reheating temperatures, but decreased the ferrite grain size at low reheating temperatures.

(6) Increasing the holding time after rolling, caused an increase in the ferrite grain size.

(7) The ferrite grain size depended on the nucleation and growth of the ferrite during austenite transformation. Niobium in solution decreased the ferrite nucleation rate and the ferrite growth rate.

Also niobium in solution and as strain induced Nb(C,N) precipitates, retarded austenite recrystallization and hence increased the nucleation rate for ferrite.

(8) The grain growth of impinged ferrite grains was retarded by Nb(C,N) precipitates.

(B) (Nb+V) Steels.

(9) Combined additions of niobium and vanadium increased the ferrite grain refinement after most of the thermo-mechanical treatments, due to increased retardation of recrystallization by NbV(C,N) precipitates.

(10) An increased nitrogen content in (Nb+V) steels refined the ferrite grain size after high reheating temperatures prior to thermo-mechanical treatments, whilst it had no effect after low reheating temperatures.

(11) Decreasing the reheating and rolling temperatures refined the ferrite grain size in both the (Nb+V) steels.

(12) The effect of holding temperatures on the ferrite grain size was similar to that observed in niobium steels.

(13) Increased holding time at 950°C and 750°C did not affect the ferrite grain size, therefore it is suggested that the addition of vanadium to niobium steel, tends to maintain a fine ferrite grain size even after prolonged holding times.

(C) Vanadium Steels (Low nitrogen).

(14) Vanadium in solution increased the hardenability of steel although the effect was complex due to its carbide and nitride forming tendencies and the ease of precipitation during transformation.

(15) Vanadium refined the ferrite grain size, particularly after rolling at low temperatures and there was no systematic relationship between ferrite grain size and vanadium content.

(16) There was no consistent effect of reheating temperature on the ferrite grain size, which varied with the thermo-mechanical treatment.

(17) Holding in the austenite range after rolling, coarsened the ferrite grain size whilst continuous cooling immediately after rolling refined the ferrite grain size.

(18) An increase in holding time up to 1000s at 750°C and 950°C did not affect the ferrite grain size significantly in vanadium steels, but consistently caused a coarser ferrite grain size in the base steel.

(19) Decreasing the rolling temperature and increasing the amount of deformation, refined the ferrite grain size, particularly at low rolling temperatures.

(D) Vanadium Steels (High nitrogen)

(20) An increase in nitrogen to 0.02% in vanadium steels increased the hardenability of steel, although the effect was small.

(21) High nitrogen vanadium steels gave consistently finer ferrite grain sizes than low nitrogen steels.

(22) As observed in low nitrogen steels, there was no systematic variation of ferrite grain size with vanadium content in high-nitrogen steels.

(23) Decreasing the reheating and rolling temperatures refined the ferrite grain size, particularly in high nitrogen vanadium steels.

(24) Holding at 950°C after rolling, refined the ferrite grain size in all the high nitrogen vanadium steels, and it should be noted that in niobium and low nitrogen vanadium steels the ferrite grain size coarsened when held at 950°C. The different effects of holding temperature in these steels have been explained on the basis of Al-N-V interaction in high nitrogen steels.

(25) Holding at 750°C coarsened the ferrite grain size at high reheating temperatures but refined the ferrite grain size at low reheating temperatures.

(26) Increasing the holding time from 100s to 1000s at both 950°C and 750°C, refined the ferrite grain size, and the effect was more pronounced after holding at 950°C compared with 750°C. This effect was opposite to that observed in niobium and low nitrogen vanadium steels, where the ferrite grain size coarsened with an increase in holding time.

Mechanism of Transformation and Occurrence of Mixed Ferrite Grain Sizes.

(27) The nucleation sites for ferrite were the austenite grain boundaries

and triple junctions, deformation bands, second-phase particles, sub-structure or polygonised sub-grain boundaries, and twin non-coherent boundaries.

(28) The ferrite nucleation rate at the austenite grain boundaries was high when the grain boundary was deformed. The mechanism of such increased ferrite nucleation due to deformation has been discussed.

(29) Various mechanisms for mixed ferrite grain size formation in controlled rolled products have been suggested and discussed. It has been shown that a mixed austenite grain size prior to rolling, the occurrence of multiple ferrite nucleation, rolling in the critical temperature range, and non-uniform strain in the through thickness direction, leads to the formation of mixed ferrite grain sizes.

(30) In the case of partially recrystallized austenite and non-uniform unrecrystallized austenite resulting from mixed austenite grain sizes, the occurrence of mixed ferrite grain sizes has been shown to be prevented by heavy deformation prior to transformation, inorder to create more intragranular nucleation sites, coupled with fast cooling rate to increase ferrite nucleation within the coarse unrecrystallized austenite grains.

Precipitation Strengthening.

(A) Niobium Steels

(1) Precipitation of Nb(C,N) in ferrite caused precipitation strengthening which increased with increasing reheating temperature.

(2) Precipitation of Nb(C,N) in the austenite did not cause precipitation strengthening and decreased the amount of niobium in solution. This decreased the subsequent precipitation strengthening.

(3) Strain induced precipitation in the austenite was more pronounced during rolling at 950°C than during rolling at both higher and lower temperatures.

(4) Increasing the rolling reduction increased the amount of strain-induced Nb(C,N) precipitated in the austenite.

(5) Increasing the holding time at both 950°C and 750°C decreased the

intensity of precipitation strengthening.

(6) The intensity of precipitation strengthening increased with increasing Nb:(C+N) ratio up to the stoichiometric ratio of about 8 and above this the precipitation strengthening decreased.

(7) The presence of large quantities of undissolved Nb(C,N) lowered the precipitation strengthening due to precipitation of Nb(C,N) on these prior precipitates.

(B) Vanadium Steels.

(8) To achieve maximum precipitation strengthening for a given vanadium content it is necessary to:-

- dissolve all the vanadium carbo-nitride in austenite,
- prevent strain-induced precipitation of vanadium nitride or vanadium carbide in austenite,
- control the size and distribution of precipitates which are produced by interphase precipitation.

(9) Although solubility data can be used to decide the reheating temperature for complete solution of vanadium nitride and vanadium-carbide, it is also necessary to consider the kinetics, particularly in high vanadium steels where large quantities of precipitates are present.

(10) Strain-induced precipitation of vanadium carbide in austenite occurred at a maximum rate at 830-850°C. An increased strain-induced precipitation of vanadium nitride and vanadium carbide in austenite, decreased precipitation strengthening.

(11) Decreasing the holding temperature from 950°C to 750°C decreased precipitation strengthening due to the precipitation of both vanadium carbide and nitride in austenite. Such a decrease in precipitation strengthening was more pronounced when the austenite was unrecrystallized, due to much faster precipitation in such austenite.

(12) An increase in rolling reduction, depending on whether recrystallization had taken place, either lowered or did not alter precipitation strengthening. Unrecrystallized austenite produced by high deformations, increased the rate of strain-induced precipitation of vanadium nitride in austenite and thus decreased the precipitation strengthening.

(13) Precipitation strengthening increased with an increase in V:C ratio up to the stoichiometric ratio for V_4C_3 i.e. 5.65, and a further increase in the V:C ratio decreased the precipitation strengthening. This suggested that the precipitating phase was V_4C_3 rather than VC.

(14) An interaction between vanadium, aluminium and nitrogen occurred because of the slow rate of precipitation of aluminium nitride. In spite of the higher affinity of aluminium than vanadium for nitrogen, vanadium nitride precipitated in preference to aluminium nitride in austenite. Precipitation of vanadium nitride in austenite lowered the precipitation strengthening, but re-solution of vanadium nitride occurred when aluminium nitride was precipitated by the use of appropriate thermo-mechanical treatments. This re-solution of vanadium nitride increased precipitation strengthening by making more vanadium available for precipitation as vanadium carbide.

(15) Incomplete precipitation of aluminium nitride in the work reported gave consistently lower precipitation strengthening in the high nitrogen steels, but an increased nitrogen should also increase the precipitation strengthening. The mechanisms by which nitrogen increases precipitation strengthening in vanadium steels have been explained.

(16) An increase in nitrogen in vanadium steels altered the 'C' curve for the effect of rolling temperature on the strain induced precipitation of vanadium carbo-nitride. In low nitrogen-vanadium steels precipitation strengthening was lower after rolling at 750°C than after rolling at 1250°C whilst, in high nitrogen-vanadium steels, precipitation strengthening at these same rolling temperatures was similar. This has been explained by the different kinetics of the precipitation of vanadium nitride and vanadium carbide.

(17) Variation of precipitation strengthening with V:C, V:N and V:(C,N) ratios in high nitrogen vanadium steels, indicated nitrogen can fill some of the interstitial vacancies in the V_4C_3 lattice.

(18) Most of the precipitation by vanadium carbo-nitride occurred in ferrite during the $\gamma \rightarrow \alpha$ transformation by an interphase mechanism, whilst a very small amount of precipitation occurred from

ferrite due to there being limited carbon available in the ferrite. Therefore, it has been suggested that to intensify precipitation strengthening, control over the interphase precipitate size and distribution should be achieved.

(19) Under ideal thermo-mechanical treatment conditions, niobium contents up to ~0.10% gave higher precipitation strengthening than equal vanadium additions by weight, but considering the difficulties in processing niobium steels under such conditions, they are unlikely to achieve higher precipitation strengthening than can be achieved by vanadium. Therefore, it has been suggested that niobium can be used as a potential ferrite grain refiner but a moderate precipitate strengthener. Vanadium on the other hand can be used as both grain refiner and precipitation strengthener.

(C) (Nb+V) Steels.

(20) When niobium and vanadium additions were made together, the precipitating phase was NbV(C,N) rather than Nb(C,N) or V(C,N).

(21) The effect of various thermo-mechanical treatment variables on the precipitation strengthening was similar to those observed in niobium and vanadium steels.

Comparative Effects of Niobium and Vanadium

(22) Small amounts of niobium imparted more precipitation than vanadium, providing that all the Nb(C,N) was dissolved and very little or no strain-induced Nb(C,N) occurred in the austenite.

(23) At higher niobium and vanadium contents, vanadium gave much greater precipitation strengthening than niobium.

(24) Precipitation strengthening in niobium steels was more sensitive to reheating temperature and other thermo-mechanical treatment variables than in vanadium steels.

(25) Precipitation strengthening due to niobium and vanadium added together was lower than the sum of that which can be achieved from niobium and vanadium added individually.

INDUSTRIAL IMPLICATION

Controlled rolling processes are in particular aimed at obtaining maximum ferrite grain refinement by controlling the austenite grain morphology prior to transformation. At present it is generally tried to obtain unrecrystallized elongated austenite grainsprior to transformation, which by virtue of their increased capacity for ferrite nucleation, refine the ferrite grain size. To ensure such unrecrystallized austenite prior to transformation, the temperature for recrystallization is increased by additions of elements such as niobium and vanadium. A high recrystallization temperature gives increased flexibility during rolling to obtain the desired austenite grain morphology. A debate has developed since the development of the controlled rolling process on the relative effectiveness of niobium and vanadium in refining the ferrite grain size. In the present work it has been suggested that an ideal comparison of these two elements in refining the ferrite grain size should be done after rolling conditions which gives maximum grain refinement in niobium and vanadium steels. These rolling conditions would be different for niobium and vanadium treated steels.

Niobium has often been suggested to have greater potential for the refinement of the ferrite grain size than vanadium, and this has been particularly related to the effect of niobium in raising the recrystallization temperature to a greater extent than does vanadium. However, it is not necessary to have unrecrystallized austenite long before transformation (i.e. at higher temperatures) for ferrite grain refinement, because it should suffice to have unrecrystallized austenite just prior to transformation. Therefore it should be possible to justify the effect of vanadium in refining the ferrite grain size because, although vanadium does not retard austenite recrystallization at as high a temperatures as niobium it does retard recrystallization just before transformation. Therefore, in vanadium steels it should be possible to refine the recrystallized grain size by a lower reheating temperature, and then finish roll in the temperature range where austenite does not recrystallize to give a very fine ferrite grain size.

Nb(C,N) precipitated in austenite has however a positive role in refining the ferrite grain size. Such an effect can also be obtained in vanadium steels, but it should be noted that V(C,N) precipitates in austenite at lower temperatures. However, as shown in high nitrogen vanadium steels, fine uniform distributions of AlN which occurs during holding at 950°C can provide a similar effect to strain induced Nb(C,N) in refining the ferrite grain size. In addition, such a precipitation of AlN in high nitrogen vanadium steels offers a distinct advantage by converting a deleterious effect of holding time in the austenitic temperature range to a beneficial one, by increasing the precipitation strengthening due to the solution of strain induced VN precipitates. On many occasions holding in the austenitic temperature range is used to obtain a low finishing temperature, but this has been shown to have an undesirable effect on the ferrite grain size. In this situation it is suggested that the use of high nitrogen V-Al steels should give optimum strength toughness combination after specially designed controlled rolling schedules.

In controlled rolling additional strengthening can also be achieved by the precipitation strengthening from niobium and vanadium. It must be appreciated that precipitation strengthening can arise from both interphase precipitation during the austenite to ferrite transformation and from precipitation occurring in the ferrite after the transformation is complete. In the case of interphase precipitation, the intensity of precipitation strengthening will be largely controlled by the M:C ratio in the bulk steel, the maximum effect being obtained at the stoichiometric ratio. However, in the case of precipitation directly from transformed ferrite, maximum strengthening is achieved at the stoichiometric ratio for the ferrite, i.e. at much lower dissolved carbon and nitrogen contents. These effects have been confirmed for vanadium steels. It should also be noted that the different precipitate morphology and distribution arising from the two precipitation mechanisms, may have different effects on the toughness.

The following conditions should contribute to an increase in precipitation strengthening in both niobium and vanadium microalloyed steels:-

(a) large amounts of niobium and vanadium in solution, i.e. the use of a high reheating temperature.

(b) small amounts of strain induced precipitation in the austenite, which can be achieved by:-

    (i) deformation at temperatures either above or below the nose of the precipitation 'C' curve.
    (ii) a sufficiently high deformation such that recrystallization is not inhibited.
    (iii) a short holding time, especially for non-recrystallized austenite.

(c) a bulk steel composition close to the stoichiometric composition.

(d) the absence of undissolved Nb(C,N) particles in niobium microalloyed steels.

(e) control of the size and distribution of precipitates which are produced by interphase precipitation.

(f) avoid holding in the temperature range where precipitates coarsen rapidely.

With present plate and hot strip rolling schedules, strain induced precipitation of Nb(C,N) always occurs, and therefore, the full precipitation strengthening from niobium cannot be attained. Hence niobium is more effective when used to promote grain refinement during rolling whilst vanadium is more effective as a precipitation strengthening addition, although vanadium also causes grain refinement. The present results have shown that VN can be strain induced at rolling temperatures of $\sim 950^{\circ}$C, but not to the extent of Nb(C,N). On the other hand there are clear indications that V_4C_3 can be strain induced at lower rolling temperatures of $\sim 800^{\circ}$C, which suggests that effective use of vanadium as a grain refining agent could be achieved by a suitable design of thermo-mechanical treatment conditions, i.e. heavy deformation at $\sim 800^{\circ}$C.

SUGGESTIONS FOR FUTURE WORK

1. In the present work, an attempt was made to identify the role of niobium in solution on the various recrystallization processes such as the nucleation and growth of the recrystallized grains. It was positively shown that niobium in solution retarded nucleation of recrystallized grains and thereby retarded the recrystallization of austenite. Further work is required in this area to obtain a quantitative effect of the niobium in solution on the nucleation processes. Also such work is needed to be done in vanadium steels so as to identify the role of vanadium in solution on the recrystallization of austenite.
2. Based on the results of the present work a controlled rolling schedule should be devised and tried during experimental rolling so as to obtain optimum mechanical properties in both 0.05% Nb and 0.1 5% V steels. The rolling practice should avoid rolling in the temperature range 1000°-850°C in order to obtain maximum precipitation strengthening.
3. In vanadium steels it has been shown that most of the V(C,N) precipitation occurred during the austenite to ferrite transformation and therefore, to achieve maximum precipitation strengthening, control over the size and distribution of the precipitates should be achieved by the interphase mechanism. Little is known about the interphase precipitation in continuously cooled steel and therefore, work is required to be done to identify the parameters during cooling which can give optimum precipitation strengthening.

   It is possible that during the transformation the ferrite growth rate may vary depending on whether transformation occurs from recrystallized or unrecrystallized austenite. Therefore, the morphology of austenite prior to the transformation might have some effect on the interphase precipitation, and it is suggested that studies should be made on this aspect, particularly in vanadium steels.
4. In high nitrogen vanadium steels, a beneficial effect of holding in refining the ferrite grain size due to the precipitation of AlN in the austenite was revealed. Use of this phenomena in controlled rolling would certainly be advantageous as besides ferrite grain

refinement increased precipitation strengthening can result. Further work should be carried out to explore the possibilities for using this phenomena in the controlled rolling of the V-N-Al steels.

5. Further work is required to obtain quantitative data on the effect of combined additions of niobium and vanadium on the precipitation strengthening, as the results obtained in the present investigation are inconclusive.

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TABLE 1

Analyses of Experimental Alloys

Series	Cast No.	Analysis (Mass %)							
		C	Mn	Si	Al	Nb	V	N_2	M/C
Base Steel	1	0.083	0.76	0.24	0.045	-	-	0.008	-
Nb series Low nitrogen	2	0.088	0.89	0.25	0.053	0.075	-	0.008	0.85
	3	0.093	0.93	0.27	0.066	0.11	-	0.009	1.16
	4	0.088	0.79	0.18	0.010	0.16	-	0.007	1.81
	5	0.088	0.82	0.23	0.033	0.46	-	0.006	5.22
	6	0.090	0.96	0.35	0.064	0.73	-	0.007	8.11
	7	0.086	0.94	0.28	0.057	1.03	-	0.007	11.98
V series Low nitrogen	8	0.086	0.84	0.25	0.022	-	0.06	0.007	0.70
	9	0.087	0.87	0.28	0.020	-	0.11	0.007	1.21
	10	0.088	0.93	0.29	0.023	-	0.14	0.007	1.59
	11	0.083	0.86	0.26	0.030	-	0.22	0.008	2.65
	12	0.086	0.85	0.26	0.047	-	0.55	0.008	6.40
	13	0.084	0.74	0.22	0.020	-	0.98	0.008	11.51
V series High nitrogen	14	0.075	0.98	0.29	0.05	-	0.05	0.016	0.66
	15	0.075	0.85	0.25	0.03	-	0.14	0.020	1.80
	16	0.074	0.91	0.24	0.03	-	0.25	0.015	3.31
	17	0.075	0.82	0.21	0.02	-	0.46	0.018	6.13
Nb-V series High & Low Nitrogen	18	0.080	0.87	0.24	0.03	0.03	0.12	0.019	-
	19	0.087	0.88	0.29	0.04	0.05	0.11	0.009	-
Low (C+N)-Nb steel	20	0.005	1.13	0.30	0.045	0.29	-	0.003	58.0

TABLE 2

Effect of Reheating Temperature on the Austenite Grain Size in Niobium Steels.

% Nb (Mass) in Steel	Austenite Grain Size, μm , at Reheating Temperature of:				
	1000°C	1050°C	1150°C	1200°C	1300°C
0.00	82	84	90	90	133
0.07	9	11	63	-	240
0.16	10	11	50	50	129
0.46	10	10	14	16	85
0.73	10	10	14	14	103
1.03	10	12	16	21	291

TABLE 3

Effect of Reheating Temperature on the Austenite Grain Size in Vanadium Steels.

% V (Mass) in Steel	Austenite Grain Size, μm, at Reheating Temperature of:				
	1000°C	1050°C	1150°C	1200°C	1300°C
0.0	82	84	90	90	133
0.11	15	80	82	99	342
0.14	12	87	97	108	272
0.22	7	8	73	93	298
0.55	9	9	89	103	253
0.98	9	9	81	98	128

TABLE 4

Effect of Reheating Temperature on the Austenite Grain Size in Vanadium plus Nitrogen Steels.

% V (Mass) in Steel	Austenite Grain Size, μm, at Reheating Temperature of:				
	1000°C	1050°C	1150°C	1200°C	1300°C
0.00	82	84	90	90	133
0.14	11	83	85	86	260
0.25	10	29	81	87	273
0.46	13	14	89	100	270
0.98	15	16	59	86	262

TABLE 5

Nb and (Nb+V) Steels

Recrystallization and Austenite Grain Size.

Reheated - 1300°C,
Rolled - 1250°C,
Held - 1250°C for various times and quenched.

50 % Reduction.						
% Nb (Mass) in steel	Holding Time at 1250°C					
	0.00 Sec.		100 Sec.		1000 Sec.	
	% Recry.	G.S. μm	% Recry.	G.S. μm	% Recry.	G.S. μm
0.00	100	53	100	56	100	133
0.07	100	39	100	51	100	93
0.16	99	39	100	43	100	42
0.46	59	29	86	33	95	41
0.73	80	52	89	42	98	35
1.03	64	55	79	72	94	45
0.03Nb+0.12V-N	100	41	-	-	-	-
0.05Nb+0.11V	100	42	-	-	-	-
20 % Reduction.						
0.00	100	55	100	118	100	200
0.07	79	40	84	74	87	92
0.16	54	39	82	62	84	72

TABLE 6

Nb and (Nb+V) Steels

Recrystallization and Austenite Grain Size.

Reheated - 1300°C,
Rolled - 1250°C,
Held - 950°C for various times and quenched.

50 % Reduction.						
% Nb (Mass) in Steel	Holding Time at 950°C					
	0.00 Sec.		100 Sec.		1000 Sec.	
	% Recry.	G.S. μm	% Recry.	G.S. μm	% Recry.	G.S. μm
0.00	100	53	100	60	100	63
0.07	100	39	100	37	100	53
0.16	99	39	100	40	100	37
0.46	59	29	93	39	97	34
0.73	80	52	87	39	93	41
1.03	64	55	87	36	94	54
0.03Nb+0.12V-N	100	41	100	41	100	38
0.05Nb+0.11V	100	42	100	42	100	44
20 % Reduction.						
0.00	100	55	100	49	100	70
0.07	79	40	100	35	100	41
0.16	54	39	93	35	96	38

TABLE 7

Nb and (Nb+V) Steels

Recrystallization and Austenite Grain Size.

Reheated - 1300°C,
Rolled - 950°C,
Held - 950°C for various times and quenched.

50 % Reduction.						
% Nb (Mass) in Steel.	Holding Time at 950°C					
	0.00 Sec.		100 Sec.		1000 Sec.	
	% Recry.	G.S. μm	% Recry.	G.S. μm	% Recry.	G.S. μm
0.00	44	77	100	47	100	47
0.07	00.0	54	1	64	38	31
0.16	00.0	54	1	55	24	35
0.03Nb+0.12V-N	00.0	75	00.0	72	00.0	71
0.05Nb+0.11V	00.0	70	00.0	72	00.0	72
20 % Reduction.						
0.00	13	70	23	106	23	78
0.07	00.0	107	00.0	150	00.0	148
0.16	00.0	104	00.0	80	00.0	81

TABLE 8

Nb and (Nb+V) Steels.

Recrystallization and Austenite Grain Size.

Reheated - 1150°C,
Rolled - 950°C,
Held - 950°C for various times and quenched.

50 % Reduction						
% Nb (Mass) in Steel.	Holding Time at 950°C					
	0.00 Sec.		100 Sec.		1000 Sec.	
	% Recry.	G.S. μm	% Recry.	G.S. μm	% Recry.	G.S. μm
0.00	72	-	97	23	100	23
0.07	00.0	31	88	18	89	19
0.16	00.0	28	93	19	97	19
0.03Nb+0.12V-N	00.0	-	48	25	57	18
0.05Nb+0.11V	6	-	24	43	38	52
20% Reduction						
0.00	11	94	89	55	100	12
0.07	00.0	32	96	16	96	17
0.16	00.0	28	94	17	95	18

TABLE 9

Vanadium and Vanadium plus Nitrogen (VN) Steels.

Recrystallization and Austenite Grain Size.

Reheated - 1300°C,
Rolled - 1250°C,
Held - 1250°C for various times and quenched.

% V (Mass) in Steel.	Holding Time at 1250°C					
	0.00 Sec.		100 Sec.		1000 Sec.	
	% Recry.	G.S. μm	% Recry.	G.S. μm	% Recry.	G.S. μm
50 % Reduction.						
0.00	100	53	100	56	100	133
0.14 V	100	44	-	-	-	-
0.22 V	100	50	100	98	100	236
0.55 V	100	35	100	60	100	170
0.98 V	100	29	100	47	100	128
0.14 VN	100	54	-	-	-	-
0.25 VN	100	37	-	-	-	-
0.46 VN	100	26	-	-	-	-
20 % Reduction.						
0.00	100	55	100	118	100	200
0.14 V	100	85	100	124	100	217
0.22 V	100	69	100	101	100	231
0.55 V	100	100	100	103	100	112

TABLE 10

Vanadium and Vanadium plus Nitrogen (VN) Steels; Recrystallization and Austenite Grain Size.

Reheated - 1300°C,
Rolled - 950°C,
Held - 950°C for various times and quenched.

50 % Reduction						
% V (Mass) in Steel.	Holding Time at 950°C.					
	0.00 Sec.		100 Sec.		1000 Sec.	
	% Recry.	G.S. µm	% Recry.	G.S. µm	% Recry.	G.S. µm
0.00	44	77	100	47	100	47
0.14 V	00.0	75	19	40	73	54
0.22 V	00.0	84	16	52	37	42
0.55 V	00.0	76	6	45	32	28
0.14 VN	00.0	84	34	29	39	26
0.25 VN	00.0	76	31	13	37	13
0.46 VN	00.0	79	22	23	35	21
20 % Reduction						
0.00	13	70	23	106	23	78
0.14 V	00.0	319	00.0	308	6	186
0.22 V	00.0	240	00.0	308	2	177
0.55 V	00.0	264	00.0	247	4	229

TABLE 11

Vanadium and Vanadium plus Nitrogen (VN) Steels.

Recrystallization and Austenite Grain Size.

Reheated - 1150°C,
Rolled - 950°C,
Held - 950°C for various times and quenched.

50 % Reduction						
% V (Mass) in Steel.	Holding Time at 950°C.					
	0.00 Sec.		100 Sec.		1000 Sec.	
	% Recry.	G.S. µm	% Recry.	G.S. µm	% Recry.	G.S. µm
0.00	72	-	97	23	100	23
0.14 V	6	49	95	25	99	26
0.22 V	5	41	95	19	96	19
0.55 V	3	53	95	16	96	61
0.14 VN	18	31	88	-	95	15
0.25 VN	21	33	70	15	77	18
0.46 VN	13	50	70	20	77	18
20 % Reduction.						
0.00	11	94	89	55	100	12
0.14 V	00.0	79	81	54	78	60
0.22 V	00.0	60	17	53	78	40
0.55 V	00.0	76	19	66	79	38

TABLE 12

(a) Amount of Nb in solution and as precipitate at different temperatures for the various steels.

% Nb (Mass) in Steel.	% Nb (Mass) in solution or as precipitate											
	750°C		950°C		1000°C		1150°C		1250°C		1300°C	
	Sol.	Ppt.	Sol.	Ppt.	Sol.	Ppt.	Sol.	Ppt.	Sol.	Ppt.	Sol.	Ppt.
0.07	0.0	0.07	0.01	0.06	0.01	0.06	0.04	0.03	0.07	0.00	0.07	0.00
0.11	0.0	0.11	0.01	0.10	0.01	0.10	0.04	0.07	0.08	0.03	0.11	0.00
0.16	0.0	0.16	0.01	0.15	0.01	0.15	0.05	0.11	0.09	0.07	0.12	0.04
0.46	0.0	0.46	0.02	0.42	0.03	0.43	0.08	0.38	0.14	0.32	0.19	0.27
0.73	0.03	0.66	0.06	0.67	0.11	0.62	0.19	0.54	0.25	0.48	0.30	0.43
1.03	0.32	0.71	0.34	0.69	0.34	0.69	0.39	0.64	0.44	0.59	0.48	0.55

(b) Maximum potential amount of Nb precipitated at different temperatures after reheating.

Nb % in Steel	% Nb (Mass) as precipitate.						
Reheating Temp. °C	1000		1150		1300		
Precipitation Temp. °C	750	950	750	950	750	950	1250
0.07	0.01	0.01	0.04	0.04	0.07	0.07	0.00
0.11	0.01	0.01	0.04	0.04	0.11	0.11	0.03
0.16	0.01	0.01	0.05	0.05	0.12	0.12	0.03
0.46	0.03	0.01	0.08	0.06	0.17	0.17	0.04
0.73	0.04	0.05	0.12	0.13	0.23	0.24	0.05
1.03	0.02	0.00	0.07	0.05	0.16	0.16	0.04

TABLE 13

Effect of Vanadium in the Low and High Nitrogen-Niobium Steels on the Ferrite Grain Size after Various Thermo-Mechanical-Treatments

Reheating Temp. °C	Rolling Temp. °C	Holding Temp. °C	Holding Time-Sec.	Ferrite Grain Size, $d^{-1/2}$, $mm^{-1/2}$		
				0.07 % Nb	0.05Nb + 0.11 V	0.03 Nb + 0.12 V-N
1300	1250	950	100	9.4	9.1	9.7
			1000	9.2	9.9	10.2
	950	950	100	11.4	10.3	11.1
			1000	11.0	10.3	11.8
1150	950	950	100	12.3	11.3	12.2
			1000	11.0	11.0	11.5
		750	100	12.1	11.3	10.7
			1000	11.4	11.3	10.0
1000	950	950	100	12.2	11.4	10.3
			1000	10.4	11.4	11.3
		750	100	13.8	13.4	13.2
			1000	13.6	13.4	13.4

TABLE 14

Ferrite Grain Size: Low-Nitrogen Vanadium Steels.

Reheating Temp. °C	Rolling Temp. °C	% Reduction	Holding Temp. °C	Holding Time Sec.	Ferrite Grain Size, $d^{-1/2}$, $mm^{-1/2}$					
					% V(Mass) in Steel					
					0.0	0.06	0.11	0.14	0.22	0.55
1300	1250	50	950	100	7.5	9.5	10.0	9.7	9.8	9.5
				1000	8.2	-	9.5	9.8	-	9.1
	950	20	750	100	-	-	8.0	7.3	-	8.0
		50	950	100	10.1	9.9	9.9	9.9	10.2	10.0
				1000	9.3	-	9.7	9.4	-	9.5
			750	100	8.7	10.1	9.7	9.6	9.9	9.7
				1000	8.8	-	9.2	9.2	-	9.4
	750	20	750	100	-	-	8.8	9.2	-	8.3
		50	750	100	12.6	10.7	11.4	10.7	11.2	10.0
				1000	11.9	-	10.4	10.5	-	8.8
1150	950	20	950	100	9.2	-	9.5	9.8	-	9.7
			750	100	9.0	-	8.7	8.1	-	8.1
		50	950	100	9.5	10.1	10.5	10.4	9.9	9.9
				1000	8.8	-	9.9	10.1	-	9.5
			750	100	10.2	9.9	10.3	10.2	11.4	10.9
				1000	9.8	-	10.5	9.7	-	9.7
	750	20	750	100	7.4	-	11.0	10.3	-	10.2
		50	750	100	12.0	12.5	11.5	12.1	11.9	-
				1000	11.9	-	11.5	12.5	-	-
1000	950	20	950	100	8.4	-	9.8	10.0	-	10.0
			750	100	9.9	-	8.7	11.1	-	11.2
		50	950	100	10.0	9.5	10.0	10.1	9.8	10.1
				1000	9.4	-	9.3	10.3	-	10.2
			750	100	11.2	9.5	10.1	10.6	12.2	-
				1000	11.0	-	10.0	11.7	-	10.0

TABLE 15

Ferrite Grain Sizes: High Nitrogen-Vanadium Steels.

Reheating Temp. °C	Rolling Temp. °C	% Reduction	Holding Temp. °C	Holding Time Sec.	Ferrite Grain Size $d^{-1/2}$, $mm^{-1/2}$			
					% V (Mass)			
					0.0	0.14	0.25	0.46
1300	1250	50	950	100	7.5	10.2	9.9	10.7
				1000	8.2	10.4	11.0	10.4
			750	1000	6.3	7.2	7.4	7.3
	950	50	950	100	10.1	10.5	10.4	9.3
				1000	9.3	11.3	11.4	10.4
			750	100	8.7	9.6	9.2	9.0
				1000	8.8	9.2	10.6	10.5
1150	950	50	950	100	9.5	9.8	10.4	10.4
				1000	8.8	11.5	11.5	10.9
			750	100	11.0	10.5	10.8	10.3
				1000	10.6	11.2	10.7	10.2
1000	950	50	950	100	10.0	10.5	11.5	11.8
				1000	9.4	11.4	12.4	11.7
			750	100	11.2	11.0	12.7	13.0
				1000	11.0	12.1	13.3	13.7

TABLE 16

Austenite Grain Sizes of Various Steels After Reheating at 1150°C, and After 50% Reduction at 1150°C.

Steel.	Austenite Grain Size, μm	
	At 1150°C for 30m	After 50% reduction at 1150°C.
Base	90	25
0.07 % Nb	63	12
0.14 % V	97	18
0.14 % V-N	85	15

TABLE 17

The Effect of Rolling Temperature on $(\Delta H)_p$ in (Nb+V) Steels.

Reheated - 1300°C,
Reduction 50 %,
Held - 750°C for 100s. and sand cooled.

Steel Composition	Rolling Temperature		
	1250°C	950°C	750°C
0.03% Nb + 0.12% V-N	34	29	55
0.05% Nb + 0.11% V	40	30	49

TABLE 18

Effect of Heating and Rolling Temperature, Holding Temperature and Time on Precipitation Strengthening, $(\Delta H)_p$

Reheating Temp. °C	Rolling Temp. °C	Holding Temp. °C	Holding Time Sec.	$(\Delta H)_p$ - HV for Nb	
				0.07%	0.11%
1300	950	950	100	34	38
			1000	26	36
		750	100	43	58
			1000	36	38
	750	750	100	81	97
			1000	58	71
1150	950	950	100	17	20
			1000	12	14
		750	100	29	30
			1000	22	20
	750	750	100	39	52
			1000	22	38

TABLE 19

Effect of Heating and Rolling Temperature, Holding Temperature and Time on Precipitation Strengthening, $(\Delta H)_p$, in (Nb+V) Steels.

Reheating Temp. °C	Rolling Temp. °C	% Reduction	Holding Temp. °C	Holding Time Sec.	$(\Delta H)_p$ - HV	
					0.03 %Nb+ 0.12% V-N	0.05 % Nb+ 0.11 % V
1300	1250	50	950	100	79	74
				1000	61	57
			750	1000	34	40
	950	50	950	100	40	48
				1000	31	37
			750	100	33	38
				1000	29	30
	750	50	750	1000	55	49
1150	950	50	950	100	16	40
				1000	28	38
			750	100	31	28
				1000	22	20
1000	950	50	950	100	32	19
				1000	31	21
			750	100	5	9

TABLE 20

The Ratios of V:C, V:N and V:(C+N) for V-N Steels.

C	V	N	V:C	V:N	V:(C+N)
0.075	0.14	0.02	1.86	7.0	1.47
0.074	0.25	0.015	3.33	16.66	2.80
0.075	0.46	0.018	6.13	25.50	4.94

TABLE 21

Effect of Nb in Solution and as NbC on Grain Coarsening of Austenite (Reheated 1300°C).

Rolling Temp. $^{\circ}$C	Rolling Redn. %	Holding Conditions	%Nb	Nb % (mass) as;-				Coarsening Effect
			in Steel	Undis. NbC	Pptd. NbC	Total NbC	In soluti.	
1250	50	1250°C-100s	0.073	0.00	0.00	0.000	0.073	Coarsening
			0.16	0.04	0.035	0.075	0.085	No Coarsening
		950°C-100s	0.073	0.00	0.063	0.063	0.010	Coarsening
			0.16	0.04	0.11	0.15	0.01	No Coarsening

TABLE 22

Effect of Nitrogen in 0.14% V Steel on the Ferrite Grain Size, $d^{-1/2}$, $mm^{-1/2}$, after Various T.M.T. (50 % Reduction).

Reheating Temp. °C	Rolling Temp. °C	Holding Temp. °C	Holding Time sec.	% N in Steel	
				0.007	0.02
1300	1250	950	100	9.7	10.2
			1000	9.8	10.4
	950	950	100	9.9	10.5
			1000	9.4	11.3
		750	100	9.6	9.6
			1000	9.2	9.2
1150	950	950	100	10.4	9.8
			1000	10.1	11.5
		750	100	10.2	10.5
			1000	9.7	11.2
1000	950	950	100	10.1	10.5
			1000	10.3	11.5
		750	100	10.6	11.0
			1000	11.7	12.1

TABLE 23

Calculated and Observed $(\Delta H)_p$ in (Nb+V) Steel.

Thermo-Mechanical Treatment.	Calculated $(\Delta H)_p$ for			Actual $(\Delta H)_p$	$\frac{(\Delta H)_p \text{ Obs.}}{(\Delta H)_p \text{ Cal.}}$
	0.05 % Nb	0.11 % V	0.05 % Nb +0.11% V		
1, Reheated-1300°C, Rolled -1250°C, Held - 950°C, 100s.	76	62	138	74	0.53
2. Reheated-1300°C, Rolled -1250°C, Held - 950°C,1000s.	64	50	114	57	0.50
3. Reheated-1300°C, Rolled - 950°C, Held - 950°C, 100s.	50	42	92	48	0.52
4. Reheated-1300°C, Rolled - 950°C, Held - 950°C,1000s.	24	38	62	37	0.60
5. Reheated-1300°C, Rolled - 950°C, Held - 750°C, 100s.	32	30	62	38	0.61
6. Reheated-1150°C, Rolled - 950°C, Held - 950°C, 100s.	20	40	60	40	0.66
7. Reheated-1150°C, Rolled - 950°C, Held - 950°C,1000s.	12	36	48	38	0.80
8. Reheated-1150°C, Rolled - 950°C, Held - 750°C, 100s.	32	28	60	28	0.46
9. Reheated-1150°C, Rolled - 950°C, Held - 750°C,1000s.	22	14	36	20	0.55
10. Reheated-1000°C, Rolled - 950°C, Held - 950°C, 100s.	6	34	40	19	0.47

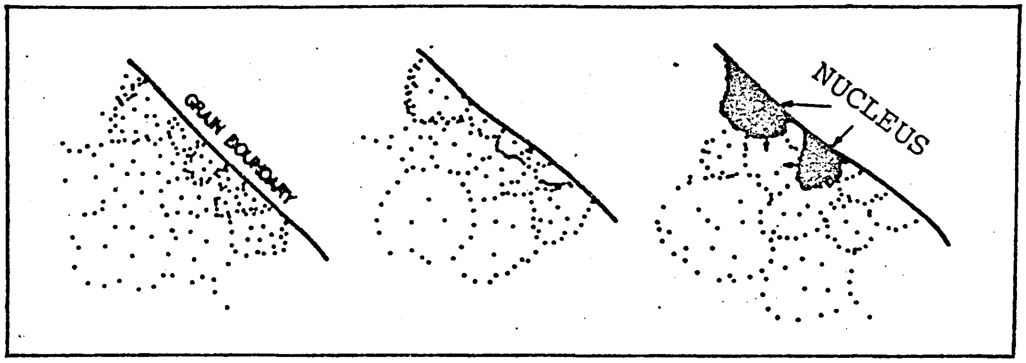


FIG. 1 NUCLEATION BY SUBGRAIN GROWTH (SCHEMATIC): Subgrain boundaries thickly populated by dislocations (dots) have a high misorientation angle, and are the most likely to migrate.

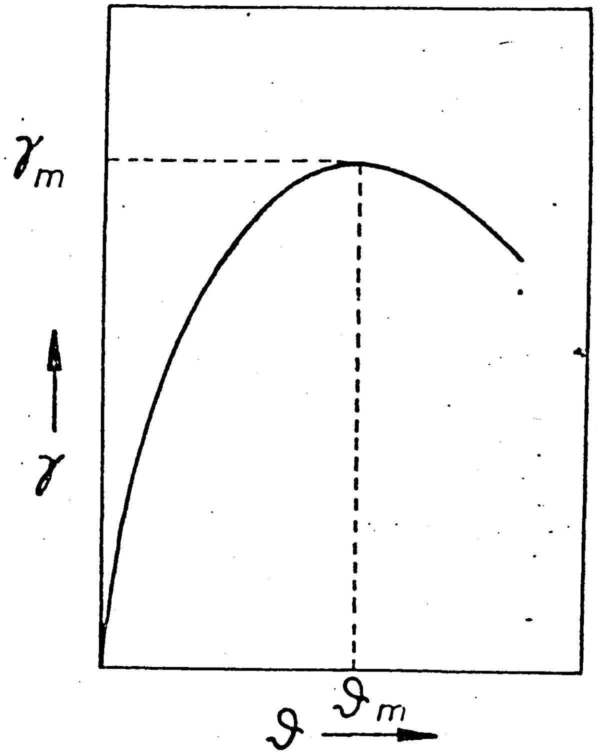
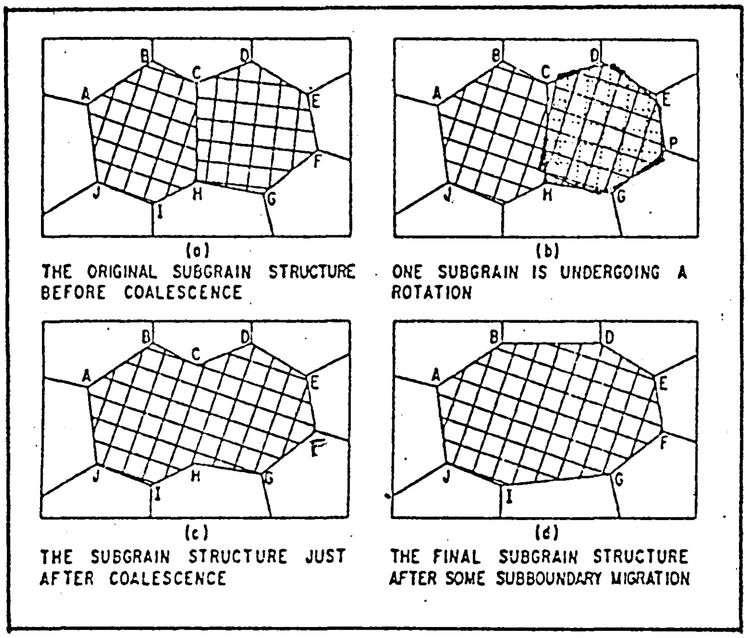


FIG. 2 ENERGY OF AN EDGE DISLOCATION BOUNDARY AS A FUNCTION OF MISORIENTATION ANGLE.



(a)
THE ORIGINAL SUBGRAIN STRUCTURE BEFORE COALESCENCE

(b)
ONE SUBGRAIN IS UNDERGOING A ROTATION

(c)
THE SUBGRAIN STRUCTURE JUST AFTER COALESCENCE

(d)
THE FINAL SUBGRAIN STRUCTURE AFTER SOME SUBBOUNDARY MIGRATION

FIG. 3 SCHEMATIC REPRESENTATION OF SUBGRAIN COALESCENCE BY SUBGRAIN ROTATION.

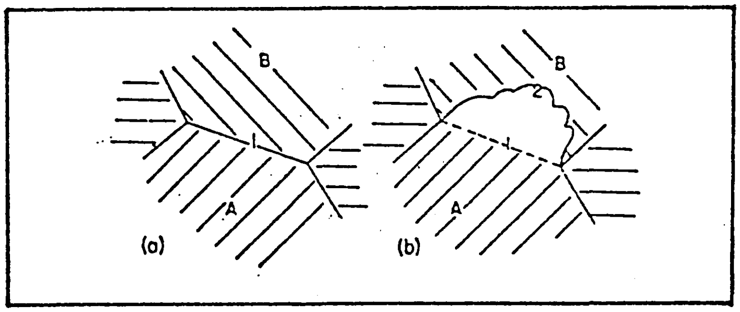


FIG. 4 SCHEMATIC REPRESENTATION OF STRAIN - INDUCED BOUNDARY MIGRATION.

(a) Configuration before annealing.

(b) The boundary between the two cold-worked grains A and B has migrated from position 1 to position 2.

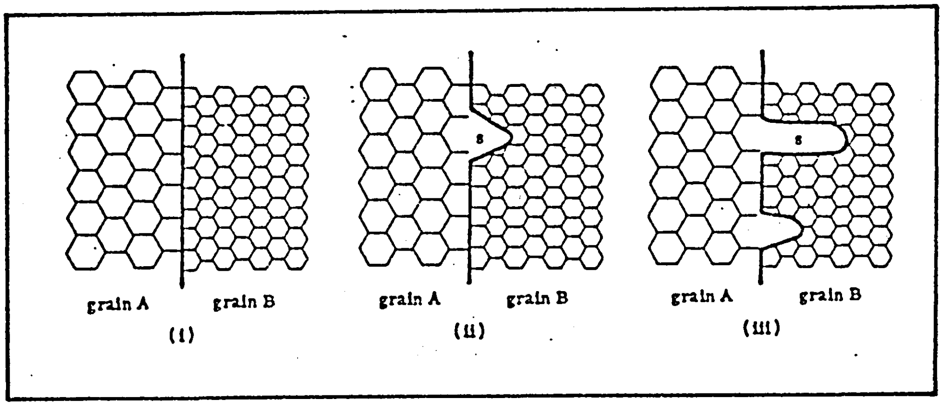


FIG. 5 SCHEMATIC REPRESENTATION OF PRIMARY RECRYSTALLISATION BY STRAIN-INDUCED GRAIN BOUNDARY MIGRATION.

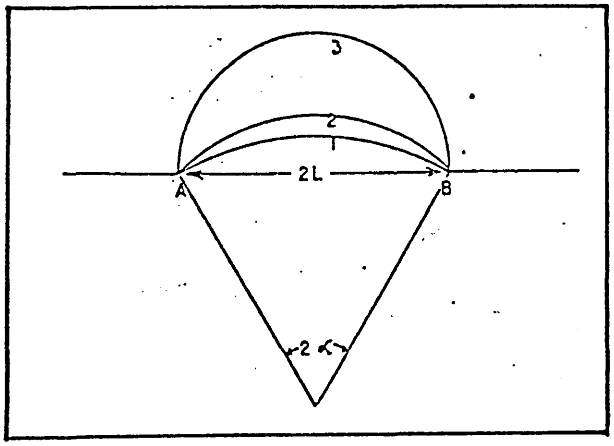


FIG. 6 MODEL FOR HIGH-ANGLE GRAIN BOUNDARY MIGRATION PROCESS IN RECRYSTALLISATION.

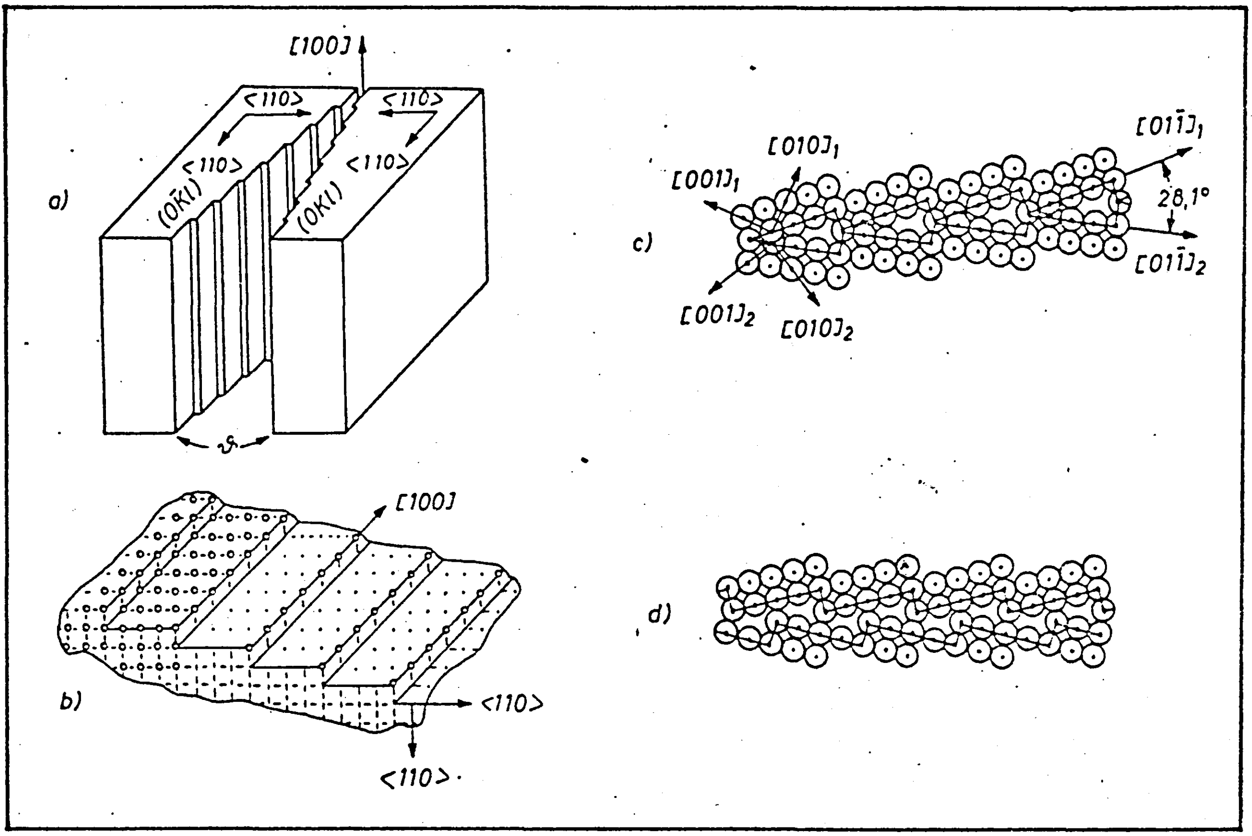


FIG. 7 GEOMETRICAL MODEL OF A SYMMETRIC ⟨100⟩ TILT BOUNDARY WITH IDEAL BOUNDARY COINCIDENCE IN A F.C.C. LATTICE.

(a) Formation of the boundary by two adjoining lattices with a misorientation angle ϑ ;

(b) Visualization of atomic steps in a partition surface between the two lattice regions;

(c) Arrangement of atoms in the grain boundary (as seen along the common ⟨100⟩ direction) showing exact coincidence of the atoms lying in the boundary plane;

(d) Arrangement of atoms after having removed one of the "overlapping" atoms adjoining the coincidence atoms in (c).

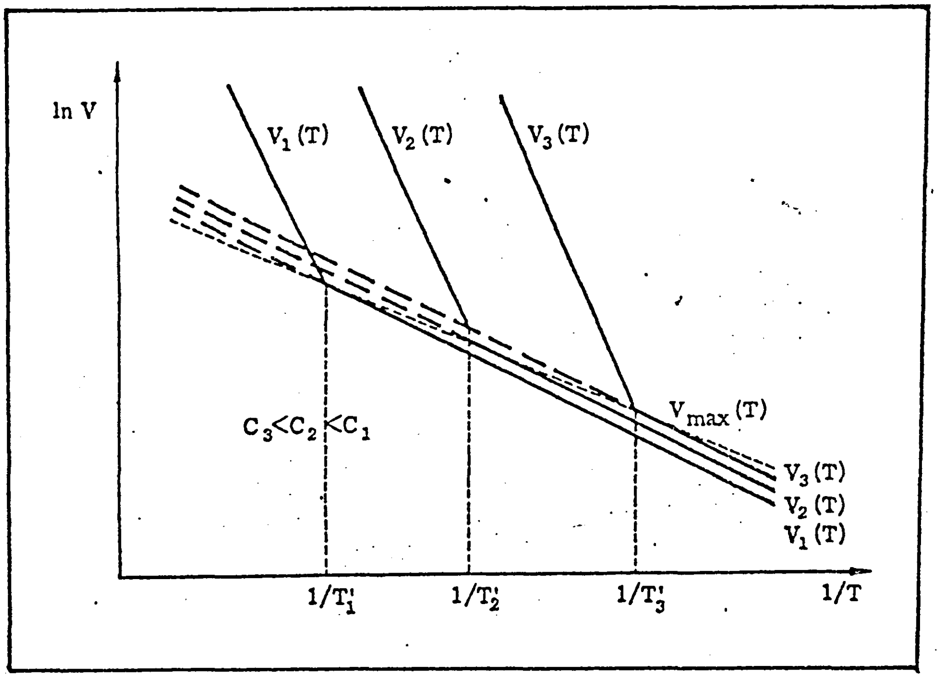


FIG. 8 SCHEMATIC REPRESENTATION OF THE TEMPERATURE DEPENDENCE OF THE GRAIN BOUNDARY VELOCITY, (V), FOR VARIOUS SOLUTE CONCENTRATIONS, (C), DURING PRIMARY RECRYSTALLISATION.

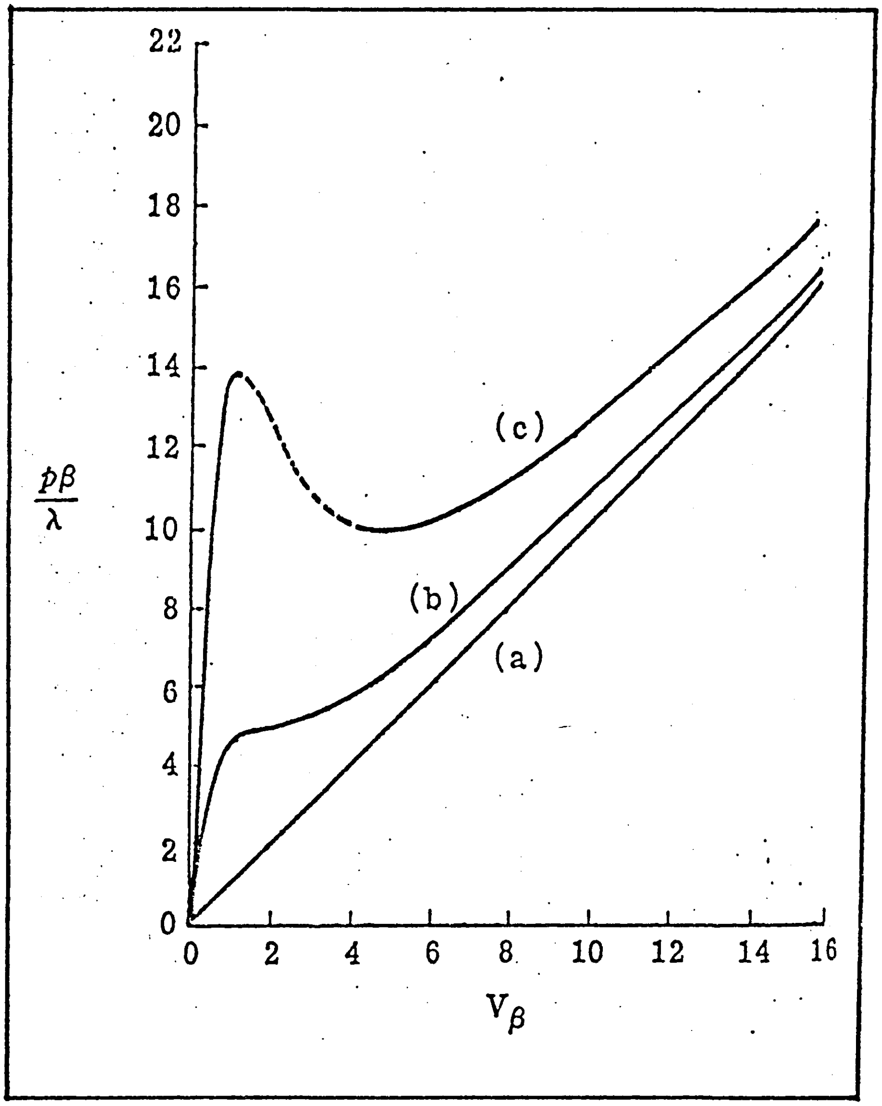


FIG. 9 THE DRIVING FORCE FOR GRAIN BOUNDARY MIGRATION AS A FUNCTION OF THE BOUNDARY VELOCITY.
Curve (a) represents a pure metal,
Curves (b) and (c) represent solid-solution alloys of increasing solute content.

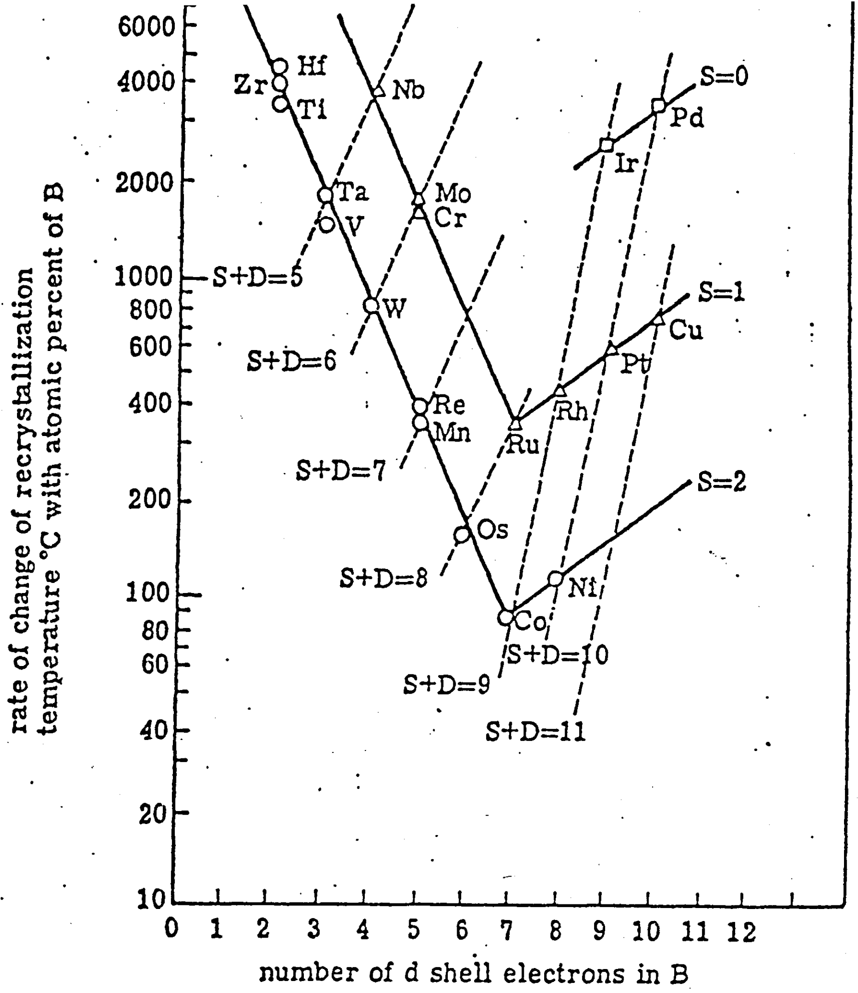


FIG. 10 RATE OF CHANGE OF RECRYSTALLISATION TEMPERATURE, PER ATOMIC % SOLUTE ELEMENT, IN IRON AS A FUNCTION OF THE NUMBER OF OUTERSHELL ELECTRONS OF THE SOLUTE ELEMENT.

