Influence of environment on intergranular fracture of 18/8 niobium stabilised stainless steel.

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INFLUENCE OF ENVIRONMENT ON INTERGRANULAR FRACTURE
OF
18/8 NIOBIUM STABILISED STAINLESS STEEL.

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PREFACE.

This dissertation is submitted for the degree of Doctor of Philosophy of the Council for National Academic Awards.

The research was carried out during the period from October 1965 to October 1968 in the Department of Metallurgy, College of Technology, Sheffield, under the supervision of Dr. P. L. James, to whom I would like to express my gratitude for his encouragement, and for many fruitful discussions.

I should also like to thank Mr. D. Thacker, B.Sc., for his continued interest in this work and for making available facilities for research at the Department of Metallurgy.

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My thanks are due to Sheffield Education Committee for the award of a Research Assistantship covering the period in which this work was carried out.

During the period in which this work was carried out the author attended post-graduate courses on:

1. Electron Metallography.
2. Fracture.

and 3. Statistical Analysis.

The results obtained and the theories developed are, to the best of my knowledge, original except where reference is made to work of others.

No part of this dissertation has been submitted for a degree at any other college or university.

[redacted]

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INTRODUCTION.

This dissertation describes some experimental work carried out to investigate the influence of the external environment on intergranular cavitation in 18/8 niobium stabilised stainless steel. Most of the results described have been obtained by optical microscopy of electro-polished specimens after creep.

One of the basic problems of high temperature alloy development and a restriction on the use of many existing alloys and metals, is the formation of intergranular cavities when the material is subjected to high temperatures and low stresses. Cavities formed under such conditions tend to act as crack nuclei and hence initiate failure. This fact reduces the maximum safe working temperature of materials, which, if it were not for cavity formation could be used at considerably higher temperatures.

During investigations of intergranular cavitation in metals and alloys a number of workers have observed that the external environment has some influence on the mechanical and cavitation behaviour of the material. This could be of great importance in many industrial applications, for example, the petro-chemical and power generation industries where economics and design require metals and alloys to operate at increasingly higher temperatures and pressures in complex, and often corrosive environments.

In order to determine the influence of environment on cavity nucleation and growth in an 18/8 niobium stabilised stainless steel the form of the creep curves, microstructures, and cavity morphologies formed on subjecting the steel to test environments of air, argon, and vacuum have been examined. The micro-structural features of the test specimens, particularly the nature and magnitude of the r-type cavitation, have been related to the difference observed in the creep curve in the different environments. To obtain a quantitative measure of cavitation comparisons have been made of size and number of r-type cavities across the section of specimen.

One of the main features of cavitation in the alloy is the presence of a variation in cavitation degree with position in the cross-section in specimens tested in air, but not in specimens tested either in an argon or a vacuum environment.

Existing theories of cavity nucleation and growth have been examined and modified to account for this observation. The variation in cavitation degree in specimens tested in air is explained, in this hypothesis, by modification of the grain-boundary energy by gaseous diffusion.

A short discussion will be given at the end of each chapter so that a degree of continuity may be maintained between the chapters. A general discussion will be given at the end of the dissertation.

Chapter 1.

PREVIOUS WORK.

Of the various structural features which influence the properties of metals the grain-boundary is one which has been studied in great detail, but it is still the least well understood. In particular, its importance in creep has been appreciated since Rosenhain and Ewen[1] demonstrated grain-boundary off-sets on the surfaces of several metals after deformation at elevated temperatures, but as yet many unresolved problems exist in this field alone. Since this observation many experiments have been performed to eradicate this deficiency of information. Much of this work has been reported in reviews by McLean,[2] Gifkins,[3] Garafalo,[4] and Grant and Mullendore,[5] consequently this literature review will be limited to a brief review of tertiary creep and factors affecting it, and a more extensive review of creep fracture, mechanisms and theories.

1. 1. TERTIARY CREEP.

To discuss tertiary creep it is first necessary to define the phenomenon that constitutes tertiary creep. Figure 1. illustrates the ideal creep curve of the ideal metal. This may be sub-divided into primary creep where $\dot{\varepsilon} \propto t^{-n}$, secondary or steady-state creep where $\dot{\varepsilon} \propto t$, and tertiary creep where $\dot{\varepsilon} \propto t^{n}$. The exact location of the beginning of the tertiary creep period depends on whether a constant stress or a constant load test is being performed. In the latter test structural changes are continually taking place due to the continually changing stress system. The literature enumerates three basic reasons for the existence of the tertiary creep period, these being:

(a) Uniform reduction of cross-sectional area in the constant load test resulting in an increase in stress which exceeds the concurrent strengthening by work-hardening.

(b) Non-uniform reduction of the cross-sectional area by localised necking or intergranular cavitation.

(c) Work softening by simultaneous recovery allowing a greater degree of deformation.

The increasing creep rate during tertiary creep is associated by most authors with mechanism (b) that is localised cracking or cavitation resulting in increased stresses. However, deformation during tertiary creep is not entirely intergranular in the form of cavitation but also occurs in a transgranular manner in the form of grain-boundary sliding, grain-boundary migration and fold formation. Hence, even in the absence of such complicating factors as recrystallisation, precipitation or resolution of second-phase particles, tertiary creep remains a complex phenomenon. It is not surprising therefore that the basic knowledge of tertiary creep is increasing at a very slow rate.

1. 2. DEFORMATION DURING TERTIARY CREEP.

Tertiary creep deformation may be sub-divided into true intergranular deformation, namely cavitation, and pseudo-transgranular deformation. The latter term has been employed to differentiate between true transgranular deformation, for example slip, and deformation processes which are partially intergranular in nature. It is intended that this section of the literature review be devoted to the latter form of deformation, namely grain-boundary sliding, grain-boundary migration, and fold formation. Since the main topic of this review is creep cavitation, reference to this form of deformation will not be made at this point except where necessary for clarity.

1.2. 1. Grain-boundary Sliding.

Grain-boundary sliding may be defined as the translation of a pair of grains by a shear movement at their common interface. This definition includes cases where the shear takes place in a zone of finite width around the boundary, and cases in which it is confined completely to the interface. Sliding becomes important as a mode of deformation at temperatures above 0.45 Tm where it is believed to play an important part in promoting intergranular weakness common in metals at such temperatures. Many of the investigations into the problem of grain-boundary sliding during creep deformation have been summarised in reviews by Gifkins[5], Sully[6], and Stevens[7], and hence the subject will be dealt with only briefly in this review.

Quantitative measurements of grain-boundary sliding in metals have followed three main courses:

(1) Internal friction measurements on polycrystalline metals and alloys,

(2) Measurement of displacements and structural changes in a single grain-boundary, and

(3) Determination of the contribution of sliding to the overall creep deformation of polycrystalline metals.

It is intended to review all three type of experiments at this point, but attention will be given mainly to investigations of types (2) and (3).

1.2. 1.1. Internal Friction Measurements.

Kê[8,9] noted during investigations into internal friction by means of a torsion pendulum that polycrystalline materials exhibited a maximum in the curve of damping time against temperature, for a given frequency of oscillation, whereas no such maximum was observed when single crystals were tested. This, he proposed, was due to the presence of grain-boundaries and suggested that the peak was due to anelastic deformation in the boundaries by viscous sliding. The concept of anelastic deformation and viscous sliding allows some of the observed phenomena to be understood qualitatively, but quantitatively the agreement is poor and, as Leak[10] pointed out, there are many observations which cannot be explained by this concept.

1.2. 1.2. Sliding in Bicrystals.

Considerable controversy has arisen from bicrystal experiments as to the existence of true grain-boundary sliding, that is sliding at the grain interface without transgranular deformation. Rhines et al[11], and Voloshina et al[12] have assembled a considerable volume of evidence to prove that sliding takes place in a zone of finite width around the boundary. From this and other observations they inferred that transgranular deformation was pre-requisite to sliding. However, a number of investigators[13-16] have reported sliding in bicrystals without the development of a shear zone of finite width. Intrater et al[15] propose that the shear zone observed by Rhines et al[11] was a consequence of transgranular deformation to maintain specimen geometry and not as a result of, or a pre-requisite of sliding.

A number of investigators[12,16-19] have reported migration of the boundary during sliding experiments. This has taken the form of alternate periods of sliding and migration resulting in short stepped fiducial lines or as concurrent processes resulting in curved fiducial lines.

Observation of the displacement of a sliding boundary has shown it to be a cyclic process which may take one of several forms, a number of which are illustrated schematically in figure 2. The overall sliding rate is found to follow a relation of the form, $\rho = \beta t^{\alpha}$
where p is the displacement observed in the time t, and α and β are constants, α and β are found to vary considerably with specimen geometry, misorientation angle of the bicrystals, and other structural features.