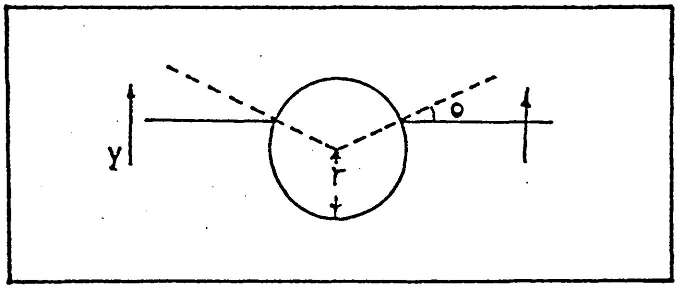


FIG. 11 INTERACTION OF MIGRATING GRAIN BOUNDARY WITH AN INCLUSION.

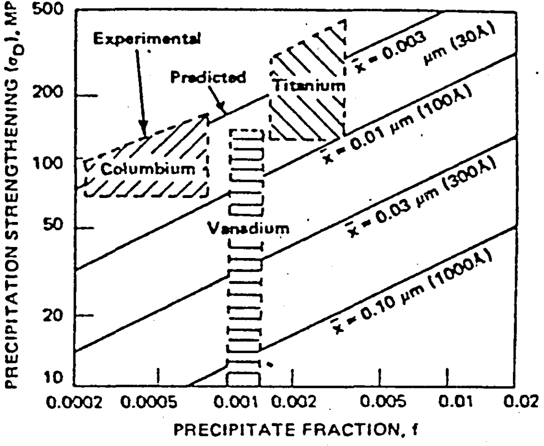


FIG. 12 QUANTIFICATION OF PRECIPITATION STRENGTHENING.

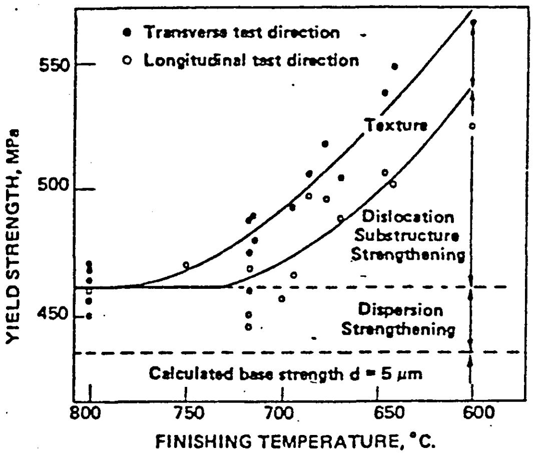


FIG. 13 FACTORS AFFECTING YIELD STRENGTH OF CONTROLLED ROLLED PLATE.

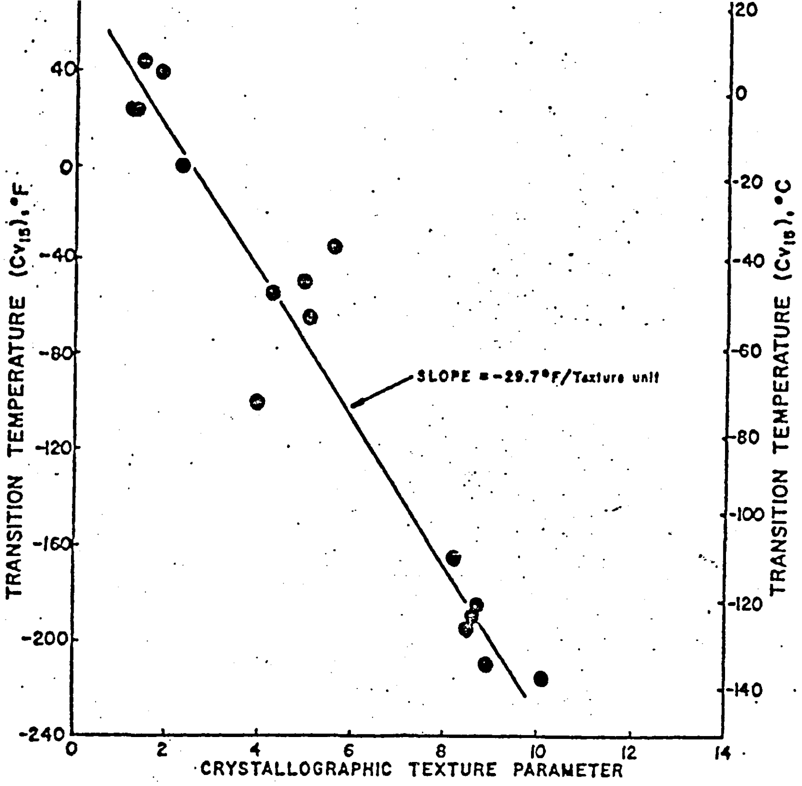


FIG. 14 A PLOT OF TEXTURE FACTOR VERSUS TRANSITION TEMPERATURE FOR THE AS - ROLLED PLATES.

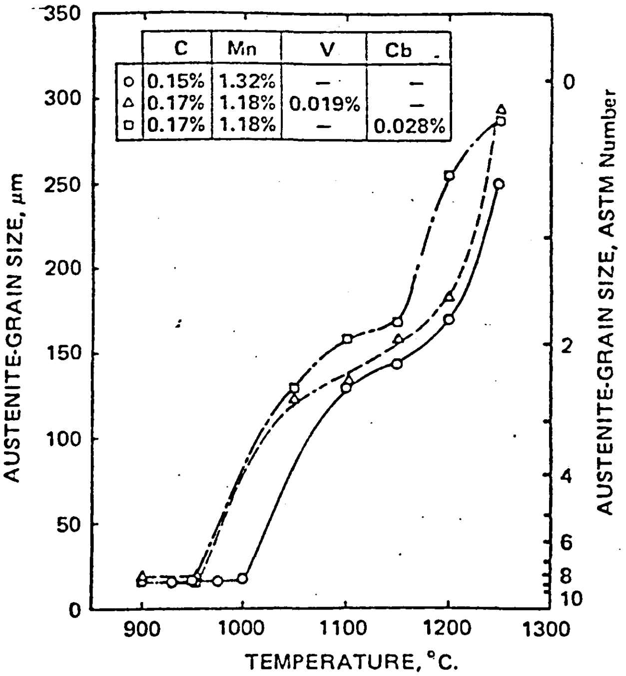


FIG. 15 HOW REHEATING TEMPERATURE AFFECTS AUSTENITE GRAIN SIZE IN THREE STEELS.

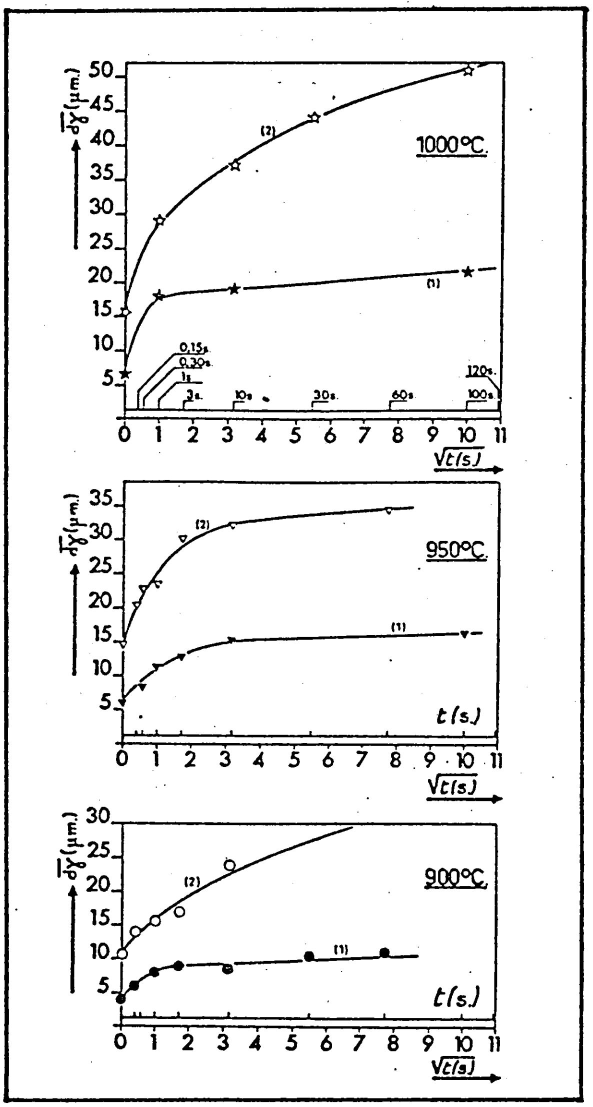


FIG. 16 ISOTHERMAL GRAIN GROWTH OF DYNAMICALLY RECRYSTALLISED AUSTENITE DURING HOLDING AT VARIOUS TEMPERATURES.

(1) Nb steel.

(2) Base steel.

Austenite Grain Size

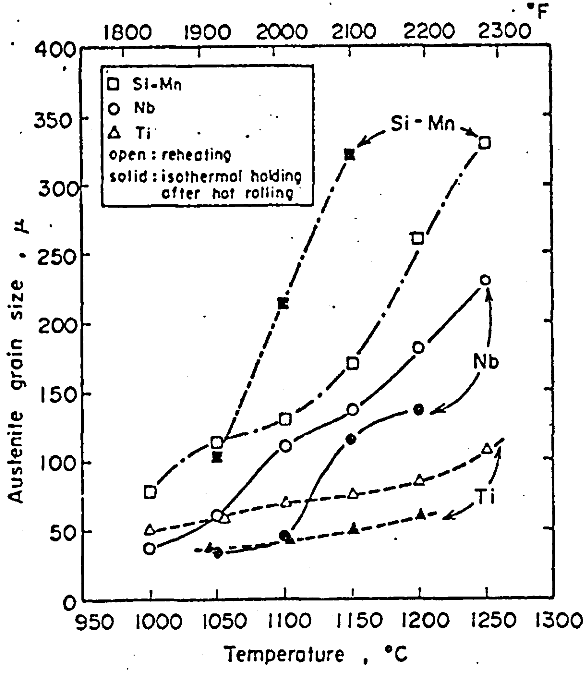


FIG. 17 GRAIN COARSENING BEHAVIOUR IN THE REHEATING AND AFTER HOT ROLLING WITH A HOLDING TIME OF 30 min.

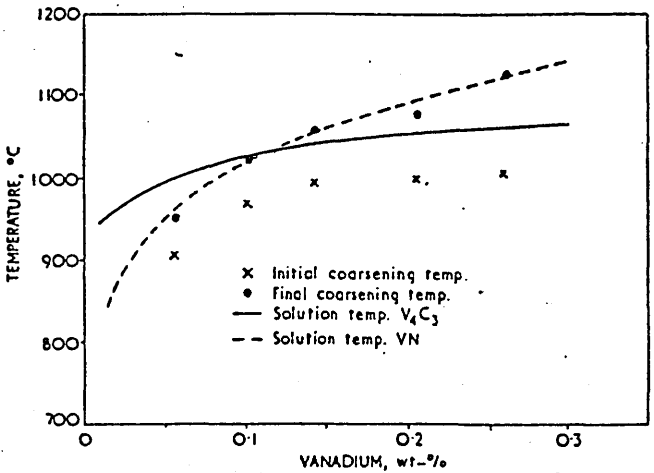


FIG. 18 EFFECT OF VANADIUM ON AUSTENITE GRAIN-COARSENING TEMPERATURE.

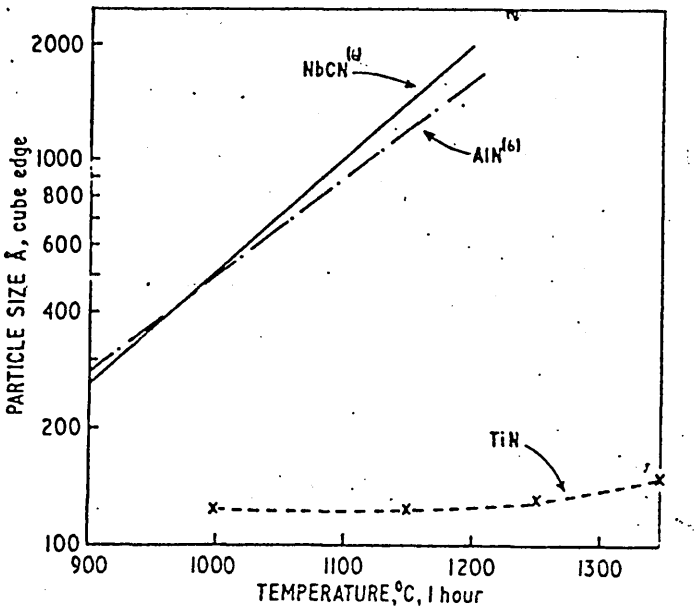


FIG. 19 A COMPARISON OF PRECIPITATE PARTICLE SIZE WITH INCREASING TEMPERATURE.

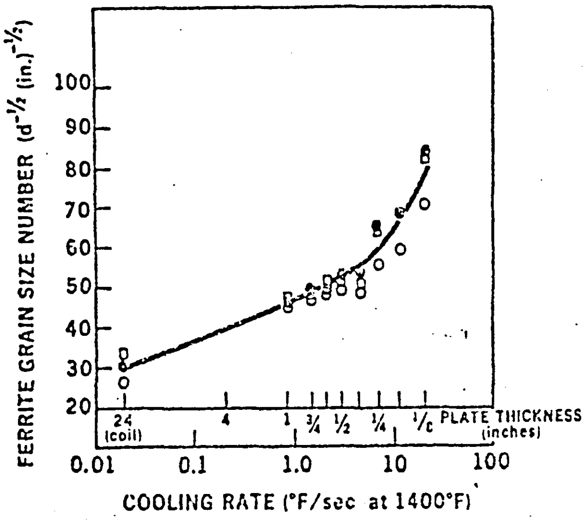


FIG. 20 EFFECT OF COOLING RATE ON FERRITE GRAIN SIZE.

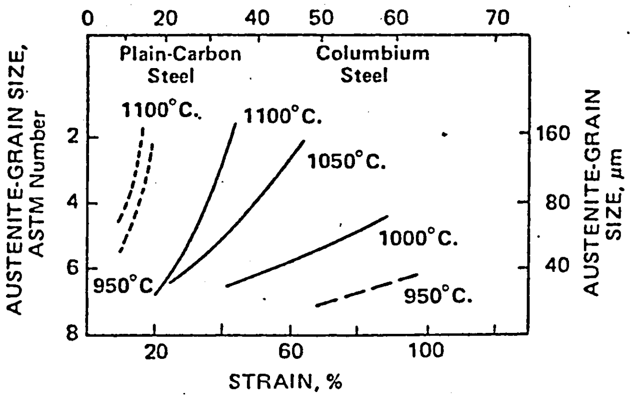
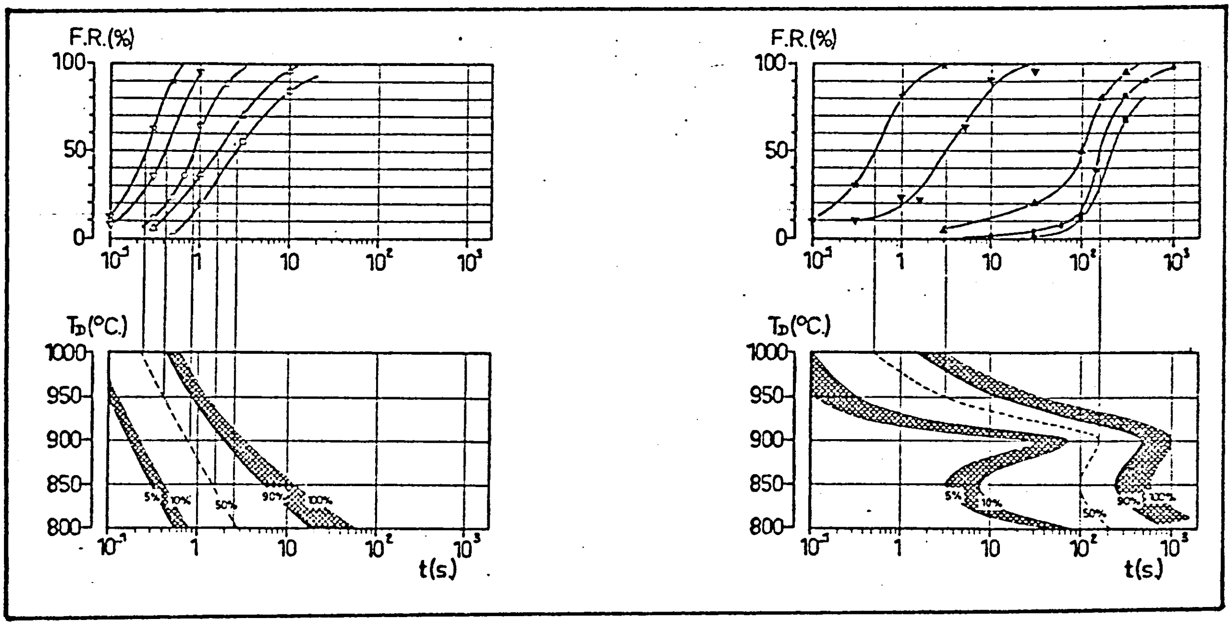


FIG. 21 EFFECT OF DEFORMATION TEMPERATURE AND INITIAL GRAIN SIZE ON CRITICAL AMOUNT OF DEFORMATION REQUIRED FOR COMPLETION OF RECRYSTALLISATION IN THE PLAIN - CARBON AND NIOBIUM STEELS.



(a) Nb free steel:

1000°C - 2.3 rev.
950°C - 3.0 rev.
900°C - 3.5 rev.
850°C - 4.3 rev.
800°C - 4.8 rev.

(b) Nb steel:

1000°C - 4.1 rev.
950°C - 5.0 rev.
900°C - 6.0 rev.
850°C - 6.6 rev.
800°C - 7.3 rev.

FIG. 22 RECRYSTALLISATION KINETICS AND R.T.T DIAGRAMS FOR SEVERELY DEFORMED AUSTENITE.

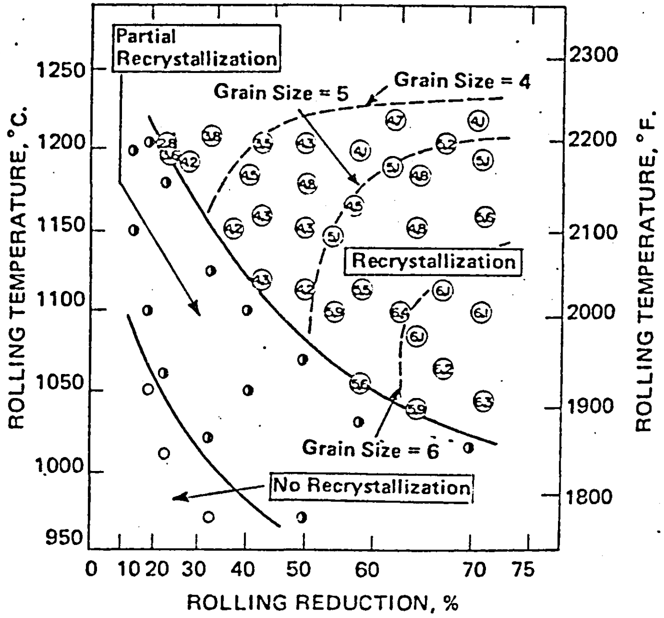


FIG. 23 AUSTENITE RECRYSTALLIZATION AND RESULTING GRAIN SIZE AS A FUNCTION OF ROLLING TEMPERATURE AND REDUCTION, FOR 0.03%Nb STEEL. The steel was reheated to 1250°C for 20 min., rolled with one pass, and quenched. The initial austenite grain size number was 1.0.

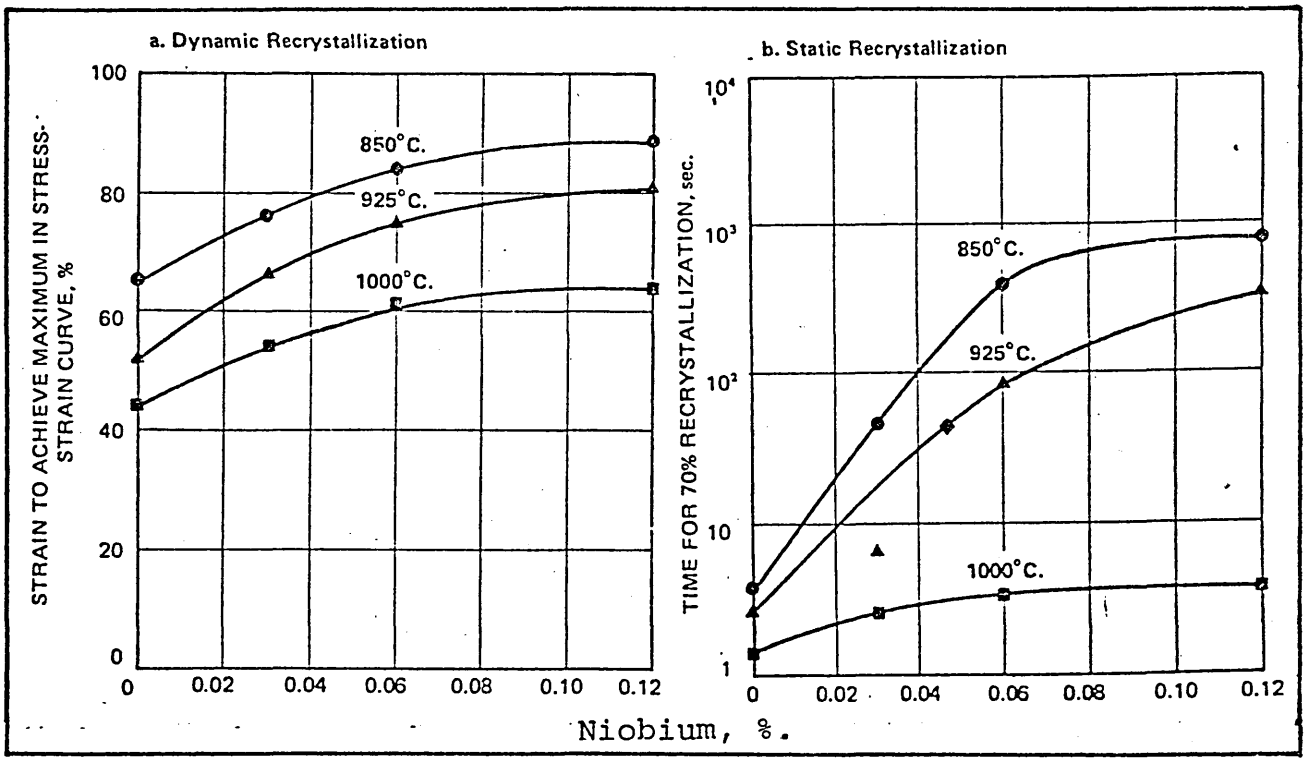


FIG. 24 EFFECT OF NIOBIUM ON THE RECRYSTALLIZATION OF A 0.05% C, 1.0% Mn STEEL.

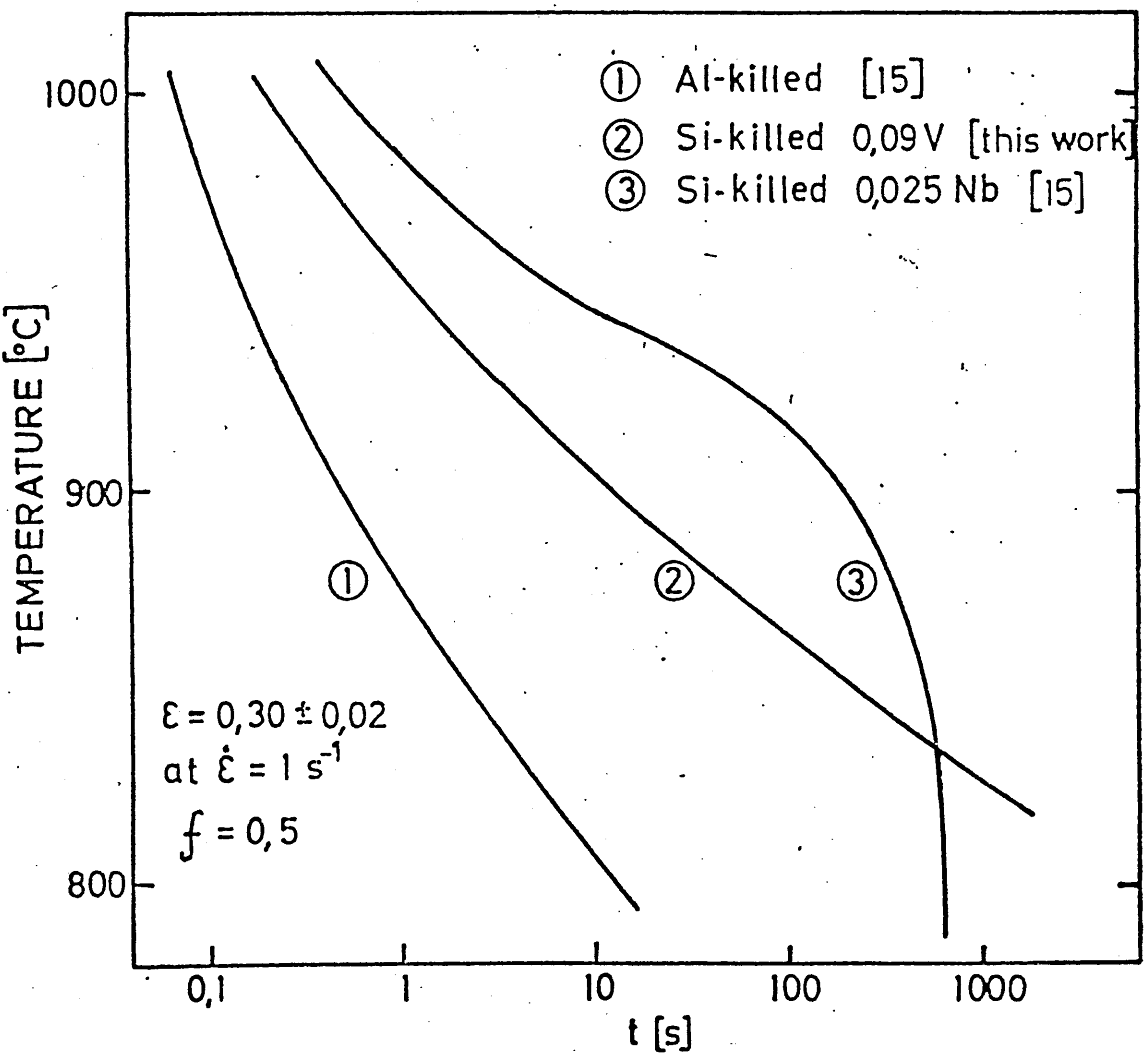
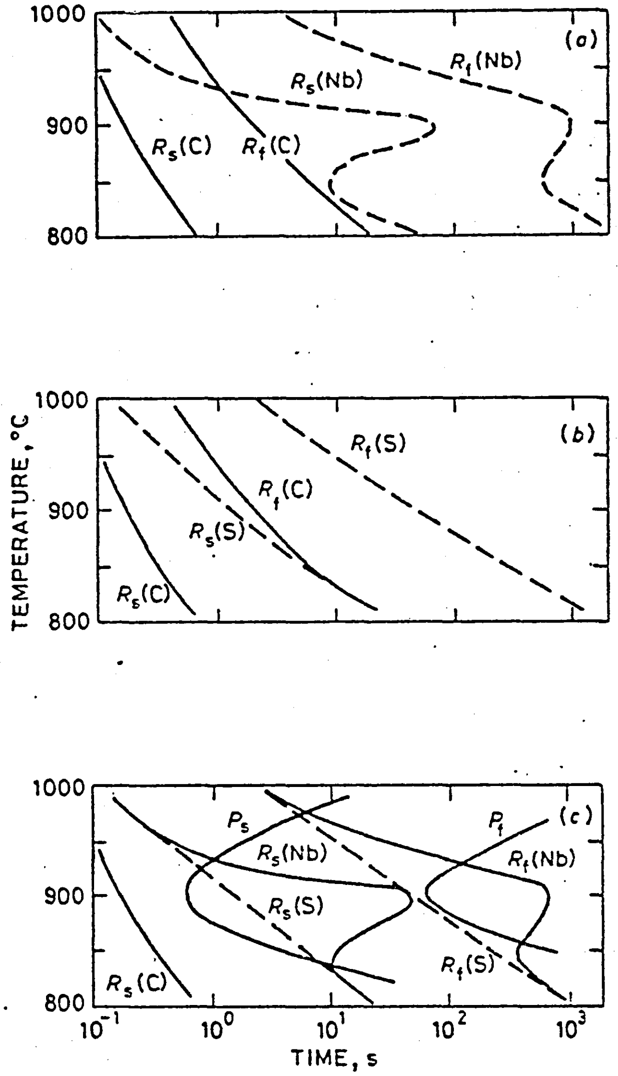


FIG. 25 THE TEMPERATURE DEPENDENCE OF THE TIME TO 50% RECRYSTALLIZATION.



(a) Comparison of recrystallization kinetics of plain carbon (C), and Nb-treated steel (125)

(b) Derived effect of Nb as solute, (S), on recrystallization kinetics of Nb-treated steel of (a).

(c) Superposition of P.T.T diagram for dynamic precipitation and derived R.T.T diagram of (b) for rate of solute modified recrystallization.

FIG. 26 INTERACTION BETWEEN NIOBIUM AS SOLUTE AND AS PRECIPITATES ON THE RECRYSTALLIZATION KINETICS.

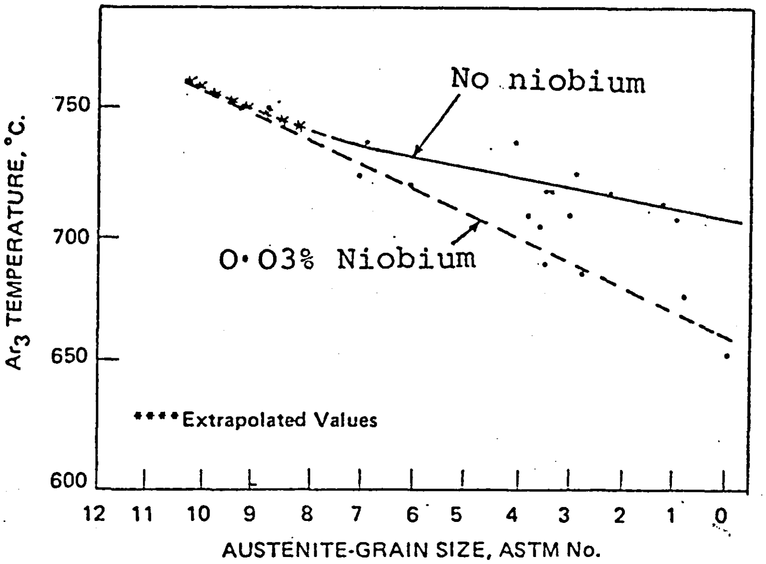
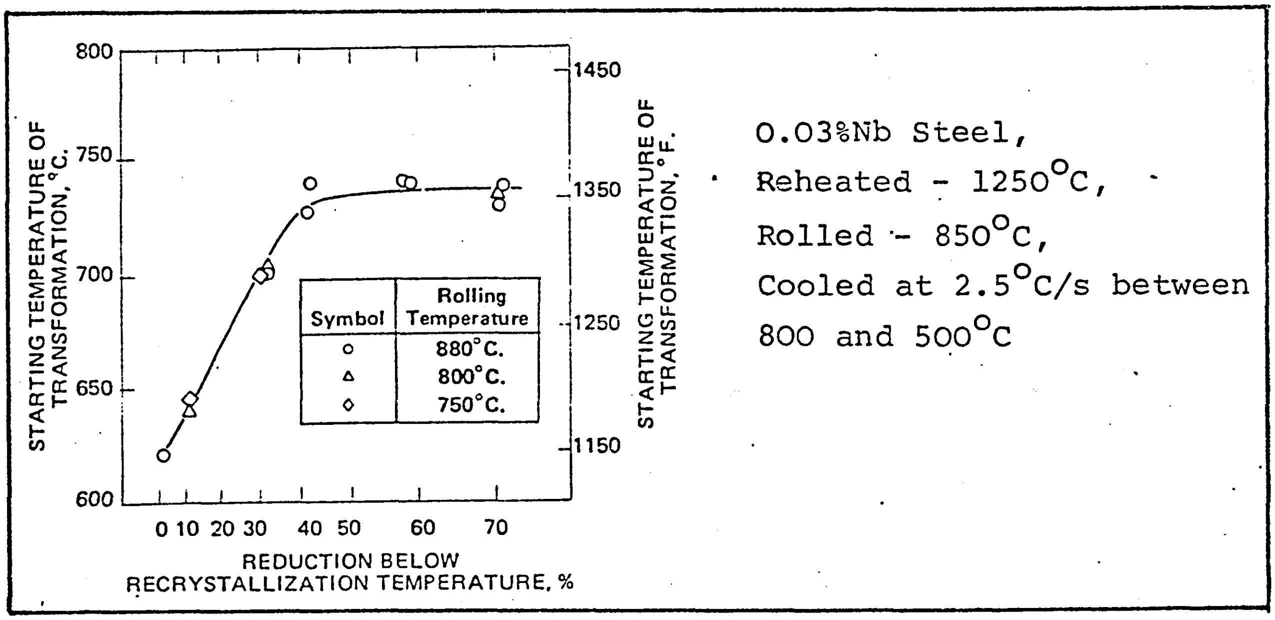


FIG. 27 EFFECT OF NIOBIUM ON THE RELATIONSHIP BETWEEN AUSTENITE GRAIN SIZE AND Ar_3 TEMPERATURE OF A STEEL CONTAINING 0.18%C and 1.37%Mn



0.03%Nb Steel,
Reheated - 1250°C,
Rolled - 850°C,
Cooled at 2.5°C/s between 800 and 500°C

FIG. 28 VARIATION OF THE AUSTENITE-TO-FERRITE TRANSFORMATION TEMPERATURE WITH THE DEFORMATION BELOW THE AUSTENITE-RECRYSTALLIZATION TEMPERATURE.

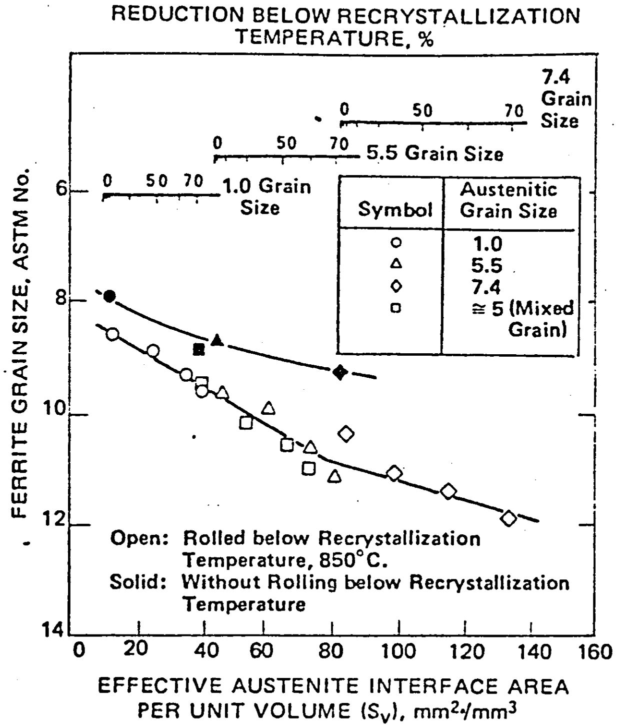


FIG. 29 VARIATION OF FERRITE GRAIN SIZE WITH INTERFACIAL AREA (S_V) IN 0.03%Nb STEEL.

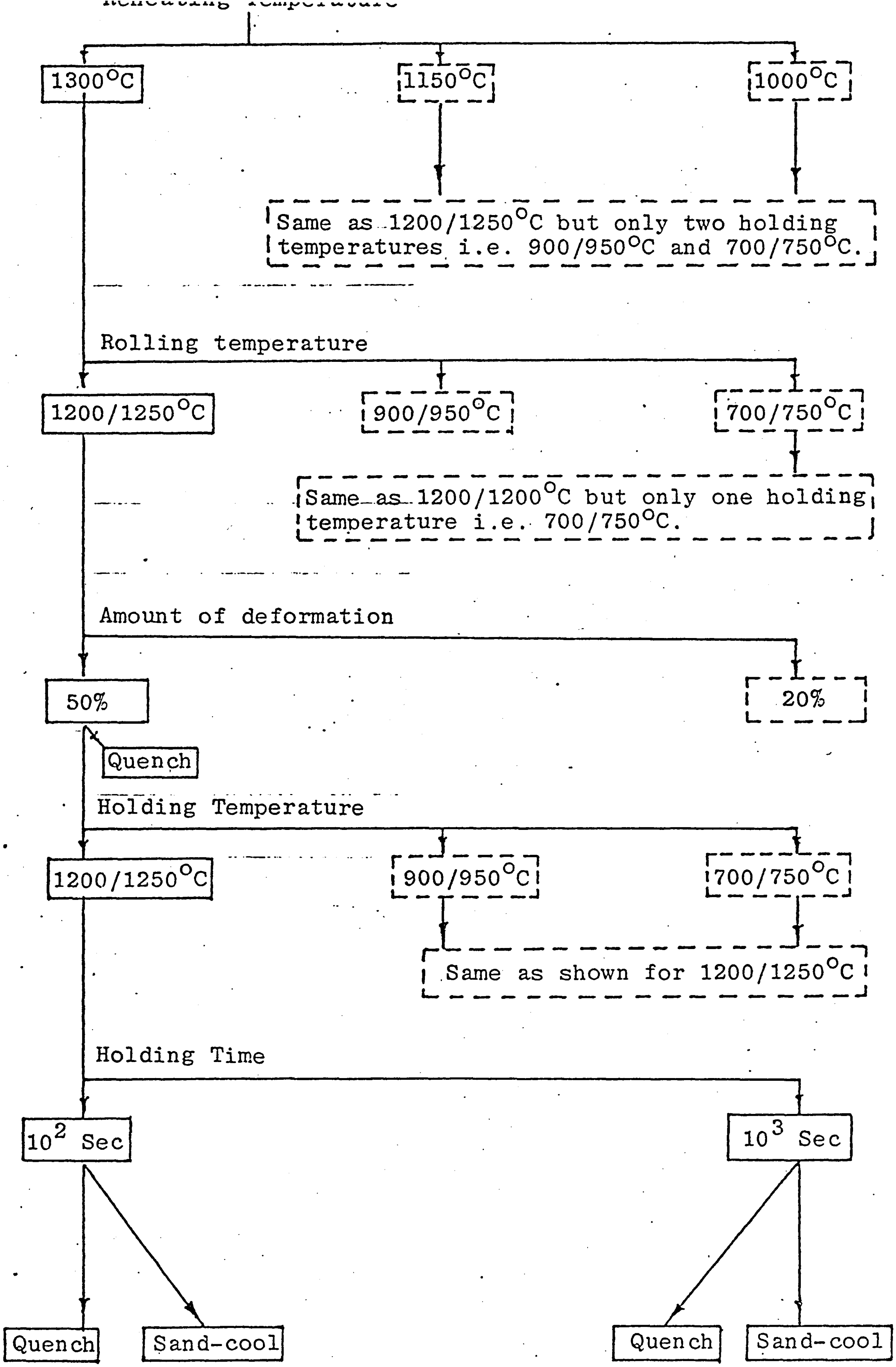


FIG. 30 EXPERIMENTAL PROCEDURE

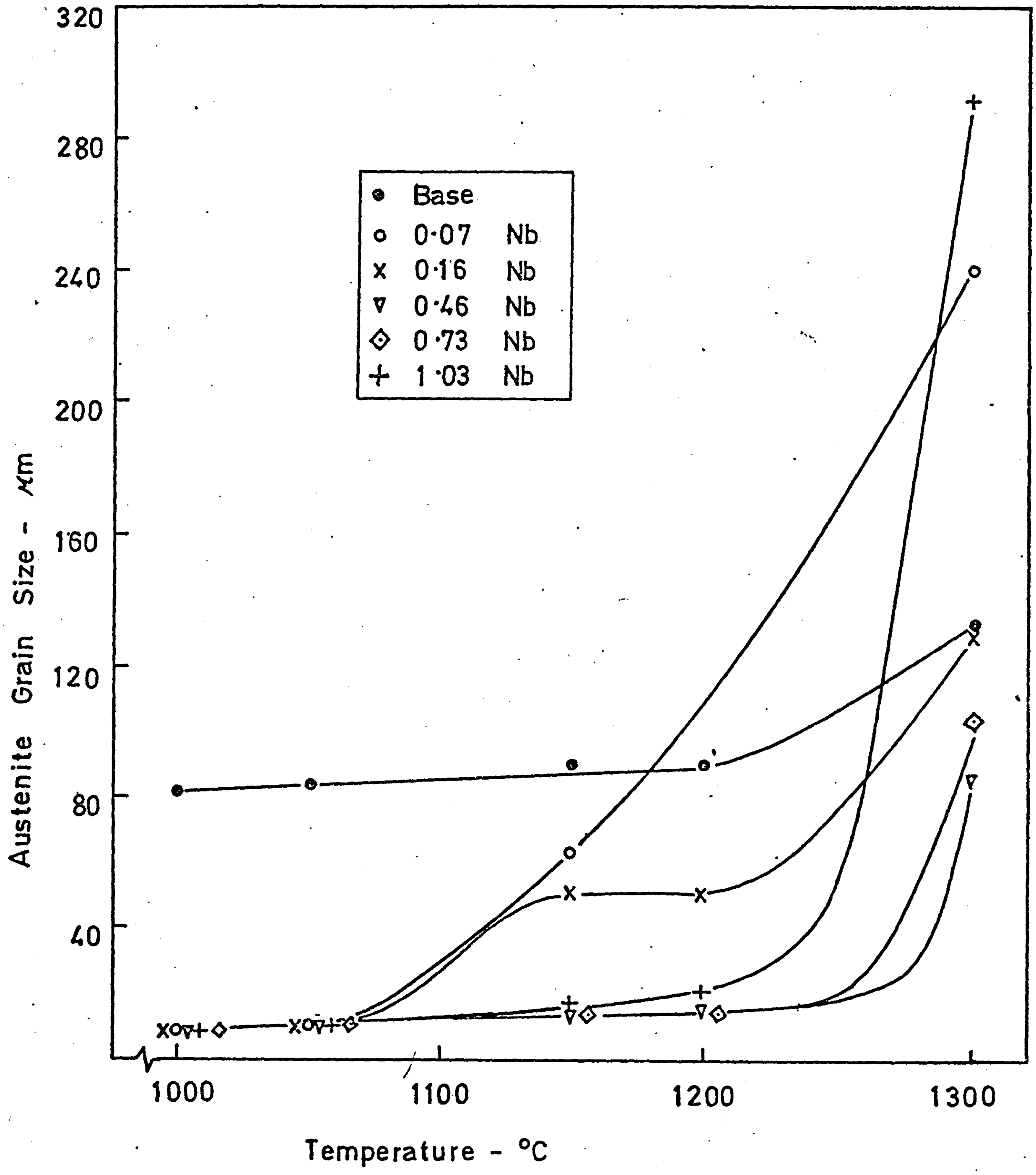


FIG. 31 THE VARIATION OF AUSTENITE GRAIN SIZE WITH TEMPERATURE IN NIOBIUM STEELS

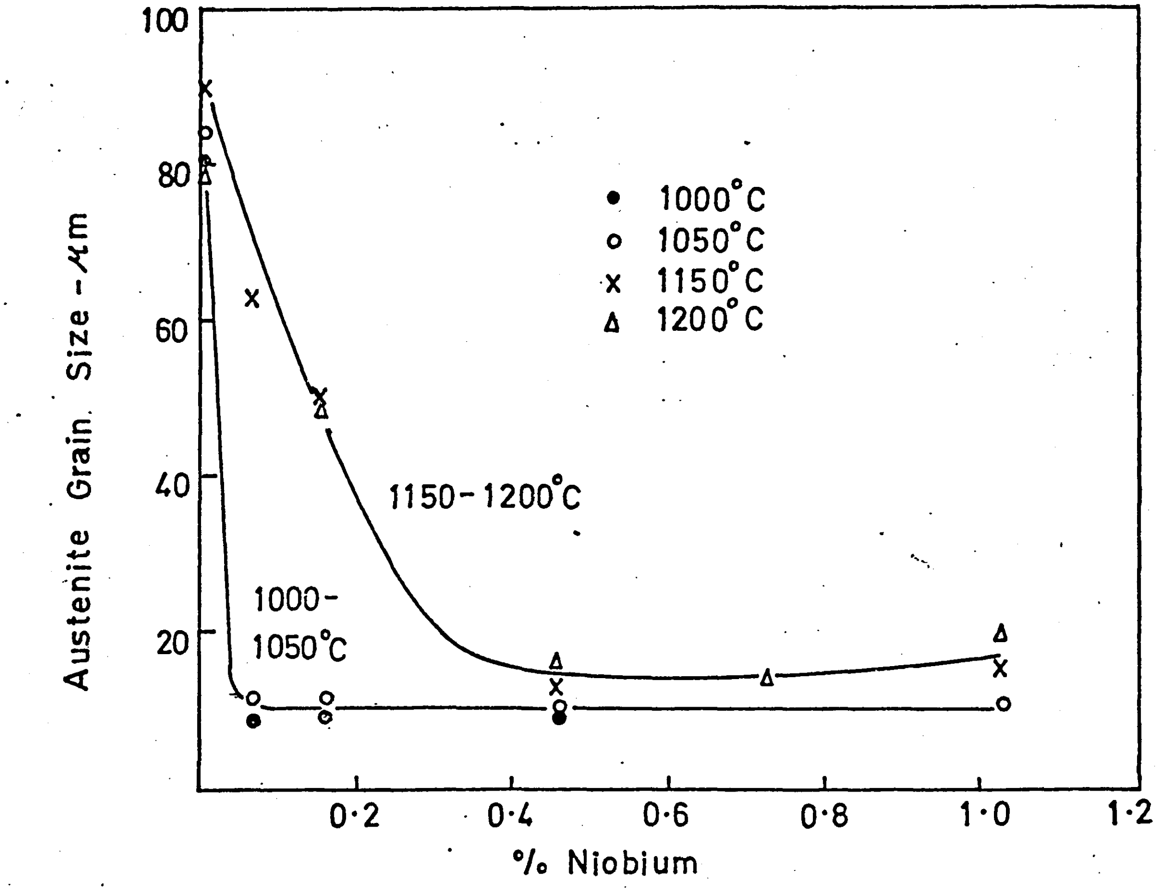


FIG-32 EFFECT OF NIOBIUM ON AUSTENITE GRAIN SIZE AT VARIOUS TEMPERATURES

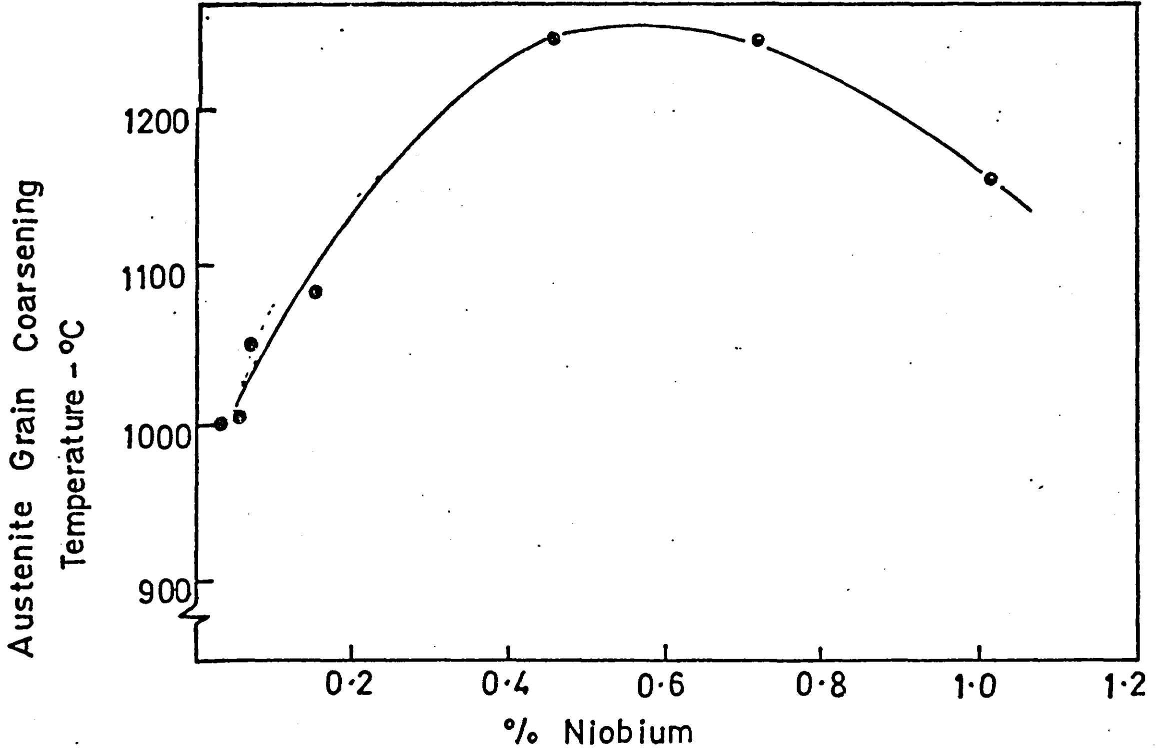


FIG-33 EFFECT OF NIOBIUM ON THE AUSTENITE GRAIN-COARSENING TEMPERATURE

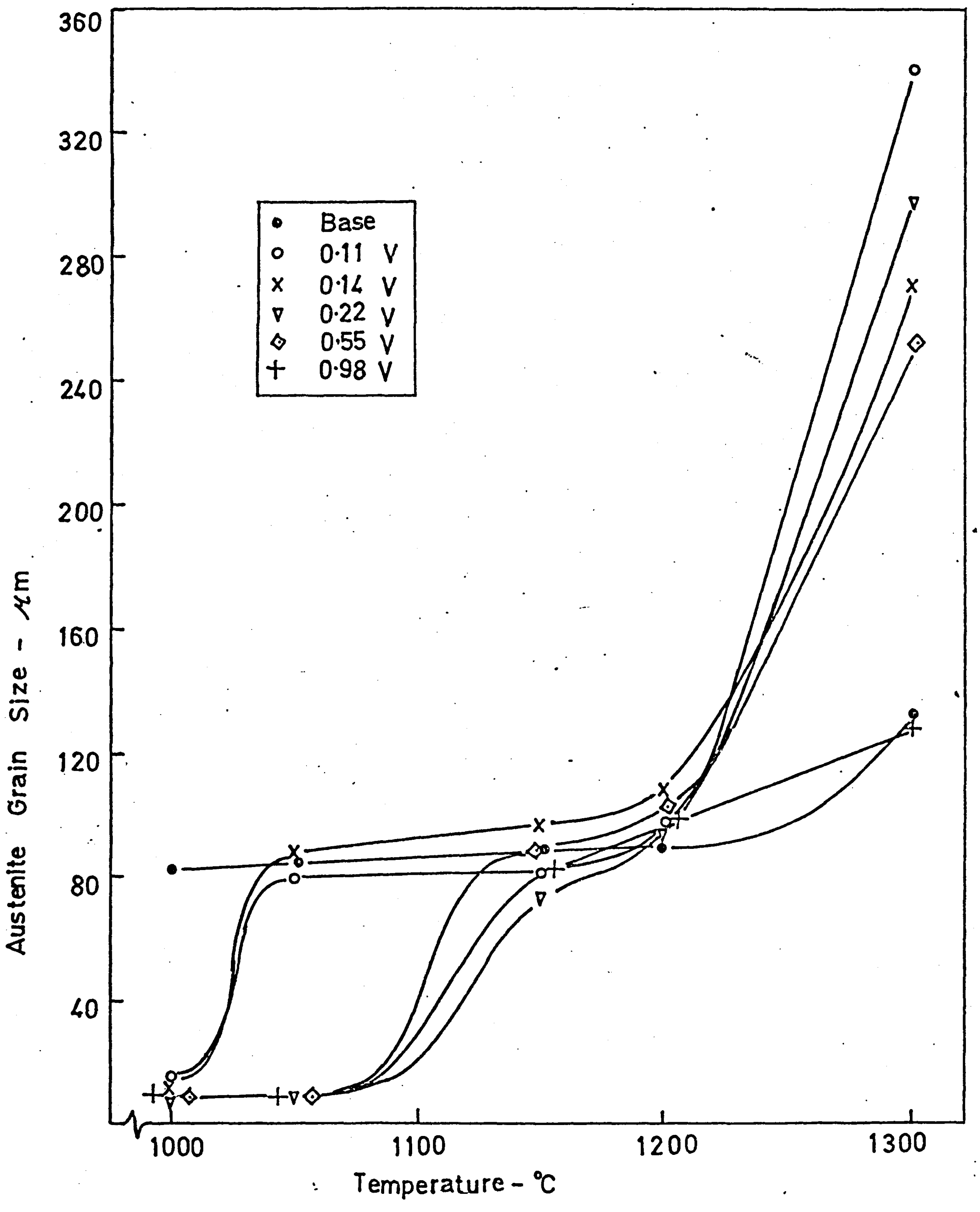


FIG. 34 THE VARIATION OF AUSTENITE GRAIN SIZE WITH TEMPERATURE IN VANADIUM STEELS

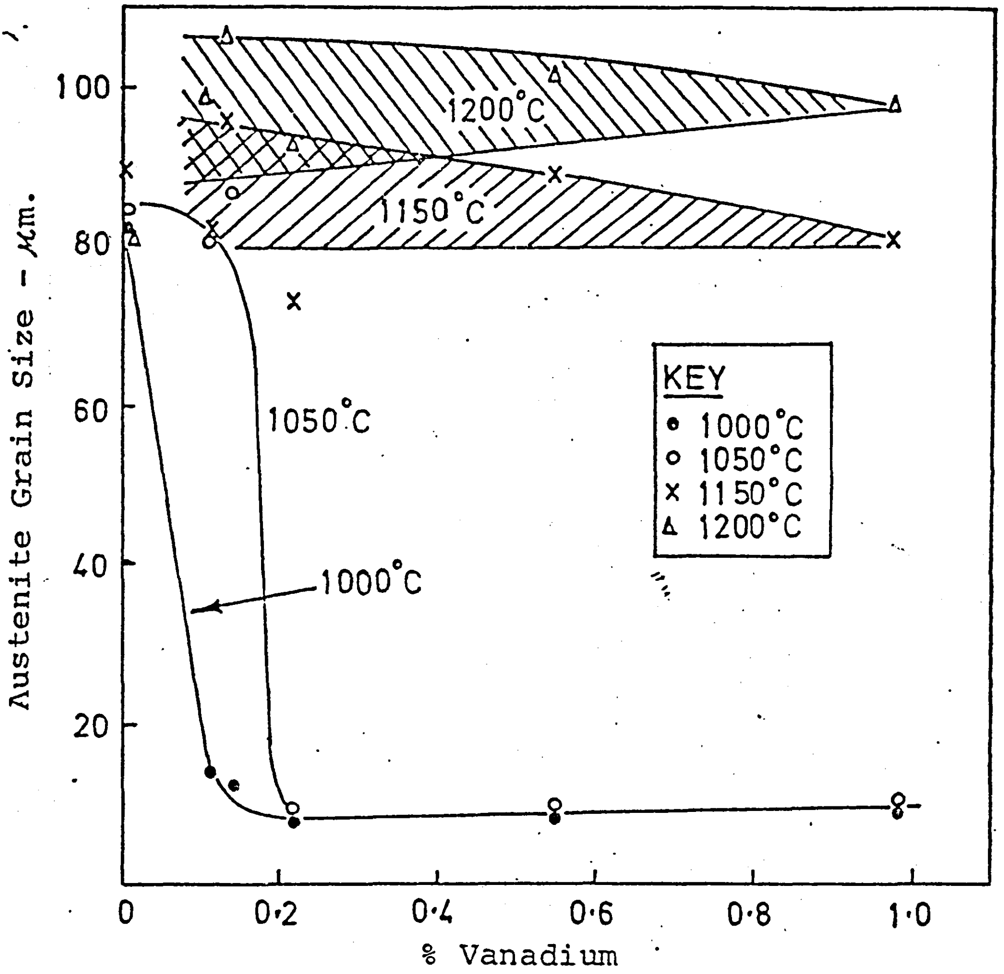


FIG. 35 EFFECT OF VANADIUM CONTENTS ON AUSTENITE GRAIN SIZE AT VARIOUS TEMPERATURES.