The effect of temperature and stress on the rate of sliding in bicrystals appears from the literature to be somewhat confused. For example, Puttick et al[20] found that the initial sliding rate in tin was proportional to the applied shear stress, Tung et al[14], on the other hand, found that in aluminium it was proportional to exp.($-\gamma_0/\gamma$), where γ_0 is constant and γ the applied shear stress. Similar behaviour was reported by Rhines et al[11]. The behaviour reported by Puttick et al[20] is similar to that observed in creep of single crystals and polycrystals at low stresses and temperatures approaching the melting point, indicating viscous behaviour. The observations of Tung et al and Rhines et al, on the other hand are typical of creep at high stress. It follows, therefore, that the zone shear type deformation observed by the latter investigators shows characteristics of transgranular creep. The general effect of increasing temperature appears to be to increase the rate of boundary sliding. This was clearly illustrated by Intrater et al[21] who observed that the sliding rate in copper bicrystals increased with increasing temperature, whereas the activation energy for the process remained virtually unchanged. It may be concluded therefore, that in general the sliding rate in a bicrystal is increased either by increasing the temperature or decreasing the stress.

The misorientation angle between the active slip planes in the two crystals of the bicrystals is found to exert considerable influence on the rate of boundary sliding. Weinborg[13] found that the rate of sliding in tin bicrystals under constant conditions of temperature and stress increased linearily with increase in misorientation angle between 30° and 85°, below this level the behaviour was erratic. Turner[22], Harper[23] and Tung et al[14] reported similar behaviour in zinc[22], copper[23], and aluminium[14]. Rhines et al[11] demonstrated that the sliding rate depended on the relative orientation of the two crystals. They defined the angle between the operative slip directions in the active slip planes in each crystal as λ and the angle between the traces of the active slip planes at the boundary as ϕ. It was found that the sliding rate varied almost linearily with $(\lambda + \phi)$. Mullendore et al[24] found it to vary with sine $(\lambda + \phi)$.

1.2. 1.3. Grain Boundary Sliding in Polycrystalline Metals.

A much wider range of measurements have been employed to determine the degree of boundary displacement in polycrystalline metals. These have included measurement of the offset of fiducial lines on the specimen surface produced by boundary sliding, measurement of the vertical displacement of boundaries by means of interferometry and profile measuring devices. A statistical method of the analysis of grain shape has also been employed to obtain an indication of the contribution of sliding to the overall creep deformation. This technique has been subjected to considerable controversy as to its accuracy and has now been superseded in a number of cases by the inert internal marker technique. This is essentially the measurement of offsets of strings of oxide particles caused by boundary sliding.

In general the behaviour of a specific grain-boundary in a polycrystalline metal is similar to that observed in bicrystals in that:

(a) Initial sliding occurs in the immediate vicinity of the boundary, however with time and displacement this form of sliding is replaced by shear in a zone of finite width. The material within the zone usually shows evidence of grain-boundary migration and lattice distortion. Thus grain-boundaries in polycrystalline metals tend to exhibit boundary zone shear type sliding rather than ideal boundary sliding.

(b) Metals which readily polygonize show more intense subgrain formation in the vicinity of the boundary than elsewhere in the grain.

(c) The displacement-time curves for short sections of a boundary show cycles or oscillations of the form observed in bicrystals. However, the curve for a full boundary closely resembles the creep curve of the metal under the same conditions.

(d) Sliding is not uniform along the length of a boundary. This is more pronounced than in bicrystals because of the restraint imposed by grain boundary junctions.

The importance of grain-boundary sliding as a mode of deformation in creep of polycrystalline metals depends on its contribution to the total creep strain and on the inter-relationship between sliding and transgranular deformation. If, for example, sliding is dependent on transgranular deformation it may serve primarily as an accommodation and not a controlling process, but if it is independent of transgranular deformation it may be a controlling process.

The majority of grain-boundary displacement values reported in the literature take the form of ratio of displacement due to sliding (Egb)to the total creep strain (ε_t), $\varepsilon_{gb}/\varepsilon_t$, usually denoted λ. λ is found to be a constant dependent on stress, and to a lesser extent on temperature and grain size. The information available concerning the influence of these parameters on λ is very meagre. Results of work on a considerable number of metals show that λ tends to increase with temperature and/or decrease in stress. In the majority of cases it was found that the activation energy for sliding and creep were of the same order indicating that the controlling mechanism may be the same in both cases. Alteration of either the grain size or the composition appears from the information available to effect. λ in a similar manner as the effect on creep deformation, for example, the increase in grain size decreases both λ and the creep rate.

Several observations have indicated that there is some form of relationship between sliding and transgranular deformation. In general, an alteration in sliding rate is accompanied by a corresponding change in the creep rate such that λ remained constant. Intrater et al[21], however, have pointed out that these observations were made on boundaries that were undergoing zone-shear type sliding and not true sliding which they have shown to be independent of transgranular deformation. Ideal sliding is thought to occur in polycrystalline metals only during the very early stages of creep, being transformed into zone-shear type sliding after the initial displacement. This results in a deformation zone of finite width around the boundary which exhibits non-uniform lattice distortion and intense subgrain formation. The latter has been associated by a number of workers with grain-boundary migration which is thought to take place during the periods of null displacement of the boundary.

1.2. 1.4. Theories of Grain-Boundary Sliding.

Sliding experiments may be sub-divided into internal-friction experiments and measurement of macroscopic movements observed in bicrystals and polycrystals. Consequently theories of grain-boundary sliding fall into two groups; those which attempt to explain the anelastic phenomena and those which attempt to explain macroscopic sliding.

Kê[8,9] proposed that the anelastic behaviour observed in polycrystalline metals could be accounted for if a grain-boundary behaves as a viscous layer of a few atoms wide such that translation of two 'solid' grains on either side could occur by neighbouring atoms squeezing past one another. The activation energy for such a process would correspond to that for grain-boundary diffusion. Mott[25] modified Kê's model and suggested that areas of good and bad fit existed in the boundary. The energy required for sliding was that required for atoms to pass the areas of good fit. Grussord et al[26] rejected both hypotheses for a number of reasons and presented a dislocation mechanism for sliding. It was proposed that a normal slip-dislocation ran into the boundary and split into a number of partials in the boundary plane. Sliding is considered to take place by movement of the partials parallel to the boundary plane. This theory has been criticised on a number of points most of which have been accounted for in modified versions postulated by Farmer et al,[27] Ishida et al,[28] and Li.[29]

Theories of macroscopic sliding may be divided into two basic groups; those in which boundary migration is considered to be the rate controlling parameter, and those in which transgranular slip is rate controlling.

Puttick et al[20] suggested that any irregularities in a grain-boundary would concentrate the stress produced by anelastic shear in the boundary. Relief of the stress by boundary migration would result in the creation of a relaxed area and a new irregularity. If a constant rate of creation and removal of the irregularities by boundary migration can be achieved a constant rate of boundary sliding can be maintained. Couling et al[30] suggested that macroscopic sliding is composed of numerous small anelastic shears of the Kê type which are rendered permanent by capture of the sheared area by boundary migration. On the basis of their activation energy measurements Intrater et al[21] proposed that in ideal boundary shear type sliding the rate controlling process is grain-boundary migration. They postulated that stress concentrations at irregularities were relieved by anelastic shear causing them to migrate thereby expanding the relaxed area. When the relaxed area reaches a critical size, fracture of tension-type 'jogs' and deformation of compression-type 'jogs' occurs to give a pulse of sliding. It was proposed that where zone-shear type sliding is prominent the rate controlling process is probably transgranular deformation.

Rhines et al[11] find no place in their model for sliding for boundary migration since they observed none in their experiments. It was proposed that the recovery mechanism was subgrain formation in a zone in each grain adjacent to the boundary and that sliding takes place by slip in the zones in a direction parallel to the boundary. It was suggested that the observed alternate periods of rapid sliding and null displacement are due to cyclic hardening by sliding and recovery by subgrain formation. Intrater et al[21] have criticised this mechanism on the grounds that Rhines et al[11] were measuring boundary zone-shear and not true boundary sliding. Weertman[31] also ascribed no role to anelastic sliding. He suggested that macroscopic sliding is a shear in the boundary region caused by dislocation movement along the grain-boundary by a combination of slip and climb. Modified, but essentially similar models of dislocation induced sliding have been proposed by several other workers[26,28,29].

A theory comprising a combination of the two basic macroscopic sliding theories has been proposed by King et al[32] and also by Fazon et al[33]. They suggest that anelastic sliding relaxes the shear stress in a boundary onto triple points and boundary irregularities, and that further shear is then controlled by deformation of these irregularities. There is a considerable amount of evidence to support this theory most of which has been summarised in a review by Stevens.[7]

1.2. 2. Grain-Boundary Migration.

Few detailed studies of the movement or migration of grain-boundaries during creep have been reported; the majority of information available being derived from observations made during investigations into other aspects of creep. In general it is considered that only low angled boundaries (less than 2°) and high angle boundaries (greater than 15°) show appreciable migration. The intermediate angles are thought to contain complex dislocation arrays which prevent their movement.