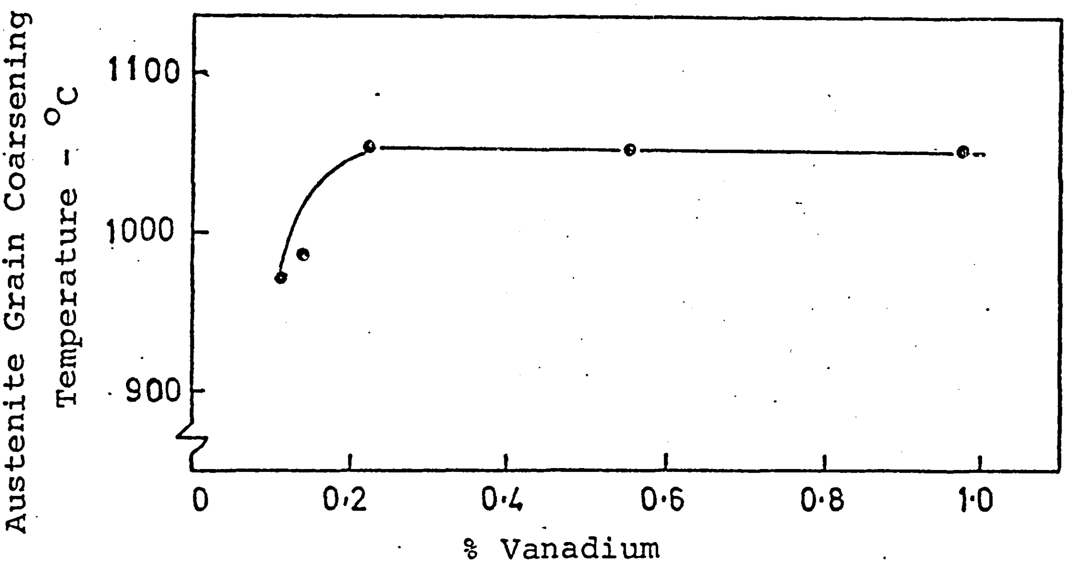


FIG. 36 EFFECT OF VANADIUM ON THE AUSTENITE GRAIN COARSENING TEMPERATURE.

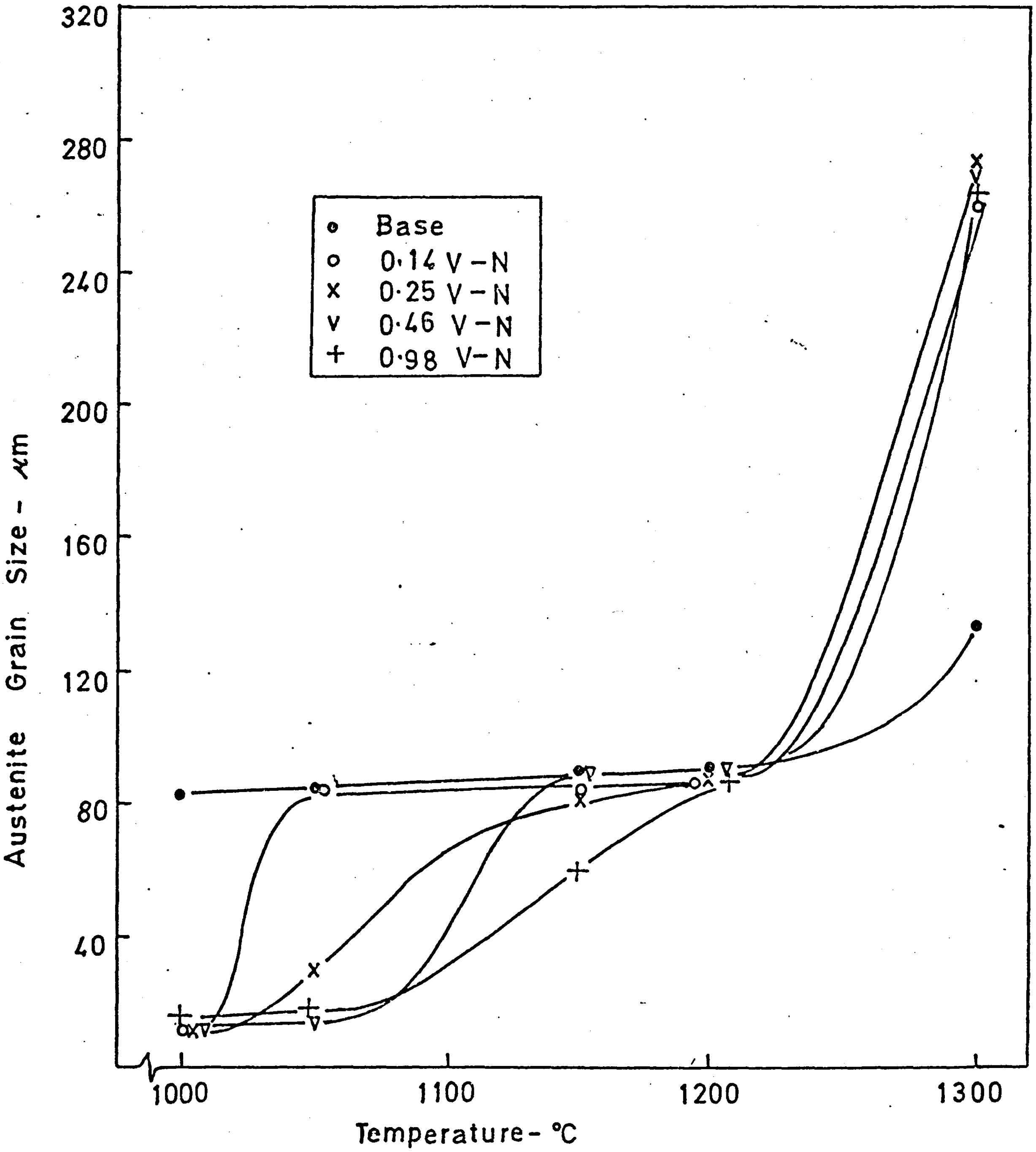


FIG.37 THE VARIATION OF AUSTENITE GRAIN SIZE WITH TEMPERATURE IN VANADIUM PLUS NITROGEN (V-N) STEELS

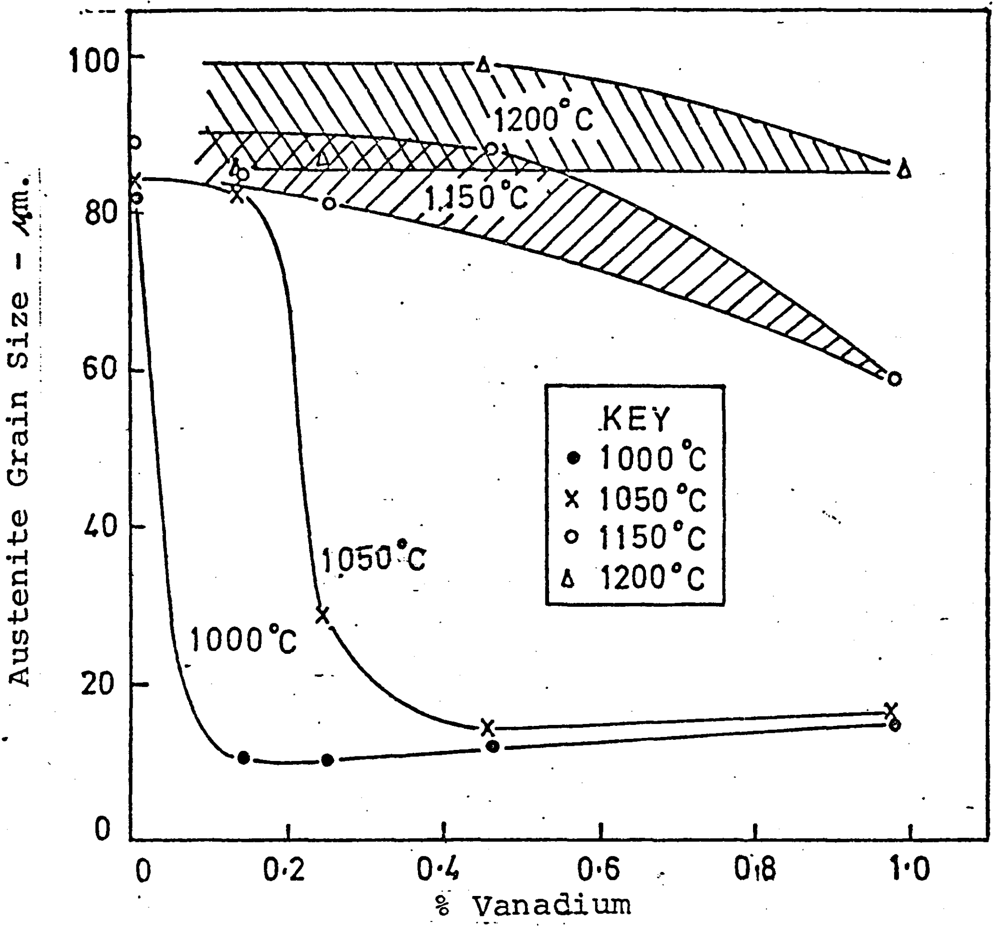


FIG. 38 EFFECT OF VANADIUM ON AUSTENITE GRAIN SIZE IN HIGH NITROGEN STEEL.

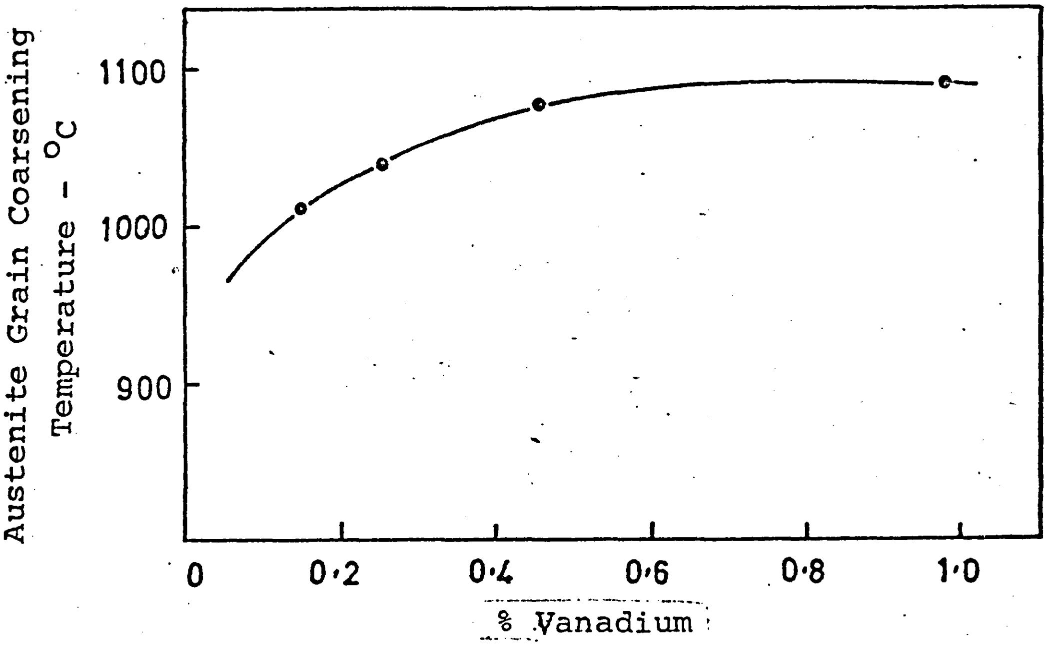


FIG. 39 EFFECT OF VANADIUM ON THE AUSTENITE GRAIN COARSENING TEMPERATURE IN HIGH NITROGEN STEEL.

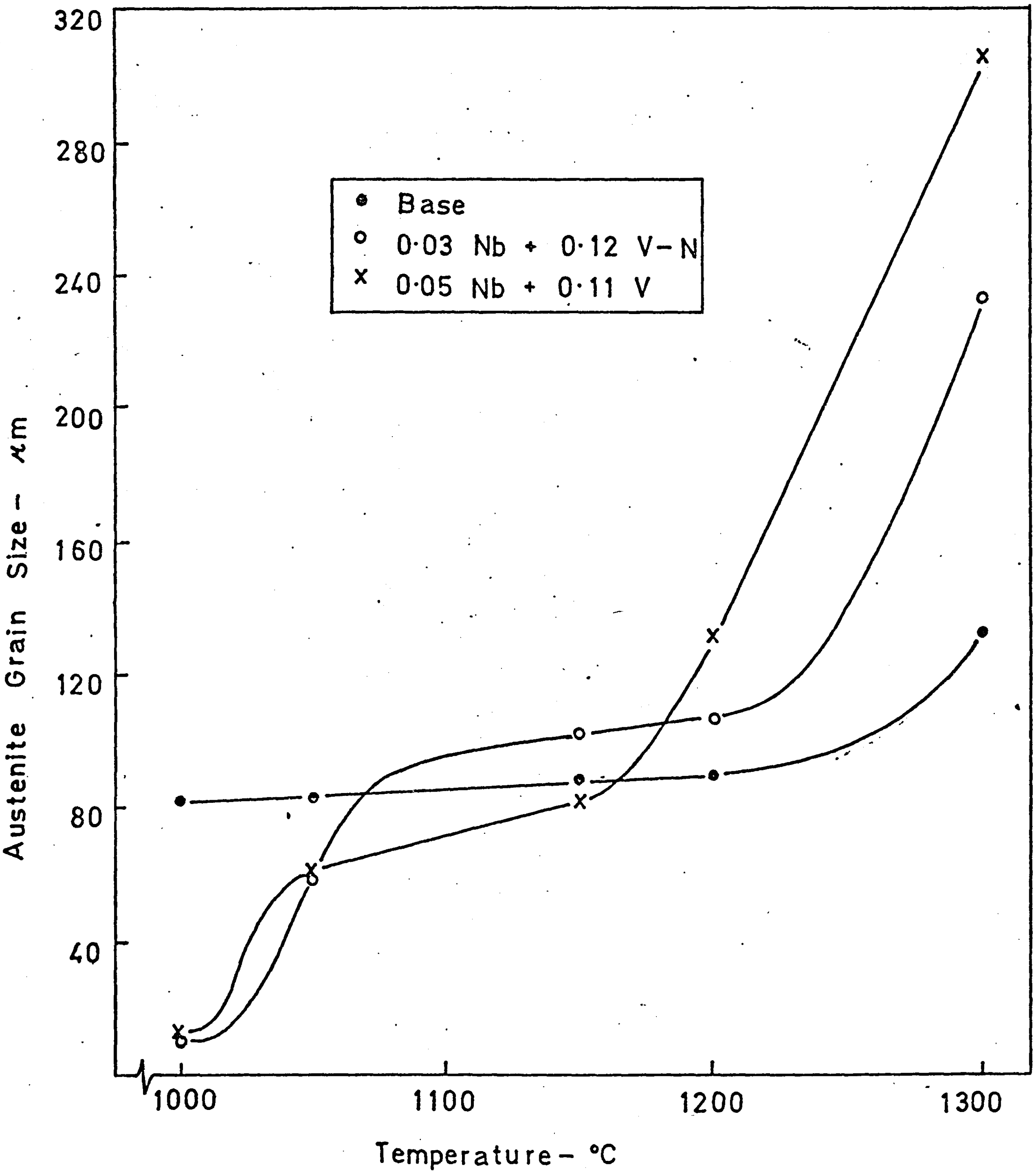


FIG. 40 THE VARIATION OF AUSTENITE GRAIN SIZE WITH TEMPERATURE IN LOW AND HIGH NITROGEN NIOBIUM PLUS VANADIUM STEELS

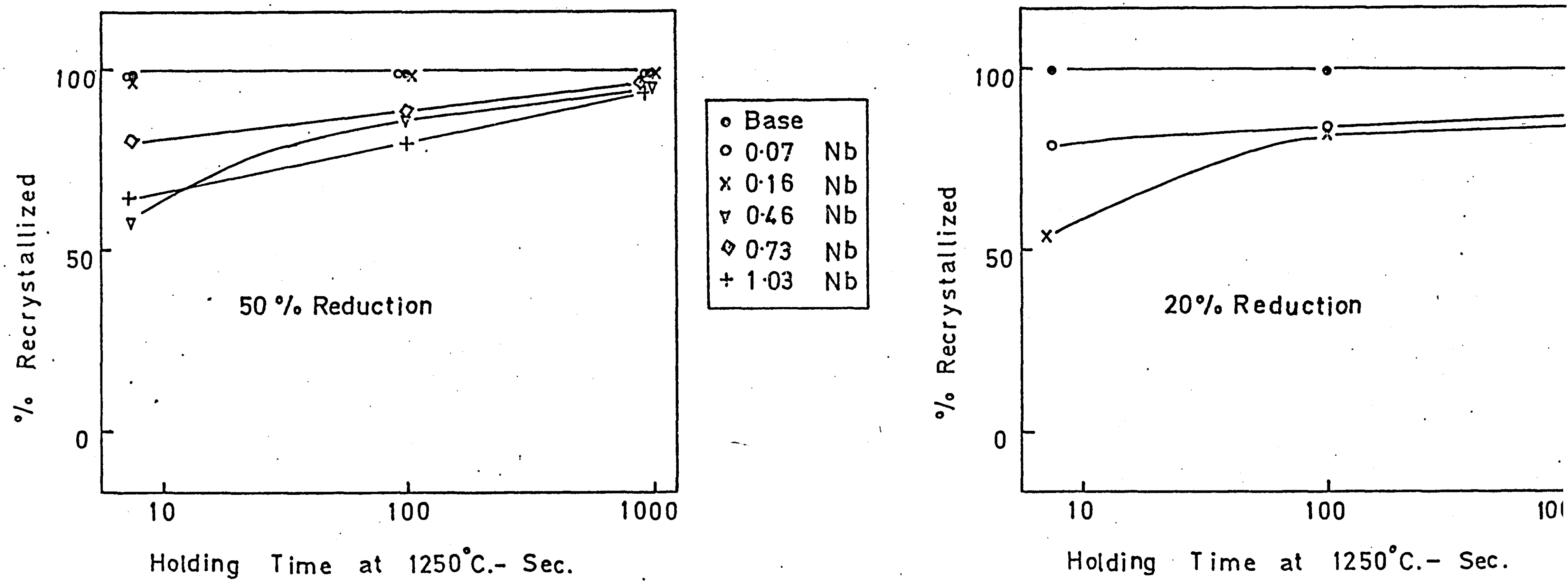
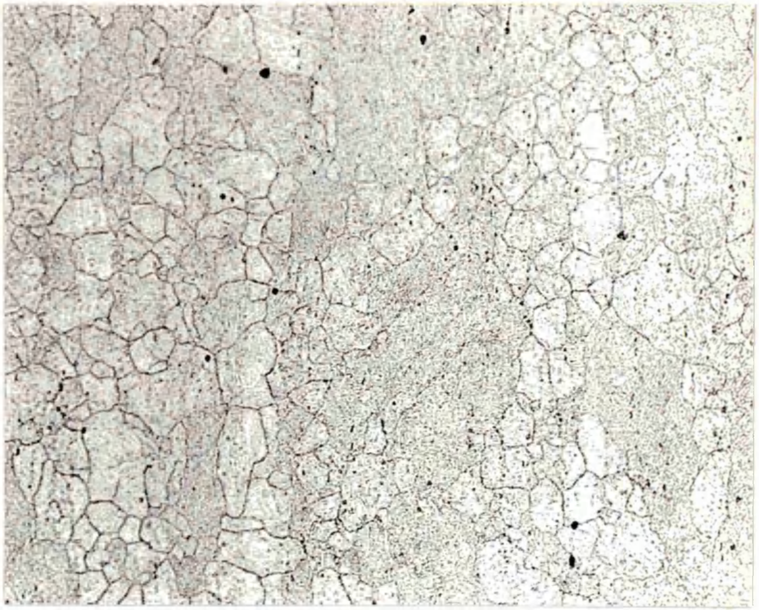
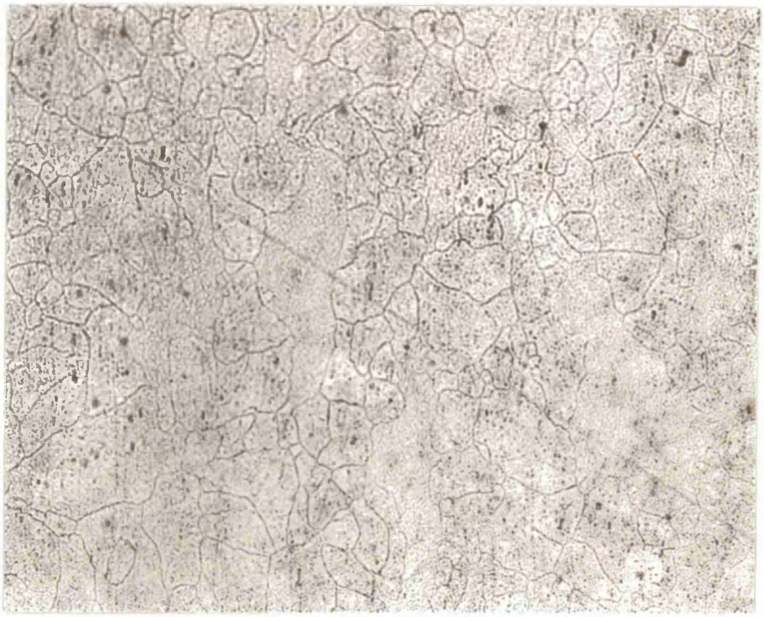


FIG. 41. EFFECT OF HOLDING AT 1250°C ON RECRYSTALLIZATION OF AUSTENITE IN Nb ALLOYS: Reheated 1300°C, Rolled at 1250°C.



(a) 0.46 % Nb Steel X 160
Reheated 1300°C,
Rolled 50% reduction at 1250°C,
Held 100s at 1250°C, Quenched.



(b) 0.73 % Nb Steel X 160
Reheated 1300°C,
Rolled 50% reduction at 1250°C,
Held 100s at 1250°C, Quenched.

FIGURE. 42 TYPICAL PARTIALLY RECRYSTALLIZED STRUCTURES.

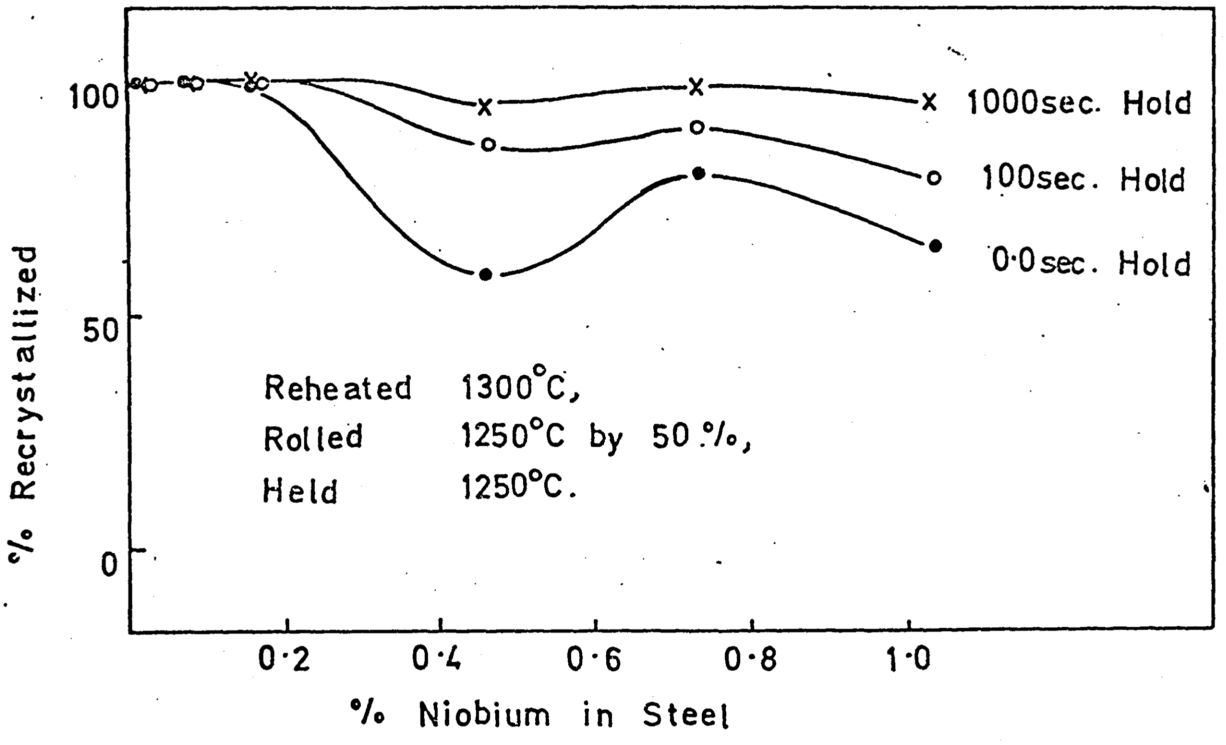


FIG. 43. EFFECT OF Nb CONTENTS ON RECRYSTALLIZATION OF AUSTENITE AT 1250°C.

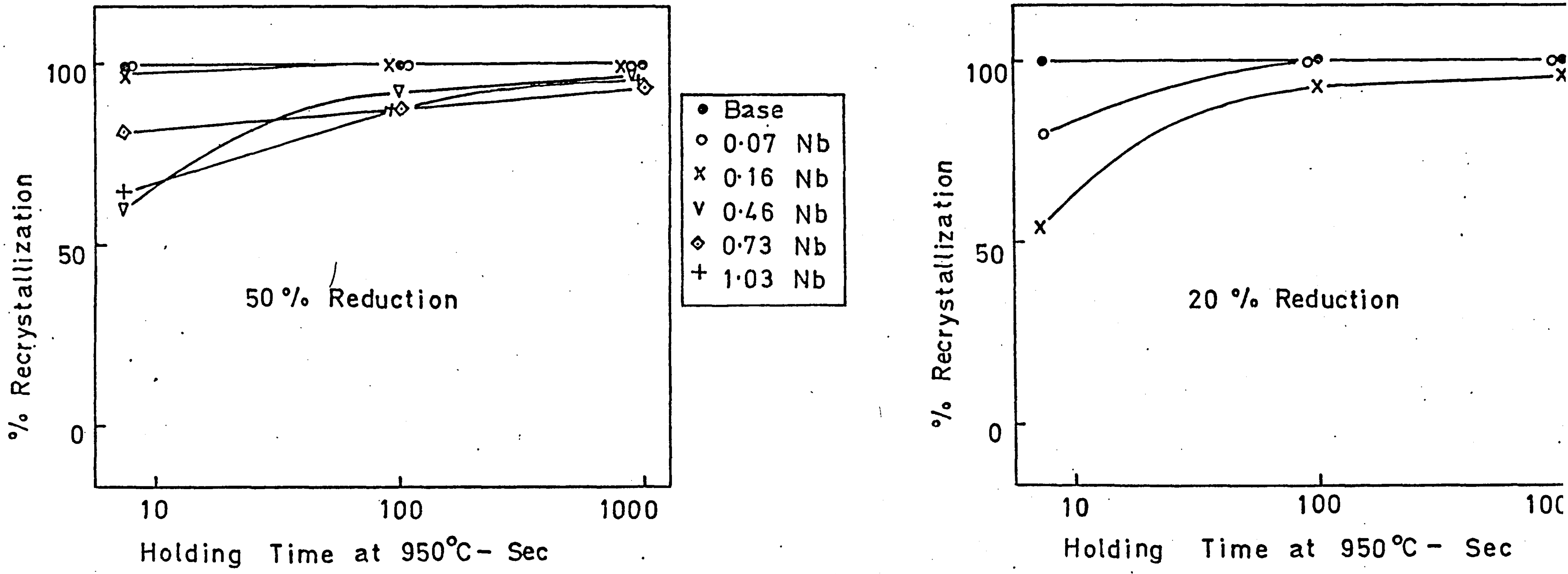


FIG. 44. EFFECT OF HOLDING AT 950°C ON RECRYSTALLIZATION OF AUSTENITE IN Nb ALLOYS: Reheated - 1300°C, Rolled - 1250°C.

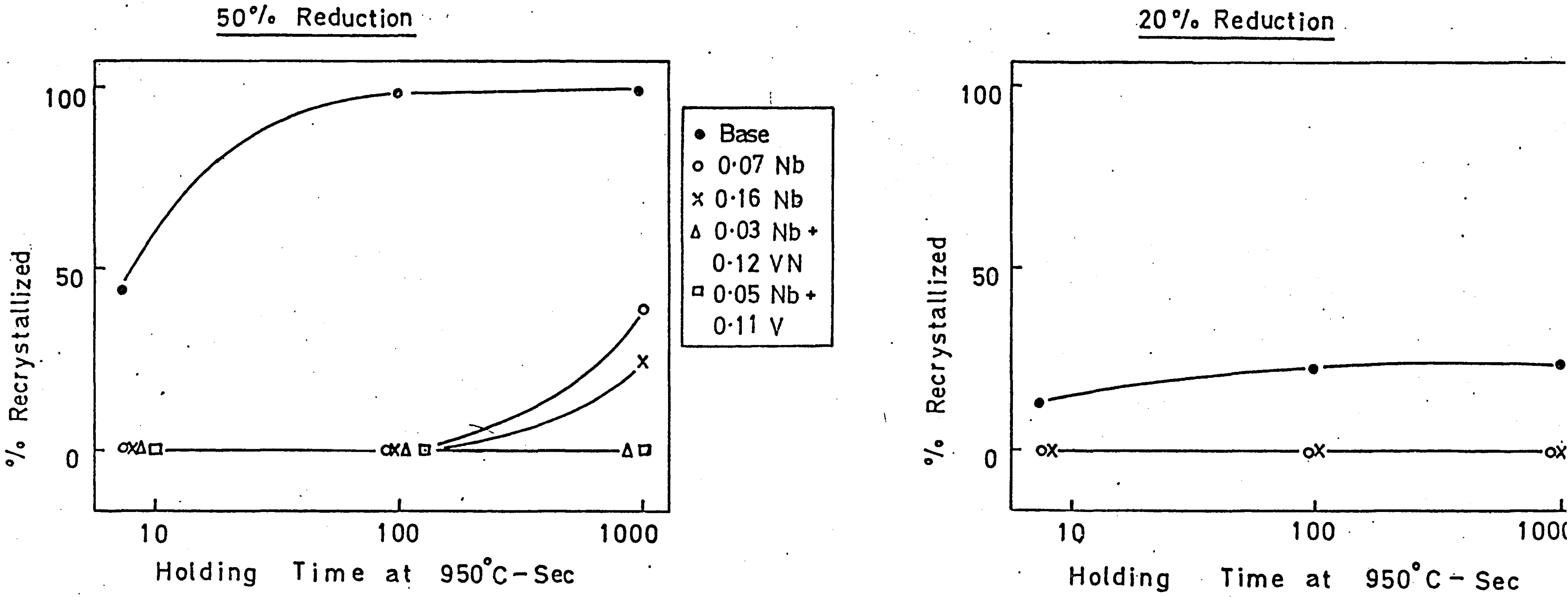


FIG. 45 EFFECT OF HOLDING AT 950°C ON RECRYSTALLIZATION OF AUSTENIT IN Nb AND Nb+V ALLOYS: Reheated - 1300°C, Rolled at 950°C.

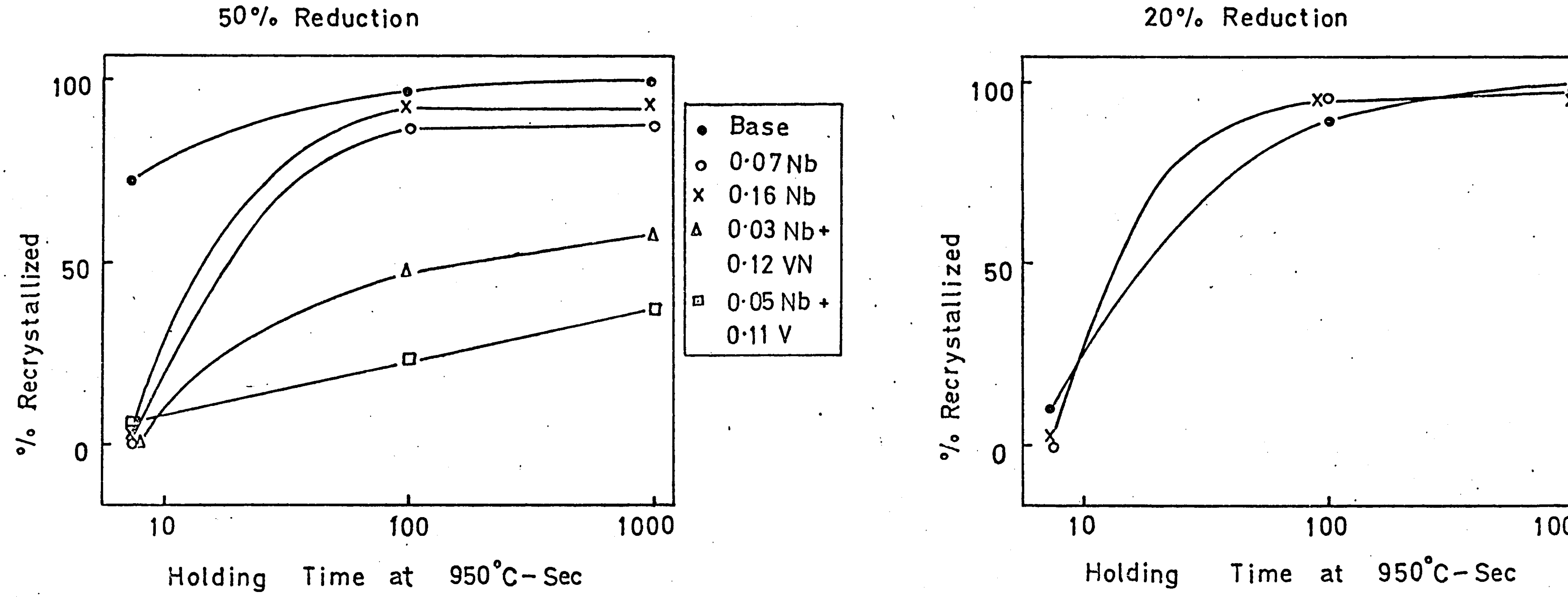
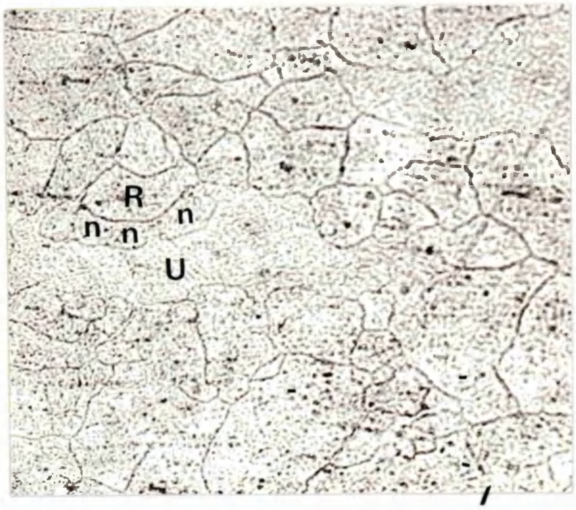
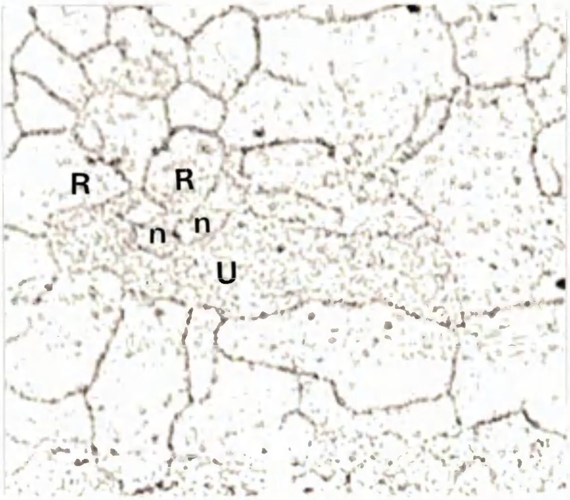


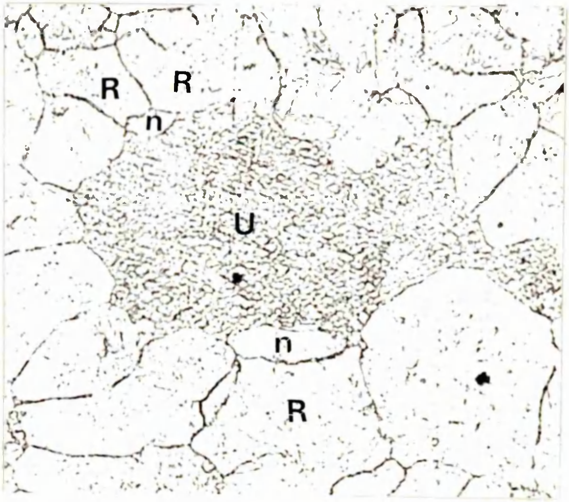
FIG. 46. EFFECT OF HOLDING AT 950°C ON RECRYSTALLIZATION OF AUSTENITE IN Nb AND Nb + V ALLOYS: Reheated 1150°C, Rolled at 950°C.



(a) 0.73 Nb
Reheated-1300°C,
Rolled -1250°C, 50% Red.,
Held -1250°C, 100s.
Quenched.



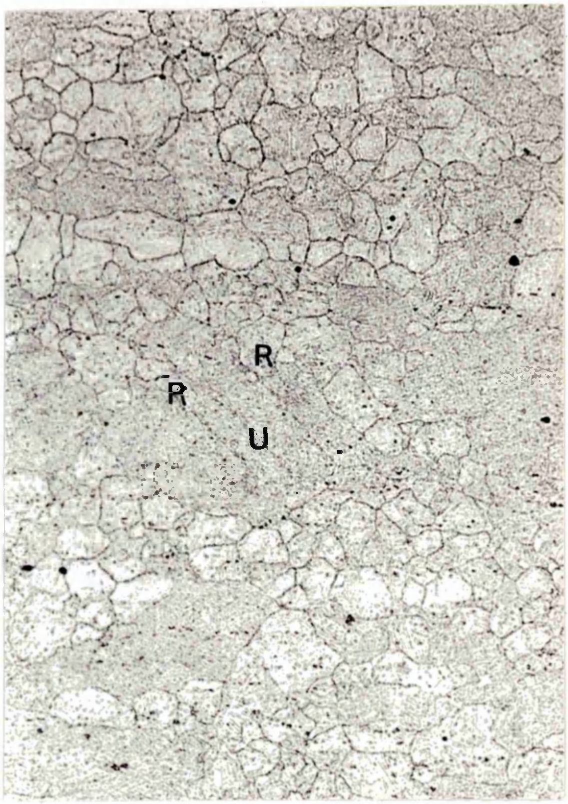
(b) 0.46 Nb
Treatment: Same as (a)



(c) 1.03 Nb
Reheated-1300°C,
Rolled -1250°C, 50% Red.,
Held - 950°C, 100s.
Quenched.

FIG. 47 NUCLEATION AT THE INTERFACE OF RECRYSTALLIZED TO UNRECRYSTALLIZED GRAINS:

U = Unrecrystallized grain, R = Recrystallized grain,
N = New grain formed.



U = Unrecrystallized grain
R = Recrystallized grains on the deformation bands.

FIG. 48 NUCLEATION AT THE DEFORMATION BANDS.

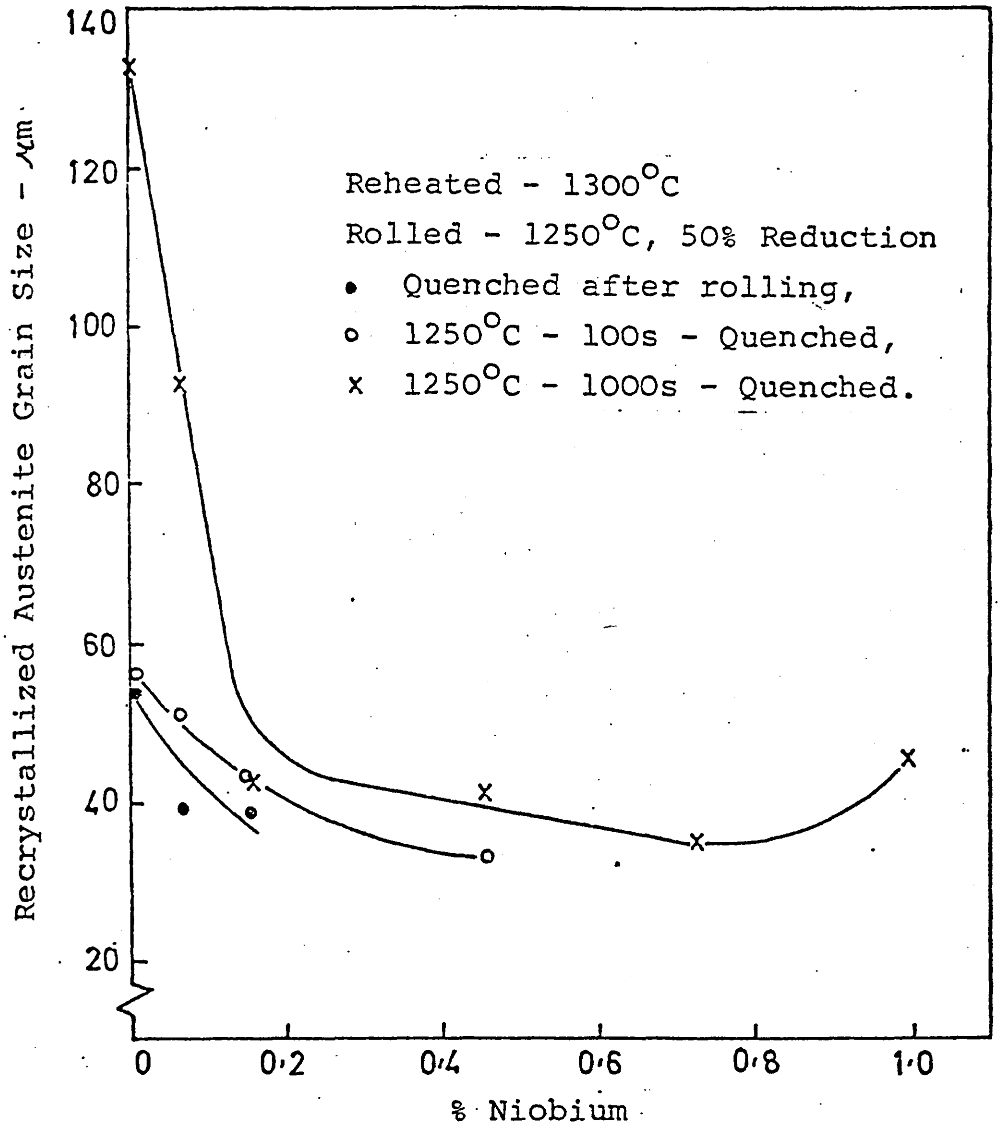
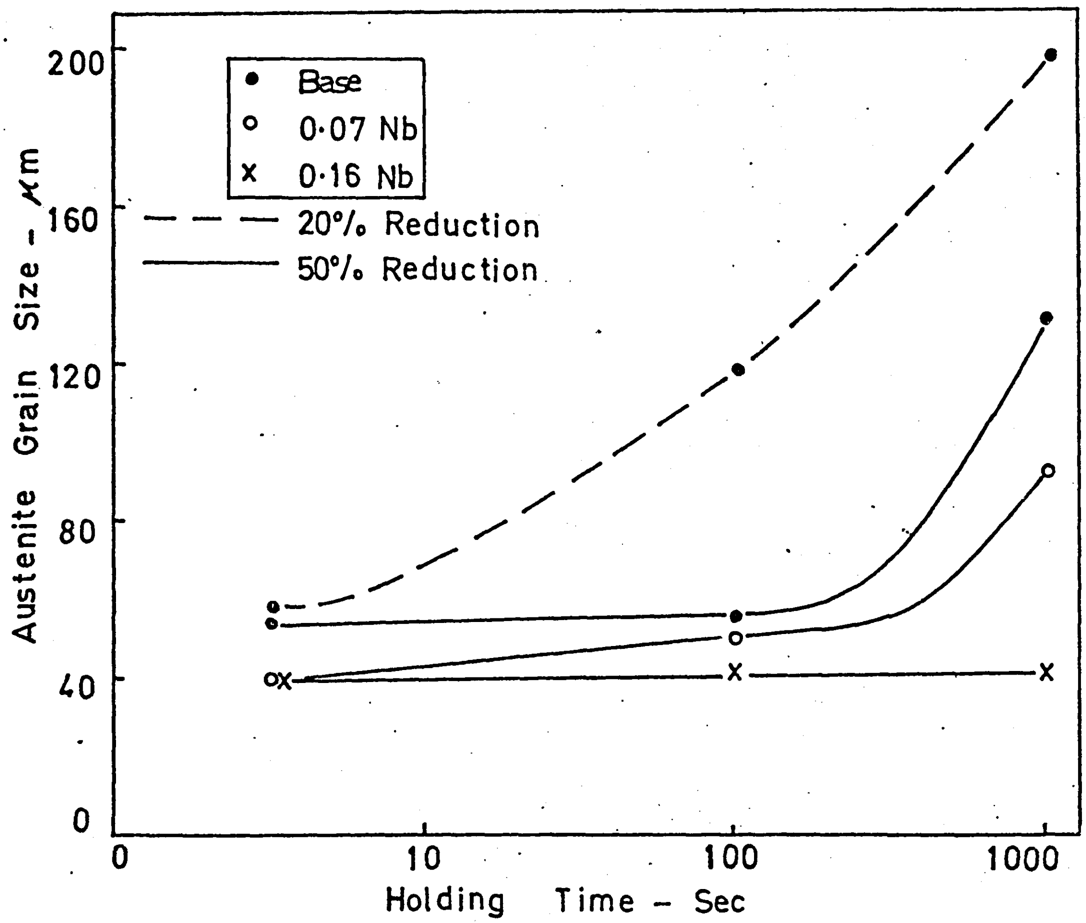


FIG. 49 EFFECT OF NIOBIUM CONTENT ON THE RECRYSTALLIZED AUSTENITE GRAIN SIZE AFTER ROLLING AT 1250°C AND HOLDING AT 1250°C.



(a) EFFECT OF HOLDING AT 1250°C ON THE RECRYSTALLIZED AUSTENITE GRAIN SIZE: Reheated - 1300°C, Rolled - 1250°C

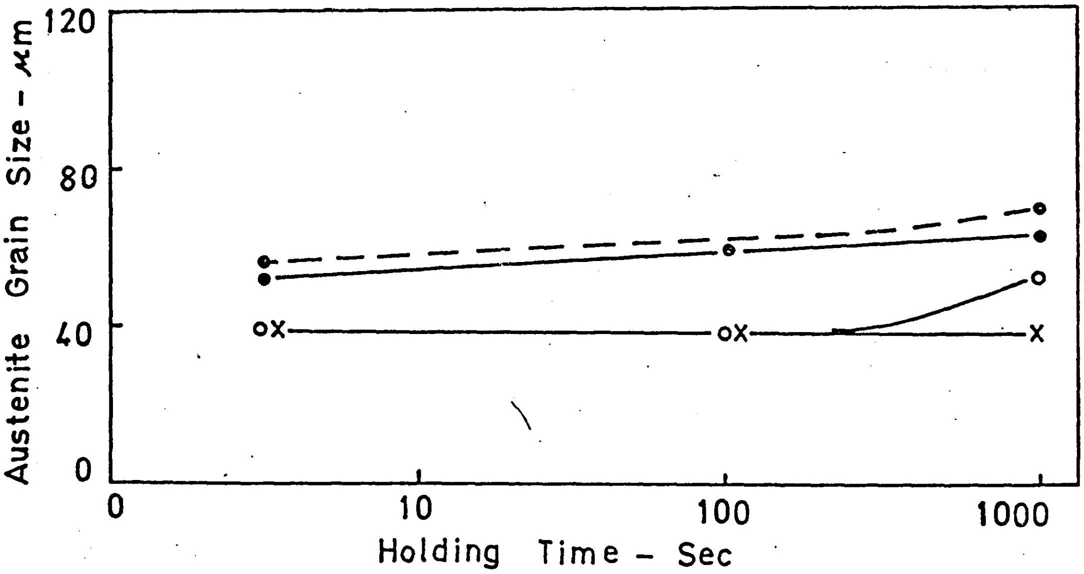


FIG. 50 (b) EFFECT OF HOLDING AT 950°C ON THE RECRYSTALLIZED AUSTENITE GRAIN SIZE: Reheated-1300°C, Rolled-1250°C.

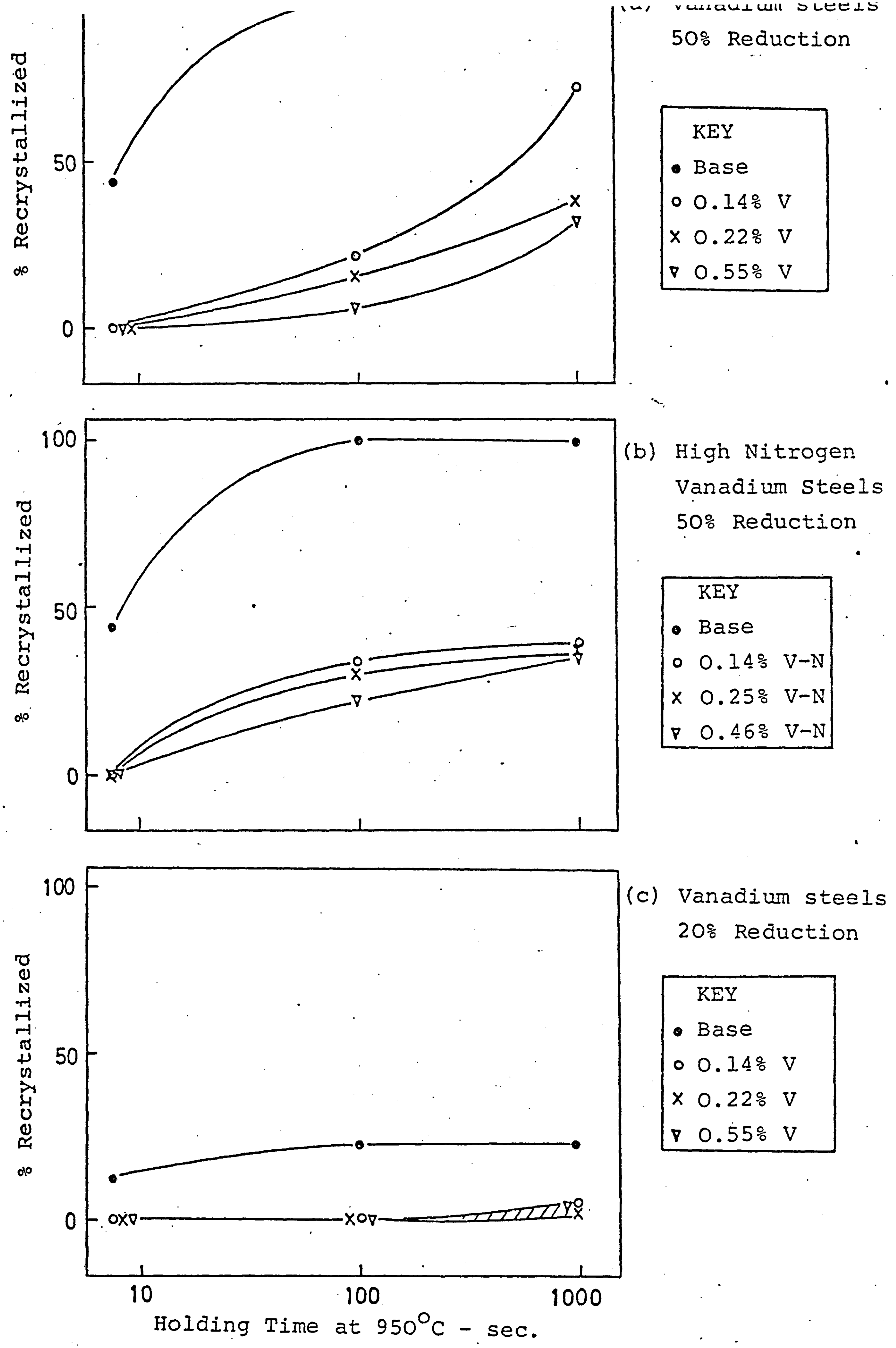
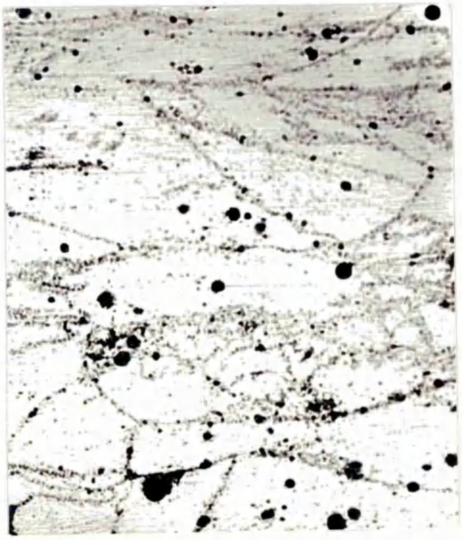


FIG. 51 EFFECT OF HOLDING AT 950°C ON THE RECRYSTALLIZATION OF AUSTENITE IN VANADIUM STEELS: Reheated - 1300°C, Rolled - 950°C

(a) 0.14% Vanadium.
Reheated - 1300°C,
Rolled - 950°C,
50% reduction,
Quenched.

(b) 0.22% Vanadium.
Treatment: Same as (a).



(c) 0.22% Vanadium.
Reheated - 1300°C,
Rolled - 950°C,
50% reduction,
Held 100s at -950°C and
quenched.

FIGURE. 52 TYPICAL UNRECRYSTALLIZED STRUCTURES IN VANADIUM STEELS.

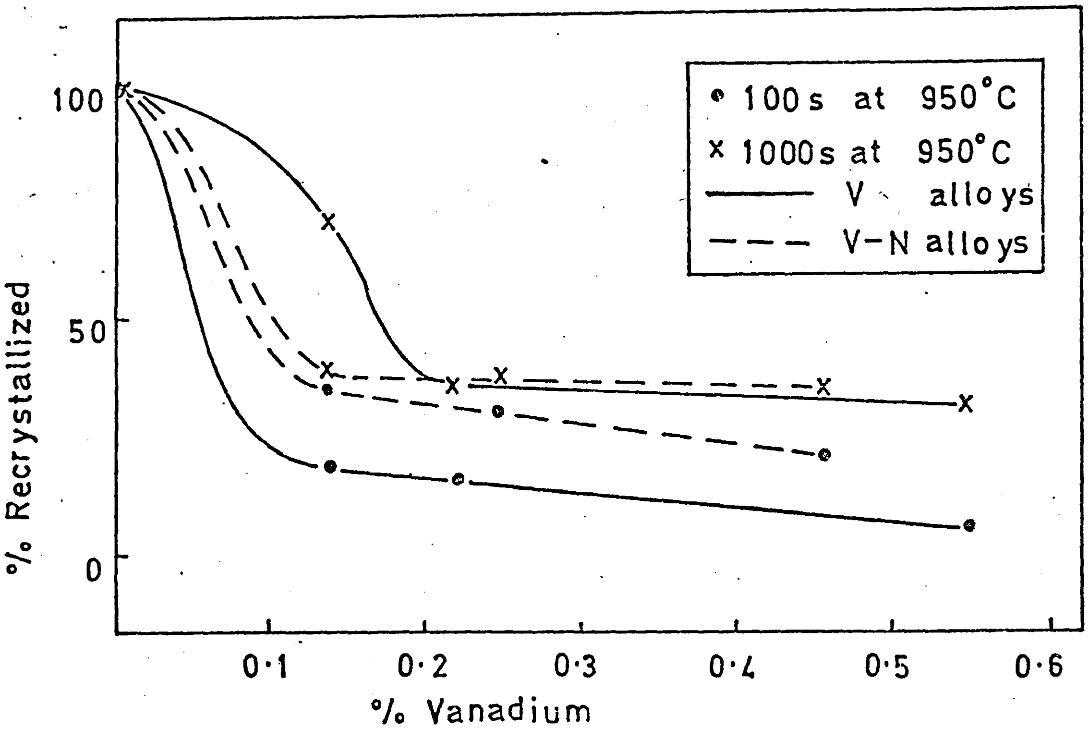


FIG.53 EFFECT OF VANADIUM AND VANADIUM PLUS NITROGEN CONTENTS ON THE RECRYSTALLIZATION OF AUSTENITE: 1300°C Reheating, 950°C Rolling By 50% and Held at 950°C for Various Times.

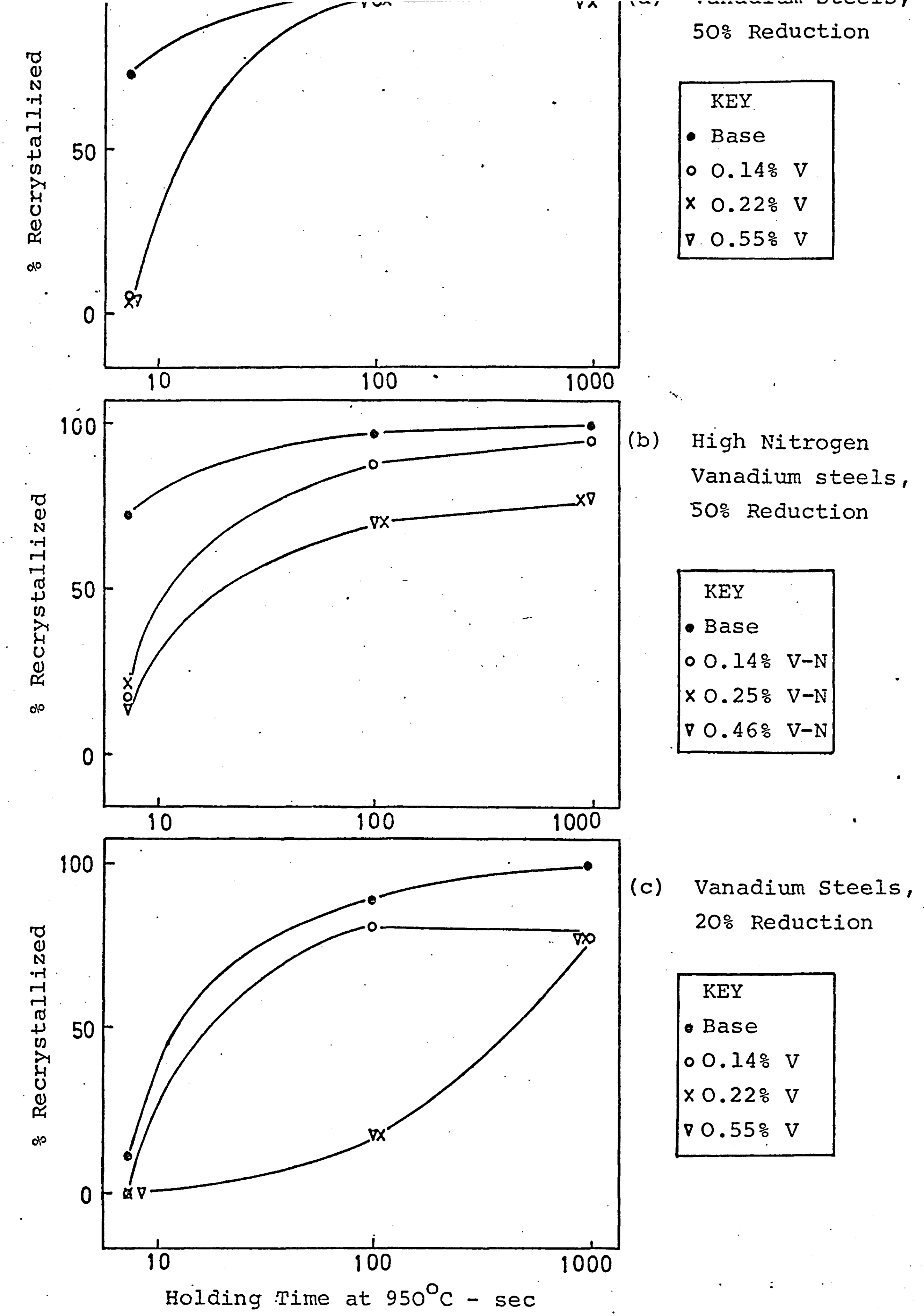
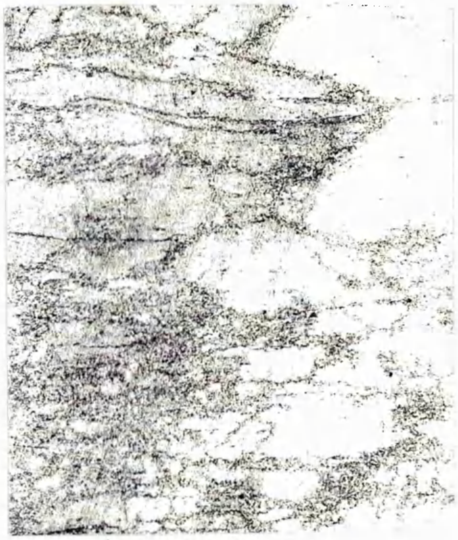


FIG. 54 EFFECT OF HOLDING AT 950°C ON THE RECRYSTALLIZATION OF AUSTENITE IN VANADIUM STEELS: Reheated - 1150°C, Rolled - 950°C.

FIG. 55 NUCLEATION OF RECRYSTALLLIZED GRAINS ON THE AUSTENITE GRAIN BOUNDARIES AND DEFORMATION BANDS.

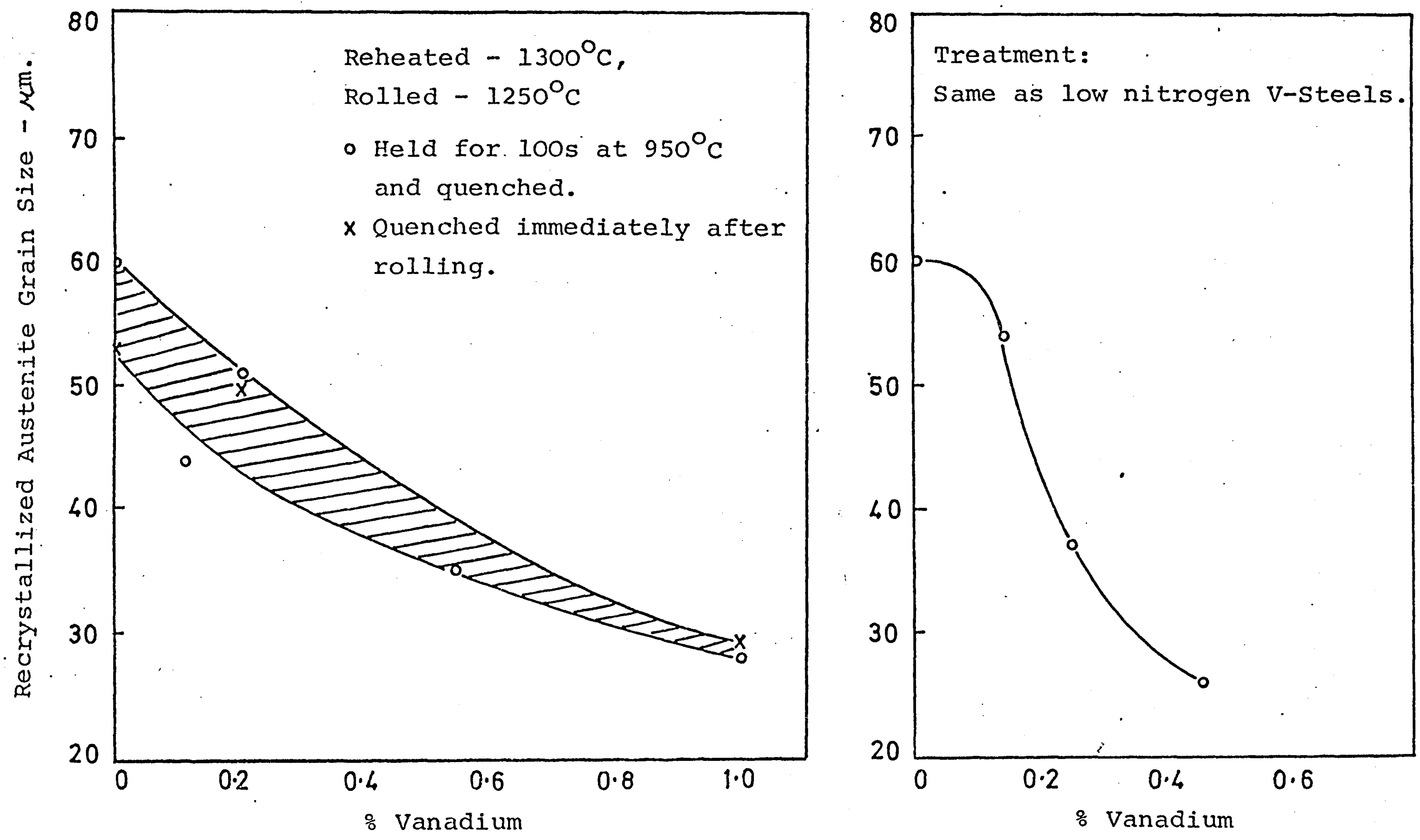
(a) Reheated - 1300°C,
Rolled - 950°C,
50% reduction,
Quenched.



(b) Same as (a) but held at
950°C for 100s and quenched.

(c) Same as (a) but held at
950°C for 1000s and quenched.

FIGURE. 56 PROGRESS OF RECRYSTALLIZATION IN 0.14% V-N STEEL AT 950°C.



Low Nitrogen Vanadium Steels.

High Nitrogen Vanadium Steels.

FIG. 57 EFFECT OF VANADIUM CONTENT ON THE RECRYSTALLIZED AUSTENITE GRAIN SIZE AFTER ROLLING AT 1250°C BY 50%.

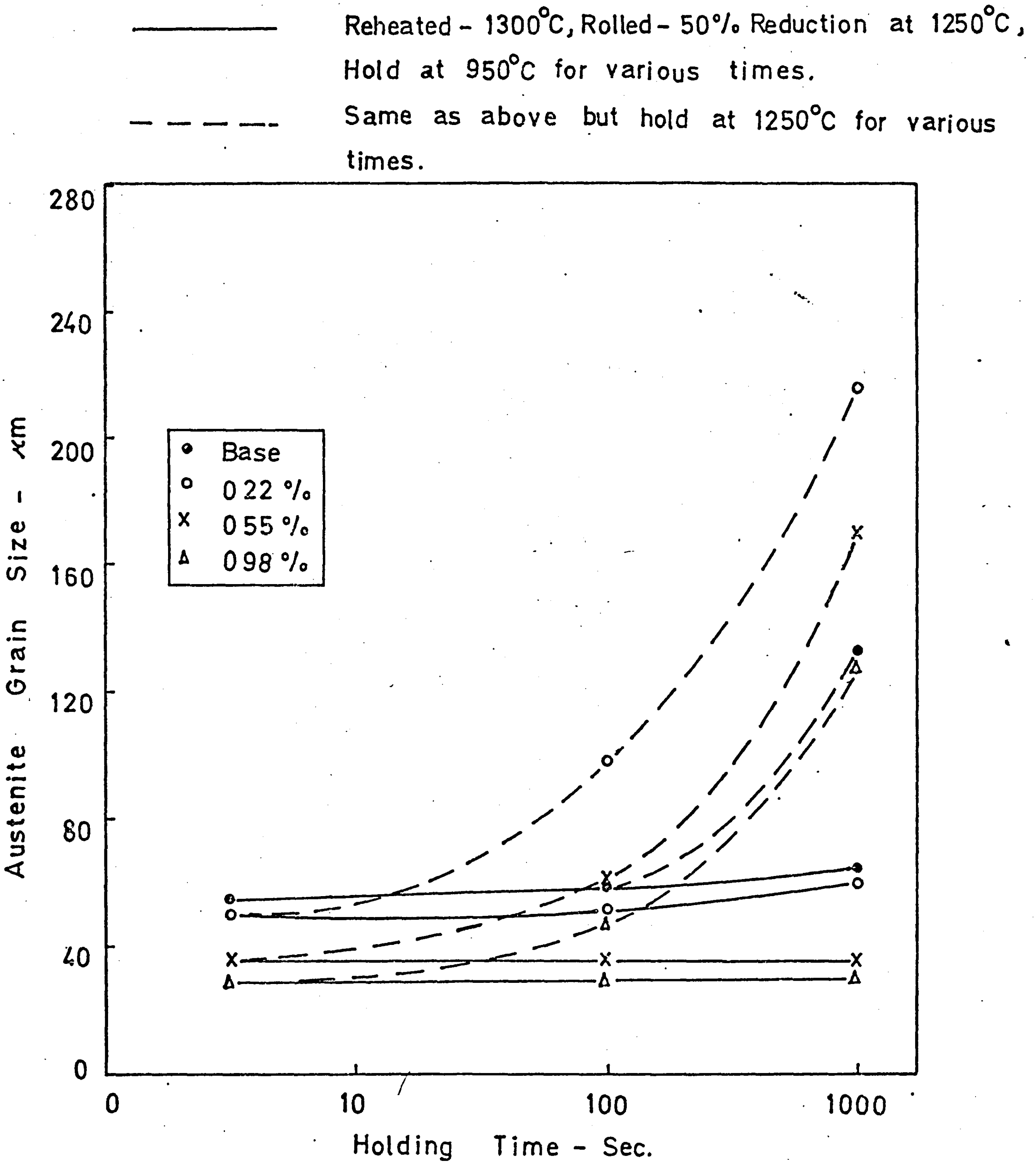


FIG.58. EFFECT OF HOLDING TIME ON RECRYSTALLIZED AUSTENITE GRAIN SIZE IN VANADIUM STEELS

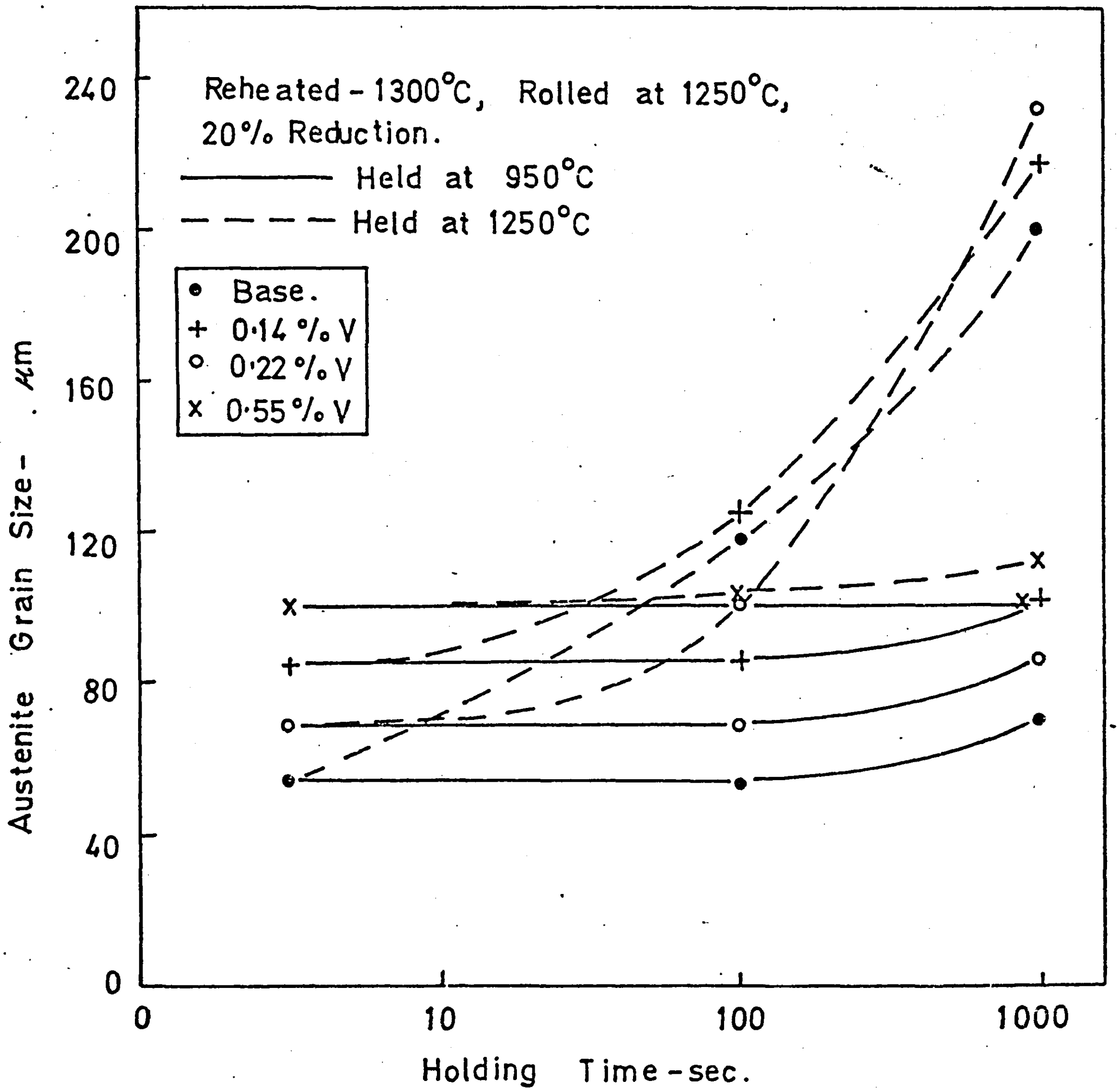
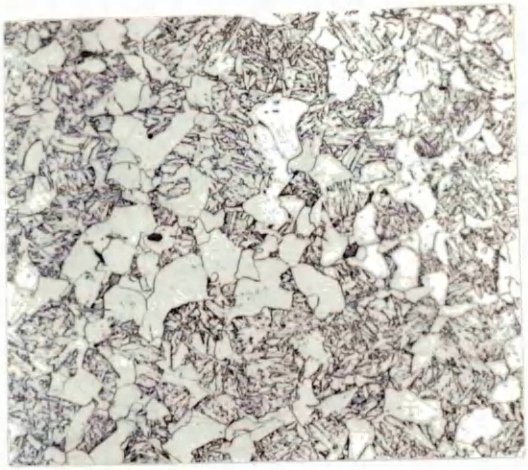


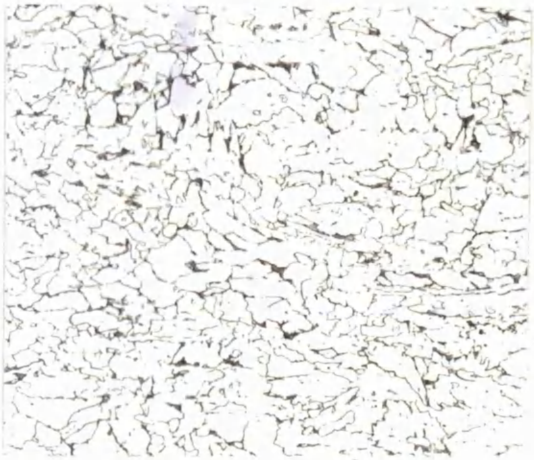
FIG. 59. EFFECT OF HOLDING TIME ON RECRYSTALLIZED AUSTENITE GRAIN SIZE IN VANADIUM STEELS.



0.16% Nb X240

(a) Reheated - 1300°C,
Rolled - 1250°C,
50% reduction,
Held 100s at 750°C and
sand cooled.

Nucleation of ferrite at prior austenite grain boundaries.



0.16% Nb X240

(b) Reheated - 1300°C,
Rolled - 950°C,
50% reduction,
Held 100s at 950°C and
sand cooled.

Large amount of ferrite due to niobium in solution reduced by rolling and holding at 950°C.

0.11% Nb X240

(c) Reheated - 1300°C,
Rolled - 950°C,
50% reduction,
Held 100s at 750°C and
sand cooled.

Less ferrite due to more niobium in solution because of less Nb(C,N) precipitation on holding at 750°C.

FIGURE. 60 TYPICAL SAND COOLED STRUCTURES IN NIOBIUM STEELS.

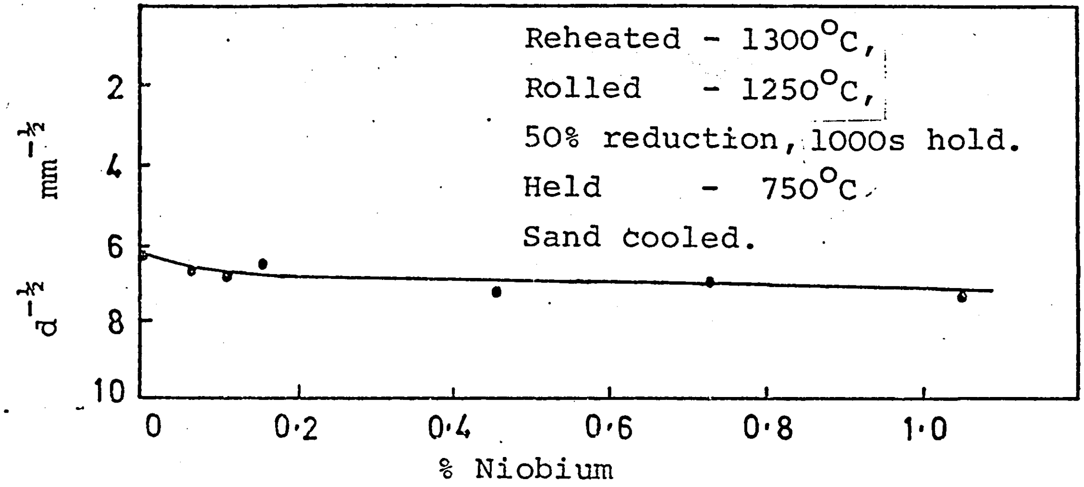


FIG. 61 EFFECT OF NIOBIUM OF FERRITE GRAIN SIZE.

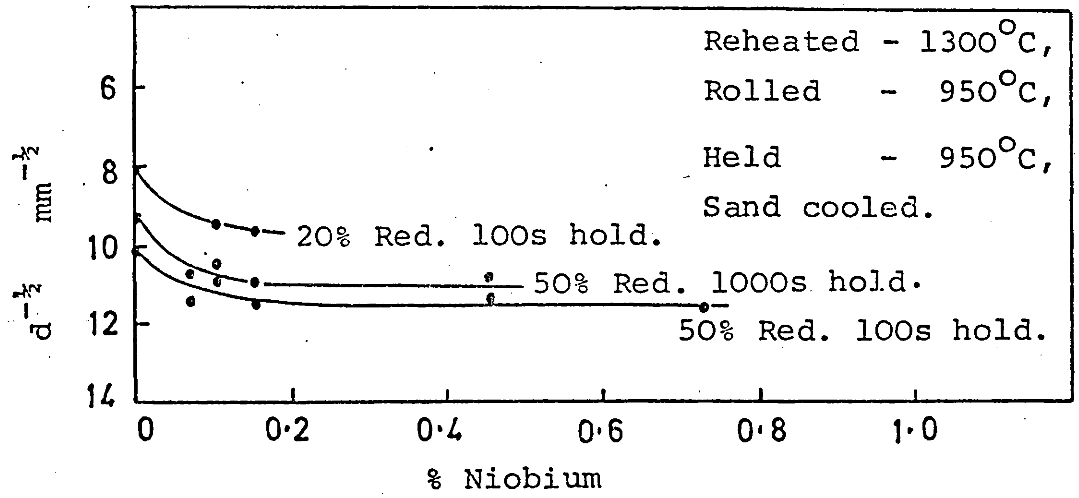


FIG. 62 EFFECT OF NIOBIUM ON FERRITE GRAIN SIZE.

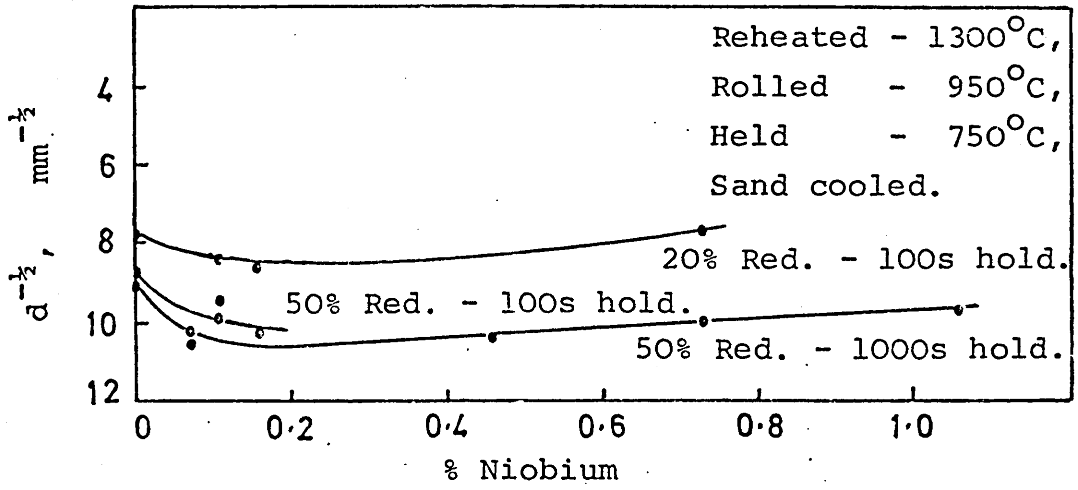
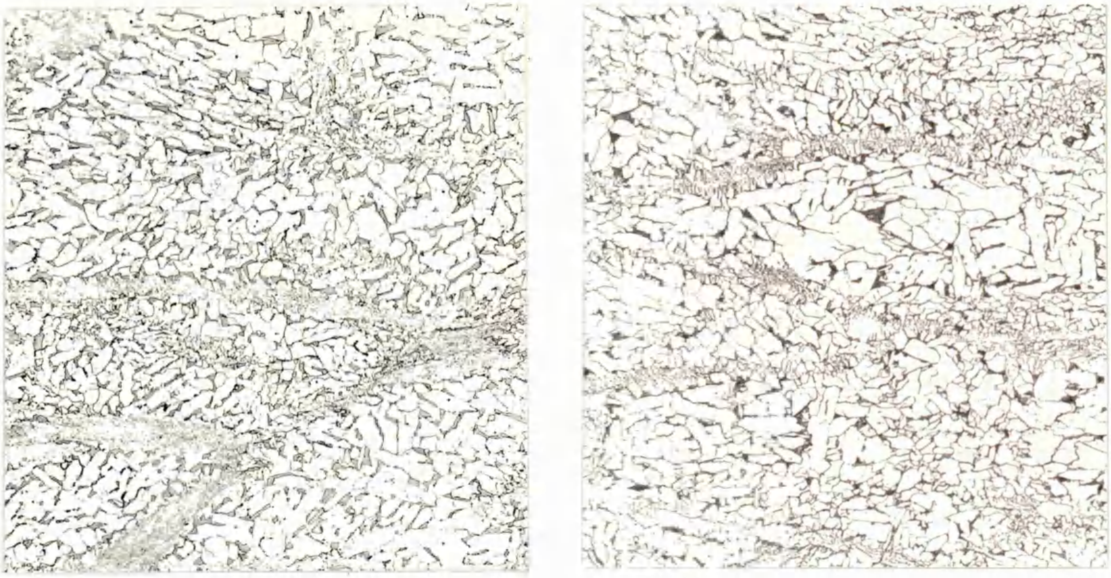


FIG. 63 EFFECT OF NIOBIUM ON FERRITE GRAIN SIZE



(a) 0.0% Nb X160

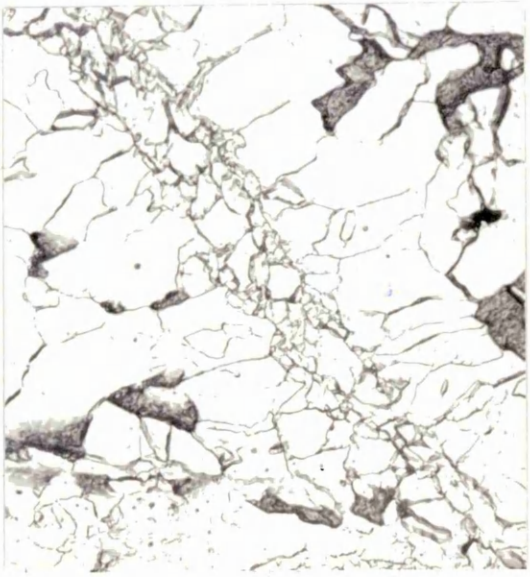
Reheated - 1300°C,
Rolled - 750°C,
50% reduction, Quenched.

Ferrite at austenite grain boundaries deformed during rolling.

(b) 0.0% Nb X160

Reheated - 1300°C,
Rolled - 750°C,
50% reduction, Held 100s at 750°C and sand cooled.

Recrystallization of deformed ferrite.



0.16% Nb X1000

(c) Reheated - 1300°C,
Rolled - 750°C,
50% reduction, Held 100s at 750°C and quenched.

Multiple ferrite nucleation at deformed austenite grain boundaries.

FIGURE. 64 EXAMPLES OF FORMATION OF VERY FINE FERRITE GRAINS.

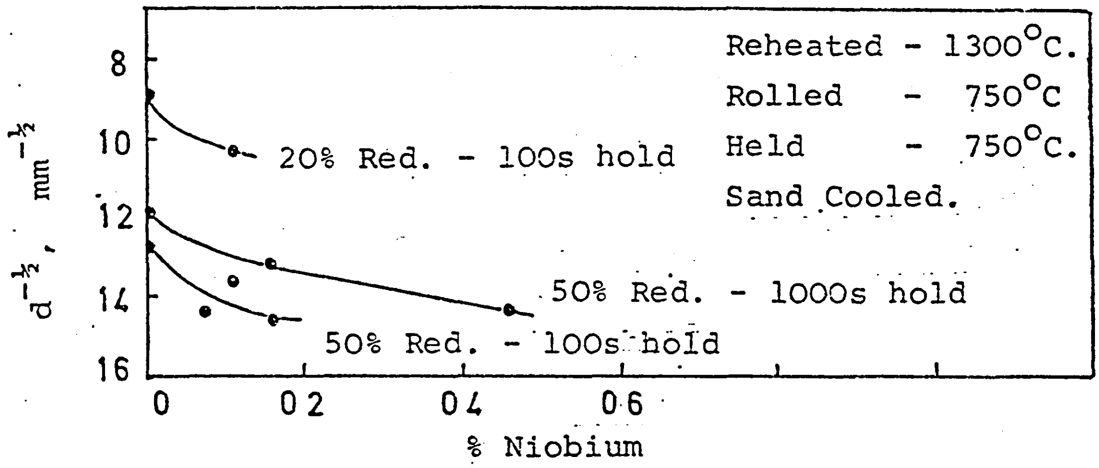


FIG. 65 EFFECT OF NIOBIUM ON FERRITE GRAIN SIZE

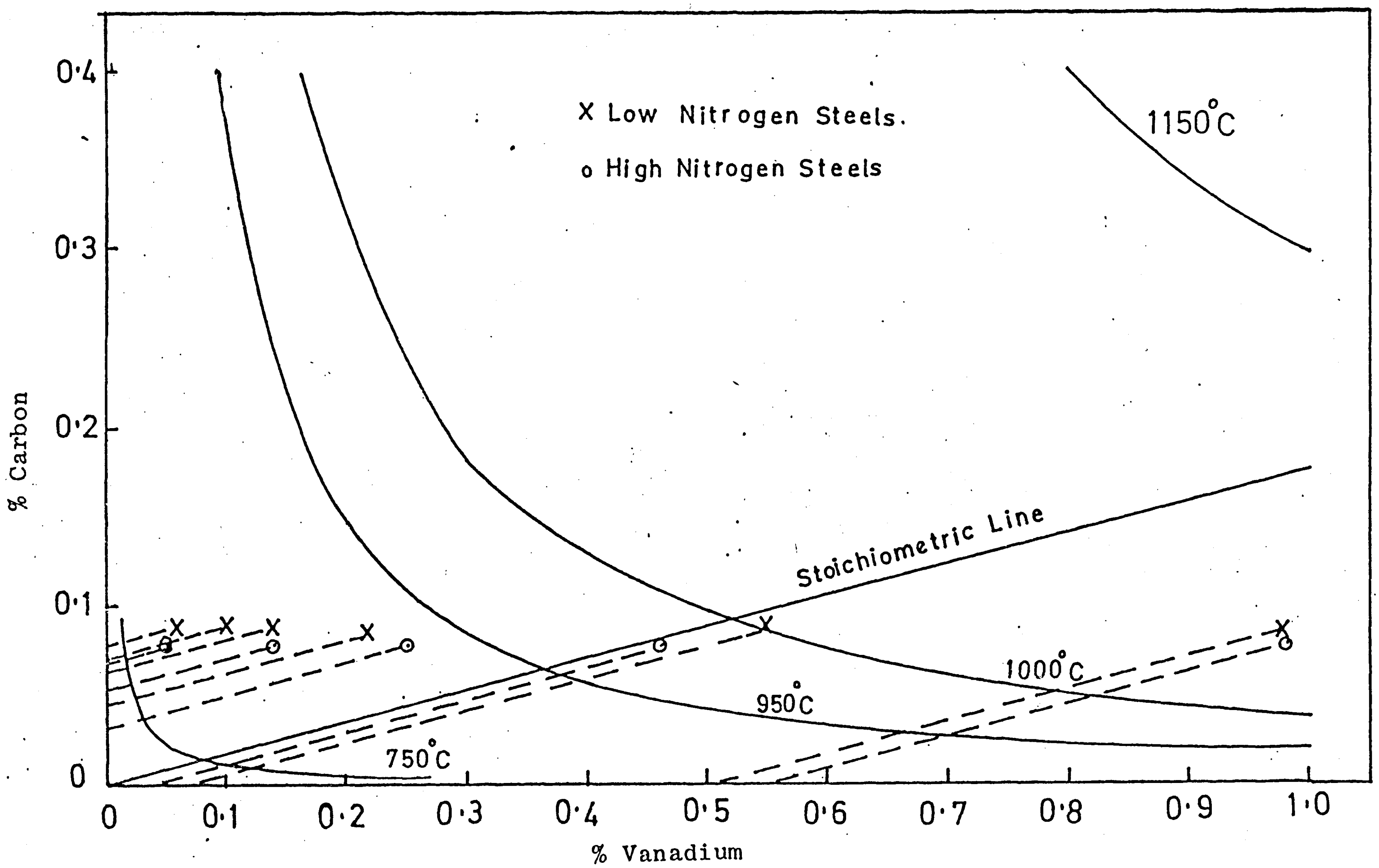


FIG. 66 SOLUBILITY OF V_4C_3 IN AUSTENITE

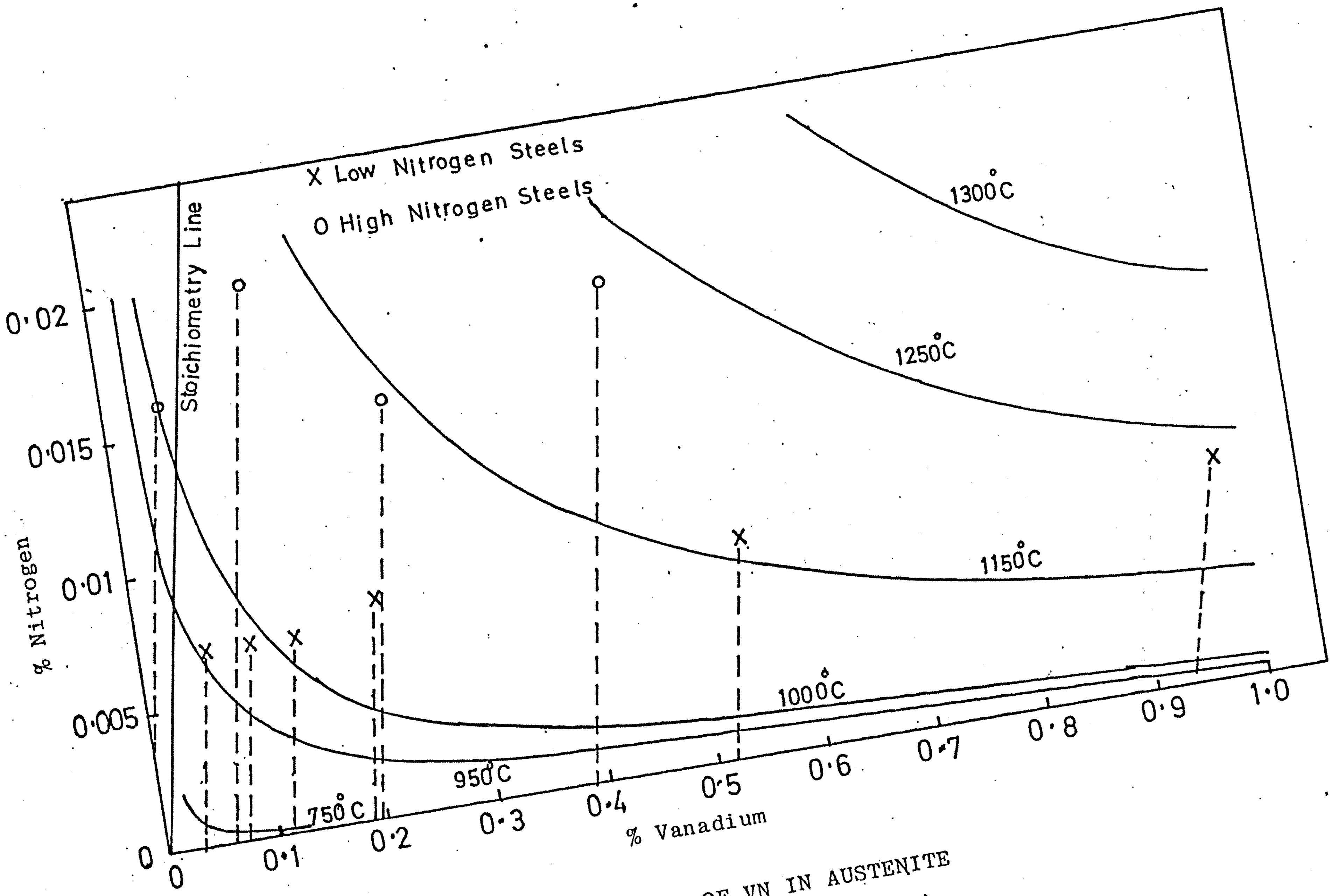


FIG. 67 SOLUBILITY OF VN IN AUSTENITE

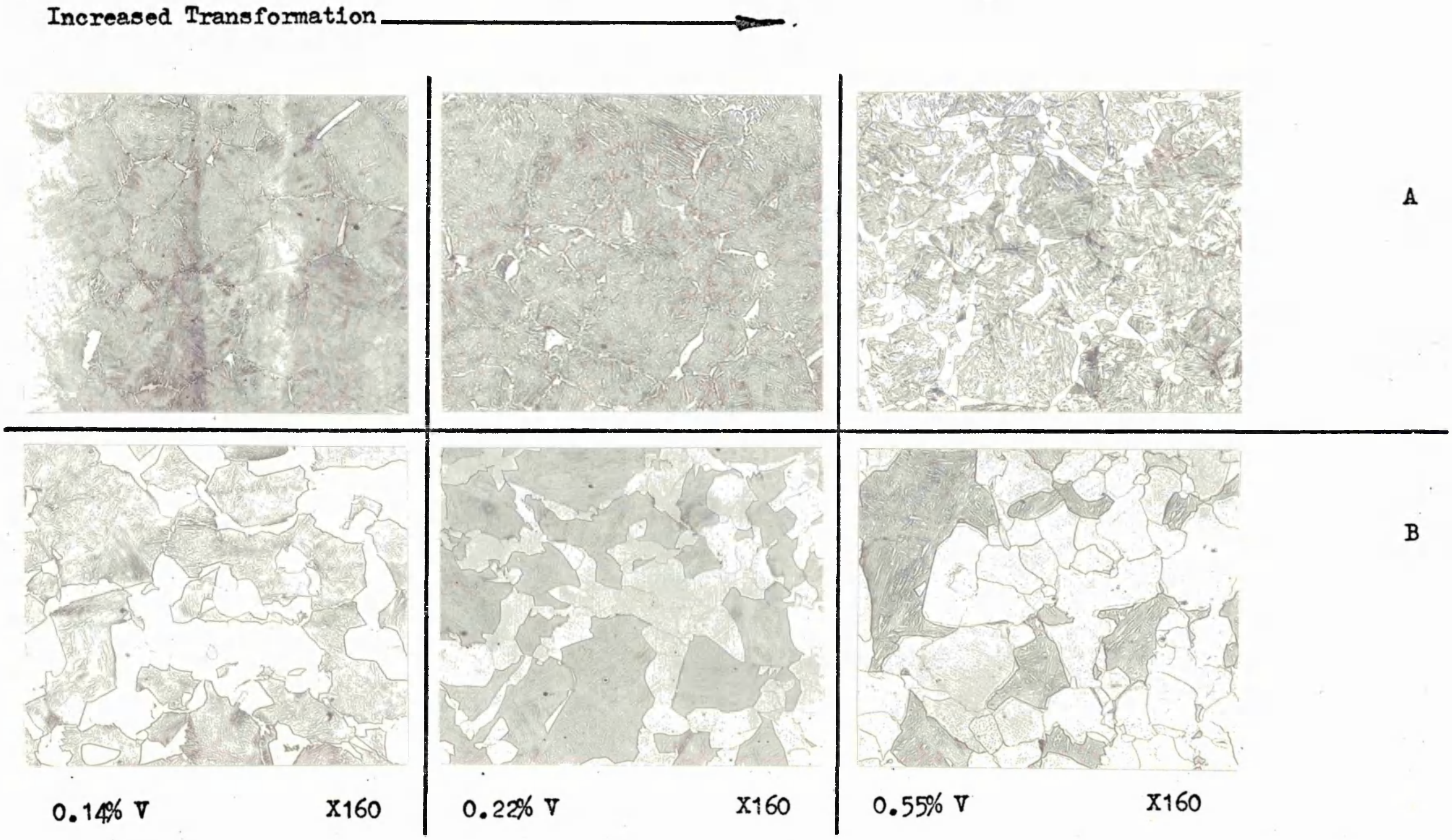
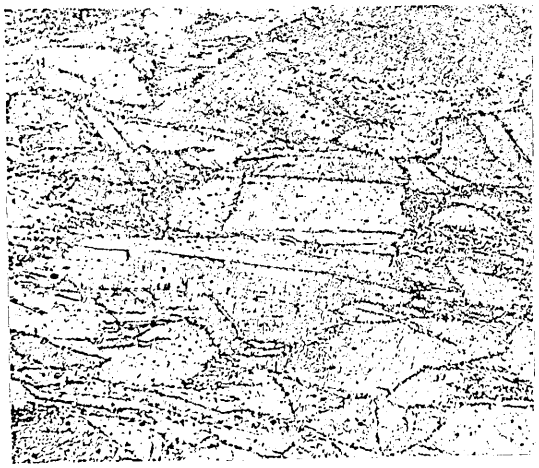


FIGURE. 68 EFFECT OF VANADIUM CONTENTS ON THE TRANSFORMATION OF AUSTENITE TO FERRITE:

(A) Reheated- 1300°C, Rolled - 1250°C by 50%, Held 100s at 750°C and quenched.

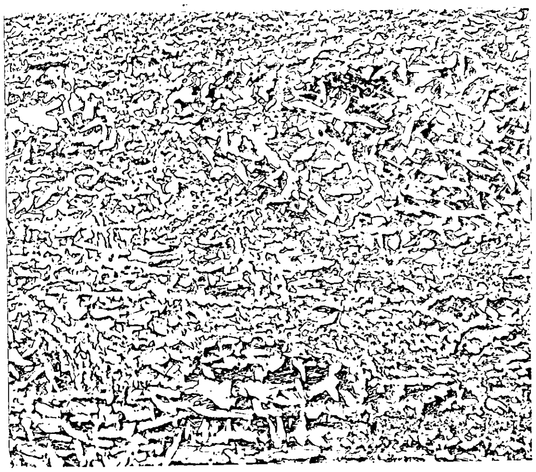
(B) Same as (A) but held at 750°C for 1000s and quenched.



X40

(a) 0.14% Vanadium,
Reheated - 1300°C,
Rolled - 950°C,
50% reduction, Quenched.

Unrecrystallized austenite.



X40

(b) 0.14% Vanadium,
Same as (a) but held at 750°C
for 100s and quenched.

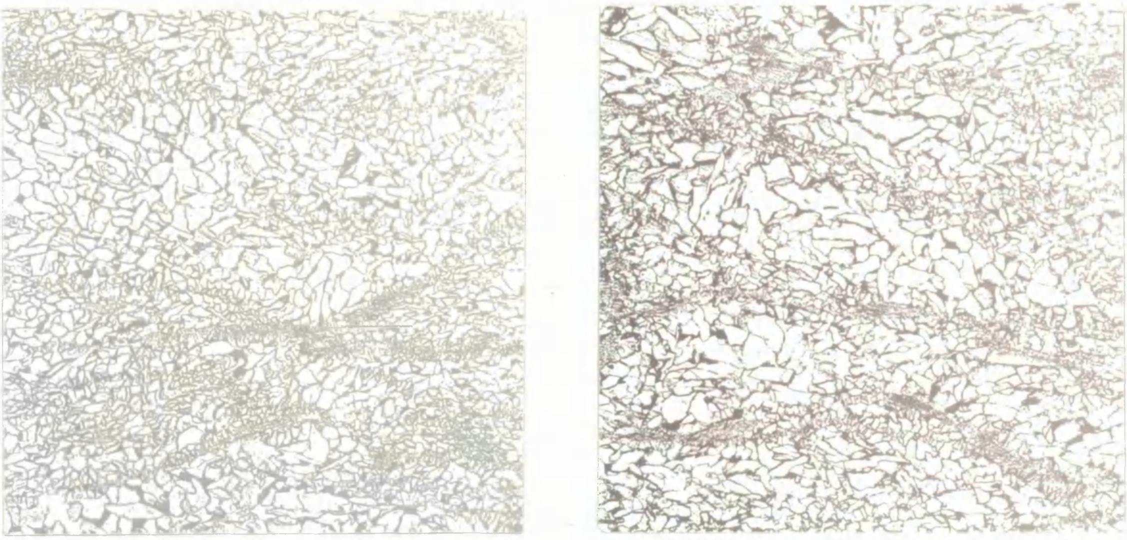
Transformation of unrecrystallized austenite.

X160

(c) 0.55% Vanadium,
Same as (a).

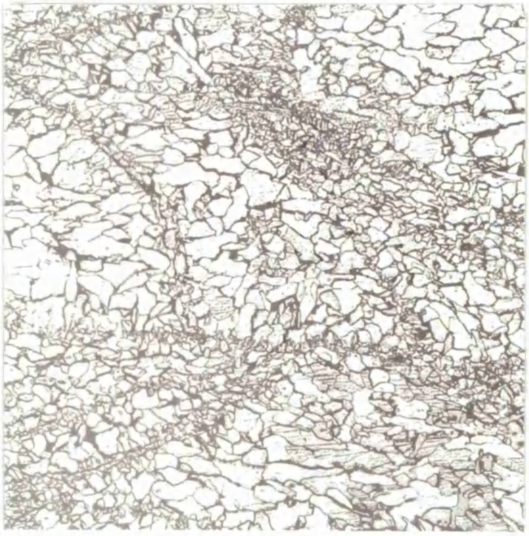
Nucleation of ferrite at deformation bands and second-phase particles.

FIGURE. 69 TRANSFORMATION OF UNRECRYSTALLIZED AUSTENITE TO FERRITE IN VANADIUM STEELS.



0.06% V X160

0.11% V X160



0.22% V X160

Treatment:

Reheated - 1300°C,
Rolled - 750°C,
50% reduction,
Held 100s at 750°C and
sand cooled.

FIGURE. 70 FORMATION OF VERY FINE RECRYSTALLIZED FERRITE GRAIN SIZE AT THE AUSTENITE GRAIN BOUNDARIES IN VANADIUM STEELS.

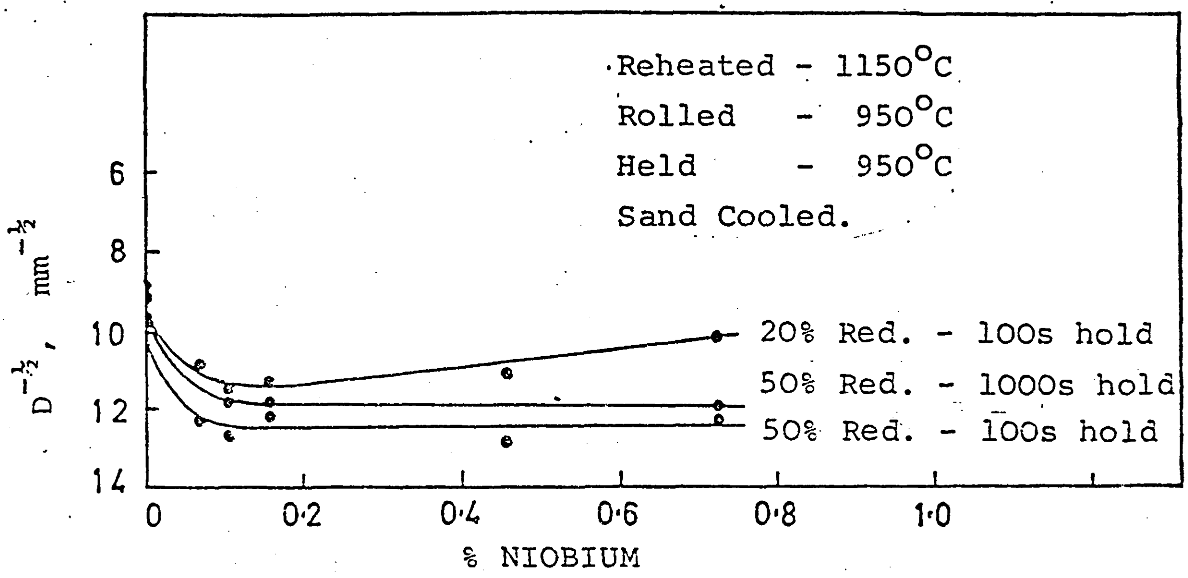


FIG. 71 EFFECT OF NIOBIUM ON FERRITE GRAIN SIZE.

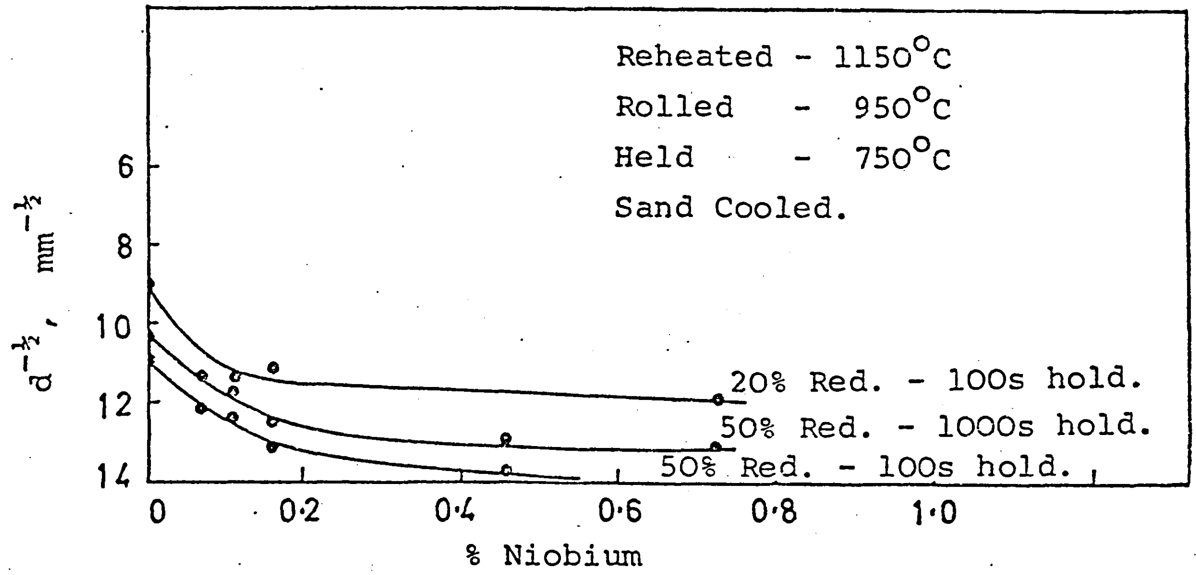
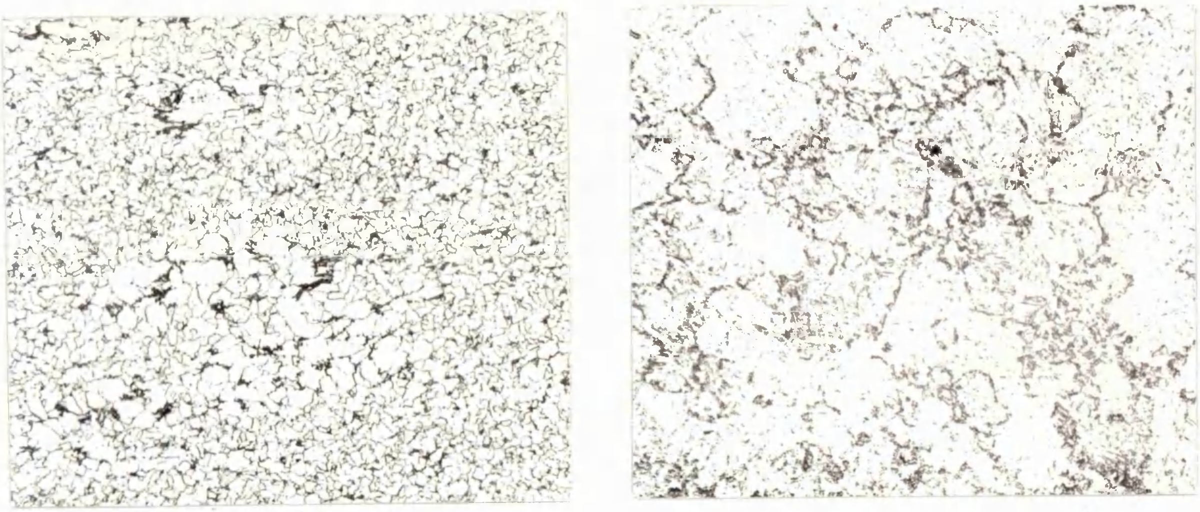


FIG. 72 EFFECT OF NIOBIUM ON FERRITE GRAIN SIZE.

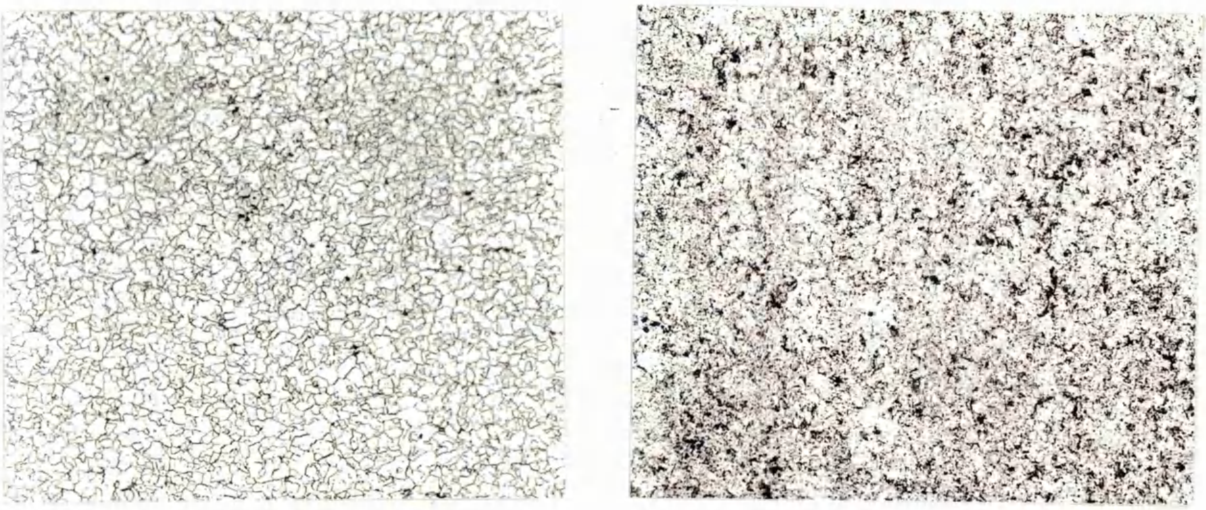


0.16% Nb X160

(a) Coarse ferrite islands resulting from coarse unrecrystallized austenite.
(Reheated-1150°C, Rolled-950°C, 50% Red., Held-750°C for 1000s, Sand cooled.)

0.46% Nb X80

(b) Variable austenite grain size obtained after reheating at 1150°C for 30 min.



0.46% Nb X160

(c) Fine uniform ferrite grain size resulting from uniform austenite grain size.

(Treatment as 'a')

0.46% Nb X80

(d) Uniform austenite grain size obtained after reheating at 1150°C for 30 min.

FIG. 73 EFFECT OF PRIOR AUSTENITE GRAIN MORPHOLOGY ON THE OCCURRENCE OF MIXED AND UNIFORM FERRITE GRAIN SIZES.

(a) 0.46 % Nb

Reheated-1150°C,
Rolled - 750°C, 50% Red.,
Held - 750°C, 100s.
Sand cooled.

Structure containing all deformed ferrite.

X240

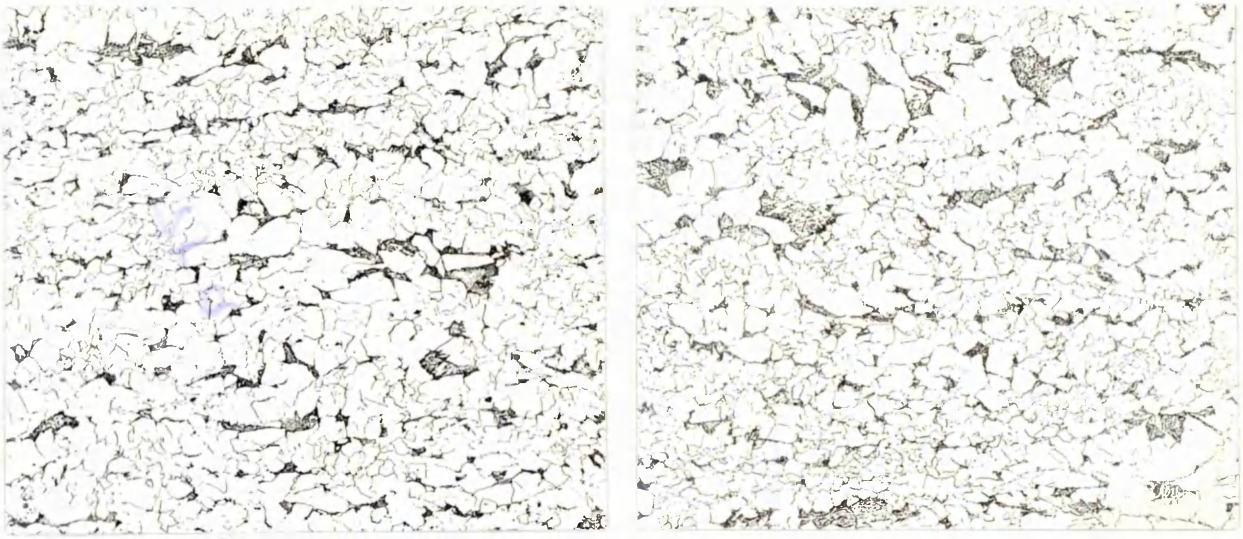
(b) 0.16 % Nb

Treatment same as (a).