The literature enumerates four possible causes of grain-boundary migration during creep, these being:

(a) To minimise departure from equilibrium stress due to concentration at triple points; the driving force being the excess free energy created by sliding of the boundary.

(b) As a consequence of the formation of subgrains in a zone adjacent to the shearing boundary. The formation of an unequal density of subgrains on either side of the boundary would create a state of non-equilibrium thereby causing migration.

(c) As an attempt to reduce the lattice energy in a strained grain or subgrain, the driving force being the energy in excess of the equilibrium energy.

(d) As an attempt to reduce the excess surface free energy and attain equilibrium angles at the junction of these surfaces. However, since grain growth in creep has to take place into a strained region boundary migration cannot be likened exactly to conventional grain growth. Evidence also exists which indicates that the direction of migration is strain influenced; that is the rate of migration in the direction of the applied stress is greater than in a direction perpendicular to it.

Grain-boundary migration, regardless of its driving force, has one important effect. It is a recovery process and hence enables regions of grain adjacent to the boundary to undergo further deformation. Migration is a diffusion process which, since it is occuring under stress will be dependent on temperature and strain ~~stress~~ rate. Guard et al[34] have shown that the extent of boundary migration is also dependent on grain size and the time of test. The degree of prior deformation has also been reported as considerably influencing the extent of migration.[35] The extent and direction of migration of a boundary is not usually constant along the length of the boundary which eventually results in inhomogenous deformation both in the boundary and the grain.

1.2. 3. Fold Formation.

One cause of resistance to boundary sliding arises from the nature of the boundary itself. Grain-boundaries under equilibrium conditions are rarely planar, consequently the direction of movement of the boundary on sliding is unique at every point., The other sources of resistance to sliding in polycrystalline metals are grain-boundary junctures where a change of orientation exists across the boundary or triple point. Stress concentrations are developed at such points by sliding of the boundary and can only be relieved by plastic deformation in the grain. The deformation which takes place in the grains at triple points as a result of sliding has been termed a 'fold' by Chang and Grant.[36] This type of localised deformation was first reported by Betteridge et al[37] in tin-antimony alloys.

The appearance of a fold depends on the geometrical relationship and orientation of the grains and grain-boundaries involved. Furthermore, the resistence encountered to the initial process of stress accommodation is certain to bring into operation secondary modes of deformation. The overall direction of a fold trace on a surface of observation does not necessarily coincide with the grain-boundary trace, but the difference in angle between these is usually very small, being of the order of a few degrees.

In conclusion, it must be pointed out that although folds have been observed in a number of metals it is difficult to envisage such a mode of deformation contributing significantly to the overall creep deformation. It is particularly difficult to envisage such a deformation mechanism being operative, in the interior of polycrystalline metals where the restraining forces, particularly normal to the fold, are considerably higher. It is interesting to note that the metals and alloys in which fold formation has been reported, namely aluminium, tin-antimony alloy, zinc, and magnesium all readily form thin tenacious oxide films at the test temperature. The possibility exists that folds observed on the surface of such metals are a reflection in the oxide film of some other form of deformation.

1.5. FACTORS AFFECTING TERTIARY CREEP.

1.5. 1. Stress and Temperature Dependence.

Very little information is available in the literature concerning the relationship between stress and temperature and the rupture life of a metal or alloy. In general it is found that an increase in temperature and/or stress decreases the rupture life of the specimen. The relationship is found to be linear and of the form:

$$tr = A_0 \ \exp.\left(\frac{\Delta H_c}{RT}\right) \sigma^{-n}$$

where A_0 is a constant influenced slightly by large changes in temperature and stress. Deviation from linearity has been observed at very high temperatures and during constant load tests towards the end of the tertiary stage when the stress is increasing rapidly with time. Activation energies calculated from this relationship are found to be slightly higher than that for bulk diffusion of the base metal. Experimentally determined values, on the other hand, are considerably below those for bulk diffusion, but comparable with those for grain-boundary diffusion. This lead Hull et al[38] to suggest that grain-boundary diffusion of vacancies controls intergranular cavity growth during creep-rupture. However, the equation as stated above does not provide specific knowledge concerning the factors controlling creep nucleation or growth of cavities during creep. It does indicate, on the other hand, that nucleation and growth of cavities may depend in some manner on creep deformation. From a practical view-point such a relation could be utilised in predicting creep life values by extrapolation in stress and temperature. It is obvious that whilst such predictions are useful they cannot be accomplished reliably until specific information is obtained on the dependence of parameters A_0 H_0, and n on stress, temperature, and structural changes occurring during creep. Extreme care must be taken therefore in undertaking such extrapolations.

1.3. 2. Composition and Microstructural Dependence.

Rupture life, like primary and secondary creep, is very dependent on composition and microstructure; small alterations in either can exert considerable influence on the creep properties of many metals and alloys, particularly the complex commercial creep-resisting alloys. Over the past thirty years a large volume of data has been published on commercial materials, most of the results however, are not amenable to generalisations which lead to sound concepts of the effect of microstructure and composition on rupture life. Nevertheless, an attempt will be made to give some indication of the findings in this area of study.

Solid solution alloying has been shown to improve both the secondary creep rate and rupture life of many non-ferrous metals[38-41]. This is found to be most pronounced where considerable lattice distortion results from accommodation of the solute atom on the parent lattice. It is generally found in such alloys that close packed structures, f.c.c. or h.c.p., have greater creep-resistance and rupture strengths than less close-packed structures at temperatures above abount 0.4 T_m.

The majority of commercial alloys employed at high temperatures contain precipitates uniformly dispersed either in the grain-boundary or the matrix. The latter structure is found to impart good creep-resistance and rupture strength to the base metal. The factors which control fracture strength in these alloys have however received little attention. It is believed on the basis of the limited experimental evidence available that optimum creep properties are obtained when an alloy contains hard particles in a soft matrix with an interparticle spacing of less that five micron. The creep resistance of such alloys is unfortunately rapidly lost at high temperatures where resolution and agglomeration of the precipitates takes place. This problem has led to the development of sintered powder-dispersion alloys which exhibit considerably higher fracture strengths than the conventional precipitation hardened alloys. Grain-boundary precipitation in commercial alloys is considered to exert considerable influence on the creep rupture-life of the material. Sufficient results are not available, however, to determine quantitatively the effect of interparticle spacing on creep-life. It is generally accepted that a continuous precipitate or film or low melting point precipitate is detrimental to creep-life.

The published literature is devoid of any extensive work on the influence of grain size on creep-life. Garafalo et al[42] report that for stainless steel the influence of grain size on the secondary creep-rate and presumably the creep-life, depends on the test temperature. At low temperatures the secondary creep-rate increases with increasing grain size, leading to lower creep strengths. At intermediate temperatures the secondary creep-rate decreases to a minimum then increases again with increase in grain size. At high temperatures the secondary creep-rate is found to decrease with increase in grain size, leading to higher creep strengths in coarse-grained metals. Similar results have been reported by Shahinian et al[43] in monel.

1. 4. FRACTURE.

Fracture during creep may be of little importance if - as might be expected - the ductility of a metal increased with temperature. Unfortunately, generally the reverse is true; many metals exhibiting brittle behaviour at temperatures in excess of 0.5 Tm. It is often found that this embrittlement is associated with the formation of cracks and cavities on the grain-boundaries of the metal. Rosenhain[1] put forward the first rational explanation of this behaviour when he suggested the existence of an 'amorphous cement' between grains. Whilst this explanation is now discounted the actual mechanism by which grain-boundaries and their properties affect the creep fracture of metals is still not fully understood. Compared with the amount of work done on the early stages of high-temperature deformation preceding fracture, very little work of a fundamental nature has been carried out on the fracture mechanism.

1.4. 1. General Observations.

As indicated previously, polycrystalline metals may fracture either transgranularly or intergranularly depending on a number of variables. In general, low temperatures and high stress favour transgranular fracture whereas intergranular fracture is favoured by low stresses and high temperatures. The actual conditions initiating the change in fracture mode are very difficult to predict due mainly to the secondary influence of such factors as composition, grain size, micro-structure, and grain-boundary deformation.

Intergranular fracture is not an unique characteristic of all metals and alloys. Recent work by Gifkins[8], Servi et al[44], and Chang et al[17] has shown that in ultra-high purity metals trangranular failure occurs at all temperatures. It is proposed that this is due to there being little or no difference between the relative strengths of the grains and grain-boundaries in metals of such purity. On the other hand, ultra-high purity aluminium has been reported to fracture in an intergranular manner at 40°K.[45] This is attributed to shearing of the boundaries by stresses developed around triple points.