Structure containing deformed proeutectoid ferrite and polygonal ferrite formed from deformed austenite.

X240

FIG. 74 STRUCTURES PRODUCED DURING ROLLING WITHIN CRITICAL TEMPERATURE RANGE.



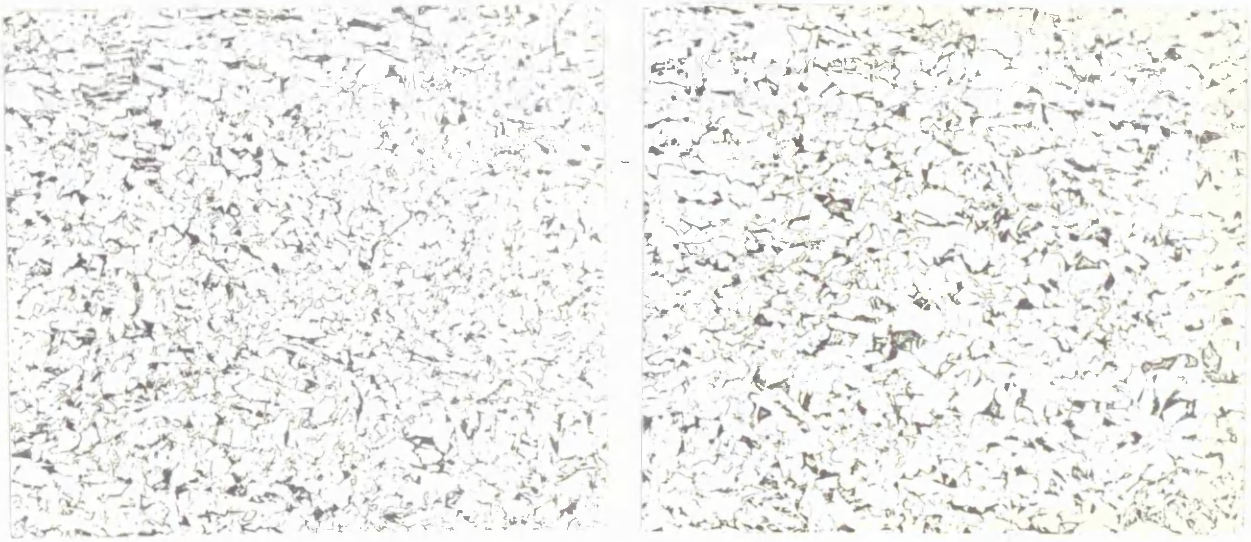
0.03 Nb + 0.12 V-N X160

(a)

0.05 Nb + 0.11 V X160

(b)

'a' and 'b' - Reheated-1150°C, Rolled- 950°C, 50% Reduction, Held- 750°C for 100s. and sand cooled.



0.03 Nb + 0.12 V-N X160

(c)

0.05 Nb + 0.11 V X160

(d)

'c' and 'd' - Reheated-1150°C, Rolled- 950°C, 50% Reduction, Held- 950°C for 100s and sand cooled.

FIG. 75 THE EFFECT OF TRANSFORMATION CONDITIONS ON THE OCCURRENCE OF MIXED AND UNIFORM FERRITE GRAIN SIZE.

X160

(a) 0.14 % V

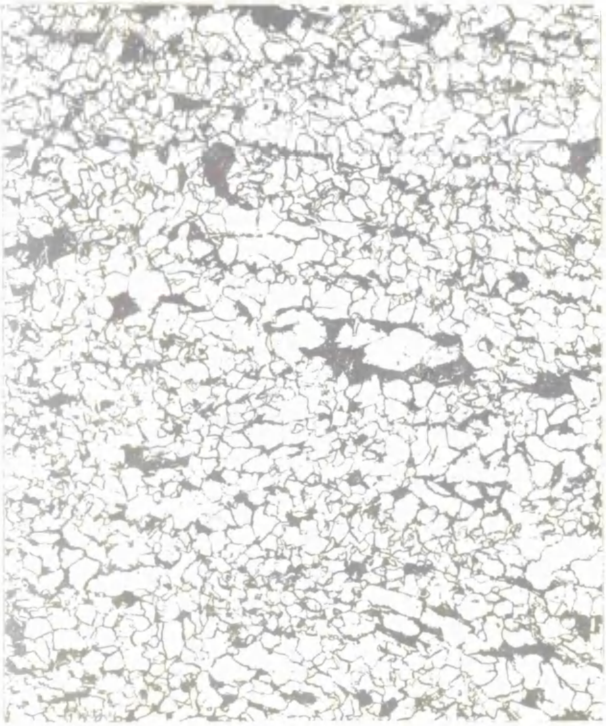
Reheated-1150°C,

Rolled - 950°C, 50% Red.,

Held - 750°C, 100s.

Sand cooled.

Less mixed ferrite grain size.



X160

(b) 0.14 % V

Treatment same as 'a' but

held for 1000s at 750°C.

Increased mixed ferrite grain size due to increased isothermal transformation of mixed austenite grain morphology.

FIG. 76 EFFECT OF TRANSFORMATION CONDITIONS ON THE OCCURRENCE OF MIXED FERRITE GRAIN SIZE.

X160

(a) 0.55 % V

Reheated-1150°C,

Rolled - 950°C, 50% Red.,

Held - 750°C, 100s.

Sand cooled.

X160

(b) 0.98 % V

Treatment as 'a'.

FIG. 77 PRESENCE OF DELTA FERRITE IN HIGH VANADIUM STEELS.

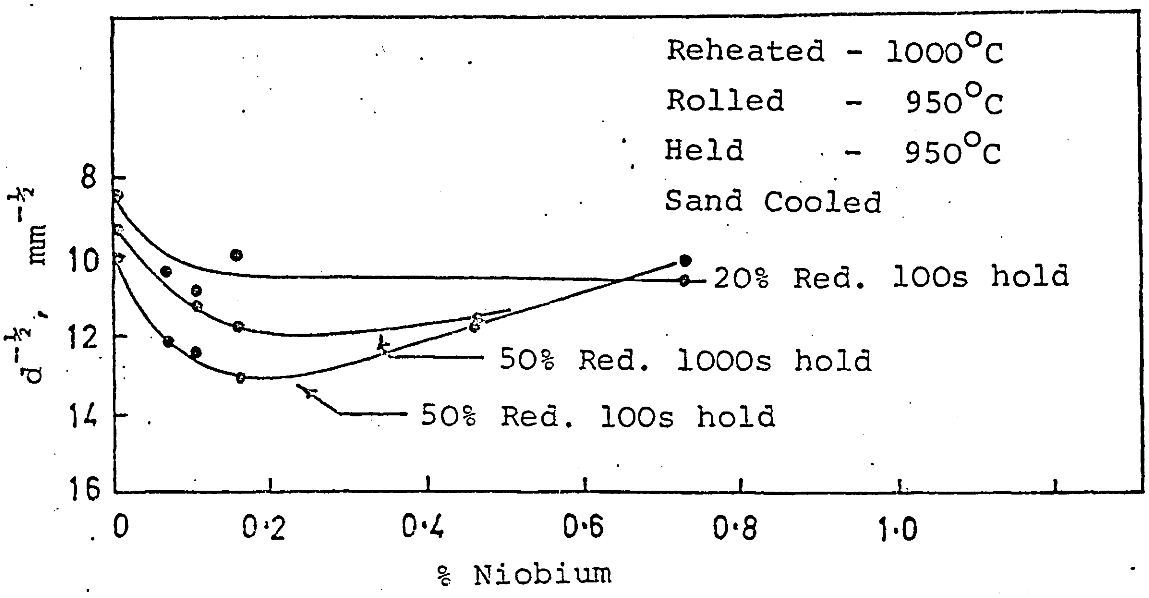


FIG. 78 EFFECT OF NIOBIUM ON FERRITE GRAIN SIZE.

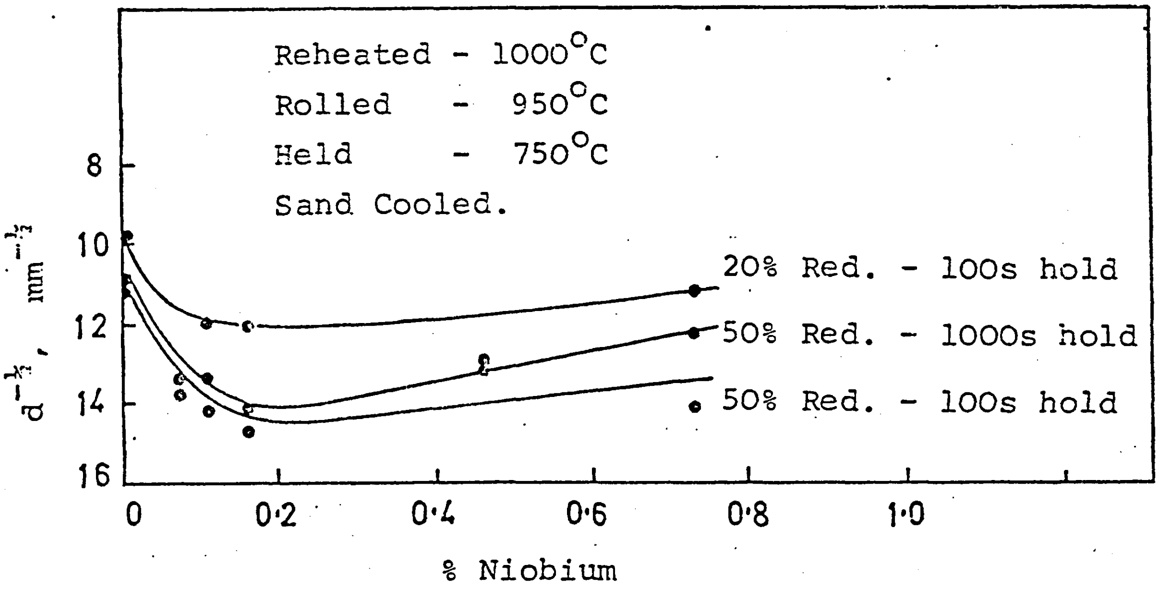
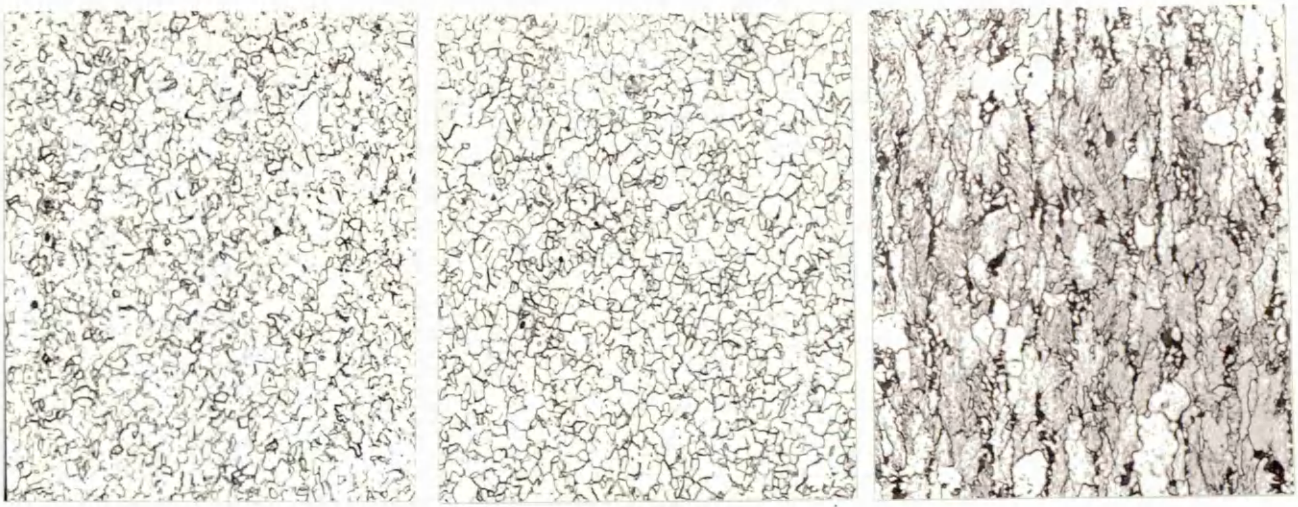


FIG. 79 EFFECT OF NIOBIUM ON FERRITE GRAIN SIZE.



(a) 0.73 % Nb X160

Reheated-1000°C,
Rolled - 950°C,50% Red.
Held - 750°C,100s.
Sand Cooled.

Fine uniform ferrite formed during holding within critical range.

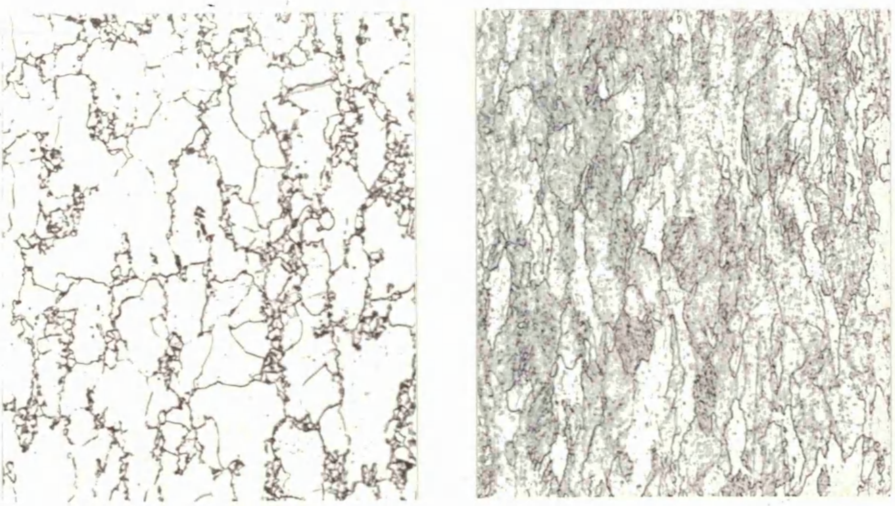
(b) 1.03 % Nb X160

Treatment as 'a'

(c) 0.0 % Nb X160

Reheated-1000°C,
Rolled - 750°C,50% Re
Held - 750°C,
Sand Cooled.

Deformed ferrite and residual austenite transformed to fine grained ferrite and pearlite.



(d) 0.0 % Nb X160

Reheated-1000°C,
Rolled - 750°C,50% Red.
Held - 750°C,1000s.
Sand Cooled.

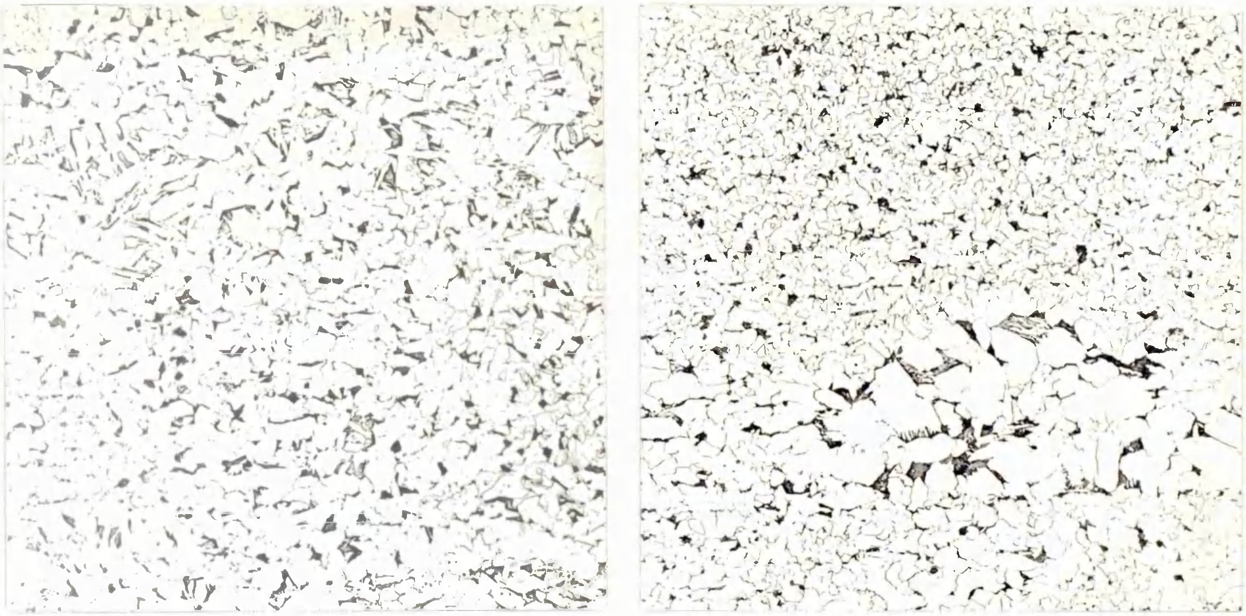
Recrystallized ferrite and fine ferrite-pearlite from residual austenite.

(e) 0.73 % Nb X160

Treatment as 'c'.

Elongated structure due to Nb retarding recrystallization and inhibiting ferrite formation.

FIG. 80 STRUCTURES PRODUCED DURING ROLLING WITHIN CRITICAL TEMPERATURE RANGE.



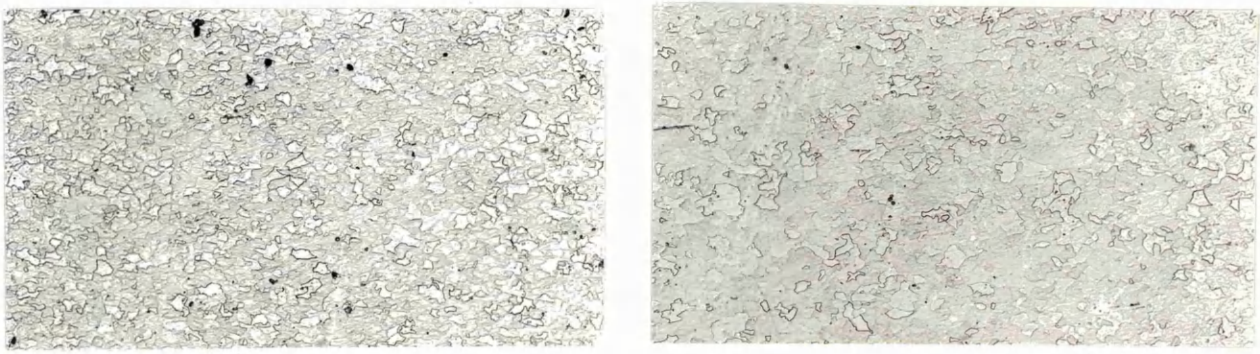
0.03 Nb +0.12 V-N X160 0.03 Nb + 0.12 V-N X160

(a) Uniform ferrite grain size. (b)Mixed ferrite grain size.

(a) Reheated-1000°C, Rolled-950°C, 50 % Reduction, Held-950°C for 100s and sand cooled.

(b) Same as 'a' but held at 750°C for 100s.

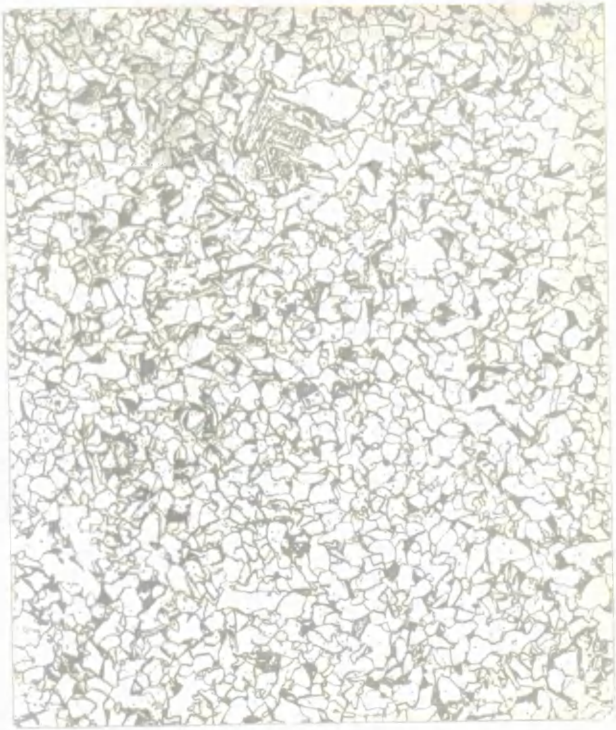
FIG. 81 EFFECT OF TRANSFORMATION CONDITION ON THE MORPHOLOGY OF FERRITE.



0.55 % V X160 0.98 % V X160

Reheated- 1000°C, Rolled- 950°, 50 % Reduction, Held- 750°C for 100s and sand cooled.

FIG. 82 PRESENCE OF δ FERRITE IN HIGH VANADIUM STEELS.



X160

(a) 0.14 % V
Reheated-1000°C,
Rolled - 950°C, 50% Red.,
Held - 950°C, 1000s.
Sand Cooled.

Uniform ferrite grain size.

X160

(b) 0.14 % V
Same as 'a' but held at 750°C
for 1000s.

Mixed ferrite grain size.

FIG. 83 THE EFFECT OF TRANSFORMATION CONDITION ON THE MORPHOLOGY OF FERRITE GRAIN SIZE.

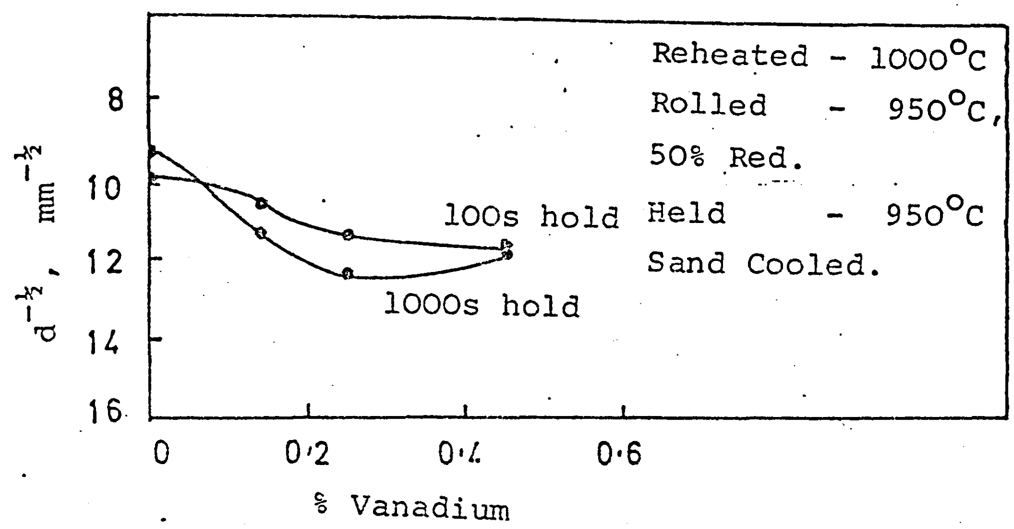


FIG. 84 EFFECT OF VANADIUM IN HIGH-NITROGEN STEEL ON THE FERRITE GRAIN SIZE.

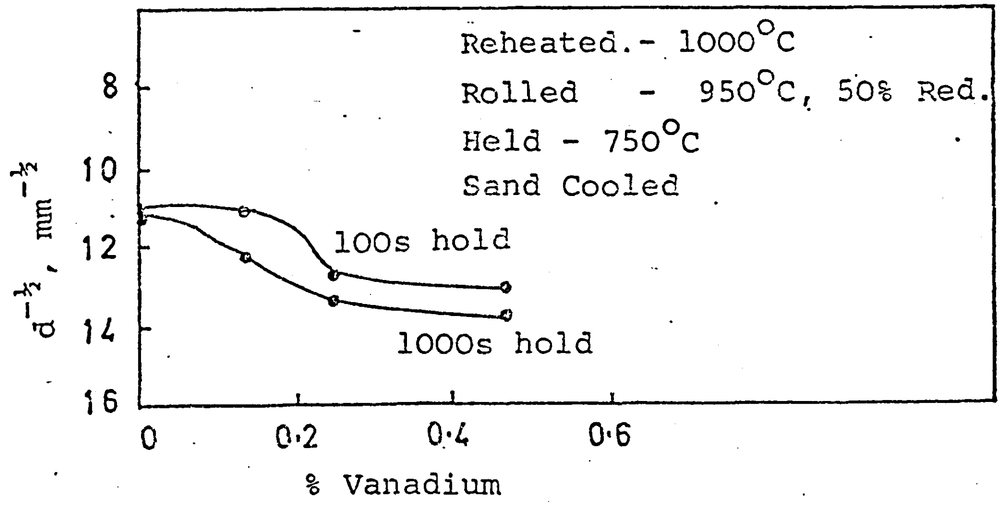


FIG. 85 EFFECT OF VANADIUM IN HIGH-NITROGEN STEEL ON THE FERRITE GRAIN SIZE.

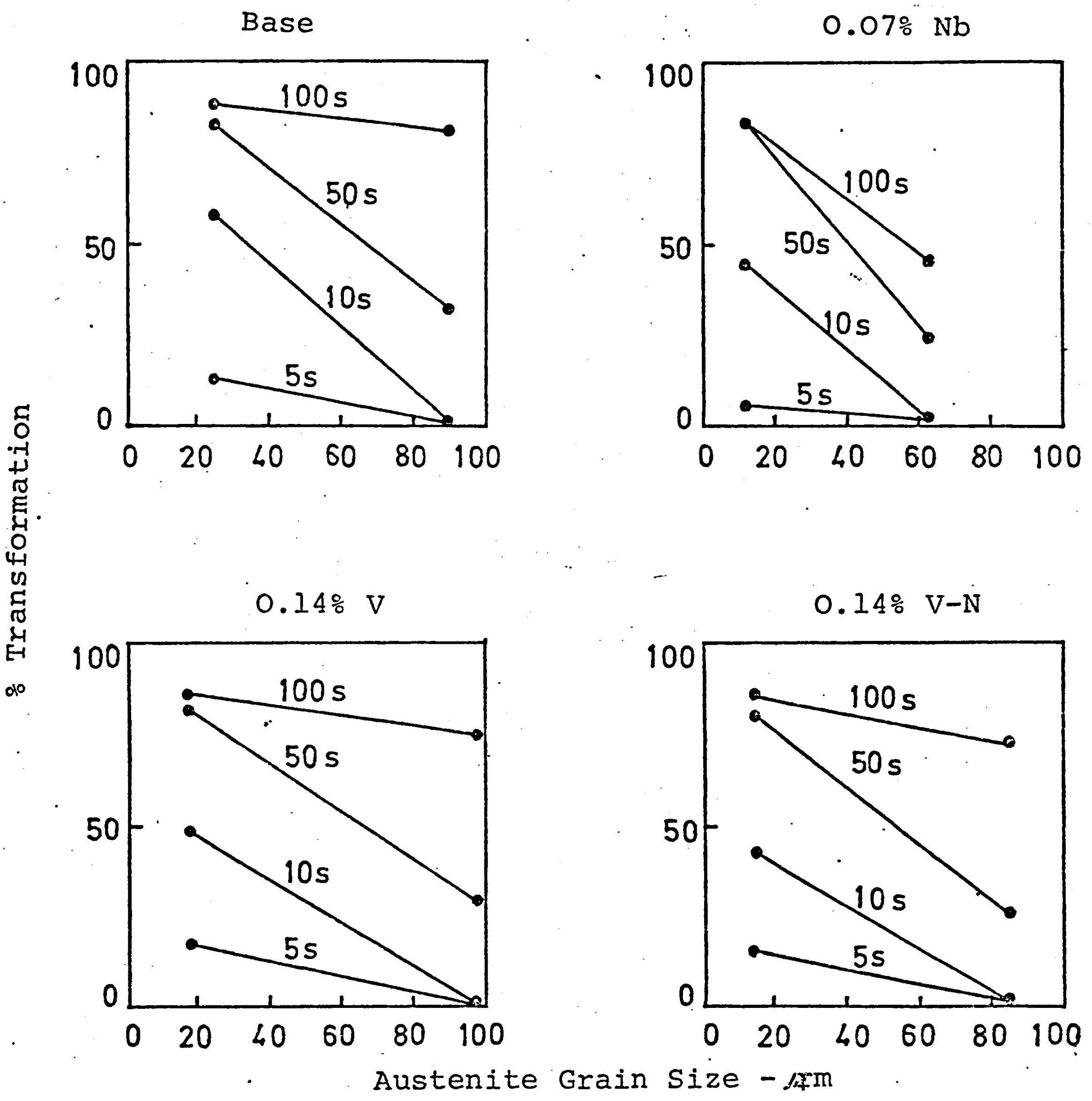


FIG. 86 EFFECT OF AUSTENITE GRAIN SIZE ON THE TRANSFORMATION AT 700°C IN VARIOUS STEELS.

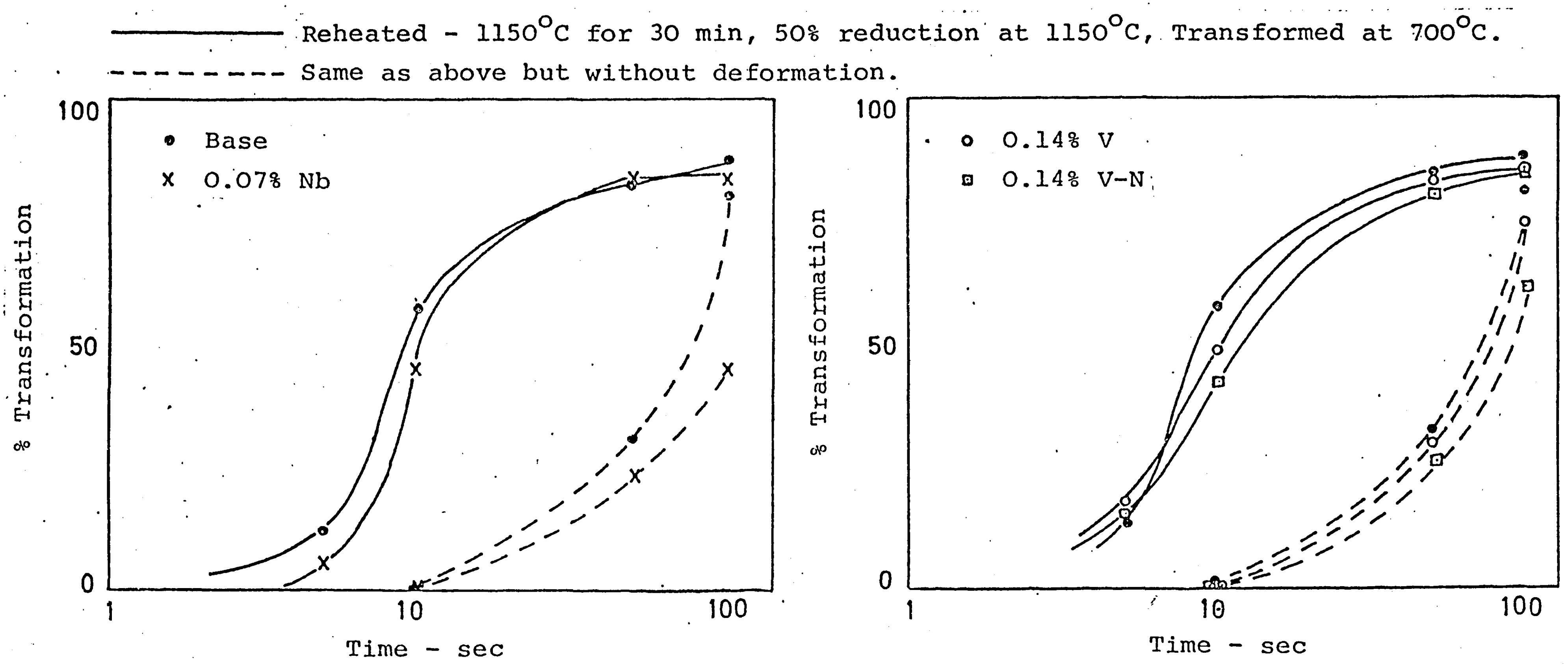


FIG. 87 EFFECT OF DEFORMATION AND MICRO- ALLOYING ELEMENTS ON THE PROGRESS OF TRANSFORMATION.

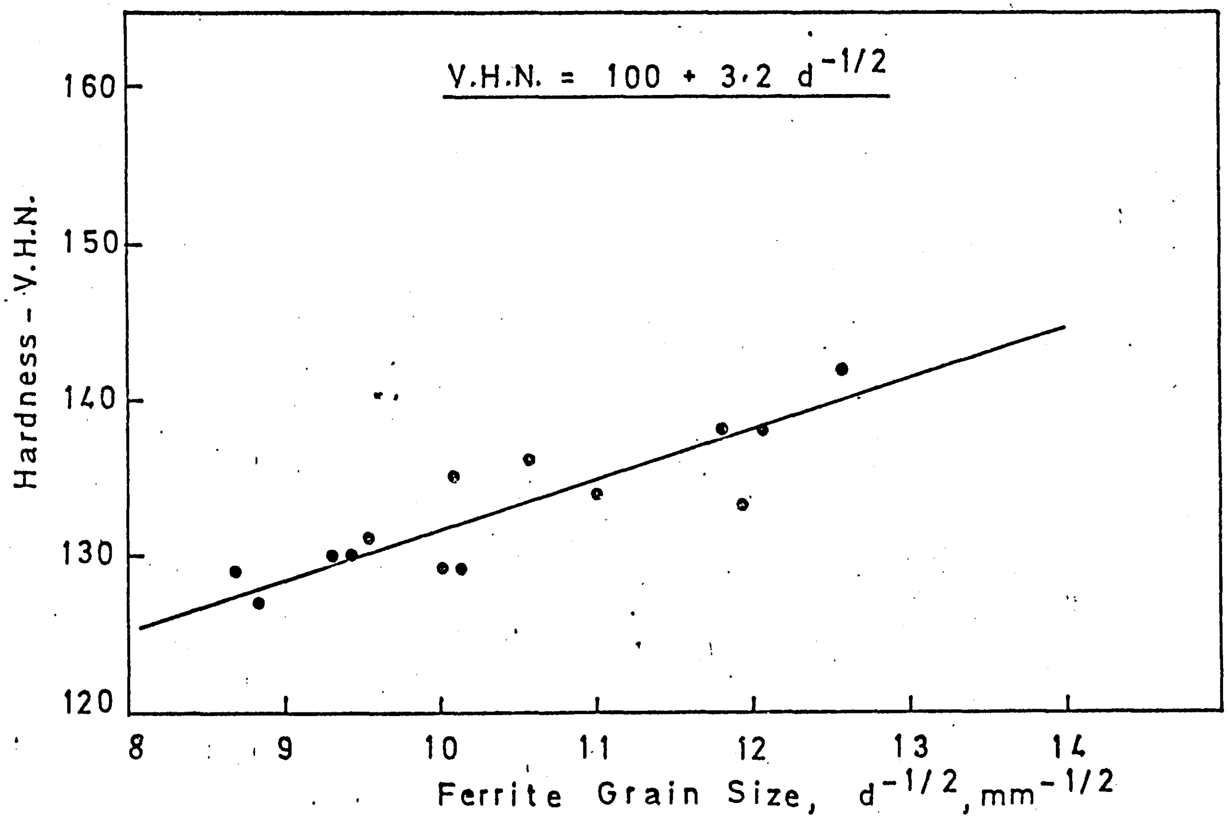


FIG. 88 EFFECT OF FERRITE GRAIN SIZE ON HARDNESS OF BASE STEEL.

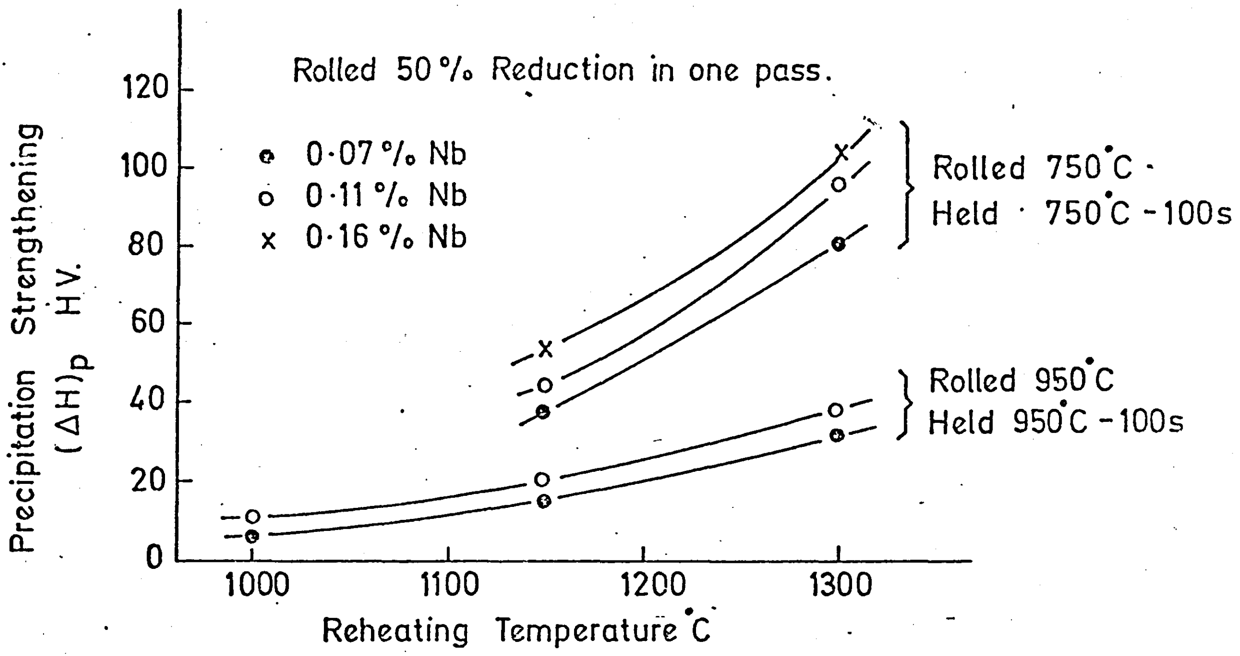
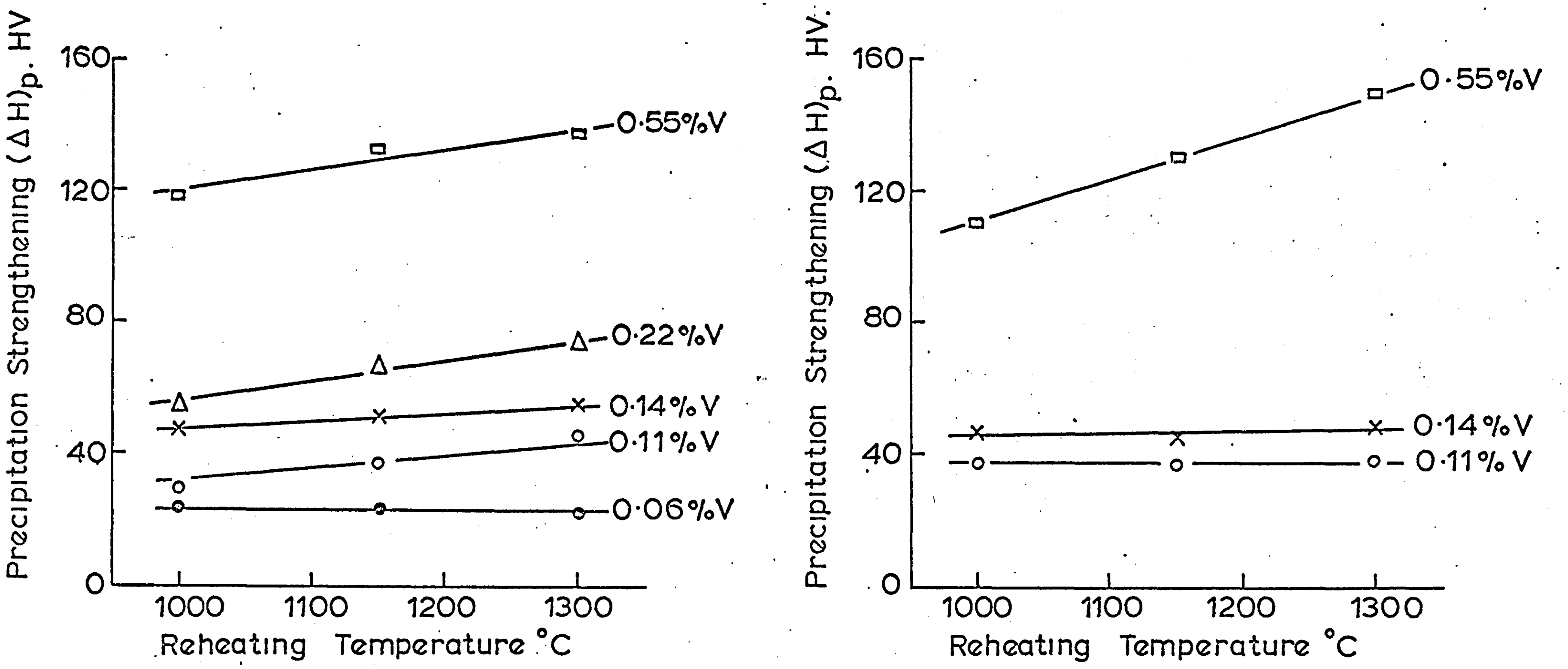


FIG. 89 EFFECT OF REHEATING TEMPERATURE ON $(\Delta H)_p$

Rolled to 50 % Reduction at 950°C.
Held at 950°C


(a) Held 100 s

(b) Held 1000s

FIG.90 THE EFFECT OF REHEATING TEMPERATURE ON PRECIPITATION STRENGTHENING IN LOW NITROGEN-VANADIUM STEELS.

Rolled to 50 % Reduction at 950°C
Held at 950°C

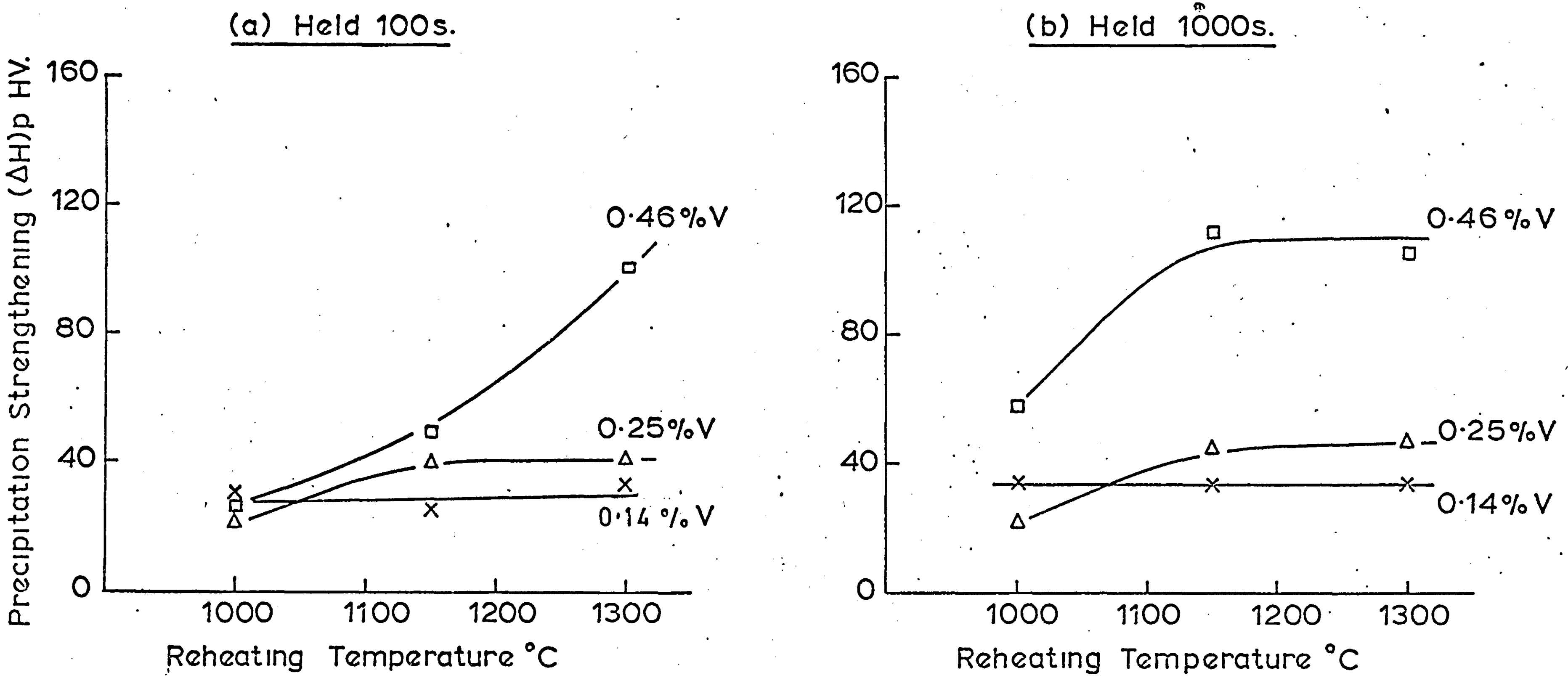


FIG. 91 THE EFFECT OF REHEATING TEMPERATURE ON PRECIPITATION STRENGTHENING IN HIGH NITROGEN-VANADIUM STEELS.

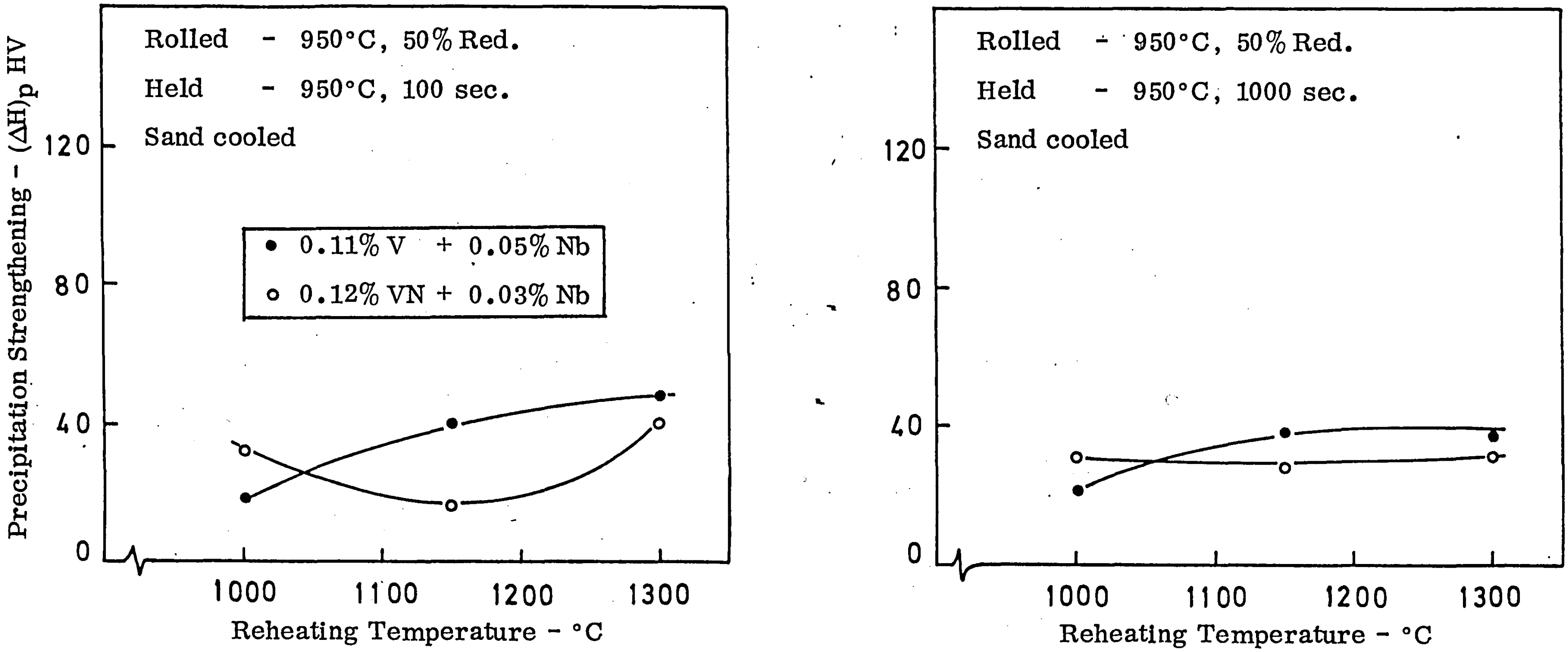


FIG. 92 EFFECT OF REHEATING TEMPERATURE ON $(\Delta H)_p$ IN Nb+V STEELS

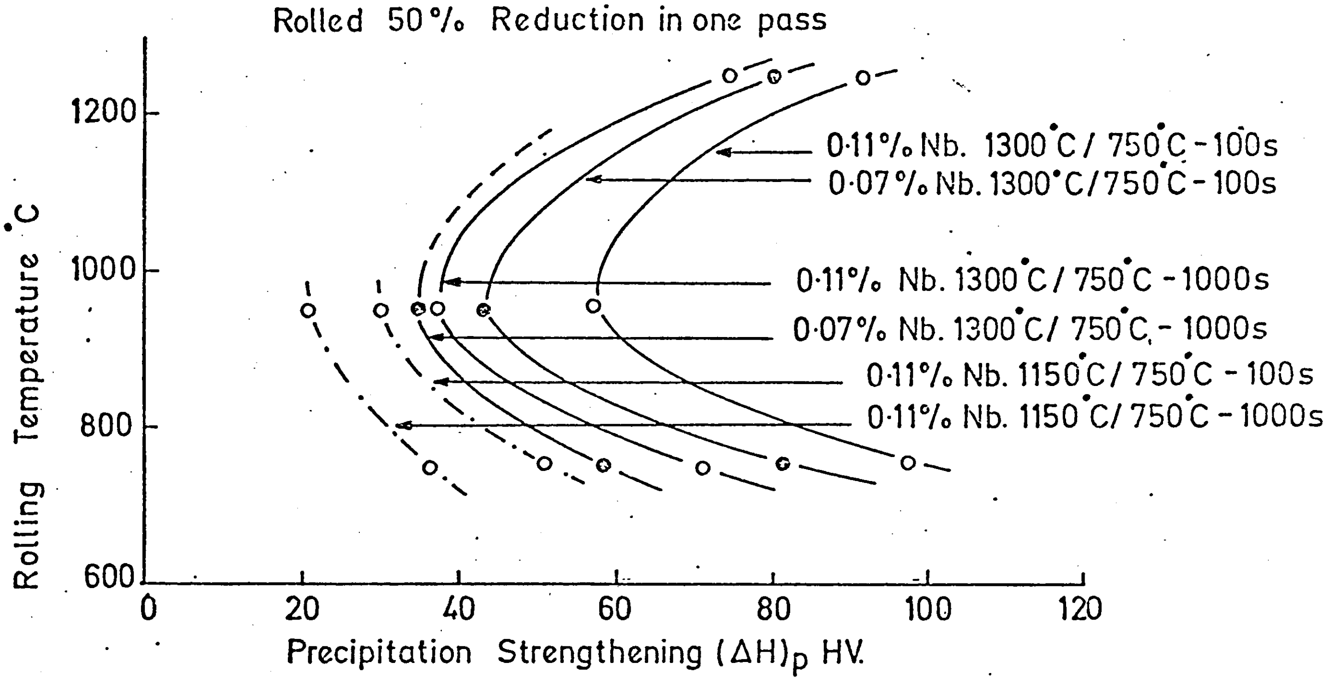


FIG. 93 EFFECT OF ROLLING TEMPERATURE ON $(\Delta H)_p$

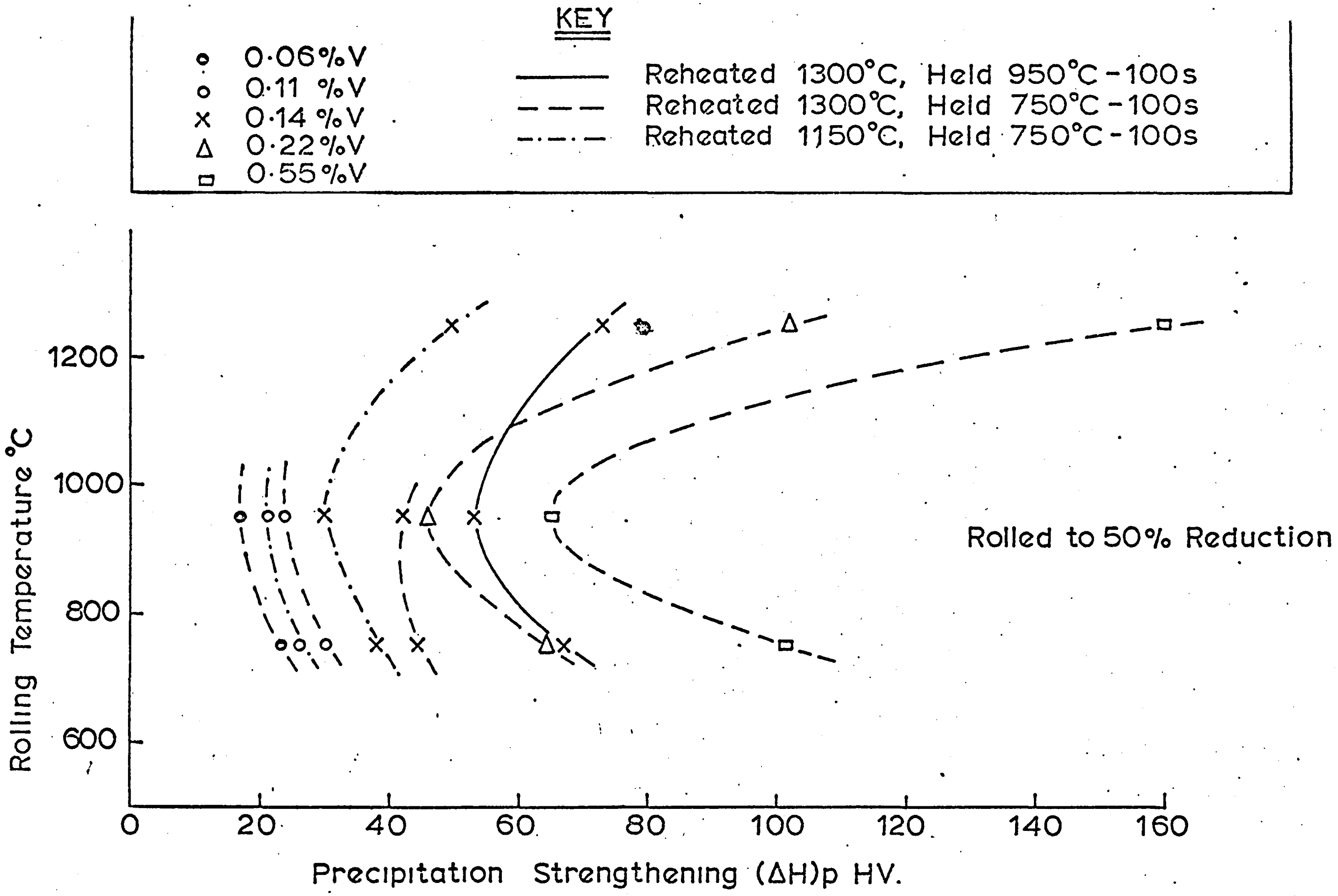


FIG. 94 THE EFFECT OF ROLLING TEMPERATURE ON PRECIPITATION STRENGTHENING IN LOW NITROGEN-VANADIUM STEELS

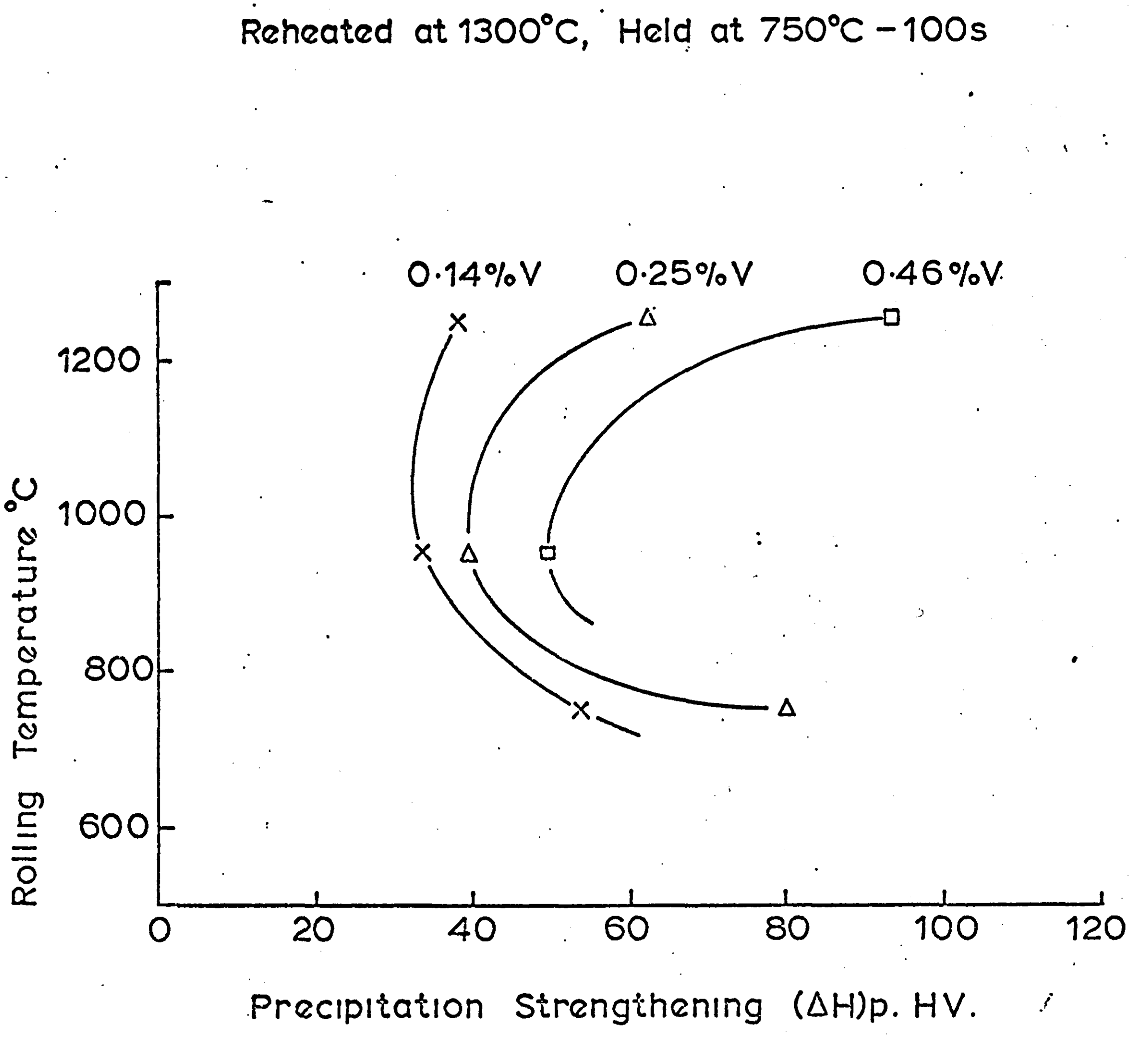


FIG. 95 THE EFFECT OF ROLLING TEMPERATURE ON PRECIPITATION STRENGTHENING IN HIGH NITROGEN-VANADIUM STEELS.

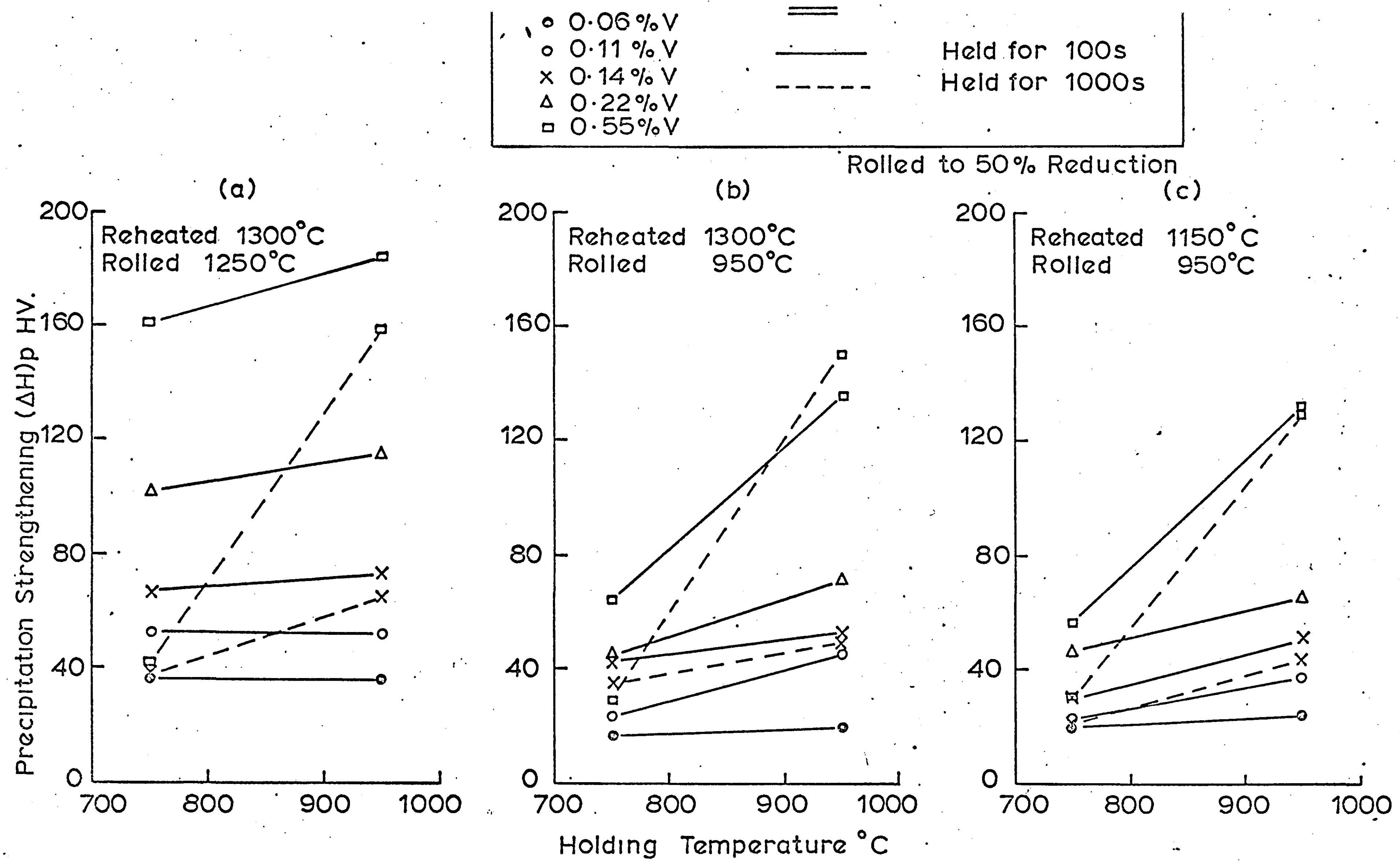


FIG. 96 THE EFFECT OF HOLDING TEMPERATURE ON PRECIPITATION STRENGTHENING IN LOW NITROGEN - VANADIUM STEELS.

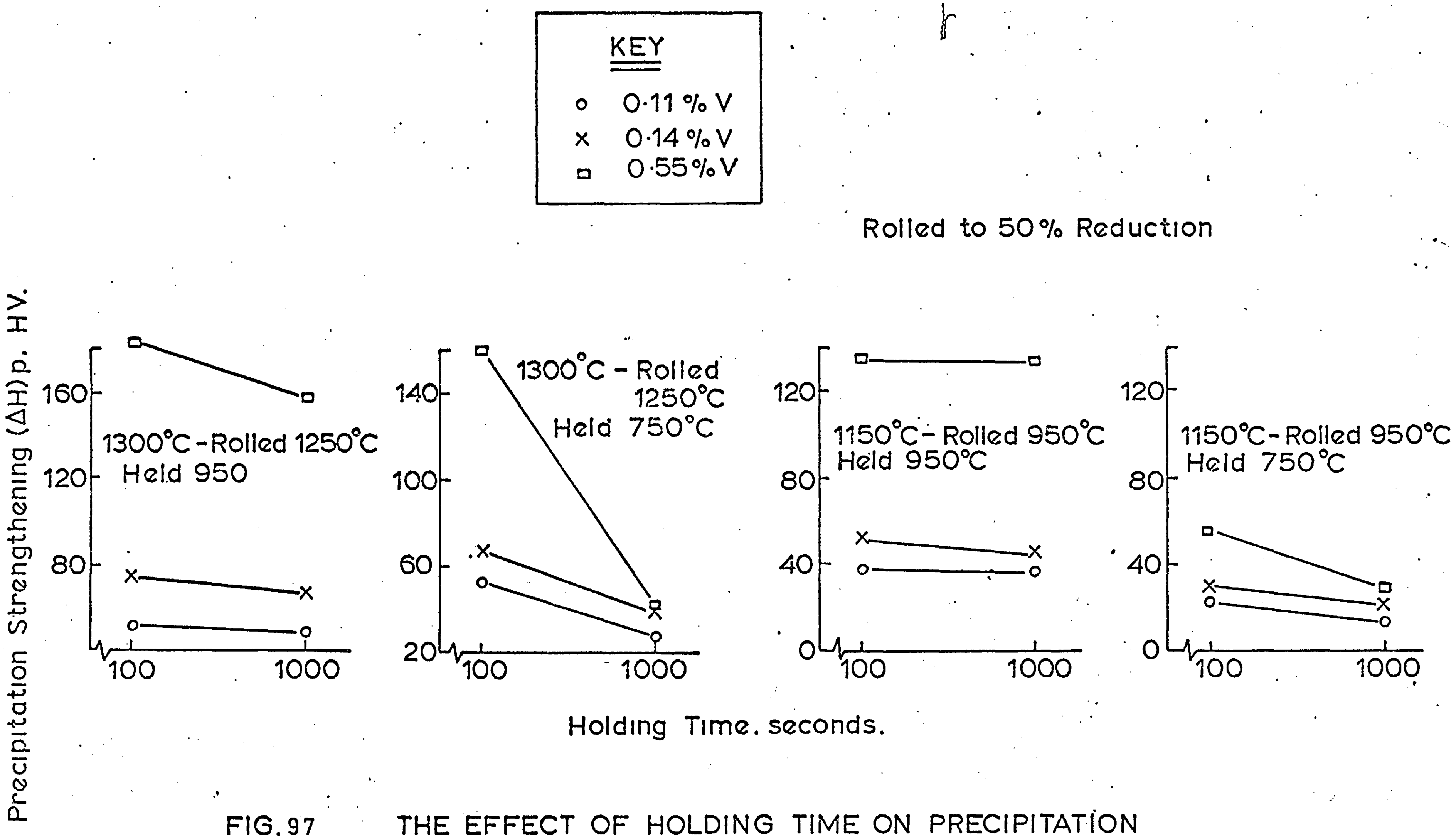


FIG. 97 THE EFFECT OF HOLDING TIME ON PRECIPITATION STRENGTHENING IN LOW NITROGEN-VANADIUM STEELS.

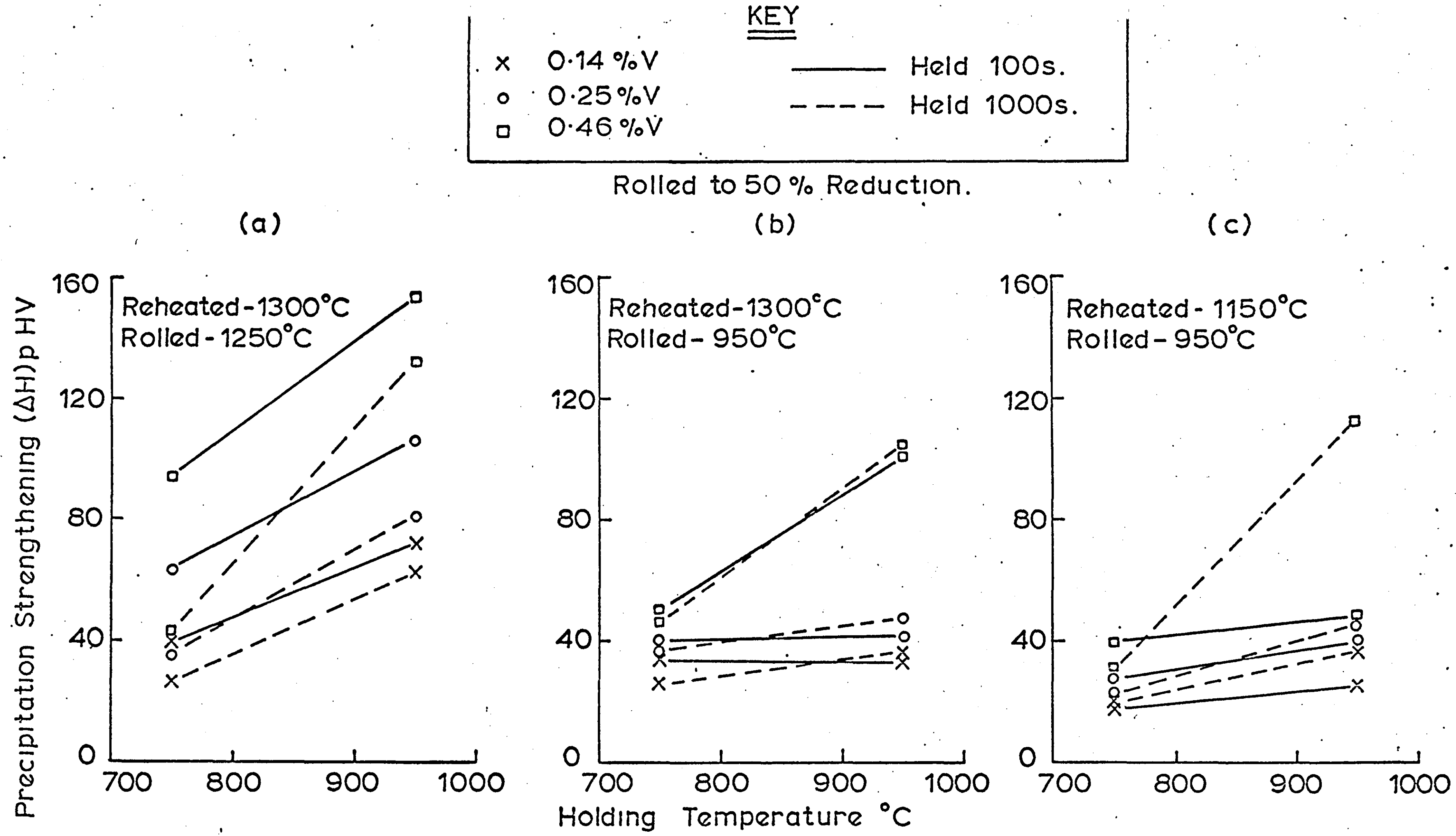
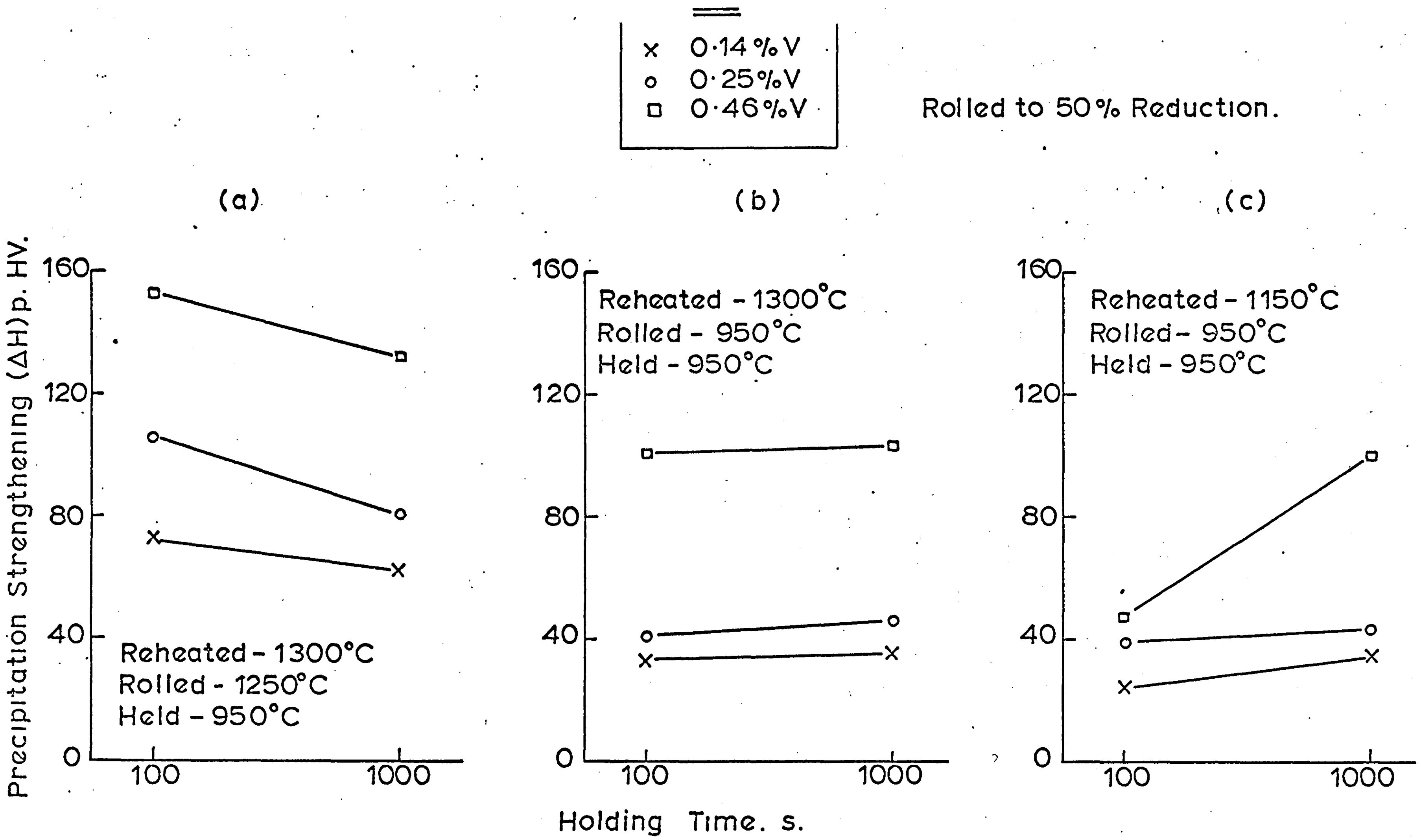


FIG. 98 THE EFFECT OF HOLDING TEMPERATURE ON PRECIPITATION STRENGTHENING IN HIGH NITROGEN - VANADIUM STEELS.



Rolled to 50% Reduction.

FIG. 99 THE EFFECT OF HOLDING TIME ON PRECIPITATION STRENGTHENING IN HIGH NITROGEN - VANADIUM STEELS.

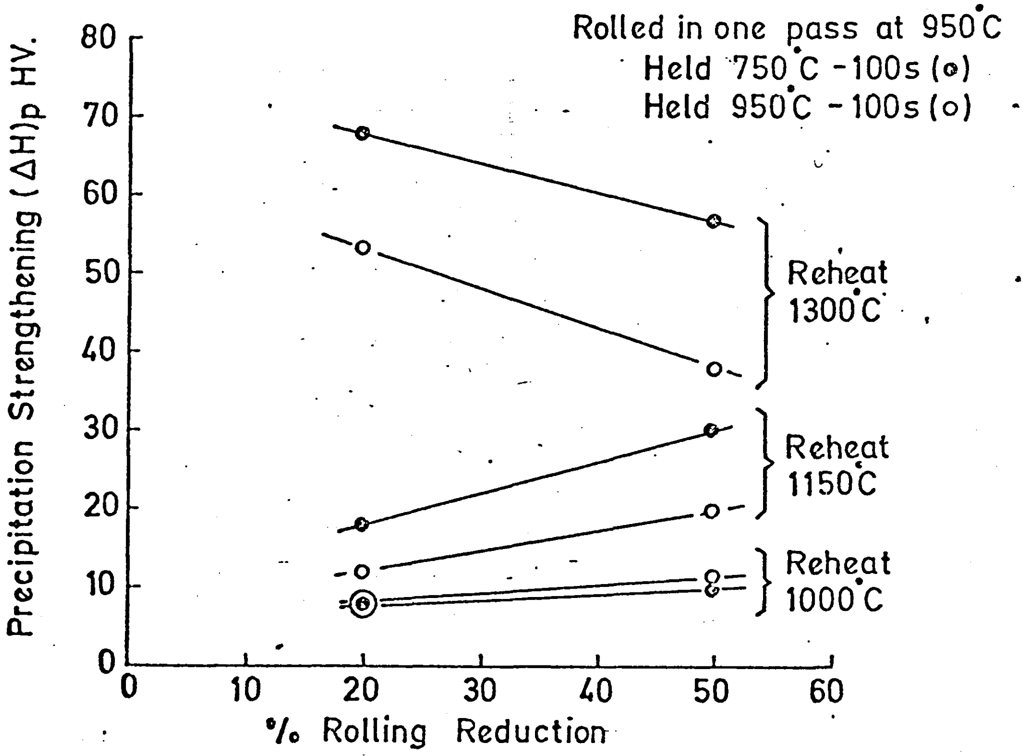


FIG. 100 EFFECT OF ROLLING REDUCTION ON $(\Delta H)_p$

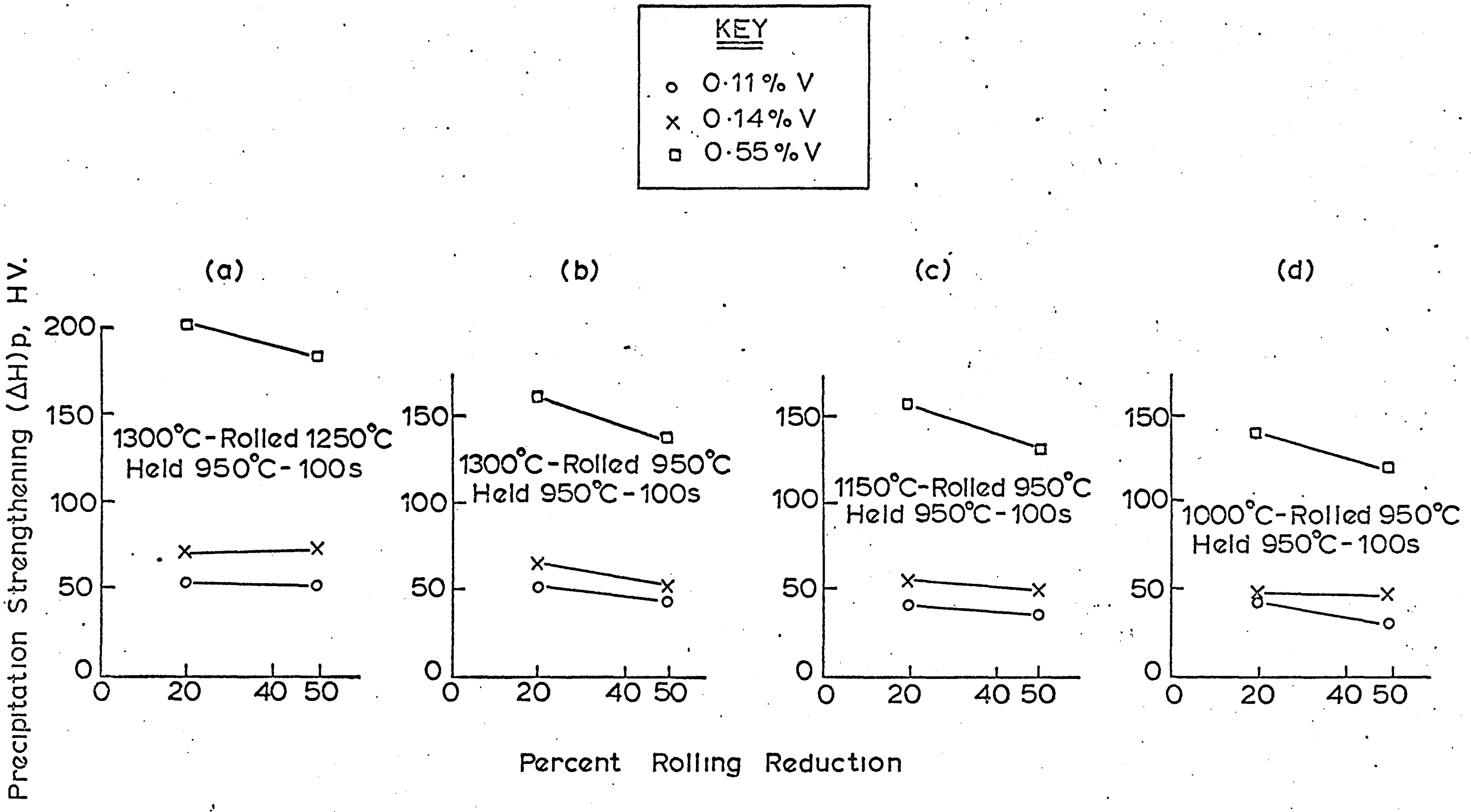


FIG.101 THE EFFECT OF ROLLING REDUCTION ON PRECIPITATION STRENGTHENING IN LOW NITROGEN-VANADIUM STEELS.

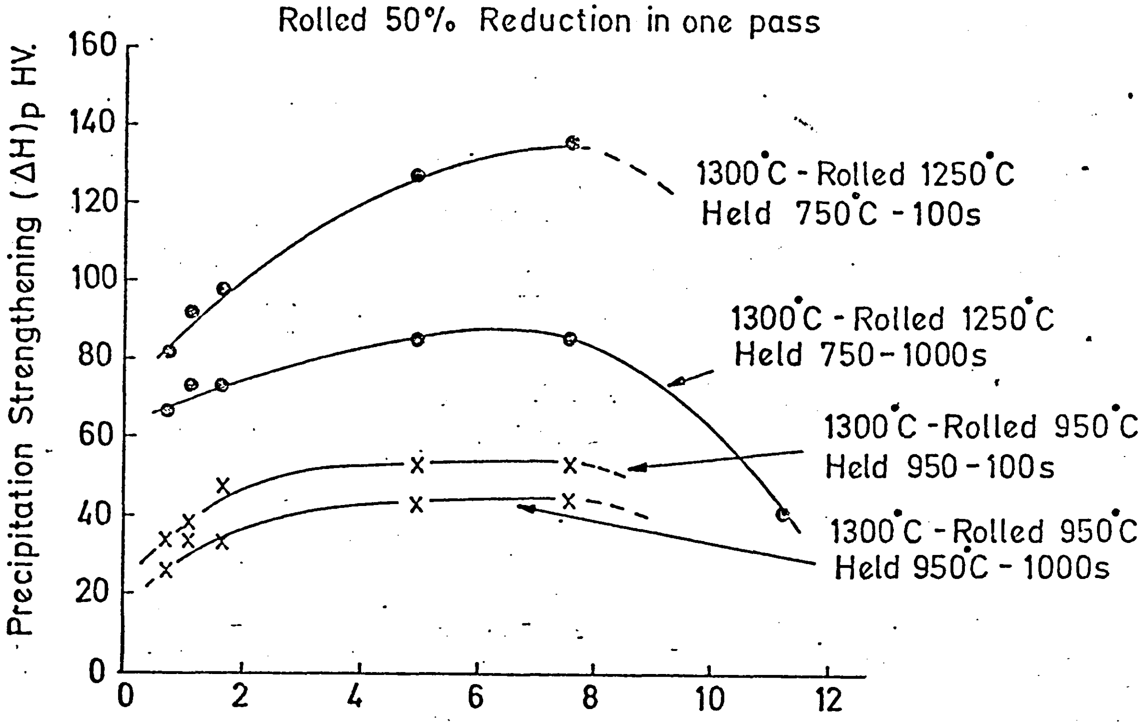


FIG. 102 EFFECT OF Nb : C_{EQ} RATIO ON $(\Delta H)_p$

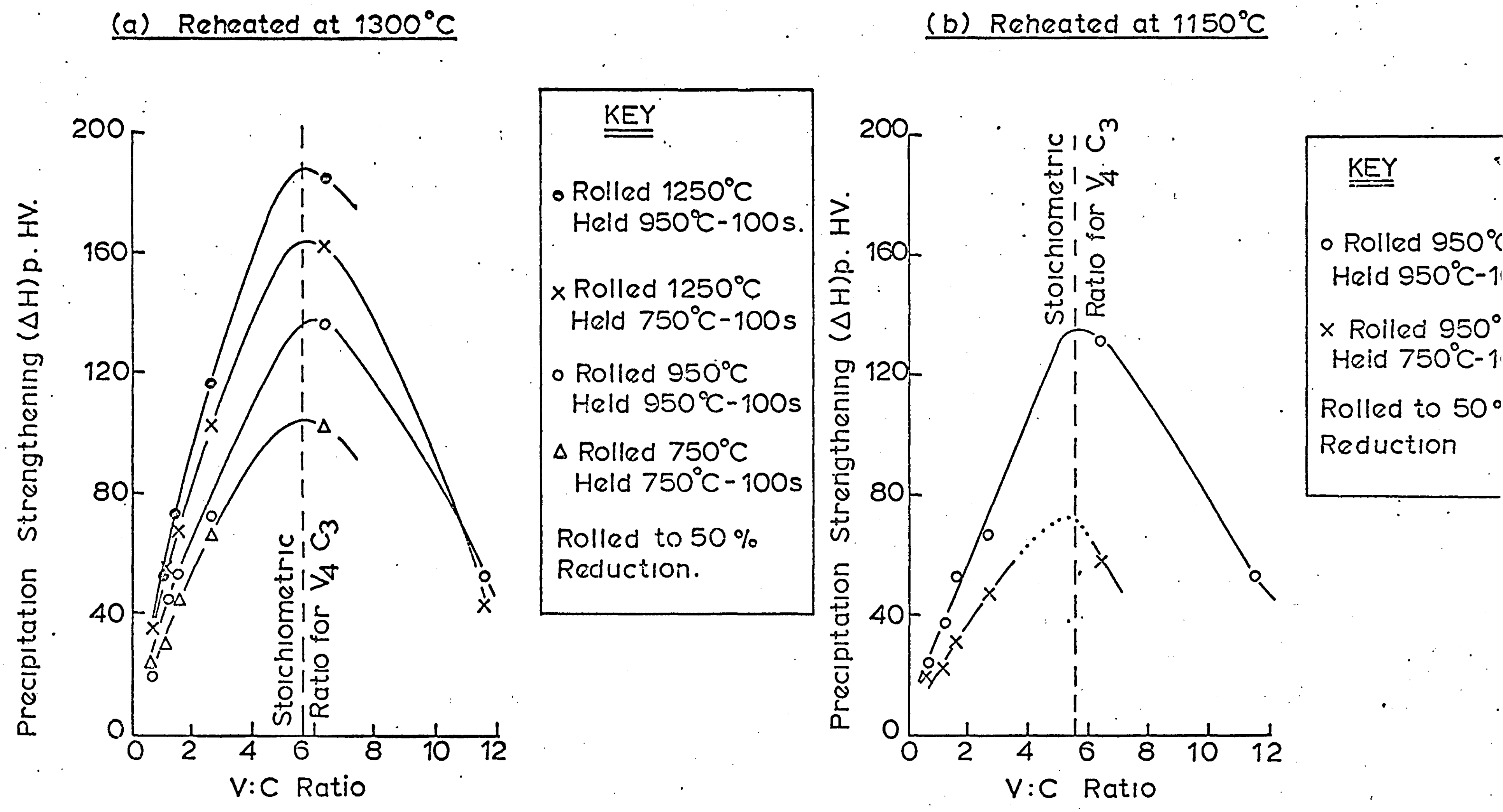


FIG.103 THE EFFECT OF VANADIUM: CARBON RATIO ON PRECIPITATION STRENGTHENING IN LOW NITROGEN-VANADIUM STEELS.

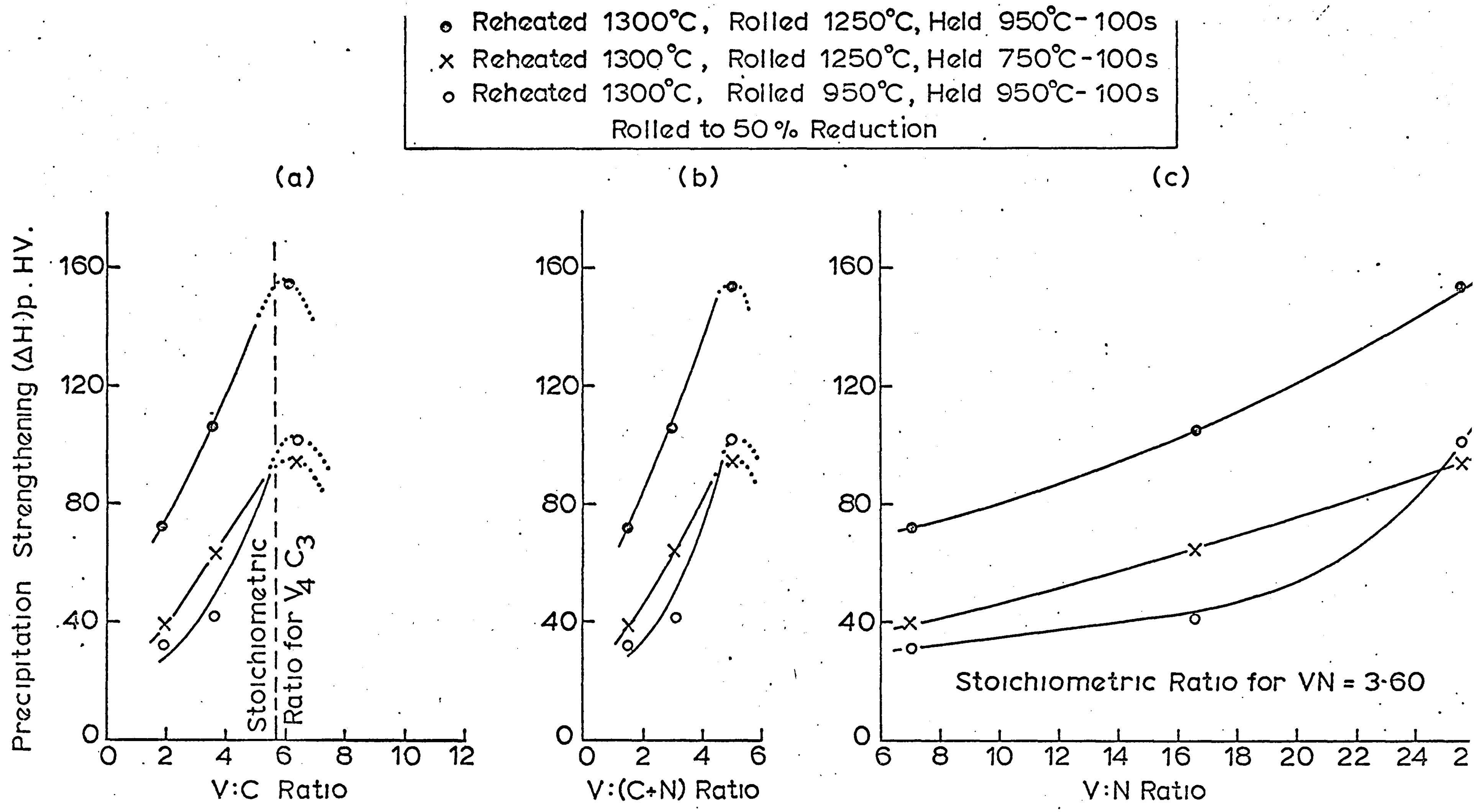


FIG. 104 THE EFFECT OF V:C, V:(C+N) AND V:N RATIO ON PRECIPITATION STRENGTHENING IN HIGH NITROGEN - VANADIUM STEELS.

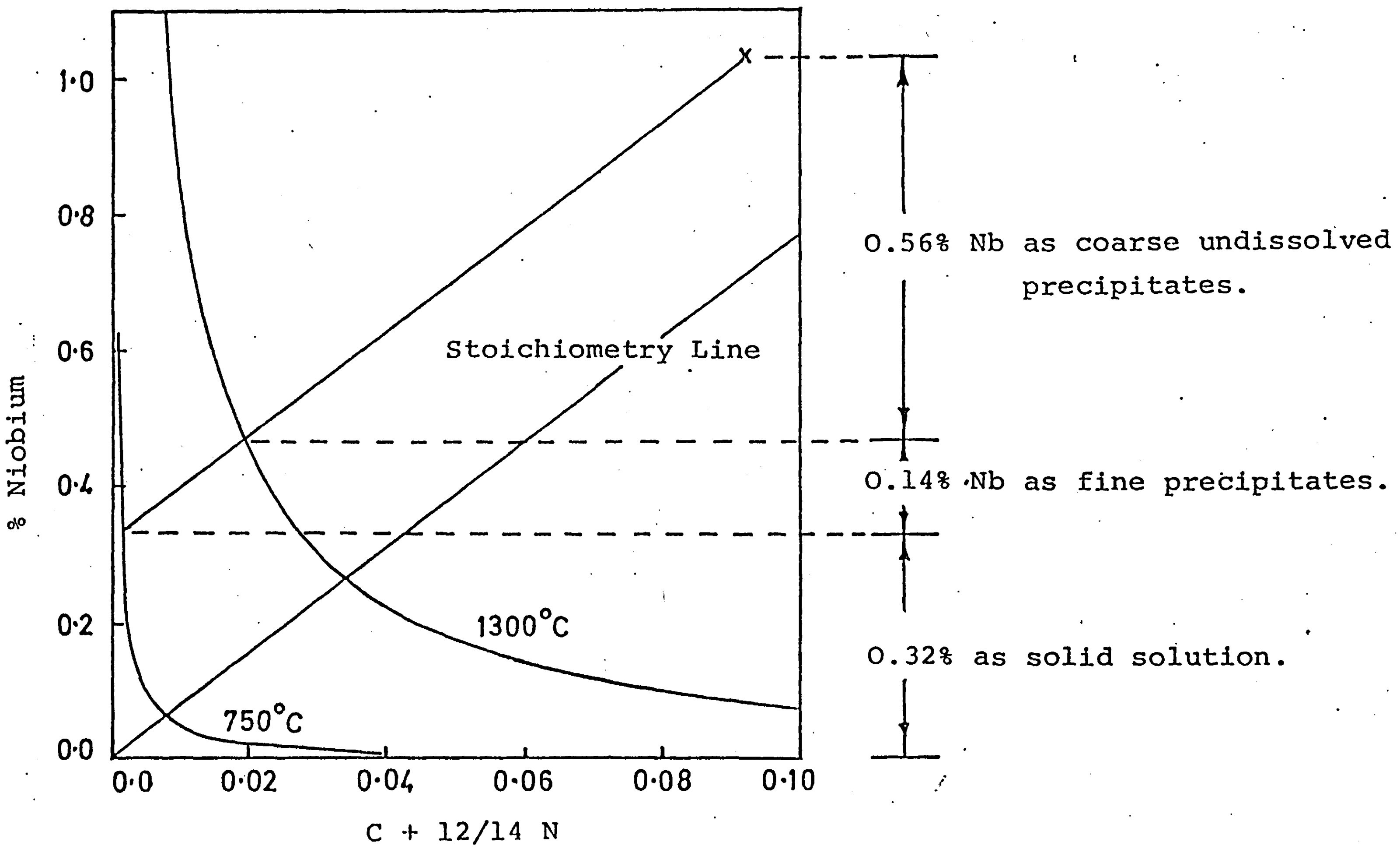


FIG. 105 VARIOUS FORMS OF NIOBIUM IN 1.03% Nb STEEL AT 1300°C.

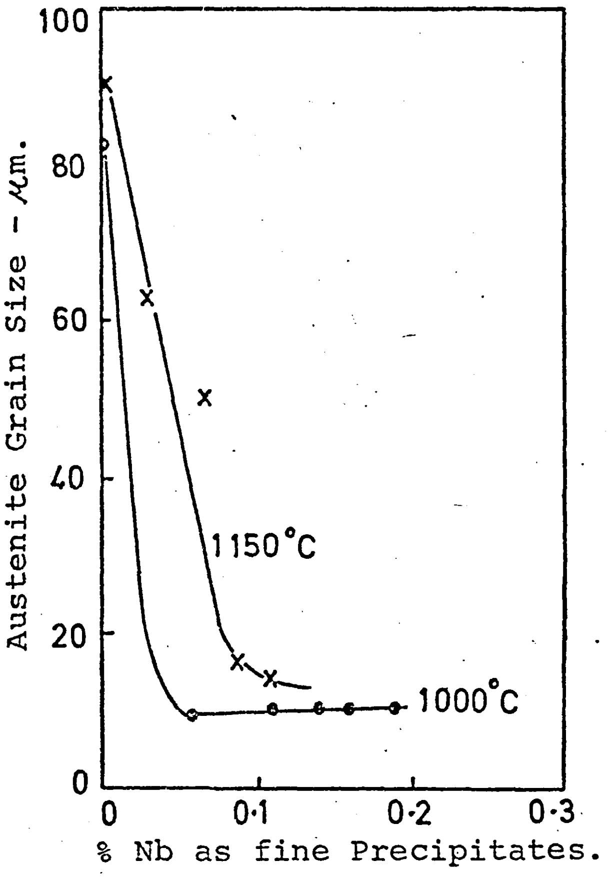


FIG. 106 THE VARIATION OF AUSTENITE GRAIN SIZE WITH % NIOBIUM AS FINE PRECIPITATES.

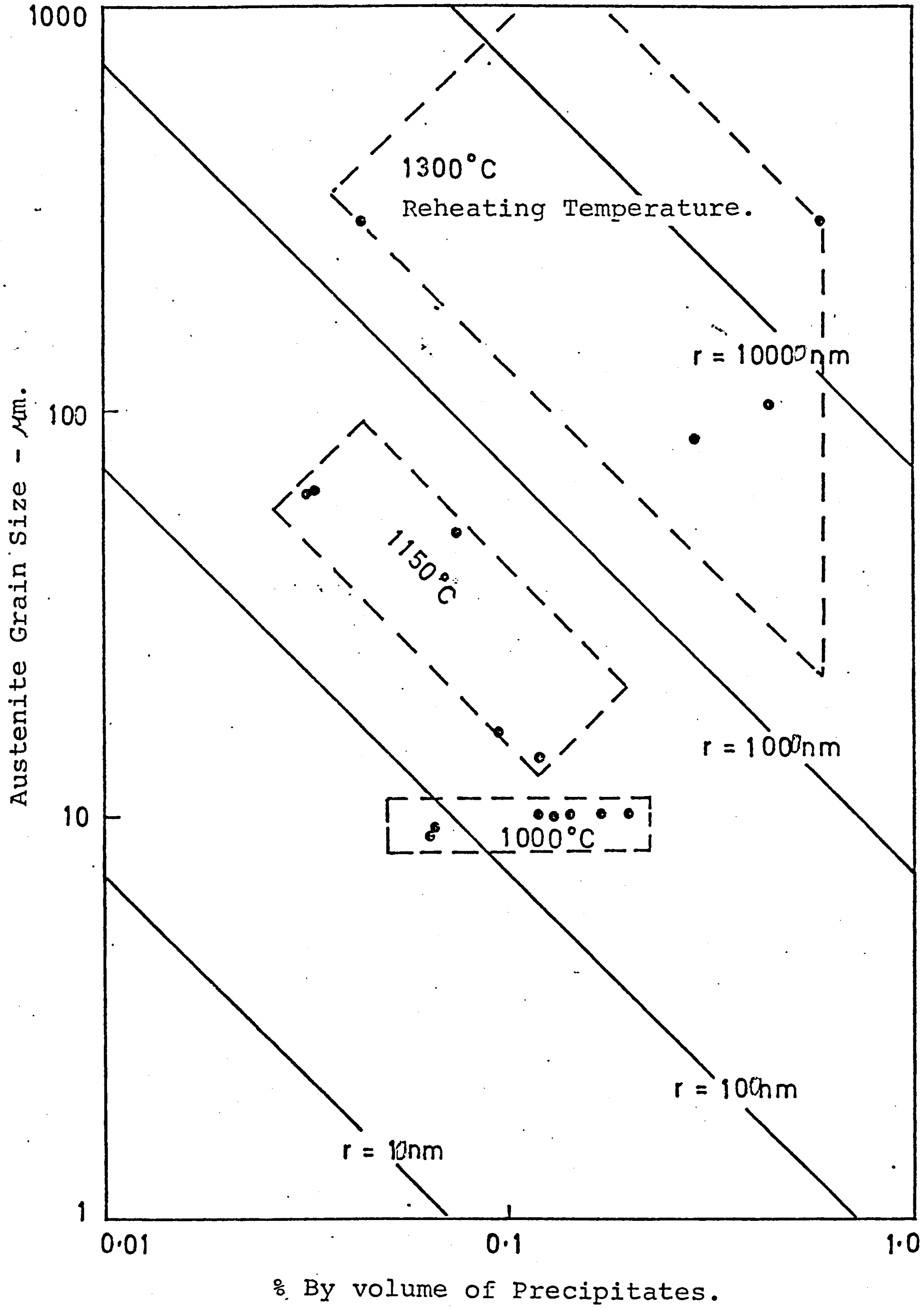


FIG. 107 EFFECT OF PARTICLE SIZE AND VOLUME FRACTION OF PRECIPITATES ON THE AUSTENITE GRAIN SIZE.

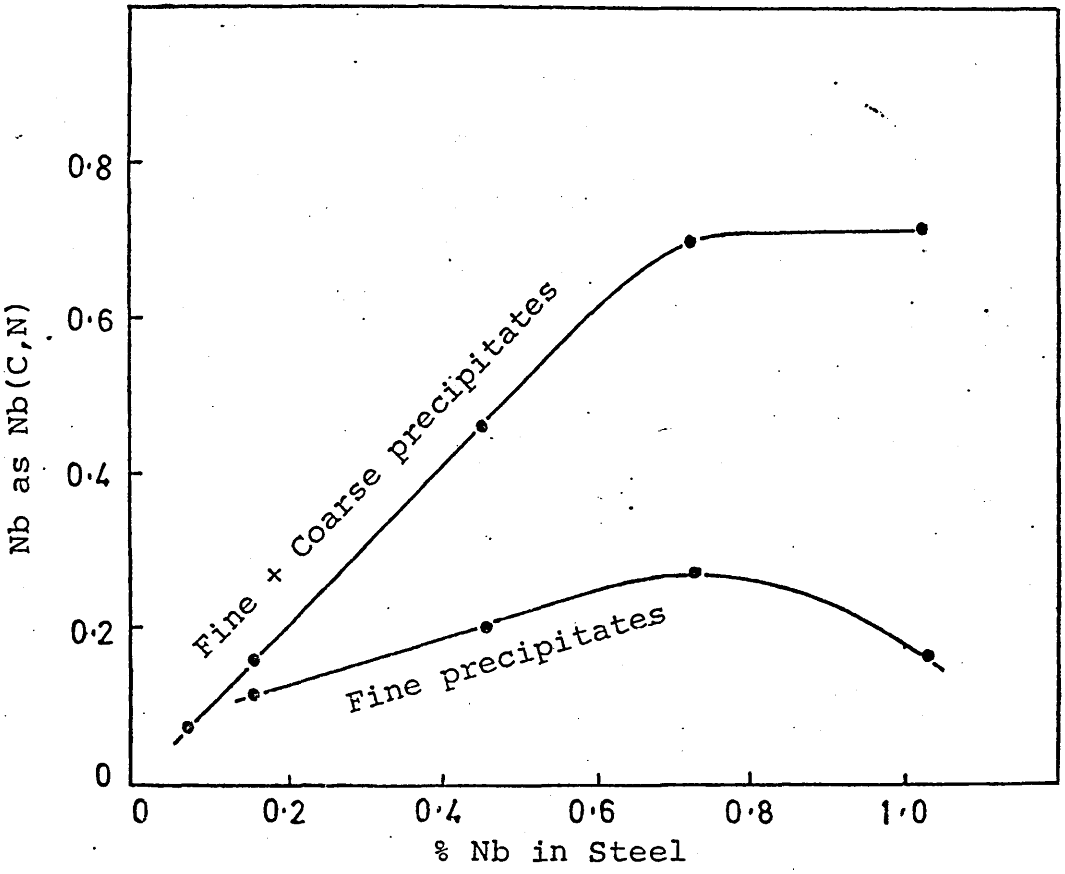


FIG. 108 THE VARIATION OF NIOBIUM AS FINE PLUS COARSE AND AS FINE PRECIPITATES WITH INCREASING NIOBIUM CONTENTS.

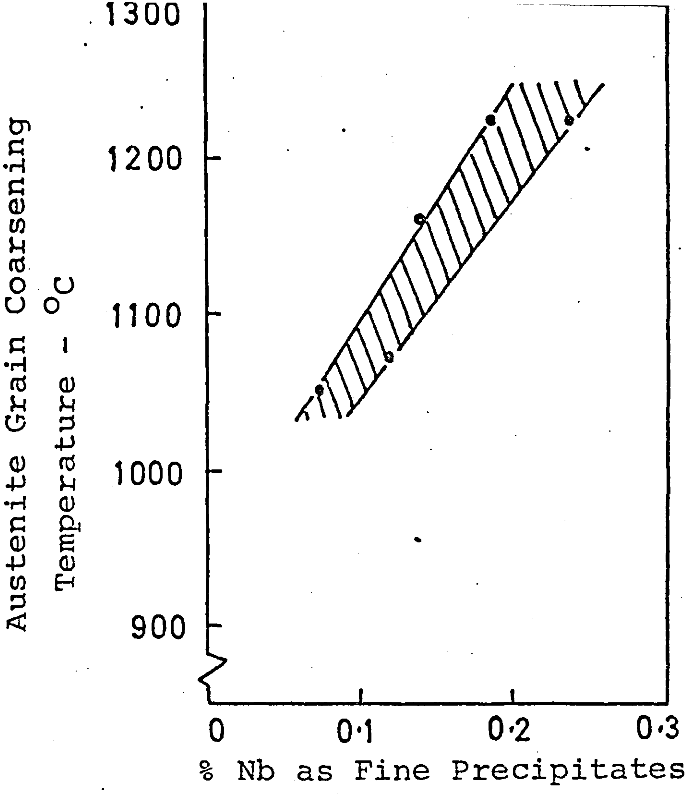


FIG. 109 EFFECT OF NIOBIUM AS FINE PRECIPITATES ON THE AUSTENITE GRAIN COARSENING TEMPERATURE.

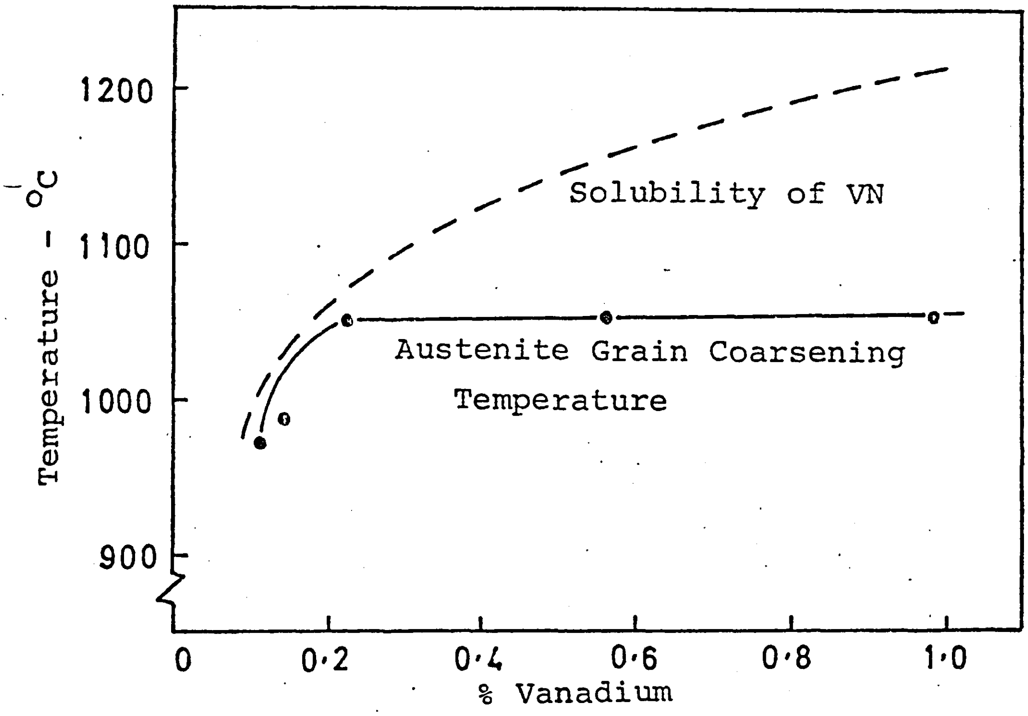


FIG. 110 RELATIONSHIP BETWEEN SOLUBILITY TEMPERATURE OF VN AND AUSTENITE GRAIN COARSENING TEMPERATURE IN VANADIUM STEELS.

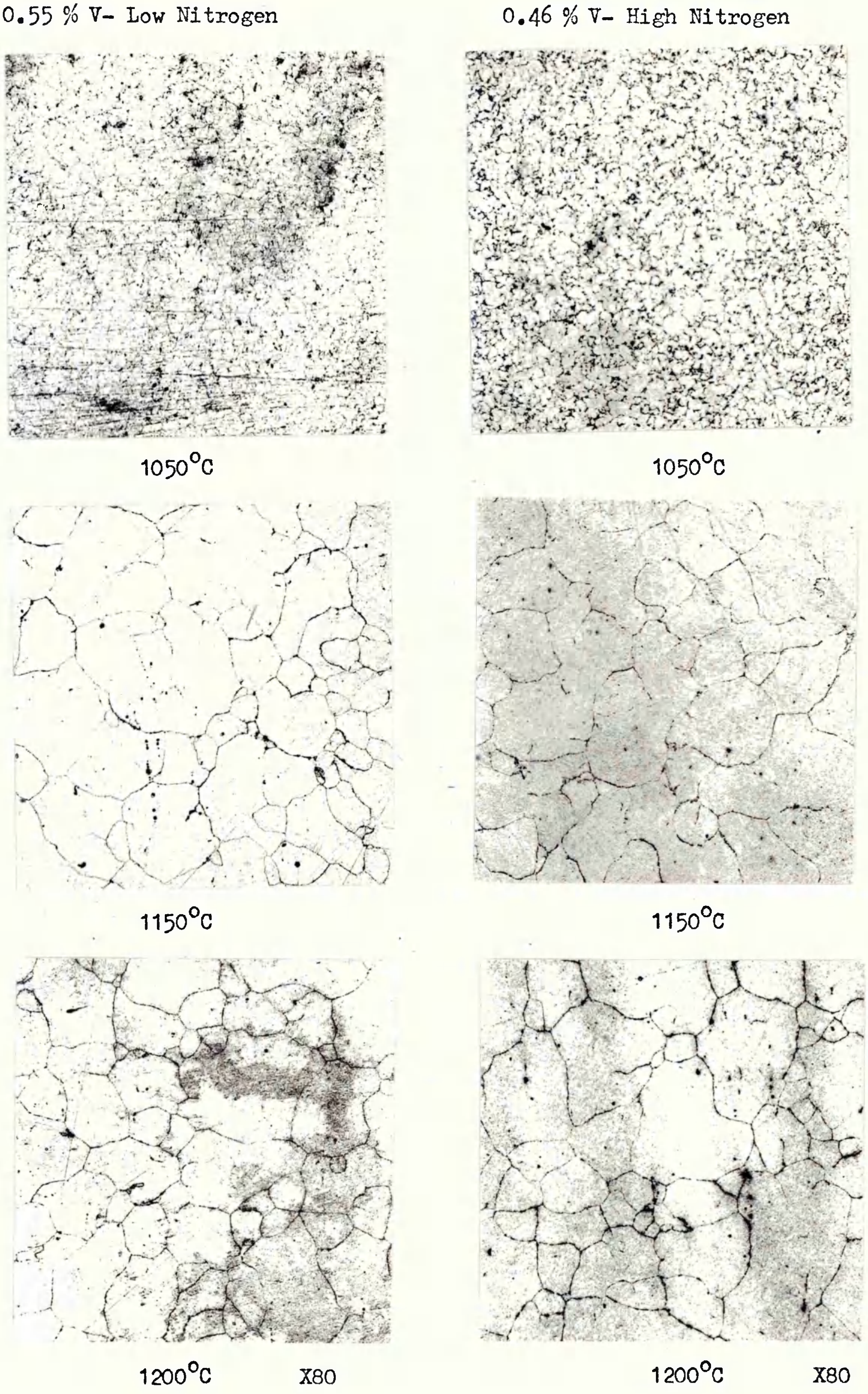
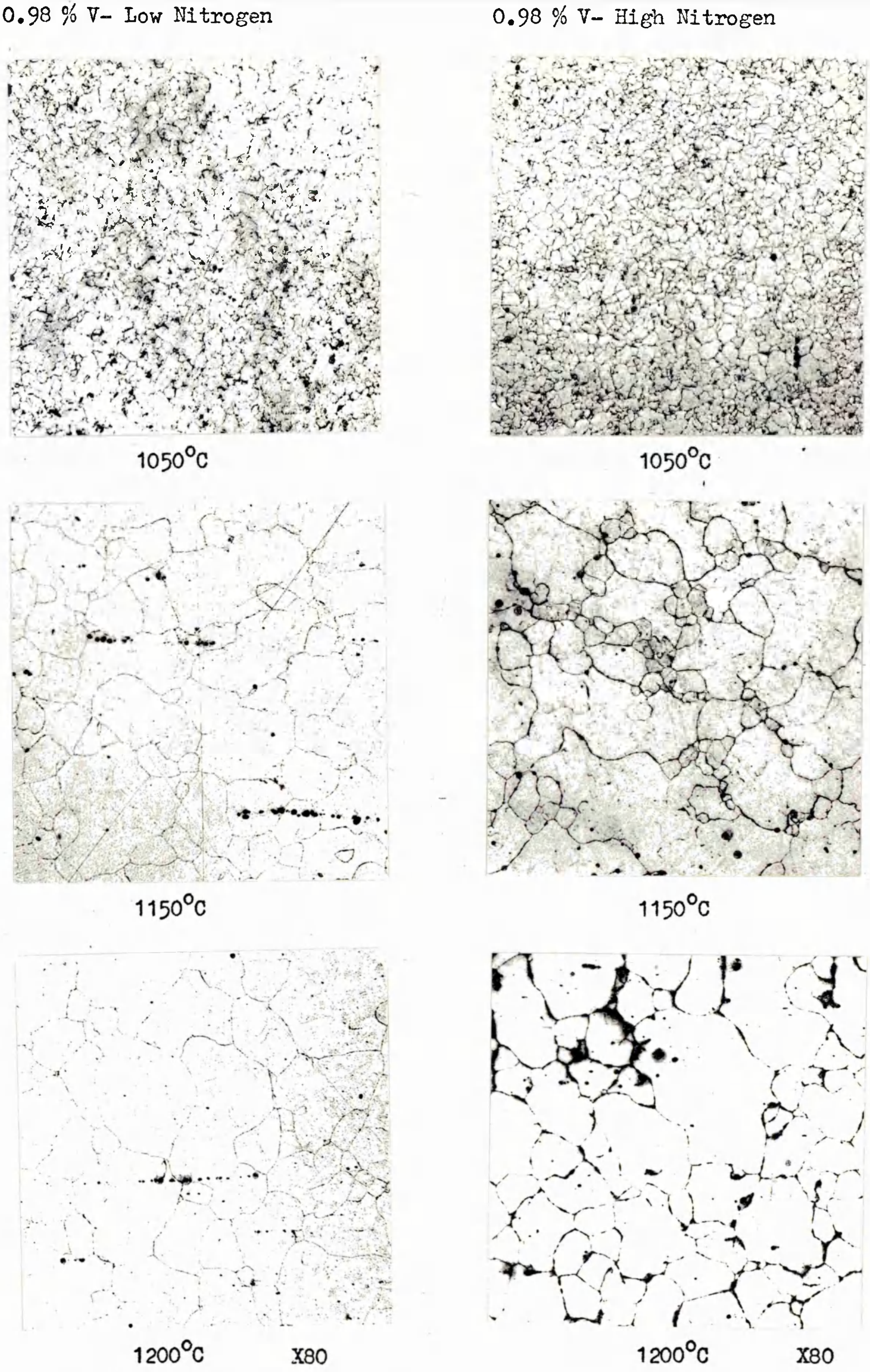


FIG. 111 (a) COMPARISON OF AUSTENITE GRAIN GROWTH IN VANADIUM STEELS CONTAINING LOW AND HIGH NITROGEN.