Impurity elements and alloying elements have been shown to exert considerable influence on rupture behaviour. At high temperatures commercially pure tungsten, zirconium, and titanium are resistant to grain-boundary cracking, whereas copper, nickel, and brass become more resistant as their impurity content is reduced. Reduction of impurity level, particularly gases, by vacuum melting and casting has been shown by many workers to be beneficial to the creep properties of metals and alloys.[46-50] Dilute nickel alloys containing copper, magnesium, or zinc have been shown to exhibit intergranular type fracture at intermediate temperatures, but transgranular at high temperatures.[40, 51] This was attributed to migration of the grain-boundary away from cavities thereby stablising them and restoring the strength of the material. Similar results and conclusions were arrived at by Chen et al[45] in commercial copper, Davies et al[52] in Nimonic 80A, and Mullendore et al[51] in dilute aluminium alloys. The change in fracture type from transgranular to intergranular is more abrupt in complex alloys than in pure metals or solid solution alloys and is usually accompanied by a pronounced fall in the ductility of the material. In many of these alloys recovery by grain-boundary migration occurs to an increasing extent with increasing temperature, but the fracture mode is found to remain intergranular.

A fall in ductility accompanied by an increase in creep life is often observed at a constant temperature if the stress is reduced. This effect is more common in complex alloys at low temperatures where the mode of fracture changes from transgranular to intergranular than at high temperatures. It is not unusual in these alloys to find that at high temperatures a decrease in stress brings about a decrease in ductility, although the fracture mode remains intergranular throughout. This is attributed primarily to grain-boundary sliding becoming the more prominent mode of deformation as the stress is reduced.

1.4. 2. Types of Intergranular Fracture Observed.

From the experimental observations discussed in the preceding section it may be concluded that low rates of deformation may induce embrittlement within certain temperature ranges in commercial metals and alloys. The materials are ductile at temperatures below the critical range and in many cases regain their ductility above this range. When embrittlement occurs the rupture is often found to be of the intergranular type.

Recent metallographic studies have shown intergranular fracture to be one of two basic types: wedge shaped or 'W-type' cracks which are usually initiated at triple points and spread more or less continuously along the grain-boundaries, and round shaped or 'r-type' cavitation in which numerous small elliptical cavities form along grain-boundaries, grow with time, and eventually coalesce to precipitate failure. In general W-type cracking is promoted by low temperatures, high stresses, and high creep-rate, whereas r-type cavitation is promoted by high temperatures, low stress, and low creep rates. The experimental observations of these two basic fracture mechanisms will be discussed separately, but because of the close inter relationship between the various metallurgical parameters on both type of failure these will be discussed as one. The hypothesis and experimental evidence put forward to explain the nucleation and growth of r-type cavities will, however, be treated in a separate section.

1.4. 3. Wedge-type Cracking.

As stated previously, this form of fracture is usually initiated at triple points where three grains meet and propagate along the grain-boundary away from this point. The direction of propagation is usually along boundaries transverse to the stress axis, although propagation by shear along 'unfavourable' boundaries is occasionally observed. Chang et al[53] have recently summarised and produced a schematic representation of the majority of wedge-type cavities observed during creep fracture, figure 3. The diagrams clearly indicate that grain boundary sliding and the creation of stress concentrations at triple points are necessary for w-type crack formation. It follows therefore that any mechanism which reduces the degree of sliding or the stress concentration will increase the ductility and creep life of the metal. Intergranular wedge-type cracks have also been observed to originate at points other than grain-boundary junctures. Weaver[54] observed w-type cracks at twin-grain boundary intersections whereas Gifkins[55] and Harris[56] observed them at precipitates. In general stress concentrations resulting in localised cracking will occur on grain-boundaries where restriction to metal flow is encounted.

Wedge-type cracking has been observed in a great number of metals and alloys, summari~~ses~~ of which are given by Gifkins[3] and Garafalo[4] in their reviews of creep rupture.

1.4. 4. Round or r-type Cavitation.

In 1954 Greenwood et al[57] reported a type of intergranular fracture, now known to be quite common, which results from the formation of small round cavities in the grain-boundary. It was proposed that the cavities increase in size and number with continuous creep and eventually coalesce to produce continuous grain-boundary cracks. These are seldom observed except at grain-boundaries and are usually, but not exclusively, found in boundaries oriented for maximum shear stress. The shape of the cavities is in dispute, although from the literature it appears that it may change with time or strain rate. Many of the early workers proposed from optical observations that initially cavities were round and grew into an elliptical form by a combination of growth by vacancy condensation and the operative stress system. Nield et al[47] obtained similar results by X-ray micrographs where it was shown that during the early stages of growth the cavities had a round structure which grew into a lenticular disc lying in the boundary with its major axis perpendicular to the applied stress. This work has been substantiated by Hyman[32 58] and Stiegler et al[59] who showed that cavities have a regular polyhedral shape. Presland et al[60] made similar observations in magnesium and proposed that the faces of the polyhedra were low index planes. Recent observations by shadowgraph electron microscopy has shown that cavities have sharp irregular outlines indicative of growth by mechanical means.

Since the initial observations of r-type cavitation by Greenwood et al[57] cavitation of this type has been reported in a considerable number of metals. Many of these and the conditions producing r-type cavitation have been summarised by Gifkins[3] and Garafalo[4] in recent review of creep fracture.

1.4. 5. Initiation and Propagation of Intergranular Fracture.

There is now considerable evidence available which shows that intergranular failure requires grain-boundary sliding, high resistance to transgranular deformation, and the absence or inhibition of recovery by, for example, grain-boundary migration. The relation between grain-boundary sliding and cavity formation has been reported in the literature by a number of workers.[38,41,47,58,62] In the majority of cases it was found that the incidence of cavitation decreased as the recovery mechanism became more predominant.

1.4. 5.1. Effect of Composition and Microstructure.

The influence of composition and microstructure on the initiation and propagation in intergranular cavitation is found to be more complex than a simple competitive interaction between the shear strength of the grain-boundary and the flow stress of the matrix. Several factors affecting cavitation behaviour of a metal have now been established. Resnick et al[48] proposed that the movement of a grain-boundary about a non-wetting particle, such as an inclusion or incoherent precipitate, can initiate cavitation by triple-point cracking about the particle. A schematic representation of this mechanism is given in figure 4. Since the observation of Resnick et al[48] cavitation of this form has been reported by a number of other workers.[38,56,58,63,64,65] The presence of grain-boundary particles or impurities has also been shown to reduce the rate of grain-boundary migration thereby reducing the rate of recovery and promoting cavitation.[40,47,49,57,66] In the majority of cases it was found that some degree of ductility returned to the material at high temperatures where grain-boundary migration may take place due to high temperature homogenisation or resolution of the particles. A third factor influencing cavitation behaviour in complex alloys is the so-called denuded zone phenomenon observed in such alloys. This effect is observed after selective precipitation of second phases at grain-boundaries which results in a narrow grain-boundary zone denuded of many of the alloying elements. The shear strength of this zone in solid-solution alloys is reduced by loss of alloying elements, whilst in precipitation hardening alloys it is reduced by a reduction in the number of precipitates in the zone. The effect of this zone on the ductility of the types of alloy, however, is different. In the solid solution alloys denudation is found to localise deformation in the region of the grain-boundary thereby promoting embrittlement.[67] In the precipitation hardened alloys, on the other hand, denudation promotes an increase in ductility by stress relief deformation in this zone.[68,69]

The structure of the grain-boundary itself may have some effect on cavity formation. Weaver[54] reported that coherent and near-coherent twin boundaries could delay or stop a propagating crack. It was shown where a twin traversed the whole grain and was sufficiently coherent to stop a propagating crack a complementary crack developed on the opposite side of the twin at the other grain-boundary - twin interface. It was thought that this was due to transmission of the stress along the twinning planes. Similar observations have been reported by McLean,[70] Greenwood et al,[57] and Hull et al.[38]

1.4. 5.2. Effect of Temperature, Stress and Prestrain.

It is difficult to separate the effects of temperature and stress on cavitation behaviour due mainly to an inability to separate completely the influence of these parameters, for example the stress level at which a creep test is conducted is usually reduced with increase in temperature to maintain the creep rate within reasonable limits. In general it is found that an increase in temperature and a decrease in stress promotes r-type cavitation whilst W-type cracking is promoted by low temperatures and high stress. This is thought to be due to there being a limiting temperature below which the extent of viscous grain-boundary sliding becomes small thereby reducing the number of cavity nuclei formed. Perhaps the most direct evidence of the influence of temperature on cavitation was obtained by Intrater et al[21] working on copper bicrystals. It was found that the number of cavities observed and the degree of cavitation for a given amount of grain-boundary sliding was independent of temperature above 650°C. At lower temperatures where sliding is strongly temperature dependent this was not the case.