0.98 % V- Low Nitrogen

0.98 % V- High Nitrogen

1050°C

1050°C

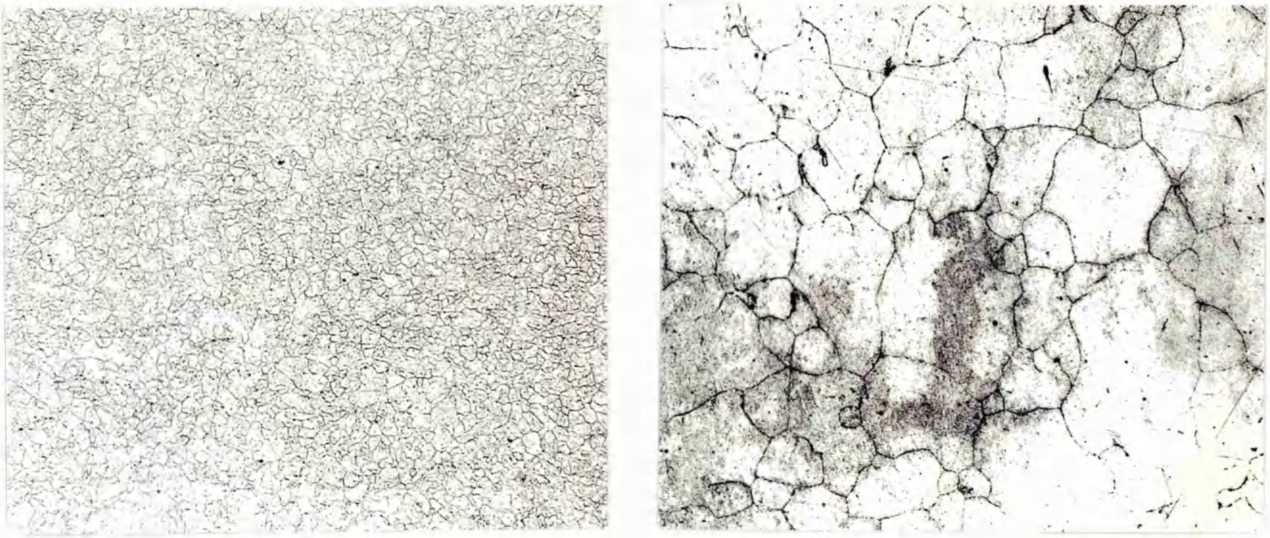
1150°C

1150°C

1200°C X80

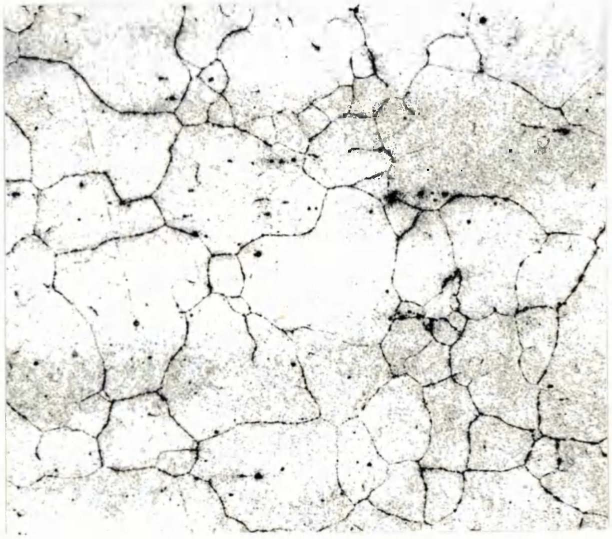
1200°C X80

FIG. 111 (b) COMPARISON OF AUSTENITE GRAIN GROWTH IN VANADIUM STEELS CONTAINING LOW AND HIGH NITROGEN.



0.46 % Nb X80

0.55 % V X80



0.46 % V-N X80

Treatment:
Reheated at 1200°C
for 30 min.

FIG. 112 THE EFFECT OF NIOBIUM AND VANADIUM ON THE AUSTENITE GRAIN SIZE.

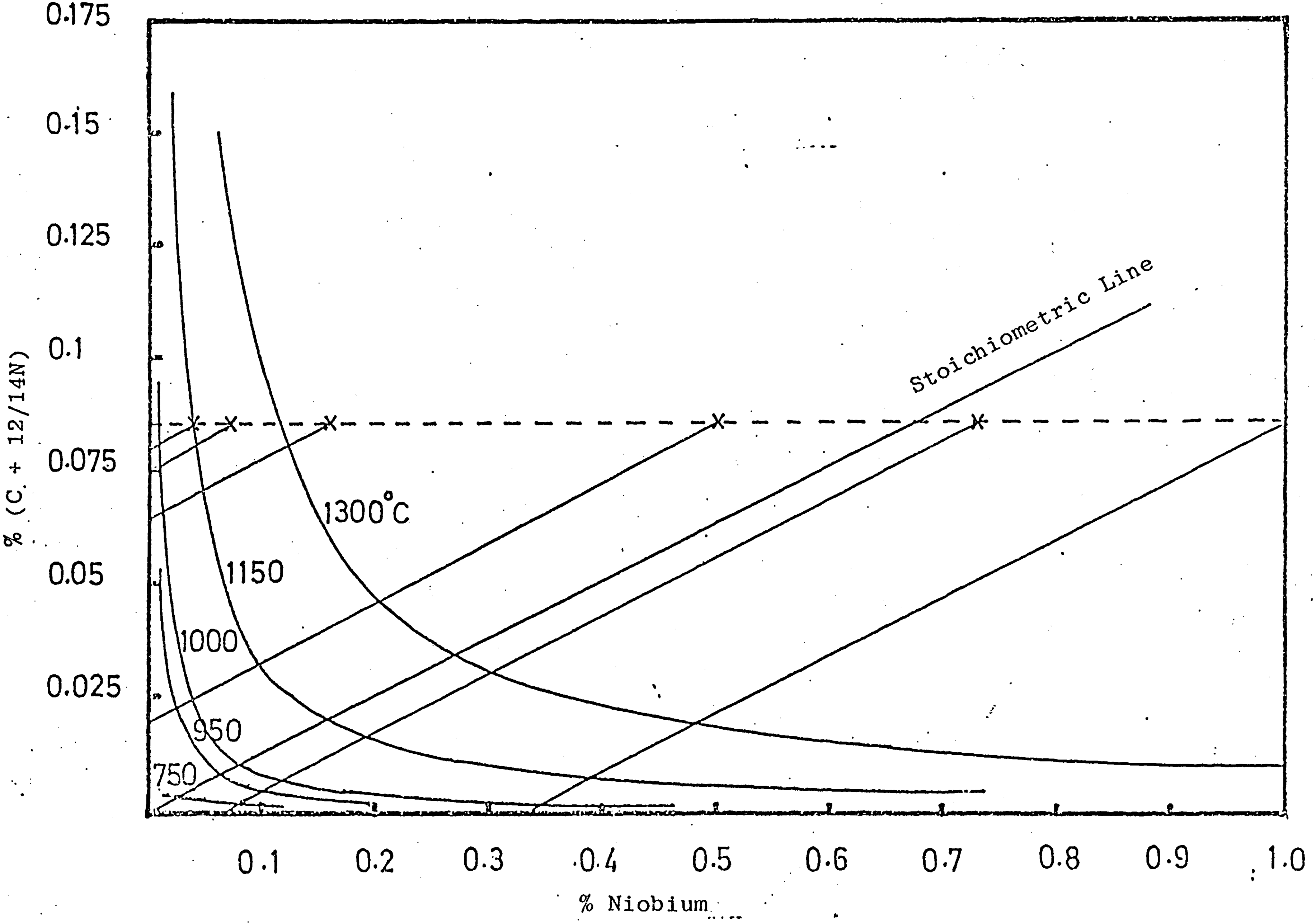


FIG. 113 SOLUBILITY OF Nb(C,N) IN AUSTENITE

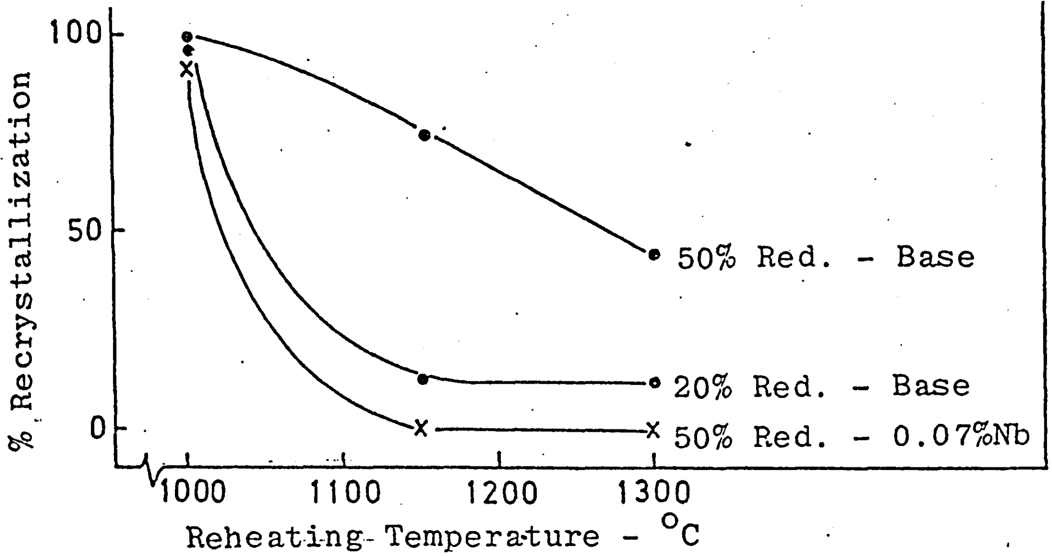


FIG. 114 EFFECT OF REHEATING TEMPERATURE ON % RECRYSTALLIZATION, Rolled - 950°C

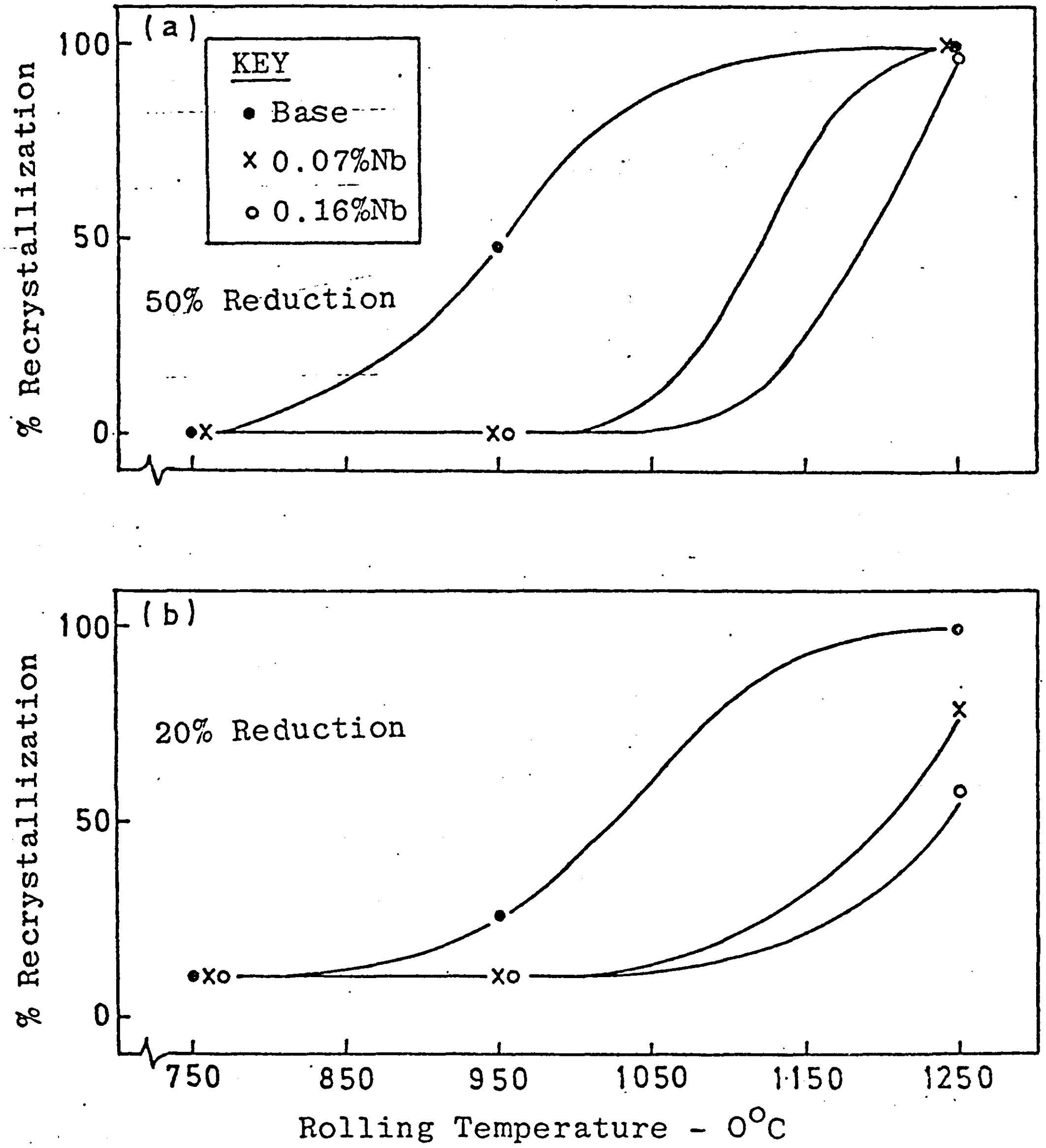


FIG. 115 EFFECT OF ROLLING TEMPERATURE ON % RECRYSTALLIZATION, Reheated - 1300°C

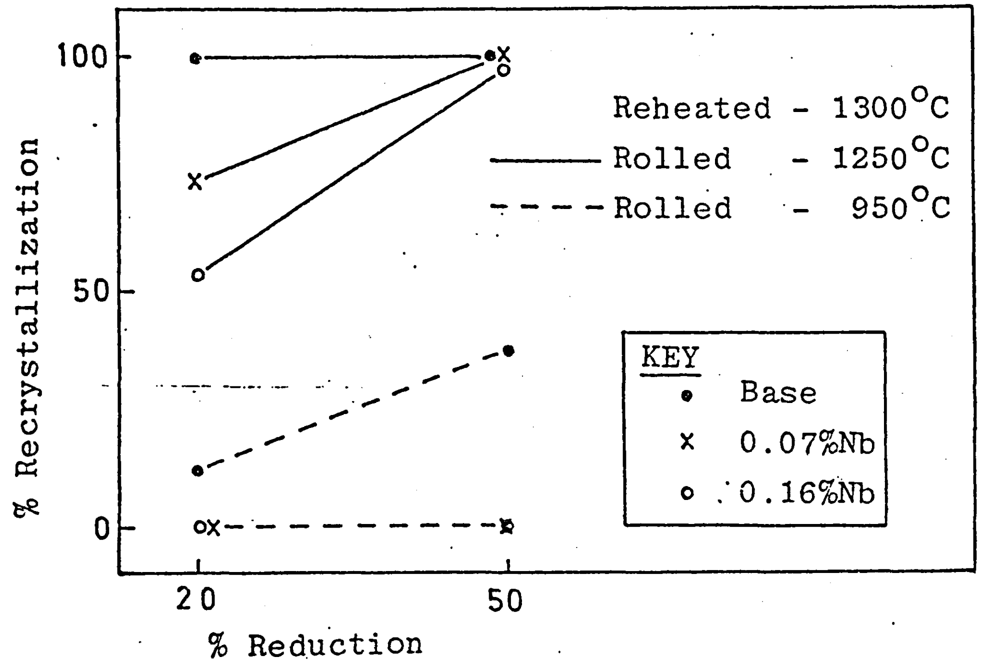


FIG. 116 EFFECT OF ROLLING REDUCTION ON % RECRYSTALLIZATION.

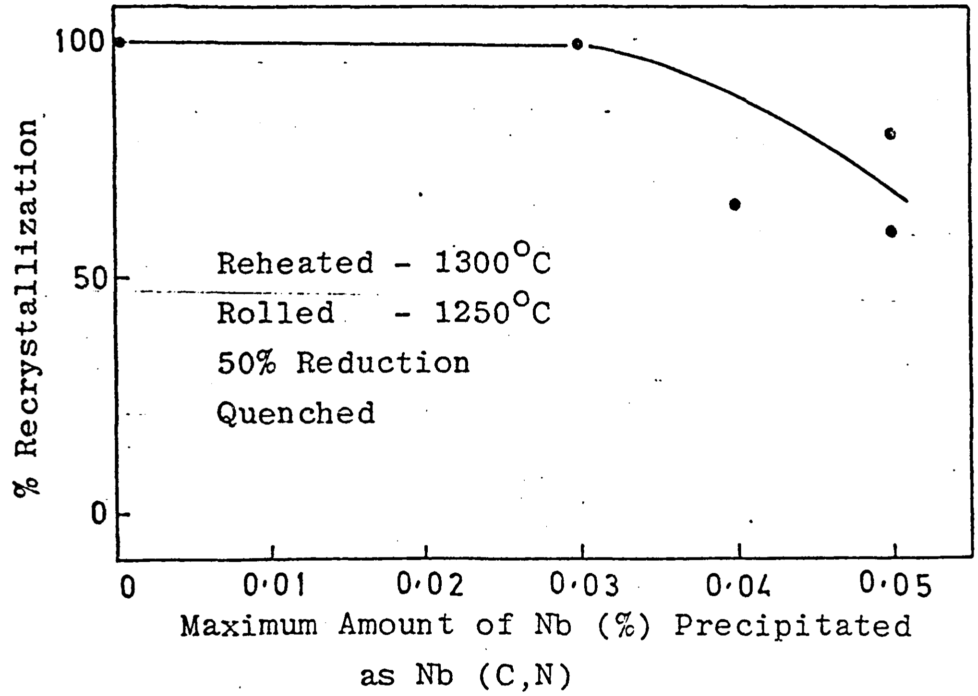


FIG. 117 RELATIONSHIP BETWEEN MAXIMUM AMOUNT OF PRECIPITATED Nb AT 1250°C AND PERCENT RECRYSTALLIZATION

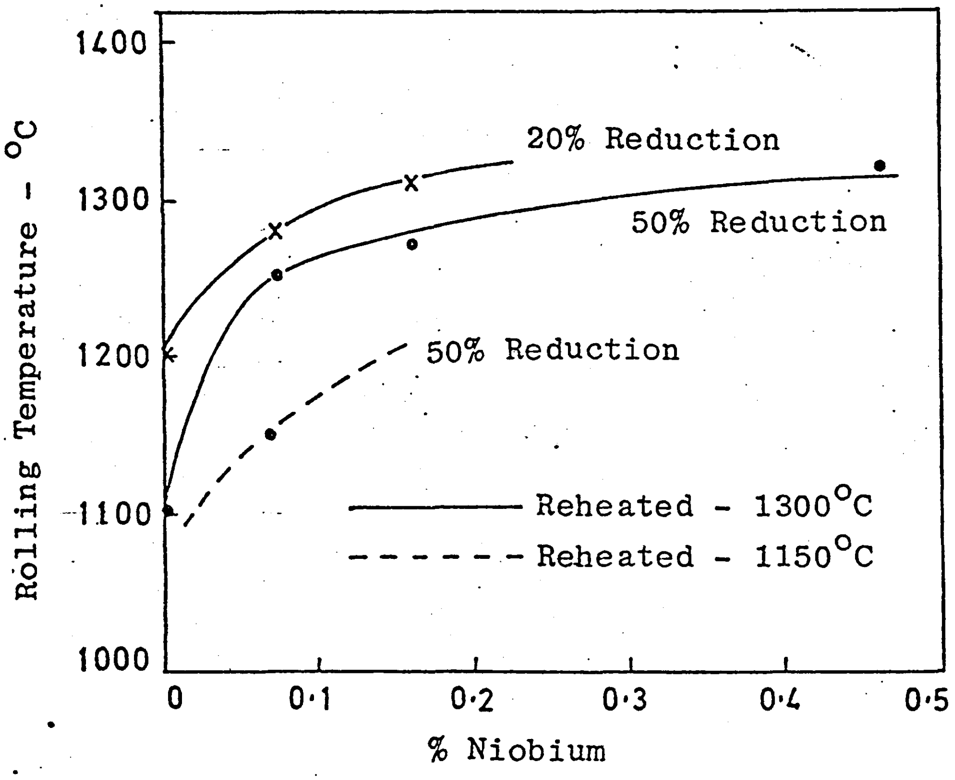
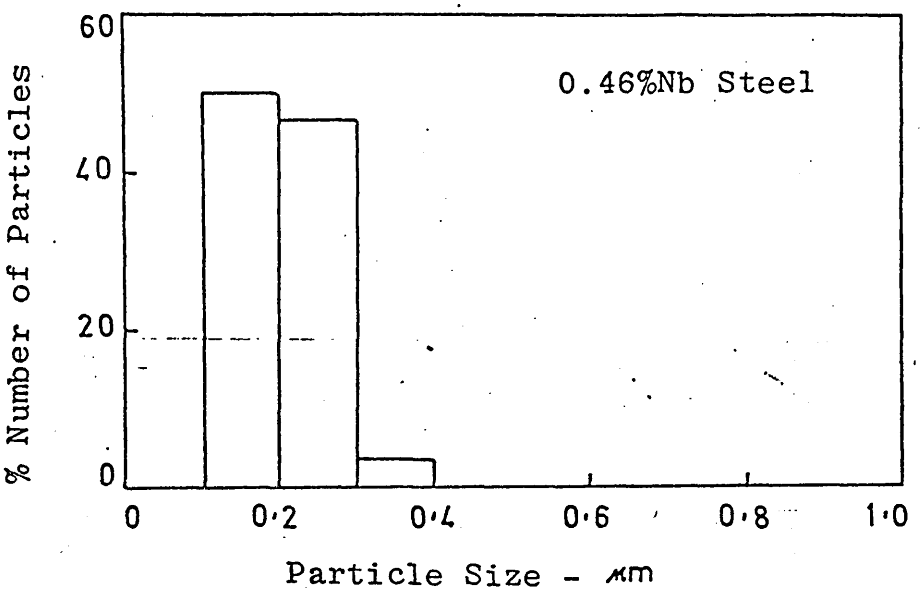


FIG. 118 EFFECTS OF NIOBIUM CONTENT ON THE ROLLING TEMPERATURE FOR COMPLETE RECRYSTALLIZATION



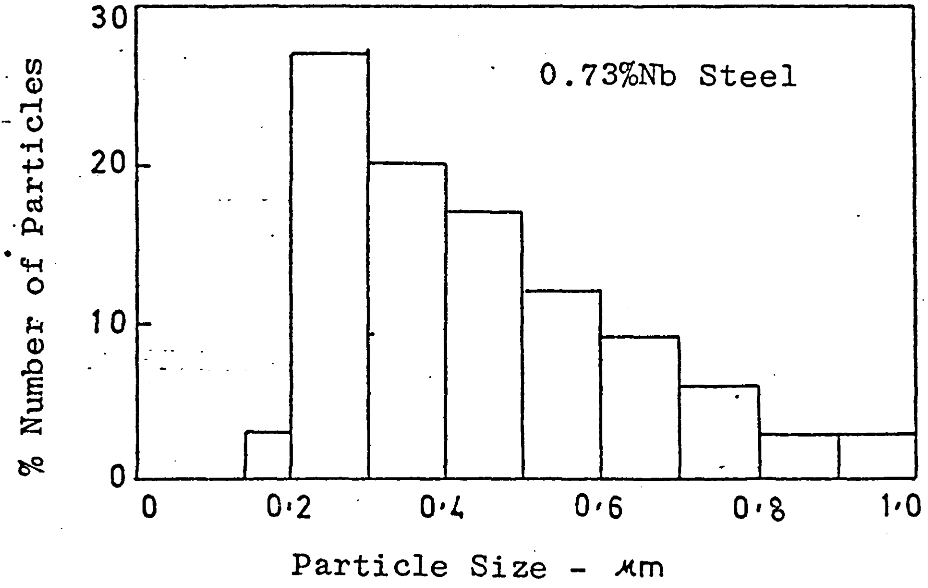
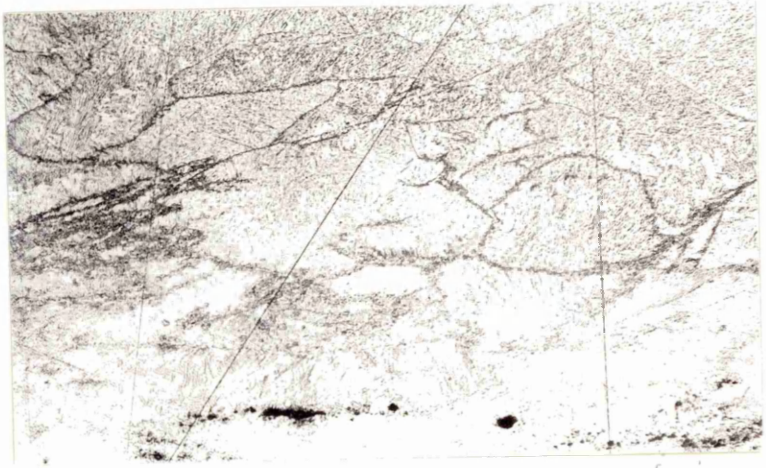
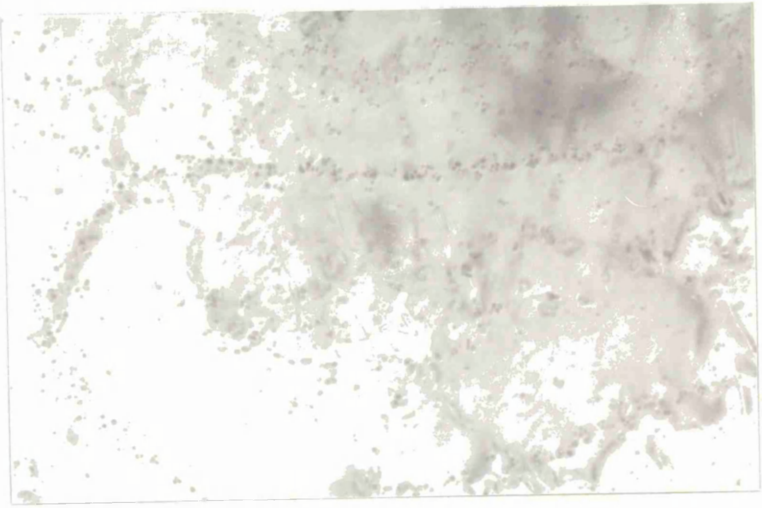


FIG. 119 PARTICLE SIZE DISTRIBUTION OF UNDISSOLVED Nb (C,N) AT 1300°C in 0.46% AND 0.73% Nb STEELS



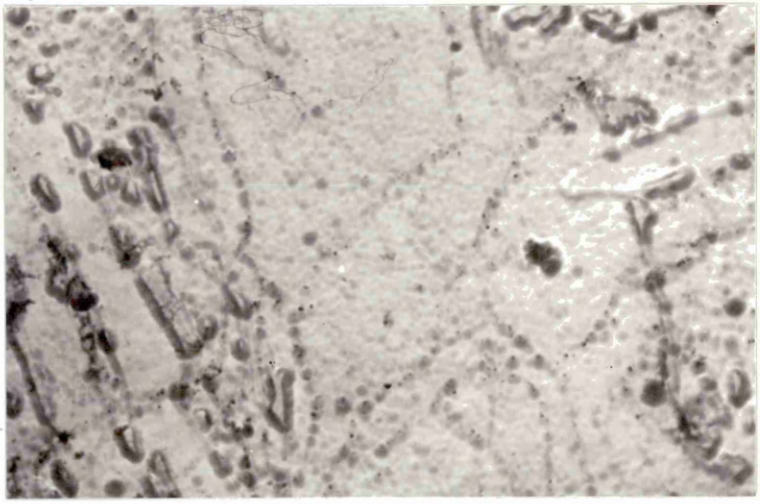
X 120

FIG. 120 UNRECRYSTALIZED AUSTENITE IN LOW INTERSTITIAL Nb STEEL:
Rolled 50 % reduction at 1250°C and quenched.



0.11 % Nb. X80,000

Reheated- 1300°C, Rolled- 950°C, 50 % Reduction, Held- 750°C for 100s, Sand cooled.



0.73 % Nb. X12,000

Reheated-1300°C, Rolled- 1250°C, 50 % Reduction, Held- 750°C for 100s, Quenched.

FIG. 121 STRAIN INDUCED PRECIPITATION OF Nb(C,N) ON SUBSTRUCTURE.

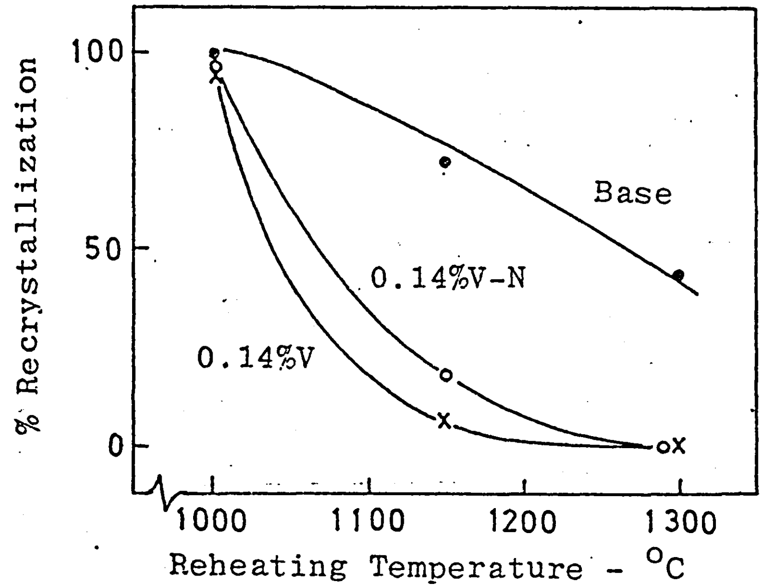


FIG. 122 EFFECT OF REHEATING TEMPERATURE ON % RECRYSTALLIZATION - Rolled at 950°C - 50% Red.

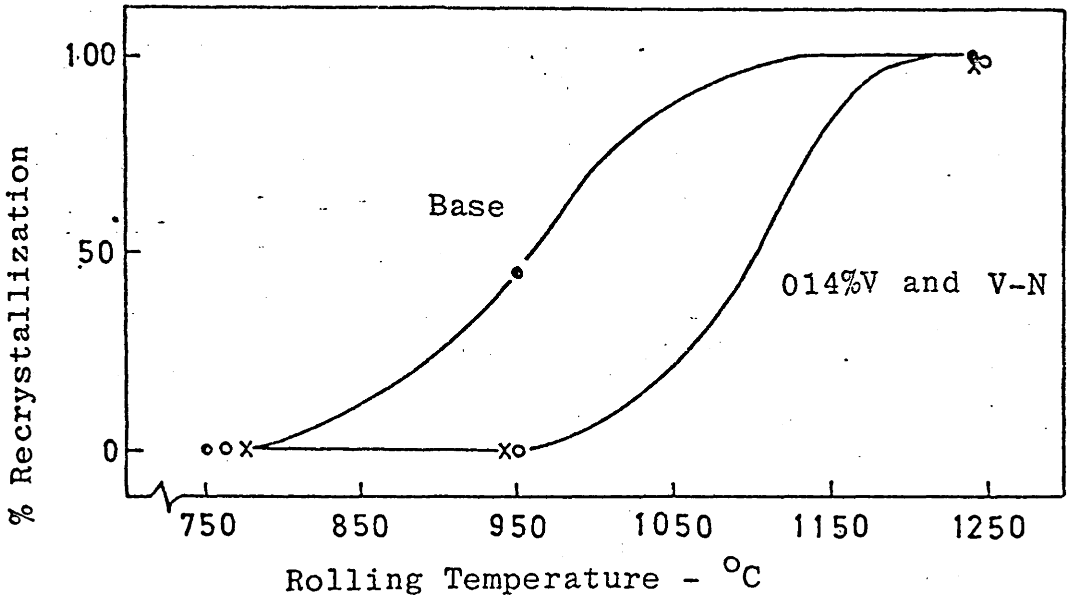
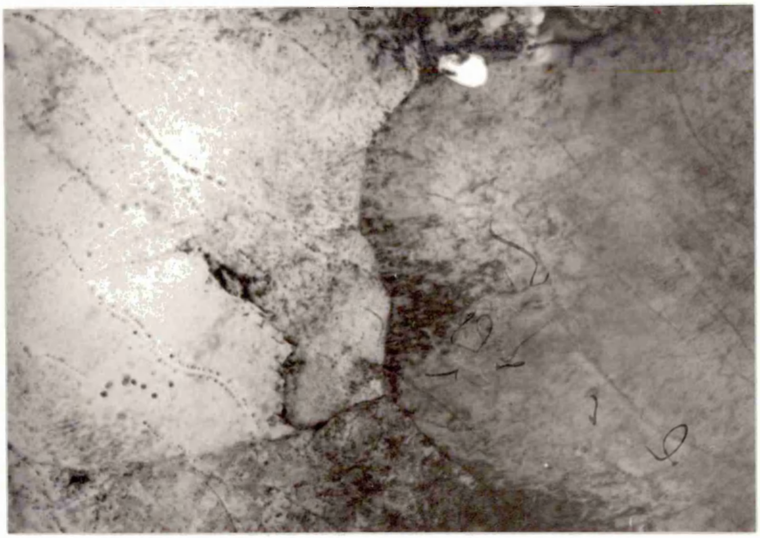
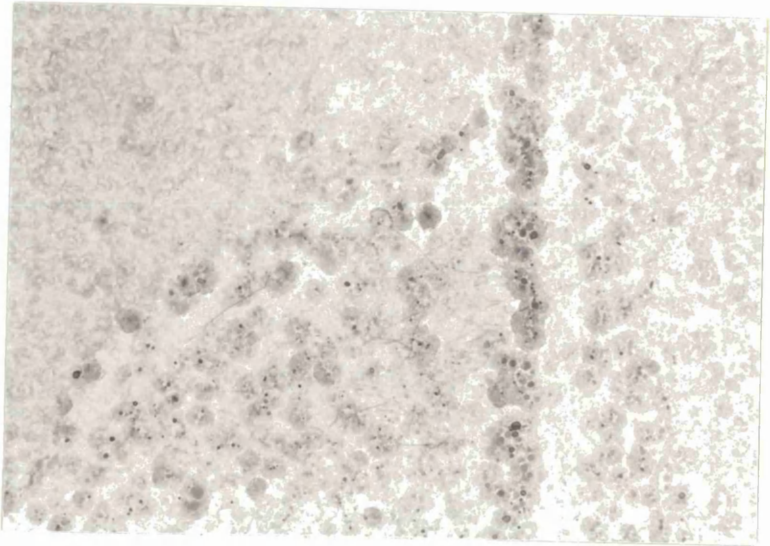


FIG. 123 EFFECT OF ROLLING TEMPERATURE ON % RECRYSTALLIZATION, Reheated - 1300°C, 50% Red.



X20,000

(a) Precipitation on substructure in 0.22 % V steel. (Reheated-1300°C, Rolled at 950°C by 50 % Reduction and held for 100s at 950°C prior to sand cooling.)



X20,000

(b) Precipitation on austenite grain boundaries in 0.55 % V steel. (Treatment same as above but quenched after holding.)

FIG. 124 PRECIPITATION OF V(C,N) IN AUSTENITE.

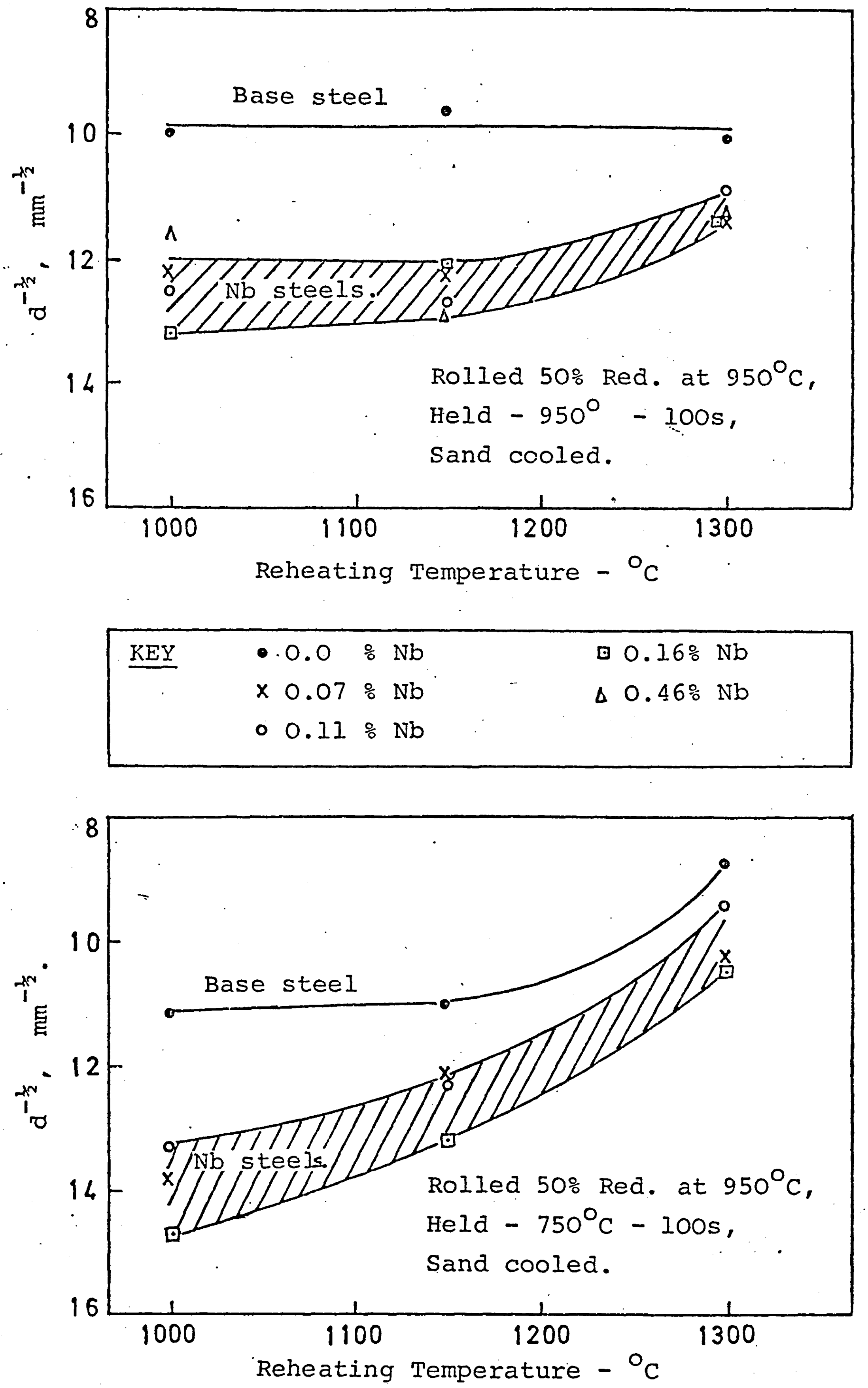


FIG. 125 EFFECT OF REHEATING TEMPERATURE ON FERRITE GRAIN SIZE.

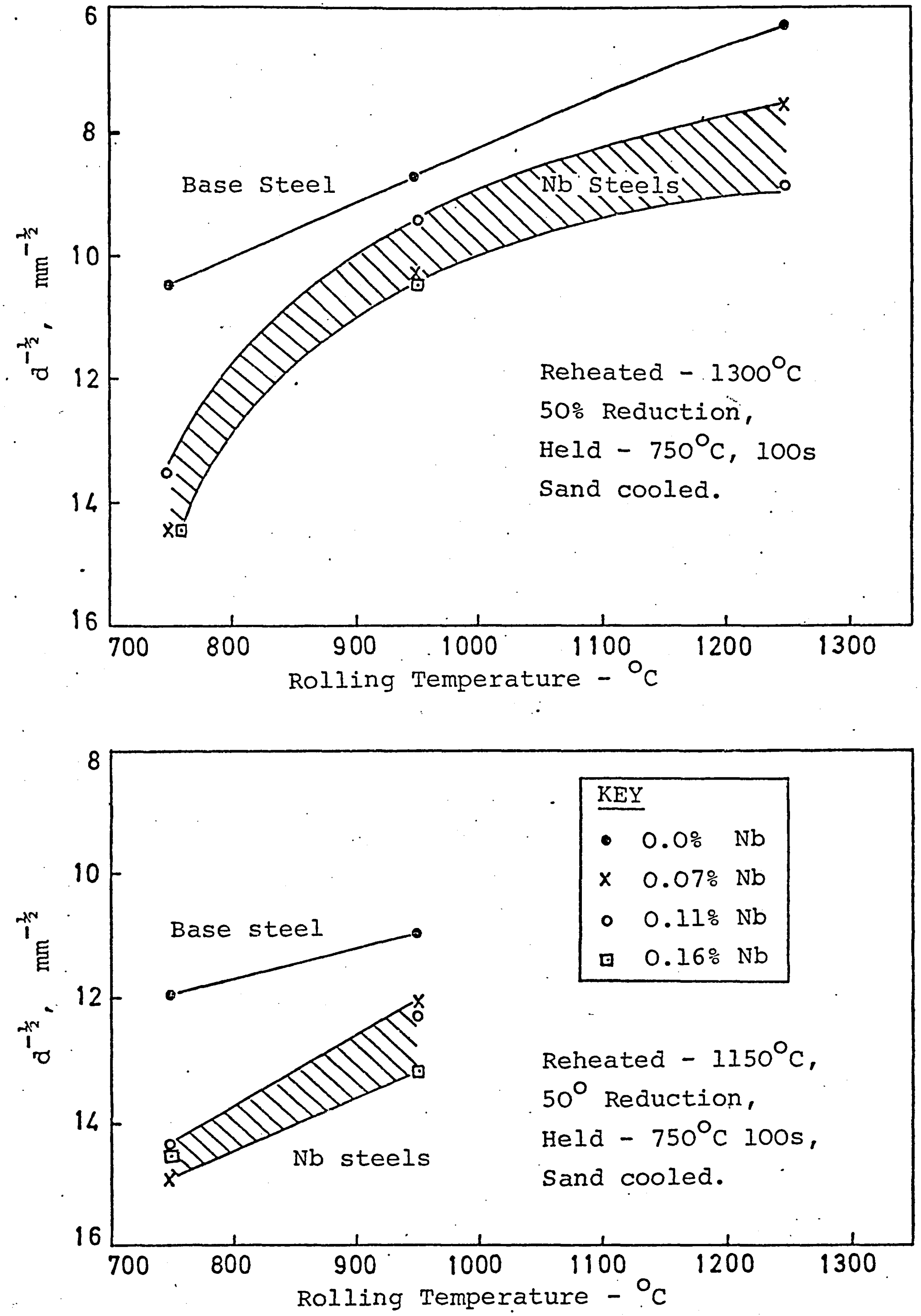


FIG. 126 EFFECT OF ROLLING TEMPERATURE ON FERRITE GRAIN SIZE.

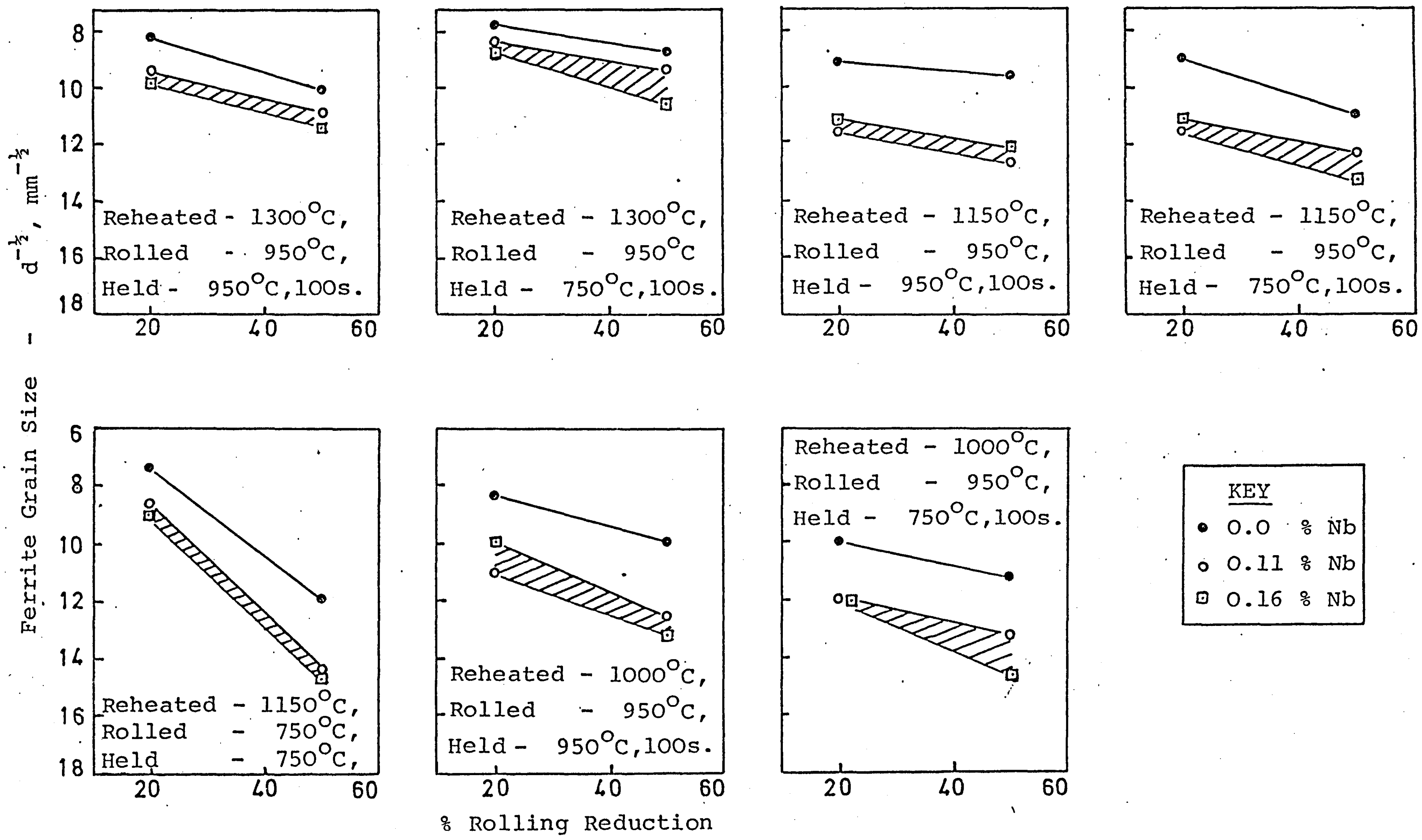


FIG. 127 EFFECT OF ROLLING REDUCTION ON FERRITE GRAIN SIZE.

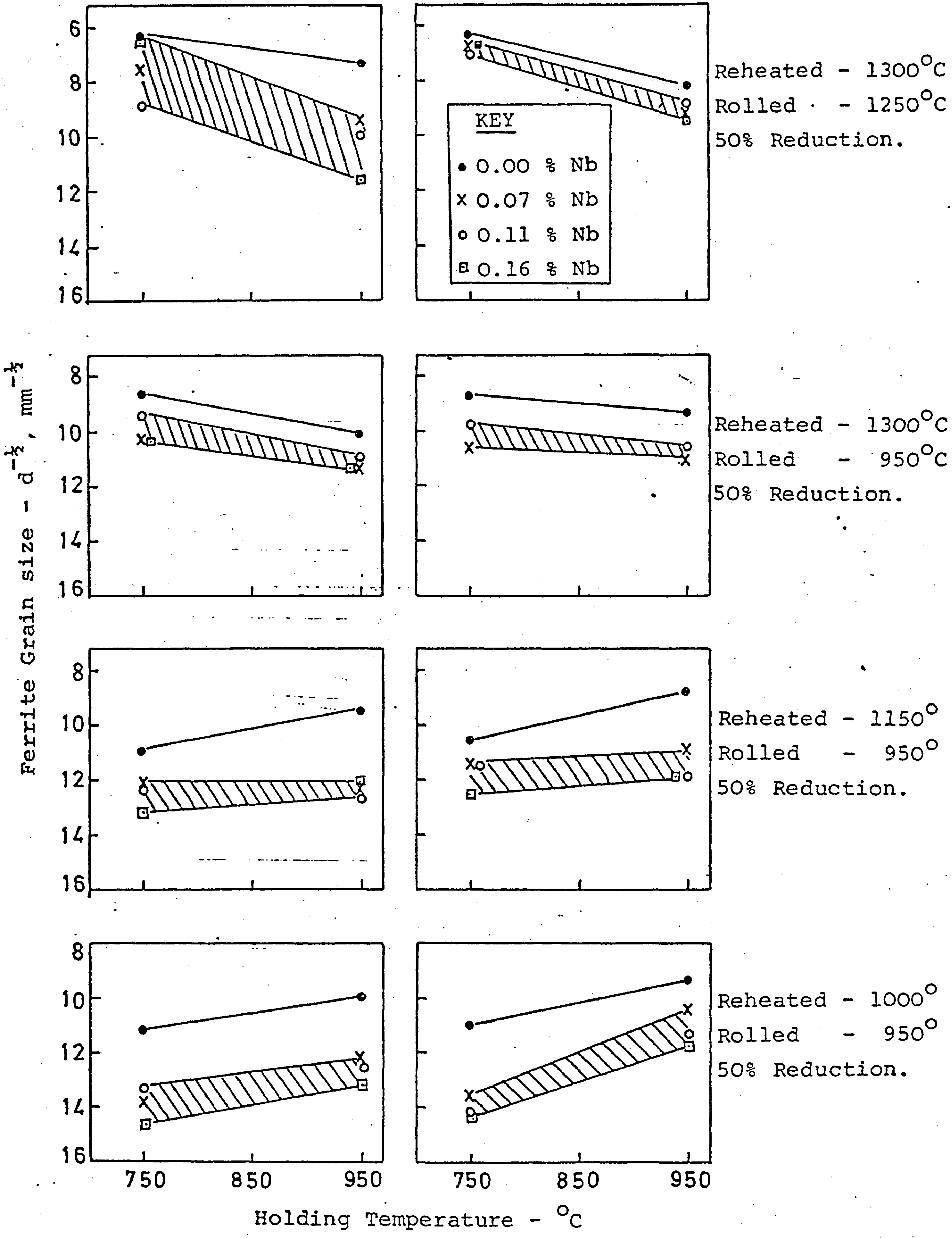


FIG. 128 EFFECT OF HOLDING TEMPERATURE ON FERRITE GRAIN SIZE.

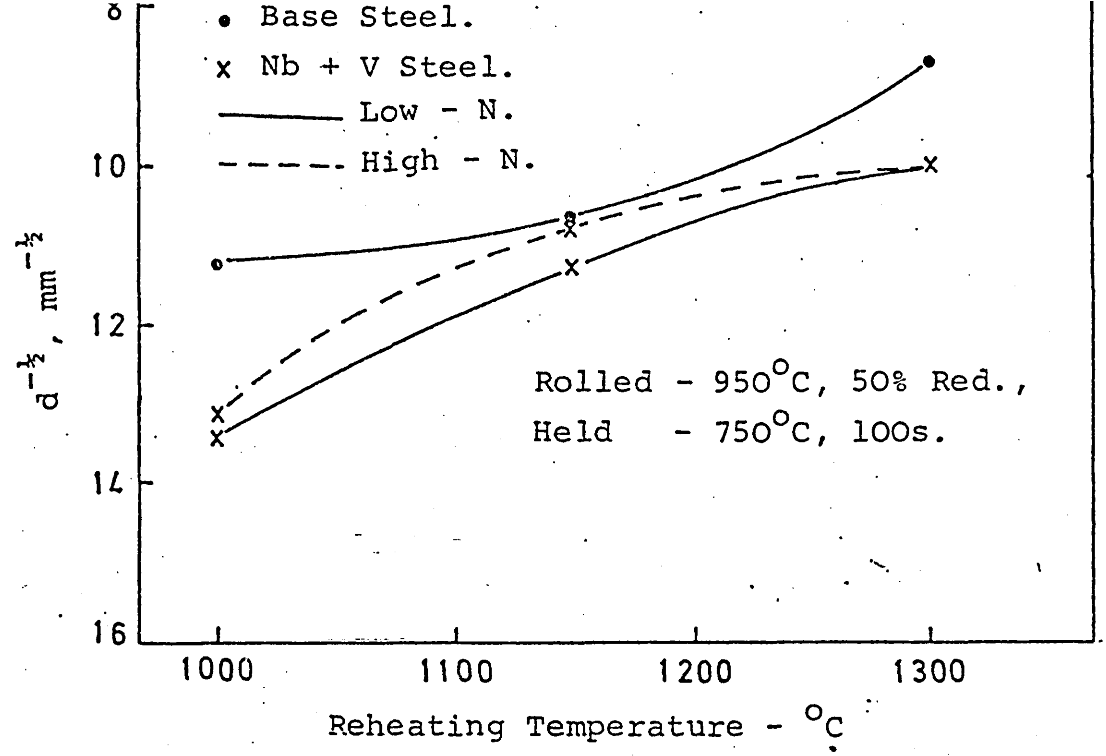


FIG. 129 EFFECT OF REHEATING TEMPERATURE ON FERRITE GRAIN SIZE.

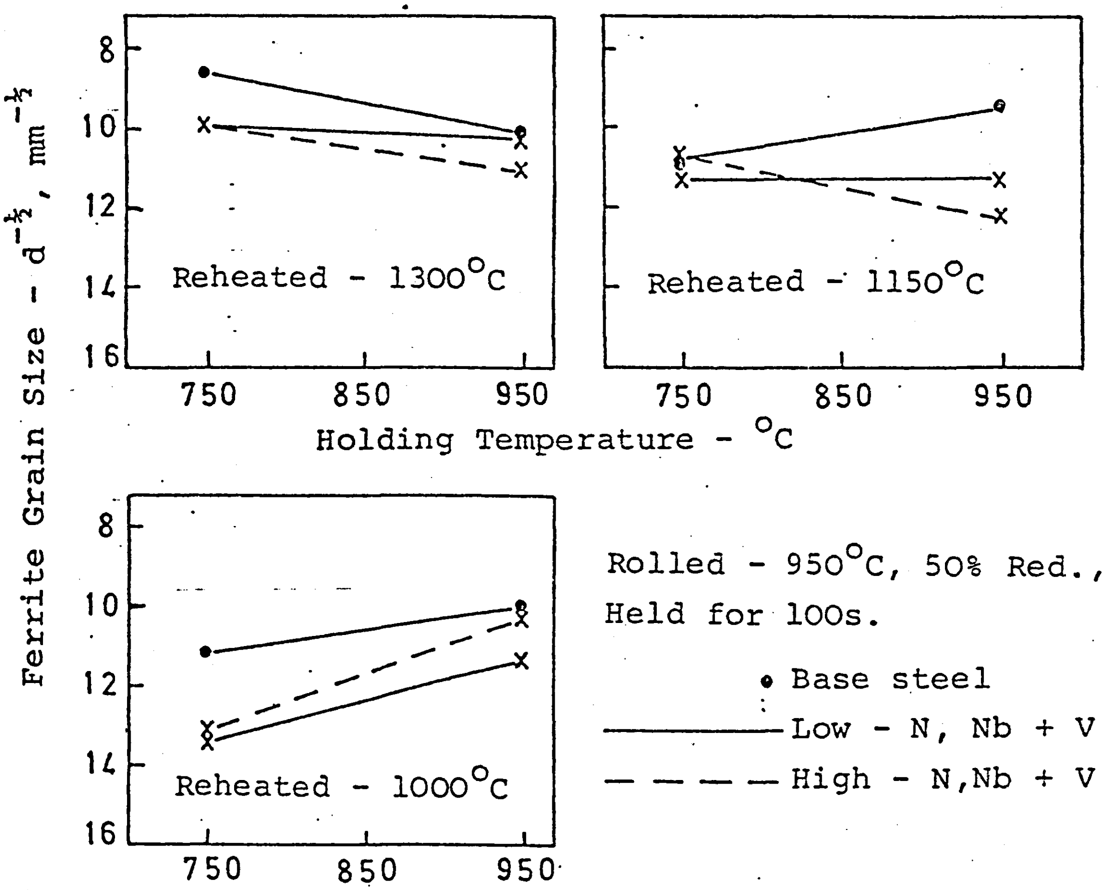


FIG. 130 EFFECT OF HOLDING TEMPERATURE ON FERRITE GRAIN SIZE.