As stated previously it has been established that in the majority of metals and alloys r-type cavitation is promoted by low stresses and w-type cracking by high stresses. The dependence of cavity formation on stress is not however a simple dependence on a stress level since it is also found to be sensitive to the orientation of the boundary to the stress axis and to the misorientation angle between two neighbouring grains. Chen et al[45], for example found that cavities did not form on the boundary of copper bicrystals subjected to 'pure' tension but did form when the boundary was subjected to a combination of shear and tensile stresses. These observations indicate an apparent relationship between crystallographic slip, grain-boundary sliding and cavity formation. The work of Chen et al[45] has been substantiated by Davies et al[71-73] who demonstrated using tension - compression creep tests that a correlation exists between the number of available nuclei sites ~~found~~ formed by crystallographic slip, the direction of sliding of the boundary, and the number and size of the cavities observed. It was proposed that it is cavity nucleation which is difficult under compressive stresses and not growth as suggested by a number of other workers. Hull et al[58] and Ratcliffe et al[79], on the other hand, have demonstrated by superimposition of hydrostatic stresses on specimens in tensile creep that growth of r-type cavities can only occur under a state of uniaxial stress.

The effect of prestrain on cavity formation appears to have been virtually neglected. Intrater et al[21] presented evidence that tensile prestrain could have considerable influence on cavity formation. The number of cavities produced by prestraining the bicrystals was found to be greater than in 'as-grown' boundaries. These findings were interpreted as indicating that grain-boundary ledges formed by slip-boundary interaction during the prestrain deformation initiate the cavities. This was substantiated by the observation that the cavity spacing increased as the coarse slip band spacing increased with rising temperature. On the other hand, it was also observed that the cavity spacing in 'as-grown' boundaries was smaller than the slipband spacing observed after test. It was concluded that a number of ledges must have been produced in the boundary prior to testing of the bicrystals. The orientation relationship between the direction of the prestrain axis and the creep stress axis has been demonstrated to exert considerable influence on the cavitation behaviour of the metal. Davies et al[71], for example, showed that under uniaxial tension maximum cavitation occurred on boundaries inclined between 90° and 60° to the stress axis. Prestraining in compression followed by an immediate reversal of the stress direction was found to increase the density of cavities formed in boundaries inclined between 60° and 30° to the stress axis. This was attributed to there being an increase in the number of available cavity nuclei sites on such boundaries after compressive prestrain. This is illustrated schematically in figure 6. It was also demonstrated that cavities formed in tension either sintered or grew in compression creep depending on whether the compression stress direction was at 180° or 90° to the original tensile direction.[73] This evidence farther substantiates that of Intrater et al[21] in that ledges formed in the grain-boundary are necessary for cavity formation. It also indicates that the direction of grain-boundary sliding in relation to boundary ledges can be of considerable importance when considering possible nucleation sites of cavities in metals.

1.4. 5.3. Effect of Environment.

Recent investigations have demonstrated that the environment may effect the mechanical properties of metals and alloys at high as well as low temperatures. Early studies have shown the flow characteristics of metals, particularly single crystals, to be sensitive to the surrounding liquid or solid environment. Although these results constitute the bulk of the evidence of environmental influence on fracture behaviour they will not be discussed in this review, rather the scope will be limited to experiments concerned with the influence of gaseous atmospheres on creep and creep-rupture properties of metals and alloys. The influence of gaseous environments on the mechanical properties of metals and alloys at high temperatures has been attributed to :

(a) energy changes produced by the absorption of gases onto a free surface resulting in weakening,

and (b) compositional changes produced by diffusion of gases into the bulk metal and possible gas-metal reactions.

With regard to mechanism (a), the surface energies of metals are small consequently the amount by which the strength may be altered by changing the surface energy, providing the surface is crack free, is also very small. If, on the other hand, intergranular cracks are produced by the deformation process the responce of the strength to surface energy changes may be marked due to its influence on the rate of crack propagation. Whilst surface energy effects can operate at all temperatures mechanism (b) becomes operative only at high temperatures where the rates of diffusion of gases in metals is considerably increased. At these temperatures it is possible for strengthening to take place as a result of gas-metal reactions and the subsequent formation of particles. It is also possible for embrittlement to occur when the product of the reaction is situated near or on the grain-boundary. Thus, whilst only one mechanism is in evidence at low temperatures, two may be operative at high temperatures.

Shahinian et al[75], working on nickel and nickel-base alloys have investigated the effect of test conditions on fracture behaviour. Under conditions which were favourable to internal oxidation, namely intermediate to high temperatures and low strain rates, considerable strengthening was observed. This was attributed first to the prevention of recovery by grain-boundary migration by oxide particles and secondly, to the filling or blocking of surface initiated cracks by nickel oxide which effectively acted as a load bearing material and maintained surface continuity of the specimen, thus reducing stress concentrations. The rupture life of the internally oxidised specimens was found, however, to be shorter than those tested in vacuum. At high stresses insufficient time is available for internal oxidation consequently it was found that the creep strength of the material in air was less than in vacuum. Shahinian et al[75] also demonstrated that the absorption of nitrogen along the grain-boundaries of impure nickel has a similar effect to oxygen at intermediate and high stresses and that it leads to excessive intergranular cracking when compared with tests in vacuum. Intrater et al[21] working on copper bicrystals found that the crack appearance differed with environment. In hydrogen isolated cavities were observed whereas in vacuum cracks propagating from the surface were found. The latter effect was attributed to the absorption of oxygen reducing the grain-boundary energy thereby promoting fracture. Boettner et al[76], on the other hand, found a slight increase in the incidence of cavitation in hydrogen compared with that in argon or air. It is interesting to note that the observed incidence of cavitation was highest at the subsurface and decreased rapidly towards the centre of the specimen. In polycrystalline copper[45] and silver[50] oxygen absorption along the grain boundaries is thought to promote cavitation by preventing or reducing grain-boundary migration.

The partial pressure of a reactive gas in an environment is found to exert a pronounced influence on the fracture behaviour of many materials in creep and elevated temperature fatigue. Thus Bleakney[77] found that the ductility of copper decreased with decrease in vacuum. In agreement with these results Snowden[52] found that the fatigue life of aluminium steadily increased with decrease in air pressure. Similar results were obtained by Achter[78] et al who found that the fatigue life of nickel depended on the partial pressure of oxygen in the environment. It was found that the fdigue life was greatest under conditions which favoured internal oxidation.

Other types of gaseous environment have been shown to affect intergranular fracture during creep of metals and alloys. For example, stress-corrosion cracking can occur in service in many 'brass alloys' if they are stressed in moist ammonia-containing environments. The number of metals that are succeptable to intergranular fracture in liquid environments is very large. Some of these involve liquid metals which cause failure by intergranular penetration or mass transport at high temperatures. Absorption of oxygen along the grain-bounderies is found to promote the former mechanism of attack.

1.4. 5.4. Rate of Nucleation and Growth.

There have been very few quantitative measurements of cavity nucleation rates reported in the literature. Intrater[21] et al from their studies of copper bicrystals concluded that the number of cavities increased monotonically with grain-boundary sliding and was independent of temperature. Greenwood[57] et al found that the spacing between cavities increased with temperature, but precise measurements were not made and the rate at which the cavities became observable was not determined. Density measurements have been employed by several workers in an attempt to obtain an indication of the rate of nucleation and growth of r-type cavities. Boettner[76] et al found that cavities were nucleated during the early stages of primary creep, but concluded that growth did not become appreciable until towards the end of this period. The rate of growth was found to increase steadily during secondary creep, then follow a parabolic increase during tertiary creep. Hull et al[38] and Gittins[64], on the other hand, concluded from their experiments that nucleation of cavities must be continuous throughout the creep life and that growth occurs at a constant rate. Conversely, Greenwood et al[74] propose that the observed change in specimen~~s~~ density with creep life cannot be accounted for unless both the nucleation and growth rate vary with creep life. The literature contains only one report of direct observations of nucleation and growth rate of r-type cavities during creep. Oliver et al[80] working on silver found that the number of visible cavities increased rapidly with time then levelled off to a constant value. They conclude that a fixed number of possible nucleation sites are present in a material for any thermal history and that the number of nuclei is not dependent on strain at a constant temperature.

Temperature is found to be an important parameter in intergranular creep since it influences the strain at which cavities became visible. Thus α- brass does not exhibit cavity formation until 50% creep strain at -193°C, but exhibits cavities after only 6% strain at 482°C.[65] Similar behaviour was found by Reid et al[62] in copper - 20% nickel alloys tested in tension at constant strain rate. Thus the strain at which cavities first become visible apparently increases with decrease in temperature. It is interesting to note the work of Davies et al[49] who found that the total strain at the end of secondary creep in pure and impure nickel and a nickel -1.16% tin alloy was the same in all cases, indicating that the rate of cavity nucleation and growth differed only during tertiary creep of these materials.

As in the case of cavity nucleation there have been very few systematic studies of the rate of cavity growth - Greenwood et al[74] and subsequently other workers[62,65,81], report that the strain at which cavities are first detectable decreased with increasing temperature. This work suggests that growth rate increases with temperature, but it must be remembered that the strain component due to grain-boundary sliding is also increased by an increase in temperature, and hence the results do not represent a simple temperature effect. In simple shear tests on copper bicrystals Intrater et al[21] found a linear relationship between the degree of sliding and size of cavity formed. They did not, however, attempt to correlate the rate of grain-boundary sliding with the rate of cavity growth. Oliver et al[80] obtained similar results for silver and found a relationship between cavity growth rate and time of the form.

$$\overline{R}_{obs} = (\tau)t + R_o$$

Where $\overline{R}_{obs}$. is the mean observed cavity radius.

t is the time of strain.

(τ) is the growth rate.

R_o is a correction factor for cavity enlargement by etching.

Weaver[63] obtained a similar linear relationship between the volume of w-type cracks per unit grain-boundary and both the time to rupture and elongation at rupture. The relationship was shown to be independent of microstructure. Weaver also reported that crack propagation may be delayed by coherent second-phase particles in the grain-boundary. Non-coherent particles, on the other hand, were found to serve as nucleation sites for w-type cracking, thereby reducing the rupture life of the material.

1. 5. MECHANISMS OF INTERGRANULAR FRACTURE.

The experimental observations reported in the preceding section show that there are two basic forms of intergranular fracture, these being wedge or w-type and round or r-type. The basic understanding of nucleation and growth of either type of fracture is very limited because of the lack of quantitative theories amenable to experimental verification. There are, however, a number of hypotheses based on physical models which define a number of mechanisms concerning nucleation and growth of both these fractures. The mechanisms of nucleation are based on the generally accepted concept that plastic flow is necessary for fracture with particular emphasis on specific modes of deformation. Thus creep deformation and creep rupture are closely inter-related and must be treated as such. This inter-relationship is necessary to explain the initiation and propagation of cracks and cavities which are formed at stresses below the theoretical lattice strength. The difference between the observed and theoretical strengths may be of the order of several magnitudes and is often attributed to the creep deformation.

1. 5.1. W-type Cracks.

Virtually all the hypotheses that have been proposed to explain the nucleation and growth of w-type cracks in high-temperature creep are based on the model originally proposed by Zener,[82] figure 6. In Zener's model the grain-boundary is considered to be a thin, viscous region in an elastic matrix. Upon application of a shear stress both the elastic matrix and viscous inclusion (grain-boundary) deform elastically in the same manner. However, if the stress is maintained the viscous region deforms to a greater extent with time, resulting in a tensile stress concentration in the elastic matrix at the ends of the viscous inclusion. In figure 6 the grain-boundary A-A' relaxes under the shear stress resulting from the applied tension produced by a stress concentration across boundary B-B', which may fracture if the stress concentration reaches the cohesive strength of B-B'.[59] Zener then assumed that, at least for an order of magnitude, the viscous boundary could be treated as a crack. However, experimental observations of the conditions leading to the formation of w-type cracks are not in complete agreement with this proposal. Flow in the viscous region should be strongly rate-dependent, and, at high stresses and creep rates little shear-stress relaxation is expected across a grain-boundary. This is substantiated by the observation that at high stress grain-boundary sliding makes very little contribution to the overall creep strain. On the other hand, w-type cracks are not observed at low stresses where complete or near complete relaxation across boundaries could be expected. There is no doubt that stress concentrations are developed at triple-points, but it is unlikely that it will be in the form of hydrostatic tension required by the Zener model. The stress concentrations in Zener's model can be partially attributed to grain-boundary sliding but it is also intensified by anisotropic effects related to the differing orientation of the adjacent grains. The formation of w-type cracks would also be dependent on the rigidity of the sliding grains and the rate of grain-boundary migration. High rates of deformation tend to increase the rigidity of the grains, that is increase the resistance to transgranular flow, and hence promote crack formation. The effect of creep rate on grain-boundary migration is not known, but nevertheless the absence of any form of cavitation behaviour in ultra-pure metals is attributed partially to the dissipation of stress concentrations by plastic flow and grain-boundary migration. The greater propensity for w-type cracking in alloys is primarily attributed to the increase in the flow strength of the grains and secondly to a decrease in the grain-boundary mobility.

The quantitative testing of Zener's model[82] has been very limited. McLean[70] has estimated the minimum stress required to form a stable crack at the head of a sliding boundary using a modification of Stroh's[83] equation for brittle fracture:

$$\tau_s^2 \geq \frac{12\, G\, \gamma_b}{\pi L}$$

where τ_s is the shear stress across the boundary,

γ_b is the surface energy per unit area of crack formed in the boundary,

G is the shear modulus,

L is the length of the sliding boundary.

It was found that except in the case of complex precipitation hardening alloys, the observed values of maximum shear stress were in good agreement with those estimated from the modified formulae. Weaver[84] pointed out that good agreement between the observed and theoretical maximum shear stress in complex alloys is obtained if the interparticle spacing of the precipitates present in the grain-boundary is substituted for the length of the sliding boundary, L. Smith et al[84], on the other hand, calculated that the minimum stress for nucleation of a crack at the intersection of two shear bands (analogous to triple point cracking) is considerably less than that predicted by McLean's modification of Stroh's equation. It was also pointed out that if the effective fracture surface energy for crack growth is greater than that for nucleation, then growth is the more difficult process and the crack will only extend with increasing strain in the shearing elements. Experimental evidence was presented which verified that the rate of crack growth at high temperatures is considerably less than that of a Griffith-type unstable crack. Waddington[85] has pointed out that the assumption by McLean[70] that the surface energy of the sliding boundary does not change with deformation is incorrect. Waddington[85] derived an equation based on the work of McLean[70] and Smith et al[84] which attempted to predict the conditions under which w-type cracks are nucleated:-

$$\sigma^{n-1} \geq 19\,\Omega\,\delta x\,\exp.\left(\frac{Q}{RT}\right)\left[RTLK_1K_2a^2\right]^{-1}$$

where σ is the applied stress

Ω is the atomic volume

δx is the grain-boundary width

Q is the activation energy for self diffusion

K_1 is a proportional constant

K_2 is a proportional constant dependent on grain size

a is the Burgers vector of the dislocation in the pile-up

n is the number of dislocations in the pile-up.

If LHS $>$ RHS then a triple point crack is initiated, conversely, if LHS $<$ RHS rupture occurs by the formation of r-type cavities. A similar concept of an inter-relationship between w-type cracking and r-type cavitation has been developed by Steigler et al.[54] It was postulated that a balance exists between the flux of vacancies entering the growing cavity nuclei from the grain-boundary, j_{gb}, and the flux of vacancies across the surface of the cavity to reduce the surface energy, j_s. If the flux of vacancies into the cavity is equal to or less than the surface flux, that is $j_{gb} \leq j_s$, then the cavity will remain polyhedral in shape, if, on the other hand, $j_{gb} > j_s$ the cavity will grow preferentially along the grain-boundary plane. In the extreme case where $j_{gb} \gg j_s$ growth will be very rapid in the plane of the grain-boundary and in the direction of grain-boundary sliding leading to the development of w-type cracks at triple points. This is schematically illustrated in figure 7. A more detailed discussion of this theory will be given in the section concerning r-type cavity growth.

1.5. 2. R-type Cavities.

At the time of their original observation of cavitation fracture Greenwood et al[57] postulated that the cavities were nucleated by the condensation of excess vacancies in the lattice. The vacancy concentration was presumed to arise from the thermal equilibrium concentration at high temperatures plus any vacancies created by deformation. Greenwood et al's[57] quantitative arguments in support of the proposal were based on the observation that the number of vacancies in a lattice increase with increase in temperature and decrease in strain-rate. Subsequent theoretial investigations[86-88] based on nucleation theory showed that the super-saturation ratio of vacancies required to nucleate cavities by condensation was many orders of magnitude greater than that normally observed in metals. In addition, as Cottrell[89] points out, there is good evidence that grain-boundaries are efficient vacancy sinks providing yet another reason why homogeneous nucleation is unlikely in grain-boundaries. Finally, Intrater et al[21] have shown that in copper bicrystals the rate of nucleation of cavities is independent of temperature over a wide temperature range in which vacancy concentration and mobility would be expected to rise sharply with temperature. As a result of these observations the original concept of Greenwood et al[67] has been generally abandoned and it is now assumed that submicroscopic cavities are already present,[2, 67] are created by slip grain-boundary interaction,[88, 90] or that heterogeneous nucleation may occur at second phase or non-wetting particle interfaces.[56, 58, 63, 76, 89]

In pure metals and alloys containing particle-free boundaries the most accepted mode of nucleation of r-type cavities is by the interaction of ledges formed by transgranular slip and grain-boundary sliding. This mechanism of cavity nucleation was first proposed by Gifkins[90] who postulated that ledges could be formed in a grain-boundary by slip accommodation across the boundary. The stress field developed by dislocations running into the pile-up that originally formed the slip-step plus the stress due to Mott's 'areas of misfit' in the grain-boundary was considered sufficient to cause fracture of the ledge-matrix interface, figure 8. Growth of the cavity nuclei was considered to occur by grain-boundary sliding. Chen et al[91] pointed out that it was highly unlikely that the stress developed by the mechanism proposed by Gifkins[90] was of sufficient magnitude to initiate fracture of the ledge-matrix interface. It was proposed that a stress of sufficient magnitude to initiate fracture could be developed across the ledge interface by sliding of the grain-boundary. The direction of sliding relative to the ledge-matrix interface was shown to be of great importance. Fracture can only occur if the direction of sliding is such that tensile stresses are developed across the interface, reversal of the sliding direction results in compressive stresses under which fracture cannot occur, figure 9. Gifkins[90] points out that such a configuration at the grain-boundary will tend to be eliminated by grain-boundary migration, and therefore, if the ledge is to persist long enough for a cavity to be nucleated the rates of grain-boundary migration must be low relative to the rates of boundary sliding. McLean[92] estimates that for stability the ledge height must be greater than four atomic diameters. Chen et al[91] and Heald et al[47] have also discussed similar models involving irregular grain-boundaries and the effects of grain-boundary sliding without specifying the origin of the irregularities which serve as cavity nucleation sites.