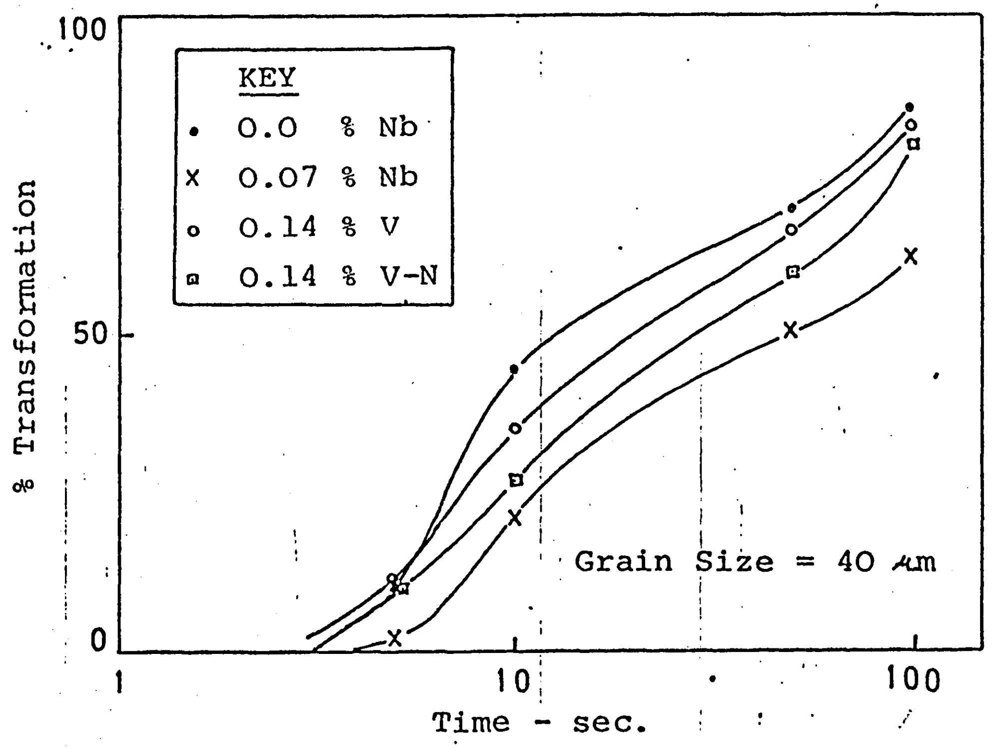


FIG. 131 KINETICS OF TRANSFORMATION AT 700°C FOR CONSTANT AUSTENITE GRAIN SIZE IN VARIOUS STEELS.

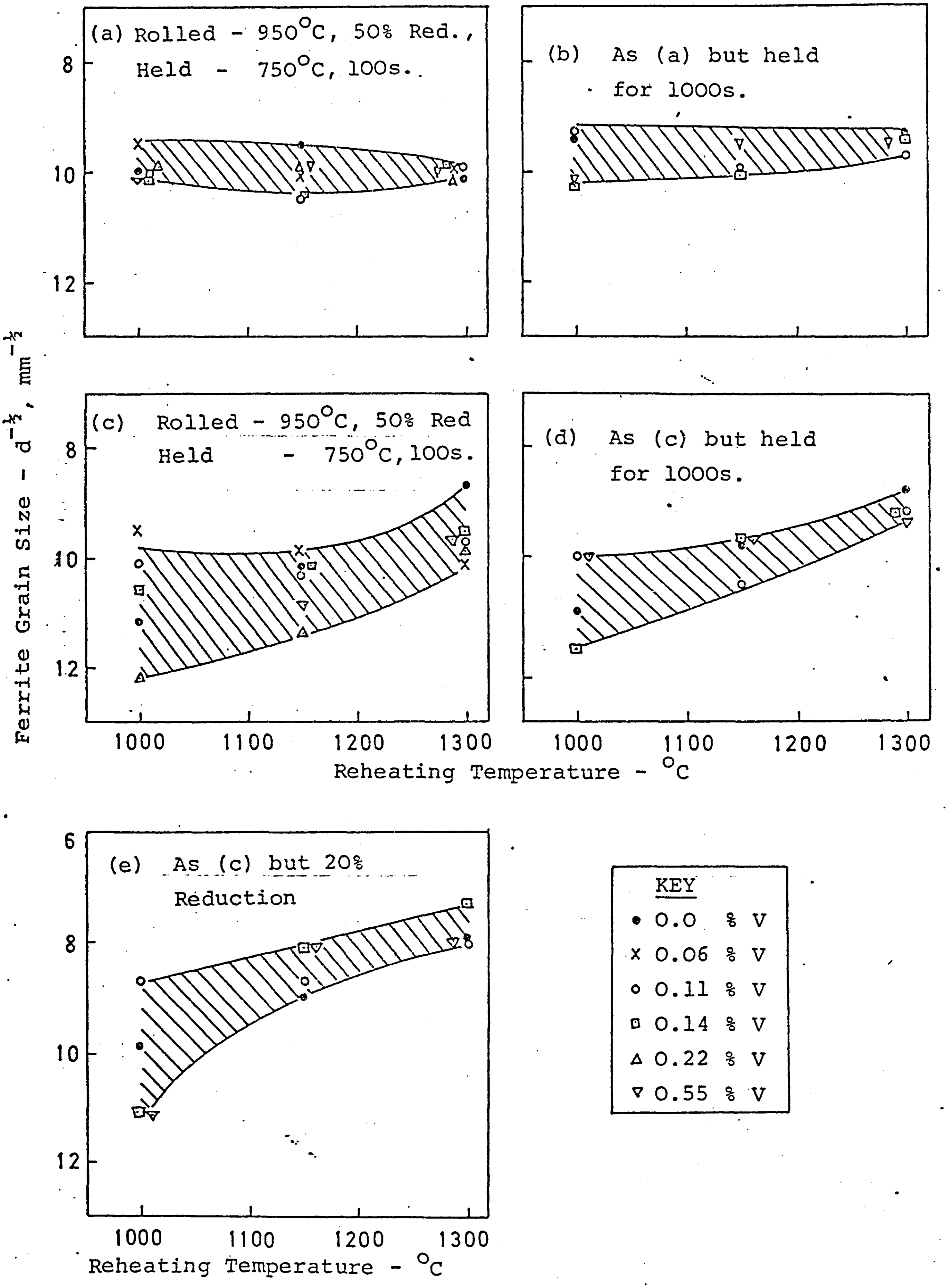


FIG. 132 EFFECT OF REHEATING TEMPERATURE ON FERRITE GRAIN SIZE.

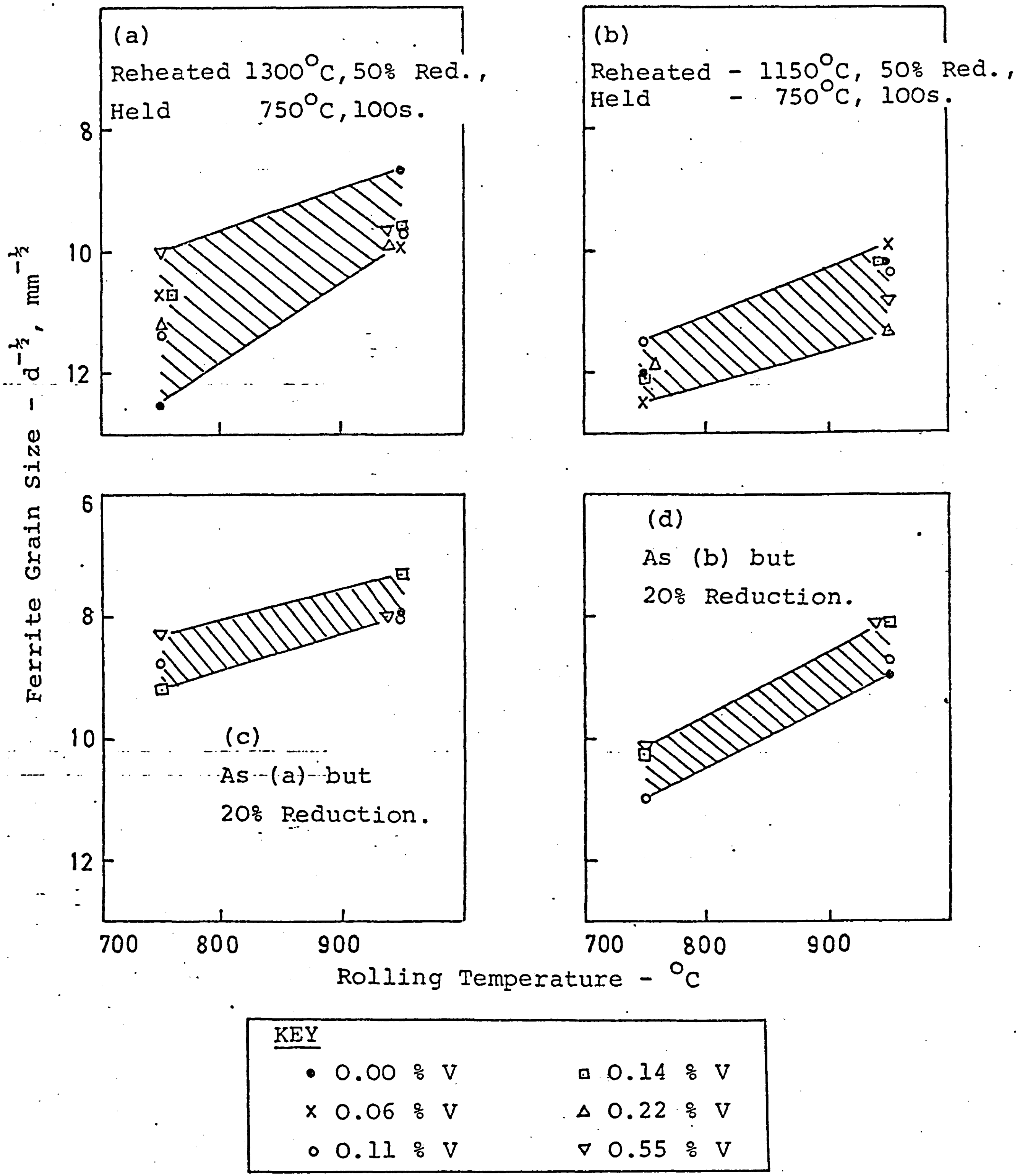


FIG. 133 EFFECT OF ROLLING TEMPERATURE ON FERRITE GRAIN SIZE.

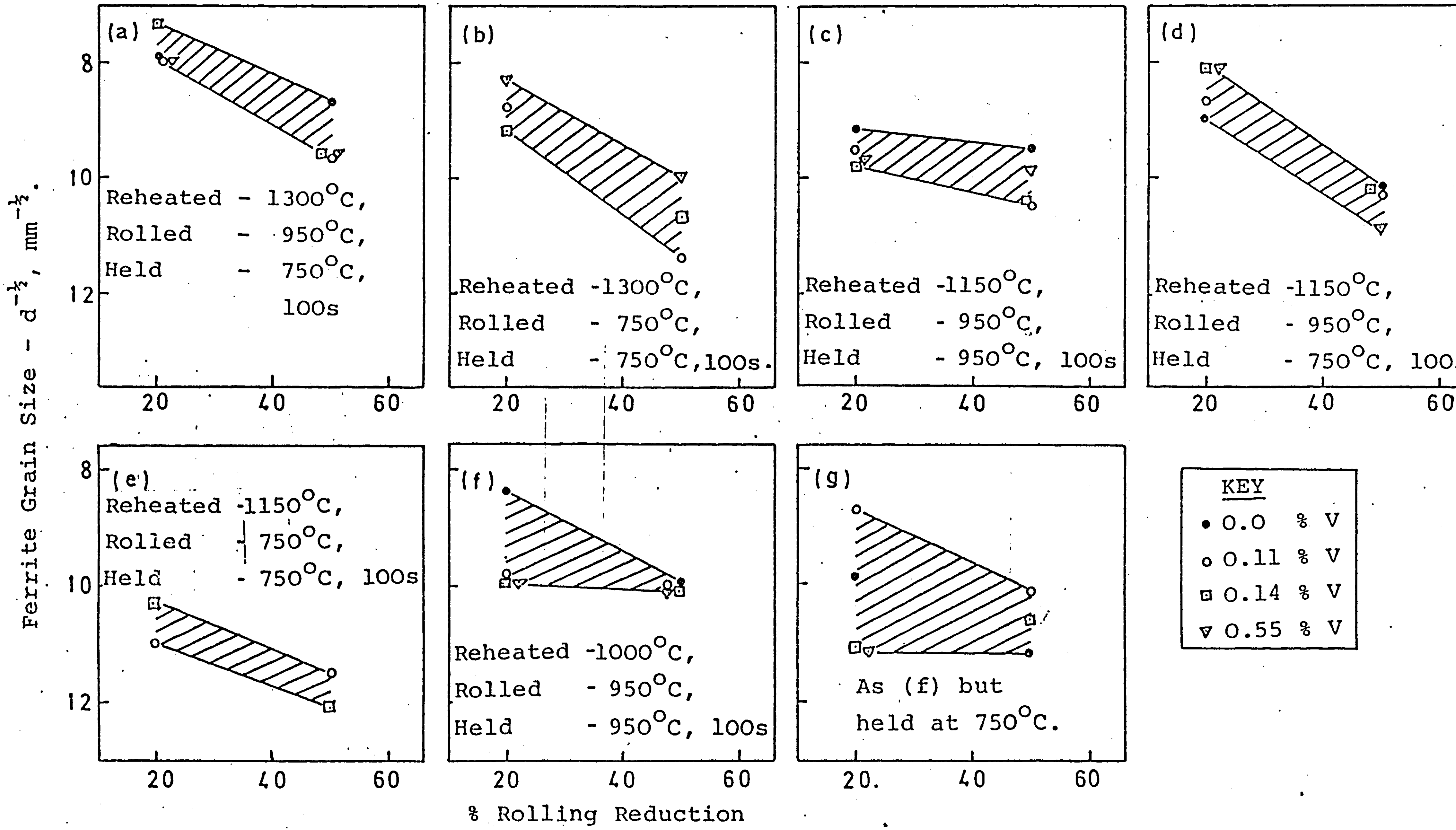


FIG. 134 EFFECT OF ROLLING REDUCTION ON FERRITE GRAIN SIZE.

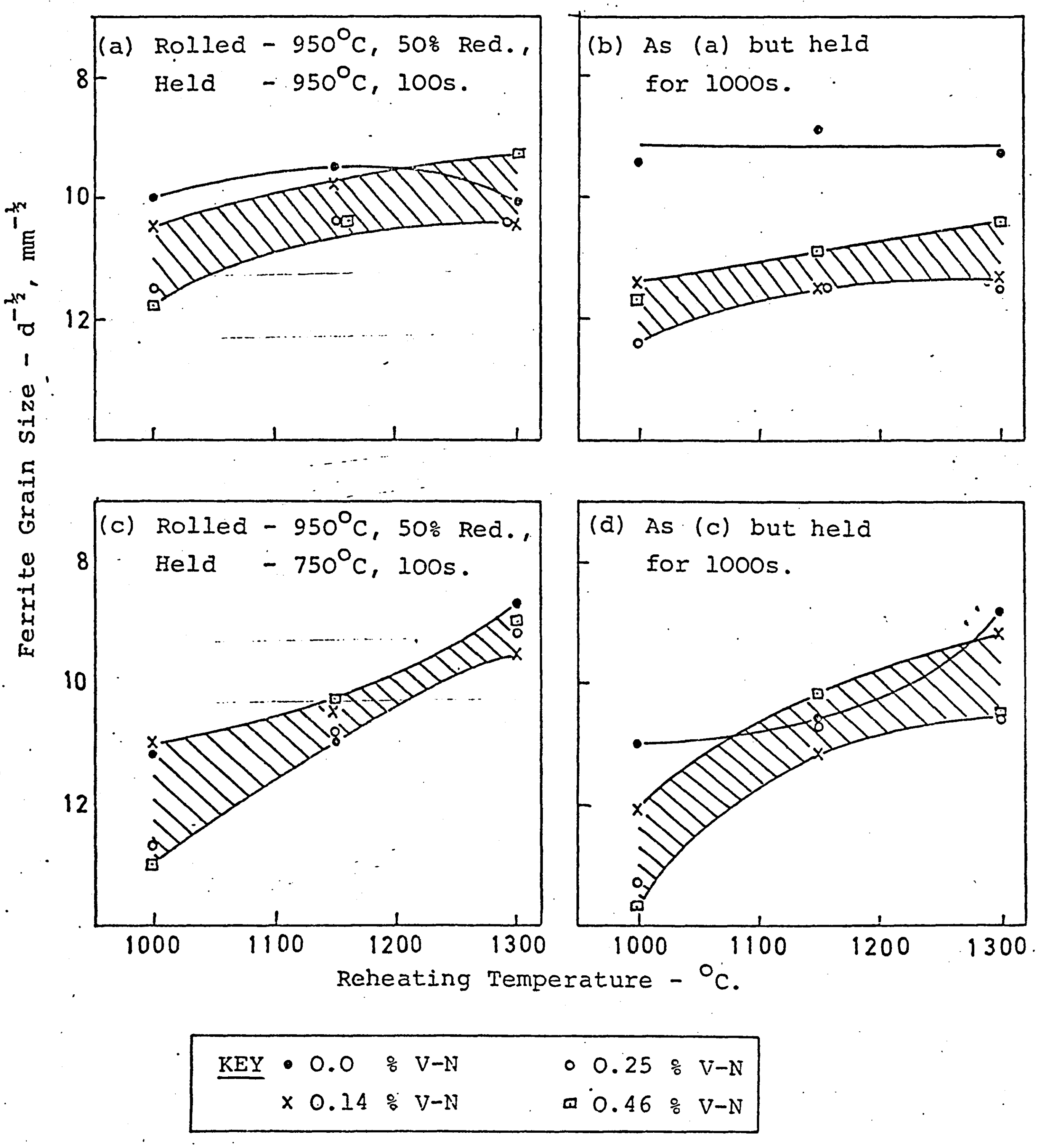


FIG. 135 EFFECT OF REHEATING TEMPERATURE ON FERRITE GRAIN SIZE.

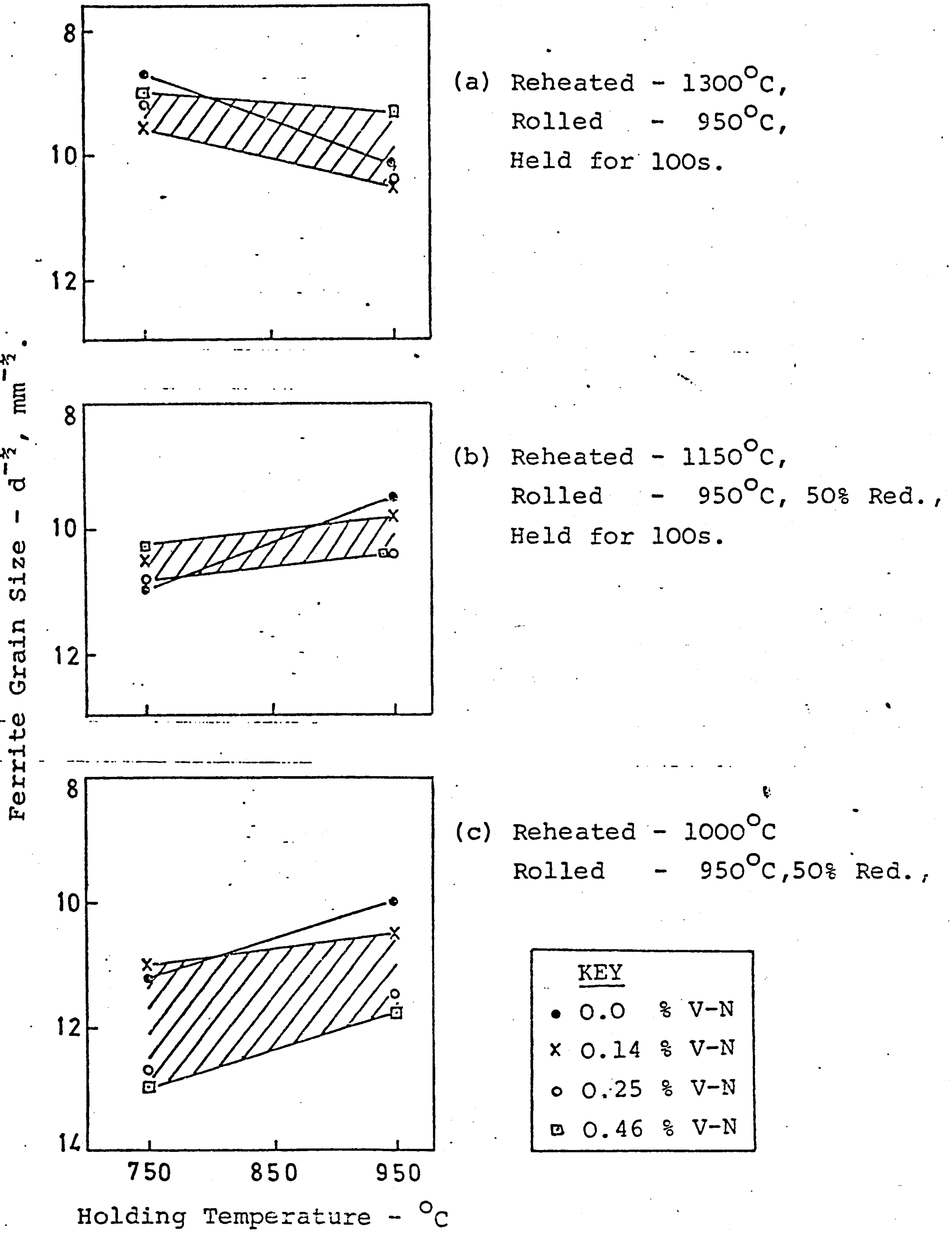


FIG. 136 EFFECT OF HOLDING TEMPERATURES ON FERRITE GRAIN SIZE.

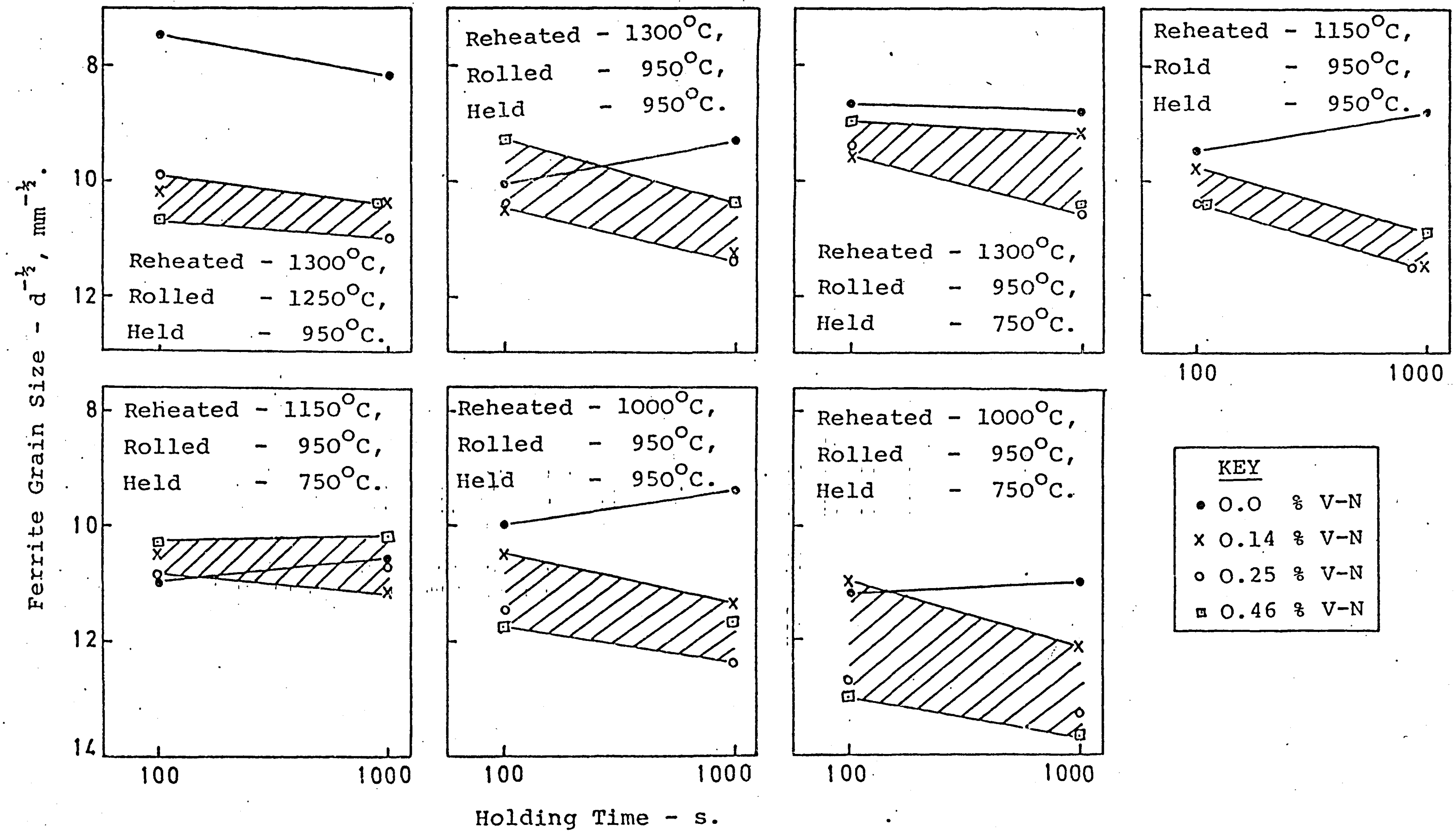
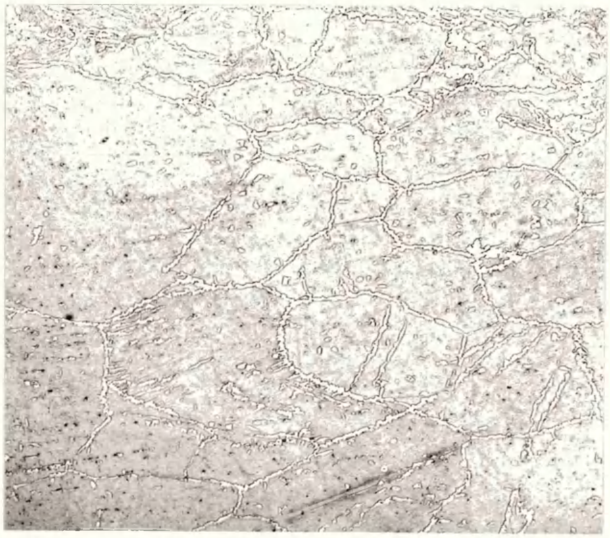


FIG. 137 EFFECT OF HOLDING TIME ON FERRITE GRAIN SIZE.

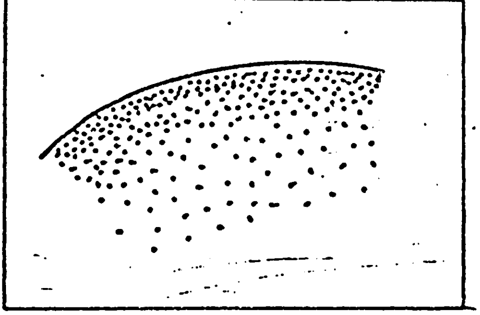
FIG. 138 NUCLEATION OF FERRITE ON SECOND-PHASE PARTICLES.



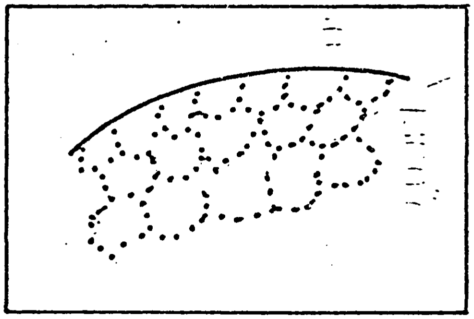
0.22 % V.
Reheated-1300°C,
Rolled - 950°C,
20 % Reduction,
Quenched.

X40

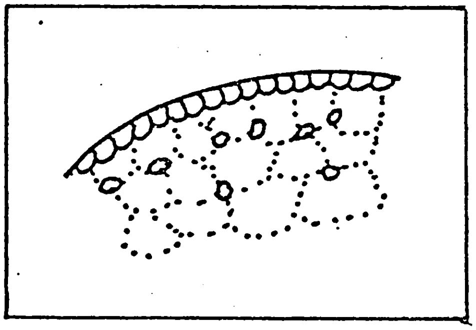
FIG. 139 FERRITE NUCLEATION ON AUSTENITE GRAIN BOUNDARIES, DEFORMATION BANDS AND SUBSTRUCTURE.



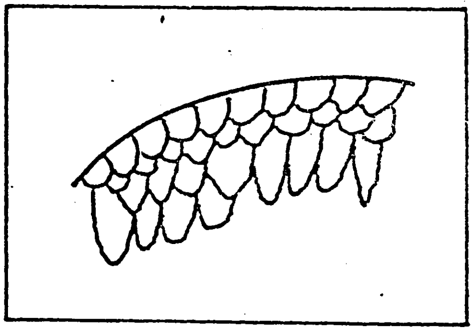
(a) After deformation the strain gradient at the austenite grain boundary develops i.e. there is a high dislocation density near the austenite grain boundary.



(b) Formation of sub-grains occurs, and precipitation of Nb(C,N) occurs on sub-grain boundaries.



(c) Ferrite first nucleates at the austenite grain boundary and this ferrite grains grow until it reaches the nearest sub boundary where the pinning effect of Nb(C,N) precipitates inhibits further growth. Also new ferrite grains nucleates at the sub-boundaries.



(d) Some distance away from the deformed austenite grain boundaries, there are no well defined sub grains and therefore no ferrite nucleation. Thus transformation occurs by continued growth of the ferrite into the austenite resulting in coarse columnar ferrite grains.

FIG. 140 MECHANISMS OF MULTIPLE FERRITE NUCLEATION AT AN AUSTENITE GRAIN BOUNDARY IN THE DEFORMED AUSTENITE.

0.14 % V.

Reheated-1300°C,
Rolled - 950°C,
50 % Reduction,
Quenched.

X40

0.55 % V.

Same as (a) but
20 % Reduction.

X40

FIG. 141 VARIATION OF STRAIN IN THROUGH THICKNESS DIRECTION.

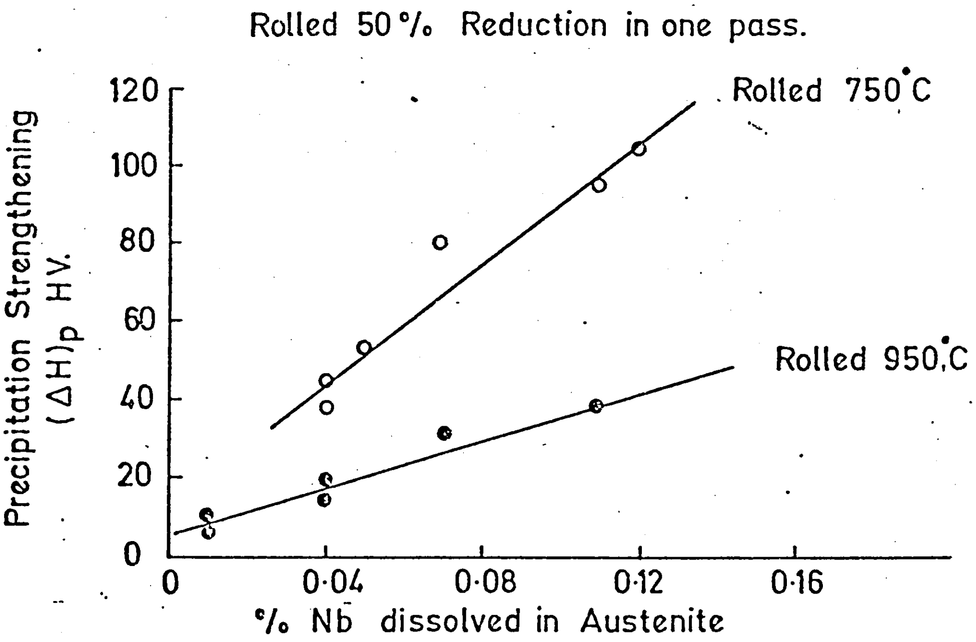


FIG. 142 EFFECT OF Nb DISSOLVED IN AUSTENITE ON $(\Delta H)_p$

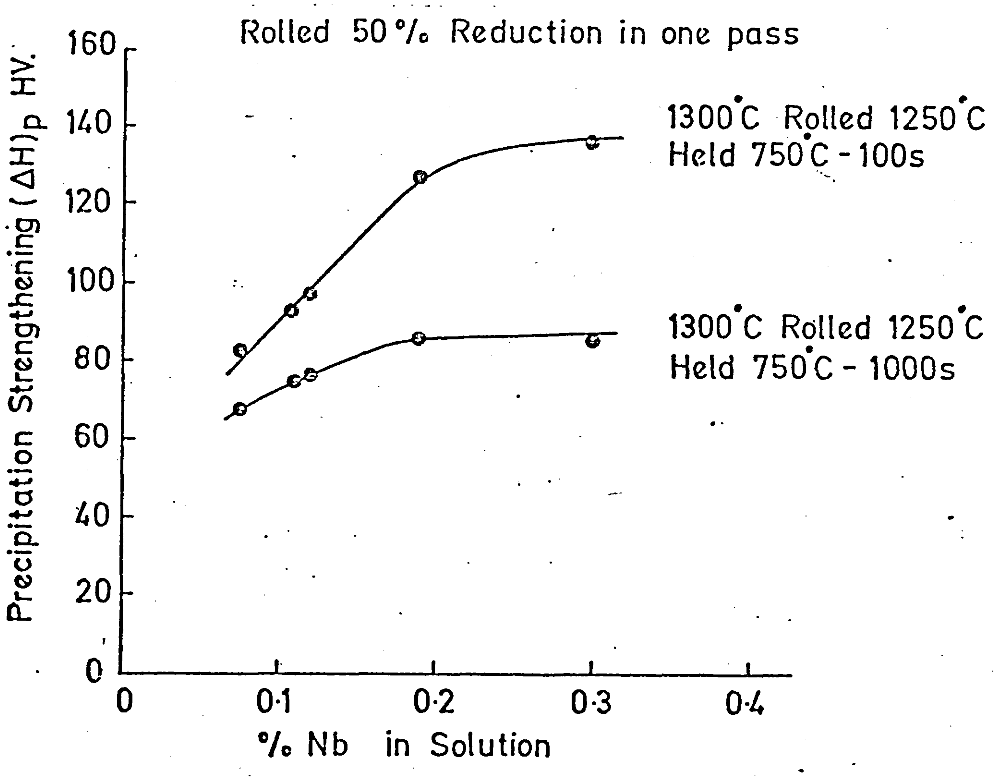


FIG. 143 EFFECTS OF Nb IN SOLUTION ON $(\Delta H)_p$

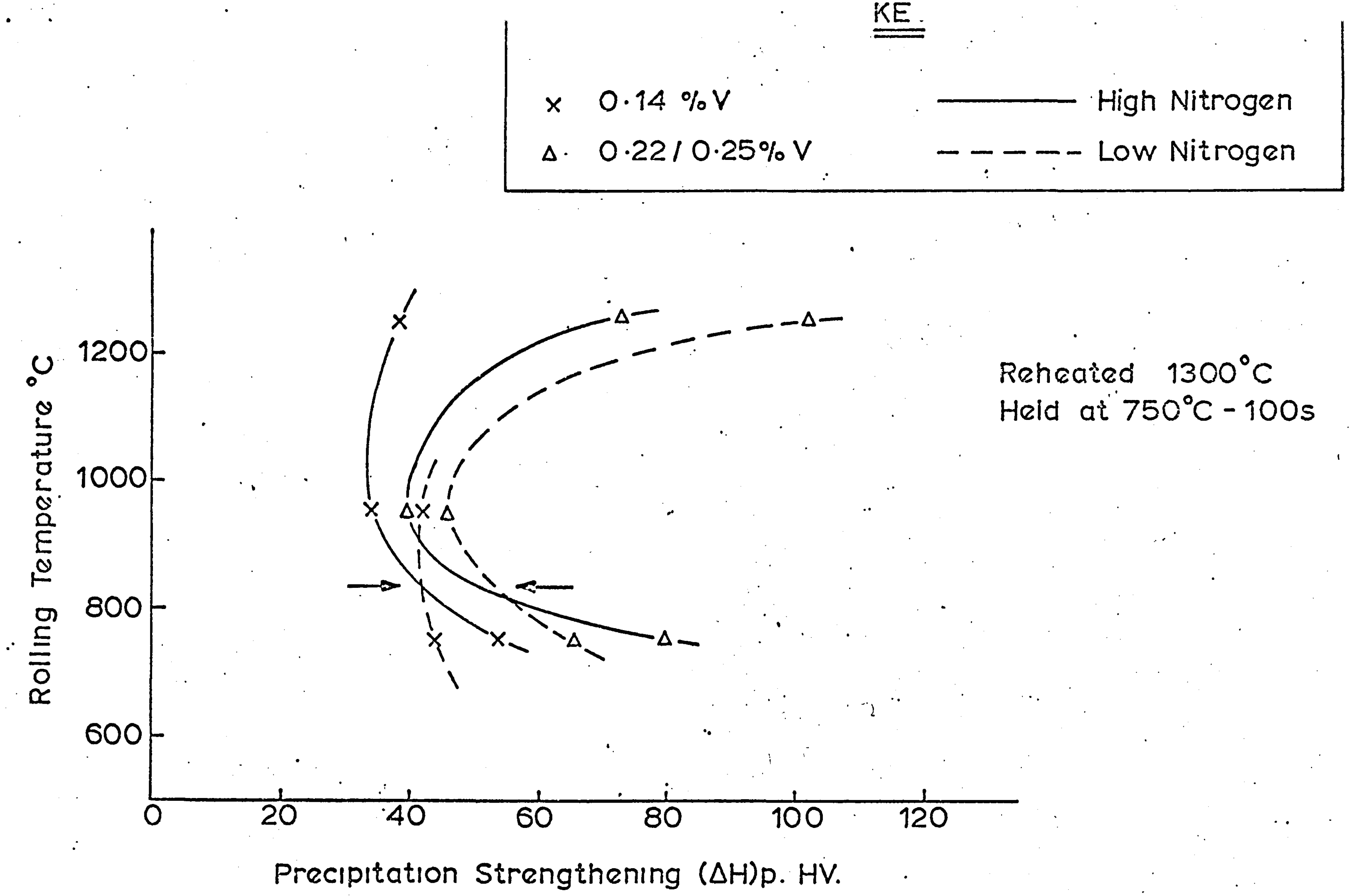


FIG. 144 COMPARISION OF EFFECT OF ROLLING TEMPERATURE ON PRECIPITATION STRENGTHENING IN HIGH AND LOW NITROGEN STEELS CONTAINING 0·14% AND 0·22/0·25%V.

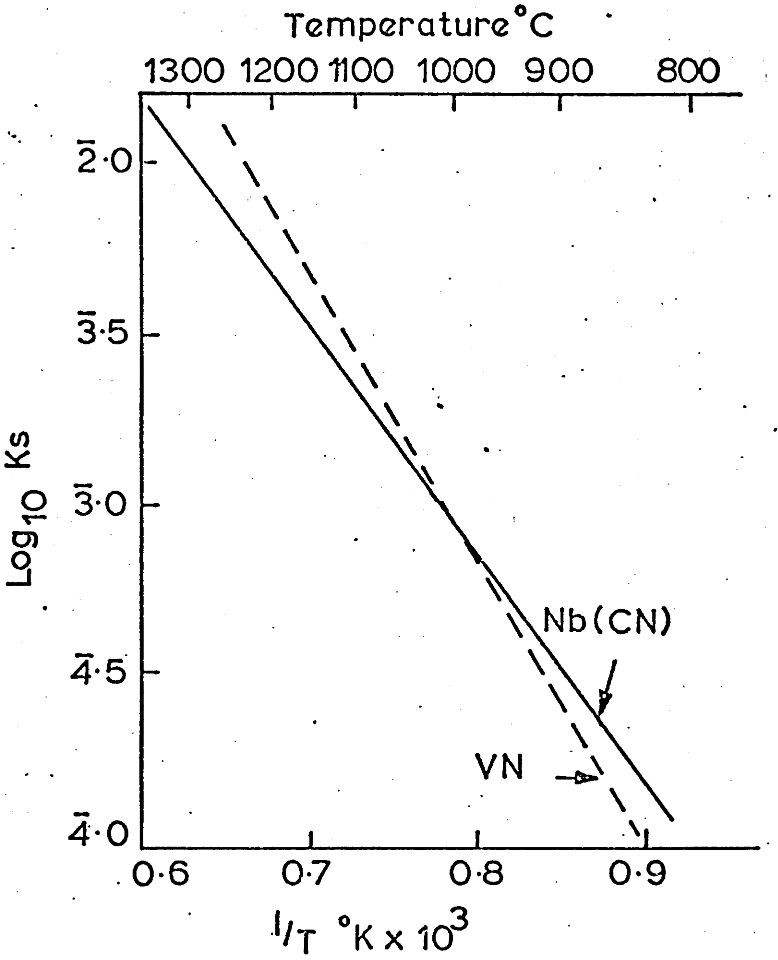


FIG.145 SOLUBILITY PRODUCTS (Ks) FOR Nb (CN) AND VN IN AUSTENITE

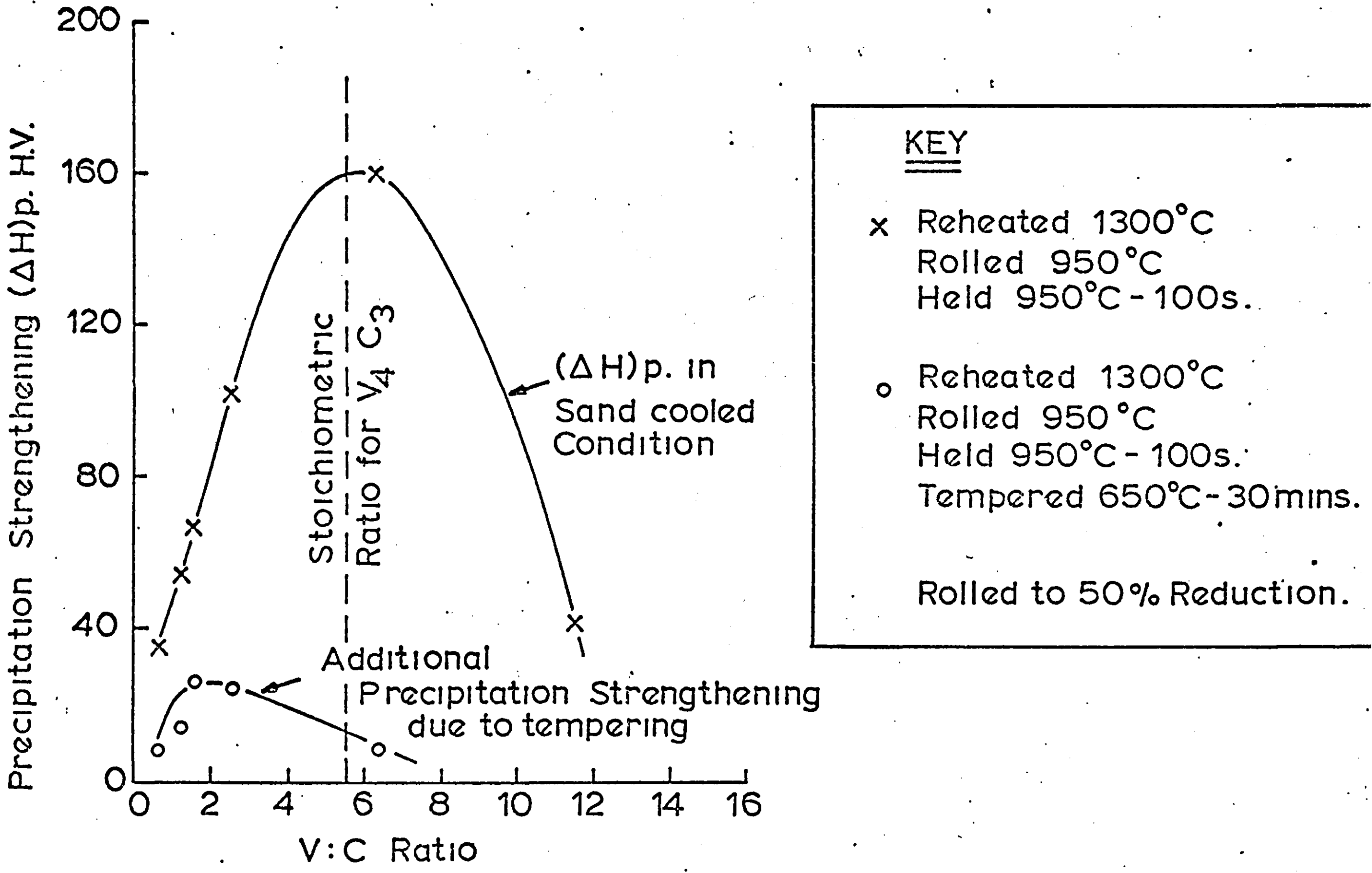


FIG. 146 THE EFFECT OF TEMPERING ON THE PRECIPITATION STRENGTHENING DUE TO PRECIPITATION FROM FERRITE.

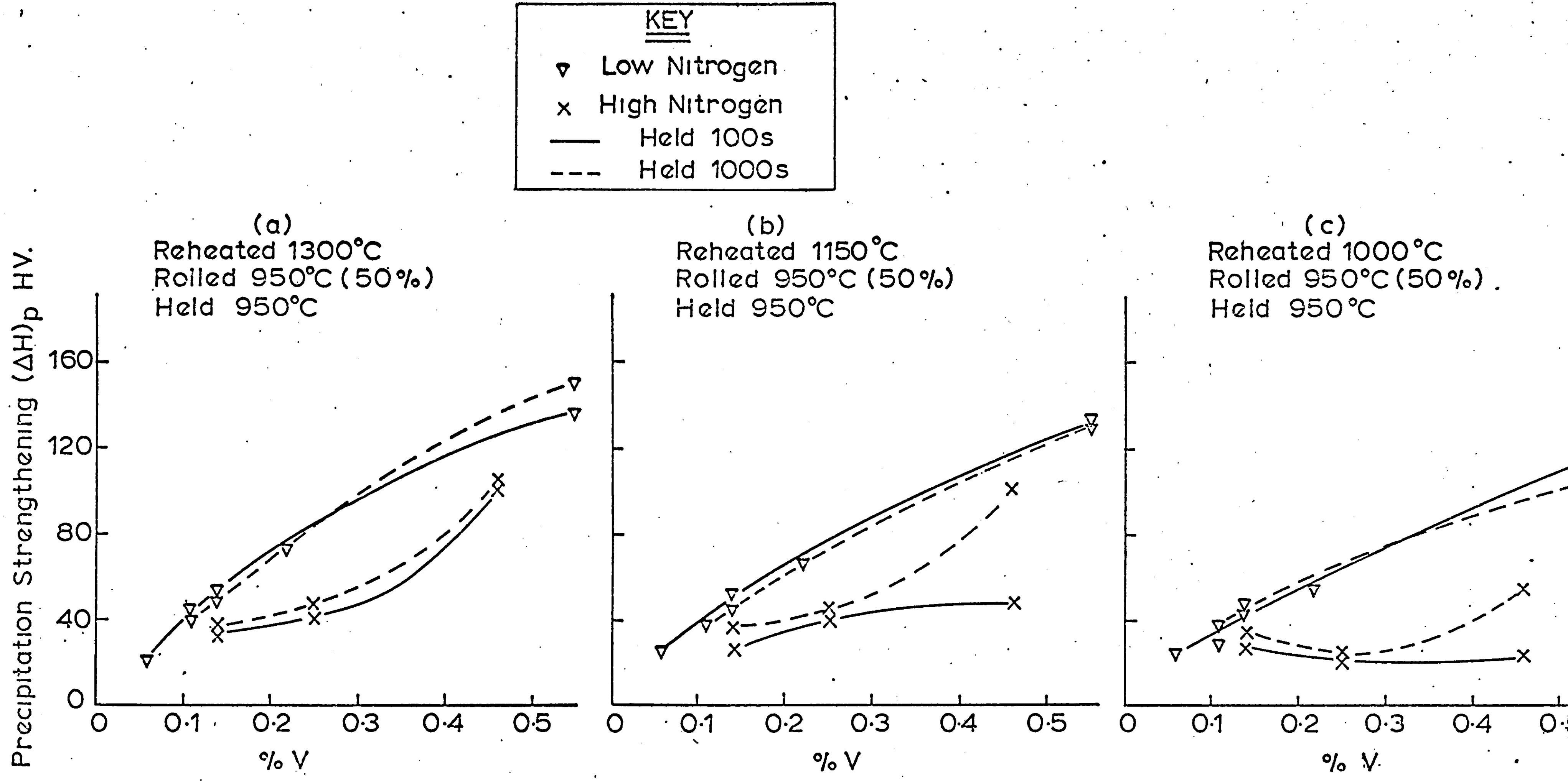


FIG. 147 THE EFFECT OF VANADIUM IN LOW AND HIGH NITROGEN STEELS ON PRECIPITATION STRENGTHENING.

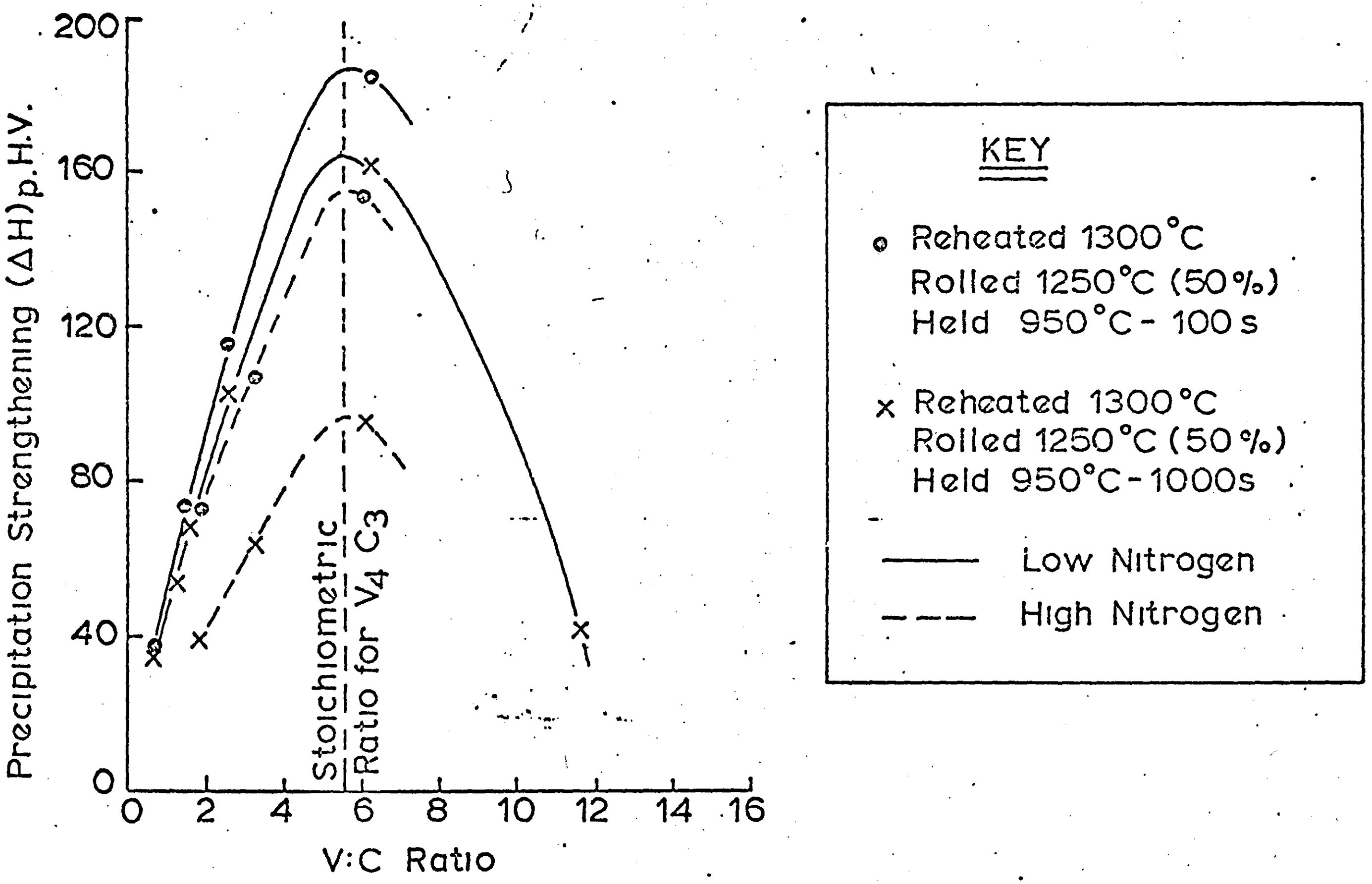


FIG. 148 THE EFFECT OF VANADIUM: CARBON RATIO ON PRECIPITATION STRENGTHENING IN LOW AND HIGH NITROGEN STEELS.

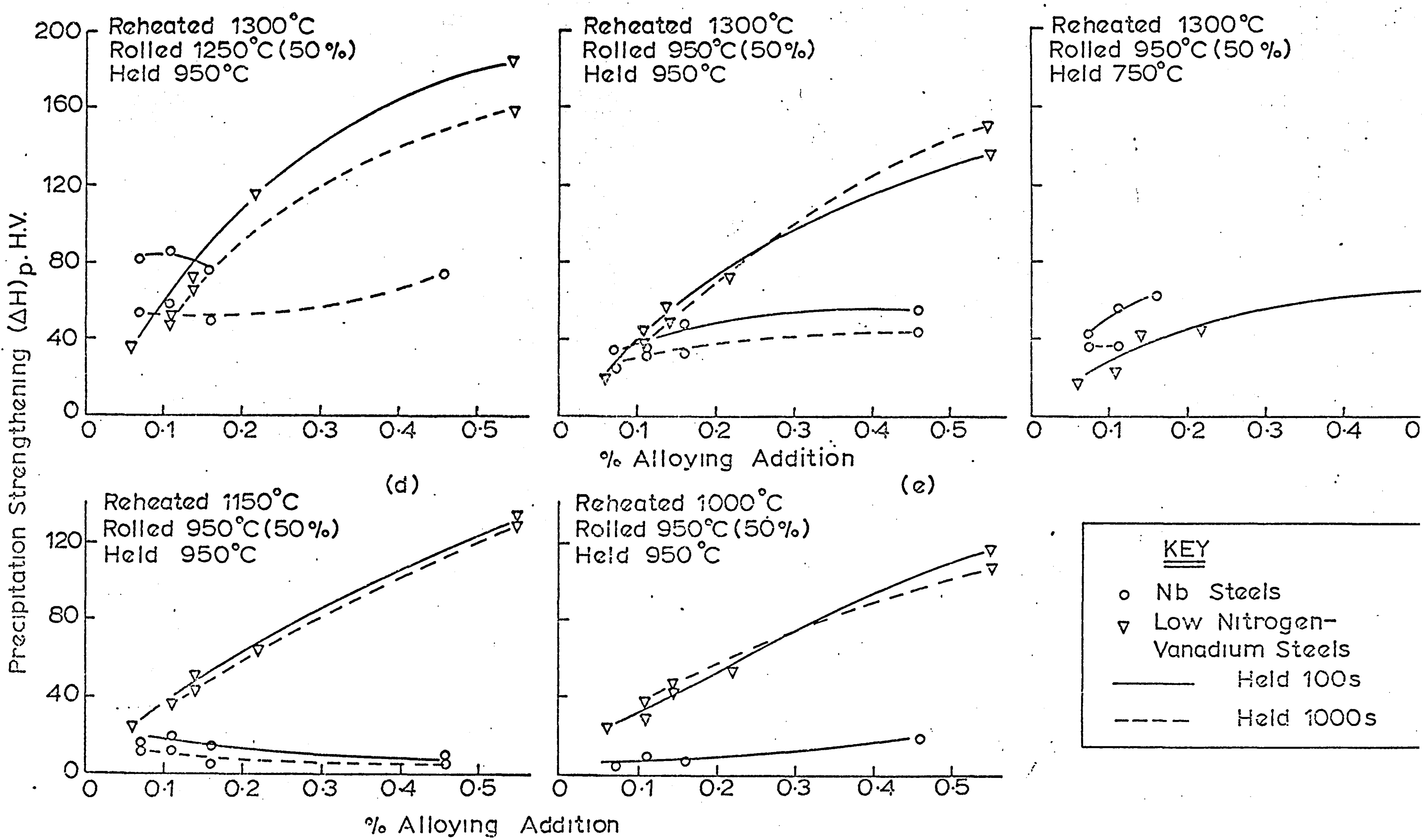


FIG. 149 COMPARISON OF EFFECTS OF NIOBIUM AND VANADIUM ON PRECIPITATION STRENGTHENING IN LOW NITROGEN STEELS.