A number of objections have been made to the ledge-sliding mechanism of cavity nucleation proposed by Gifkins[90] and Chen et al.[91] First, Intrater et al[21] have demonstrated that cavities are nucleated in prestrained copper bicrystals at intervals approximately equal to the coarse slip band spacing, but in the 'as-grown' boundaries the observed cavity spacing was less than the slip-band width. It was proposed that the 'as-grown' boundary contained 'embryo-nuclei', but the form of these was not specified. Cottrell,[89] using Stroh's criterion for brittle fracture, pointed out that it is highly unlikely that barriers in the form of ledges can nucleate fracture at stresses below that for triple-point cracking. Smith et al,[84] however, have shown that Stroh's criterion cannot be applied directly to creep fracture and that the true stress required for cavity nucleation is at least one order of magnitude lower than that predicted by Cottrell.[89] A third possible objection is that in many polycrystalline metals grain-boundary deformation zones several microns thick are observed. In view of the severe plastic deformation taking place in these zones it is unlikely that ledges of the order of 50-100 A^o in height will be formed, or if formed will remain stable sufficiently long to nucleate a cavity. To date no work on the stability of ledges in a 'dynamic shear zone' has been reported in the literature. In an attempt to overcome this objection McLean[92] proposed that instead of ledges narrow steps, approximately 100 A^o long and 20 A^o high, capable of allowing sliding on either side exist in the boundary. He presented a calculation which indicated that in a magnesium-base alloy and a Nimonic alloy reasonable rates of grain-boundary sliding exceeded the rate of sintering and was thus capable of nucleating a cavity. Harris,[56] pointed out an error in McLean's calculation which when corrected indicates apparently unrealistic rates of boundary sliding. Recent calculations by Smith et al,[84] however, have shown that a sliding rate of the magnitude required by Harris can be achieved during intermittent periods of rapid sliding of the boundary whilst the overall sliding rate may be considerably lower than that required to nucleate a cavity.

Presland et al[60] have suggested that cusps formed at the sub-boundary grain-boundary interface are possible nucleation sites for cavities in magnesium. The possibility of cusps being nucleation sites for cavities has been dismissed by Harris[56] who has shown on the basis of the figures presented by Presland et al[60] that the distance between the cusps is far too small for them to act as nuclei. A possible objection to this argument is that it is assumed that every cusp acts as a nucleus which is highly unlikely. A further objection to the theory is that cavitation occurs in pure copper which does not readily polyganise, whereas it does not occur in pure aluminium which polyganises extensively during creep deformation.

Nield et al[47] do not favour nucleation of cavities either by vacancy condensation or by direct concentration of the low stresses experienced in creep. They explain their observations of cavitation on the basis of a balance between relaxation of the boundary-transition zone by self-diffusion and grain-boundary migration. It is proposed that the relaxation process sets up tensile and compressive stresses at boundary irregularities which, unless boundary migration occurs, may combine with the stresses due to boundary sliding and nucleate cavities at the sites of tensile stresses. The mechanism as proposed by Nield et al[47] appears to be a general statement of a mechanism of the type described previously and retains the major criticism in that no indication is given as to the form of the irregularities which eventually act as the nucleant.

The possibility of cavity nucleation sites being present in situ in materials prior to creep in the form of sub-microscopic pores has been repudiated by Cottrell[89] who has pointed out that such small pores would be expected to disappear by sintering because of their small size early in the creep process. Also, if the nuclei were submicroscopic pores r-type cavities would be produced under all conditions of temperature and stress, and not, as observed, only under certain conditions.

There is considerable evidence in the literature that nucleation of cavities in complex alloys and impure metals may take place by sliding of the grain-boundary about non-wetting particles or precipitates, a schematic representation of which is given in figure 4. Much of the evidence for this mechanism of cavity nucleation is indirect, for example, an increase in the purity of most metals is accompanied by an increase in creep ductility[44,47,48,66,79]. It has been argued that this is due directly to the removal of inclusions which would otherwise act as cavity nuclei[76]. It has also been suggested that the observed improvement in ductility is a consequence of enhanced grain-boundary migration in the purer materials relieving local stress concentrations; but this explanation is not necessarily at varience with the concept of cavity nucleation at second-phase particles. The presence of oxygen in the environment surrounding specimens of copper[45,73,76,77]. and nickel[75] during creep has been shown to enhance cavitation. It is proposed that this is due to the formation of oxide particles which act as nuclei in preference to ledges, thus causing the observed rates of cavitation. Cottrell[89] suggested that the degree of cohesion between a particle and the matrix may influence its ability to act as a nucleus. In support, he pointed out that pure aluminium, the oxide of which is strongly coherent, does not cavitate during creep. This hypothesis could also explain the absence of intergranular failure in high purity lead. It must be pointed out, however, that both lead and aluminium exhibit very high recovery rates such that stress concentrations sufficiently high to nucleate cavities may never be developed. Further indirect evidence for second-phase particle nucleation is provided by Eborall[93] who suggested that pure titanium does not cavitate in creep due to its ability to dissolve its own oxide and similar compounds.

The majority of the mechanisms proposed for nucleation of both w-type and r-type fractures depend on the same criterion of grain-boundary sliding and concentration of the normal stress at line or planar obstacles. None of the proposed mechanisms are able to predict or explain directly the observation that w-type cracks occur predominently at high stresses and low temperatures and that r-type cavities occur at low stresses and high temperatures. A feasible explanation may not be possible without further knowedge of the effect of the rate of deformation and temperature on the relief of stress concentration at triple-points, grain-boundary ledges, and grain-boundary particles.

The problem of how cavities, once nucleated, may increase in size and the influence of stress on this process has been the subject of a great number of investigations. Two mechanisms have received considerable attention in the past decade, these being growth by condensation of vacancies and growth by continued sliding of the grain-boundary. Because of the conflicting nature of these two theories the evidence for and against each theory will be discussed separately and an assessment of both made at the end.

Greenwood et al[57] in their original proposal of cavity nucleation by vacancy condensation postulated that growth would occur by continued condensation of vacancies. McLean[88] also assumed that the cavities grew by the condensation of vacancies and adopted the Nabarro-Herring analysis for diffusion creep to the analysis of the problem of cavity growth in order to take into account the influence of the applied stress. Gifkins et al[86] have also examined the influence of stress on cavity growth using the Nabarro-Herring analysis and derived a critical stress relation for the growth of cavities based on the cavity dimensions. Hull et al[38] have extended this analysis by assuming that in the temperature range in which cavity formation occurs grain-boundary diffusion is the only important diffusion mechanism. A simplified form of Hull et al's[38] expression for cavity growth is as follows:

$$(\sigma - P) \geqslant \frac{2\gamma}{r_0}$$

where σ is applied stress,

P is the hydrostatic stress experienced by the cavity,

γ is the surface energy of the cavity,

r_0 is the radius of the cavity.

Hull et al[38] predicted and subsequently demonstrated that under conditions where the hydrostatic stress P was equal to the princip~~le~~al stress σ cavities cannot be formed. It was proposed that this is due to the inability of vacancies to diffuse under a hydrostatic stress. However, from the same analysis, for a constant value of $(\sigma - P)$ the rupture time should remain constant. Experiment has shown this not to be so. A correlation between predicted and experimental results could only be obtained if it is assumed that the number of cavities increased with σ at a constant value of $(\sigma - P)$. A similar analysis and series of experiments was conducted by Ratcliffe et al.[74] It was demonstrated that cavities nucleated under normal tensile creep conditions ceased to grow on the super-imposition of a hydrostatic stress equal to the principle stress. The investigators concluded that the growth cavities ceased due to the prevention of vacancy diffusion. This, it is claimed, points to vacancy condensation being an important mechanism of cavity growth. The work of Ratcliffe et al[74] suffers, however, from a similar criticism as that of Hull et al[38] in that a correlation between theoretical predictions and experimental observation is obtained only if it is assumed that the number of cavities formed increases with time. Speight et al[94] have conducted a farther theoretical analysis of the form derived by Hull et al[38] and conclude that the spacing between neighbouring cavities can considerably influence the growth rate of the cavities.

The observations of Oliver[80] et al on silver lead to somewhat different conclusions to those of Hull et al[38] and Speight et al[94]. On the basis of experimental evidence it was concluded that the nucleus size is almost zero and that the rate of cavity growth is independent of inter-cavity spacing, remaining constant even when the cavities are in contact. They postulated that if cavity growth depended on grain-boundary diffusion of vacancies the growth rate should decrease as the inter-cavity spacing decreased since the volume of grain-boundary material supplying the defects decreases. In their study of cavity growth no such decrease in the rate of growth was observed. It was concluded that the vacancies must be diffusing from the bulk grain to cause cavity growth, and, from their analysis of the kinetics of cavity growth, that divacancies are the most likely diffusing defect.

In the analysis of Greenwood et al[31], Hull et al[38], Ratcliffe et al[74] and Speight et al[94] it is assumed that the source of vacancies is deformation by sliding in the grain-boundary itself. Boettner et al[76] using considerably larger specimens than these investigators found that a substantially higher cavity volume exists in the surface zone than in the centre of the specimens. This was interpreted as indicating that the surface of the specimen, and not the grain-boundary, is the major source of vacancies.

The evidence for cavity growth by vacancy condensation has been verified many times, but unfortunately each investigator has slightly modified the experiments conducted previously without attempting a different fundamental approach. Consequently each successive experiment has retained some of the major criticisms of the original work. For example, although excellent agreement with theoretical predictions for the effect of super-imposed hydrostatic stress has been obtained, the models assumed that cavities were at all times spherical and that growth was entirely by vacancy condensation with linking by simple merging - both of which now appear untenable. The majority of investigators have employed thin wire specimens, but Boettner et al[76] have subsequently demonstrated that the degree of cavitation can vary across the section of a thick specimen and have had to considerably modify existing concepts to account for this observation. In addition, Machlin[95] has pointed out that a super-imposed hydrostatic pressure will limit growth of cavities by any mechanism, of ductile fracture. Finally, Intrator et al[21] have shown that over a wide temperature range the growth of cavities in copper bicrystals is independent of temperature but dependent on the degree of grain-boundary sliding.

In his original hypothesis of cavity nucleation, Gifkins[90] proposed that growth occurred by continued grain-boundary sliding after nucleation of the cavity. The argument continually put forward against this mechanism of growth is that cavities are not observed in compression creep tests. Davies et al[72] have pointed out that this my be due to a difficulty of nucleation, not growth. To test this hypothesis cavities were formed in a specimen by tensile creep which was then subjected to compression creep. It was found that when the direction of the compressive stress was directly opposite the direction of the original tensile stress the cavities closed and sintered, but when the two directions were perpendicular to one another cavity growth was observed. It was proposed that in the former case the boundary sliding direction was reversed on application of the compressive stress, but in the latter it was in the same sense. Taplin et al[96] dispute this observation and suggest that the shrinkage of the cavities was due to localised plastic deformation and vacancy diffusion and not a reversal of the boundary sliding direction. It was also suggested that the cavity growth observed is due to vacancy condensation, growth by boundary sliding serving only to balance shrinkage by sintering. McLean[97] endorsed the views of Gifkins[90] and Davies et al[72] and showed that cavity growth was possible by a combination of transgranular deformation and continued grain-boundary sliding. Garafalo[4] strongly opposes this mechanism on the grounds that if this were the only mechanism of growth the cavities would be expected to maintain a plate-like shape which has been observed only on rare occasions. The cavity shape usually observed is a lenticular disc of thick section and is very often almost spherical. This he argues indicates that surface diffusion tends to spheroidise the cavities to minimise the total surface energy. The observation that these cavities grow below the critical Griffith size is maintained as another reason why no significant growth by this mechanism occurs. Garafalo's[4] argument concerning the shape of the cavities is invalidated if one considers carefully the geometry of cavities produced by McLean's[97] mechanism. Since the cavities are of the form of thin lenticular discs the possibility of observing a planar or near planar section of such a disc in a conventionally prepared micro section is negligable, hence the rarity of the observation. Similarly, the comment that the majority of cavities observed are either round or thick lenticular discs may be accounted for if one considers the possible geometrical sections of a thin lenticular disc and the extent to which the outlines of such shaped cavities may be distorted by mechanical and/or electro polishing.[98] The possibility does exist, however, that some "rounding-off" of the cavities may occur by vacancy condensation or surface diffusion, but it is unlikely that this will contribute much to the growth rate.

McLean et al[97] have presented a theory of cavity growth which they claim overcomes the difficulties of both the vacancy condensation and grain-boundary sliding theories. They propose that dislocations move along the normal glide-planes under the influence of the applied stress until they are stopped by the grain-boundary, figure 10. Under the action of the applied tensile stress the dislocations then tend to move along the boundary in the direction indicated by the arrow, causing sliding. However, as the grain-boundary does not contain a glide-plane the movement of the dislocation along the boundary is a combination of glide and climb and emits vacancies as it moves. It thus tends to open up the cavity, as shown in the figure, ahead of it. The width of the cavity is considered to increase by one atomic layer for every dislocation entering the cavity. Consequently, as the cavity diameter increases so does the thickness, the resulting shape being a lenticular disc.

Cavities of the shape postulated by McLean have been observed by Nield et al[47] using X-ray microscopy, by Presland et al[60] using thin foil microscopy and more recently by Taplin et al[96] using thick thin foil microscopy[99] and fractography[100]. Presland et al[60] showed the presence of polyhedral-shaped cavities in magnesium the faces of which it was suggested were low index planes. Nield et al[47] observed similar shaped cavities but made no comment on the form of the walls. The shape observed by Taplin et al[99,100] was found to be an irregular angular plate of finite thickness rather than the lenticular disc predicted by McLean[97].. It was proposed that this was due to quenching immedi~~ally~~ately on unloading the specimen. It was considered that under less drastic cooling conditions sufficient surface diffusion and stress relief deformation could occur to "round off" the cavities and produce the polyhedral and lenticular disc shaped cavity observed by other investigators.

On the basis of observations made during a fractographic investigation into creep fracture in tungsten Stiegler et al[54] proposed that r-type cavitation and w-type cracking are the result of the same deformation mode. From Hull et al's[38] analysis they obtained a relationship between vacancy flux and growth of the cavity of the form:

$$j_{gb} \approx \frac{D_{gb}\,\Omega}{KTa}\left(\sigma_n - \frac{2\gamma}{r}\right)$$

where j_{gb} is the vacancy flux into the cavity,

D_{gb} is the diffusion coefficient in the boundary,

K is the Boltzmann's constant,

a is the intercavity spacing,

T is the temperature,

where σ_n is the stress normal to the cavity,

γ is the surface energy of the cavity,

and r is the radius of the cavity.

It was proposed that if the cavity is to maintain a spherical or polyhedral shape vacancies entering it must be distributed over the surface of the cavity as rapidly as they enter it. If surface diffusion is the predominant mechanism of material transport, the surface current or flux of vacancies, j_s, is given by the expression:

$$j_s \approx \frac{D_s \Upsilon \Omega r}{KT} \cdot \frac{\partial K}{\partial s}$$

where D_s is the surface diffusion coefficient,

Υ is the number of atoms per unit area,

Ω is the atomic volume of the fluxing material,

$\frac{\partial K}{\partial s}$ is the rate of change of radius of curvature with respect to change in position on the surface of the cavity.

It should be noted that this expression is independent of the applied stress, unlike the former, and depends only on the temperature and shape of the cavity.

The shape of the cavities observed by other investigators can now be explained in terms of the relative importance of the vacancy flux in the grain-boundary, j_{gb}, and the vacancy flux across the cavity surface, j_s, under a given set of creep conditions.

If j_s is high enough to accommodate all the vacancies arriving at the cavity then the cavity will maintain a polyhedral shape. If the vacancy flux into the cavity increases due, say to an increase in stress, equilibrium between j_{gb} and j_s cannot be maintained, and the cavity will grow primarily in two directions along the grain-boundary. The higher stress may also lead to an appreciable growth component from dislocation motion and sliding of the boundary. Depending on the relative rates of these two growth components growth may be three dimensional, ie. polyhedral shaped cavities, or two dimensional, ie. lenticular disc shaped cavities. The former condition is most likely to prevail under conditions of low stress and high temperatures whilst the latter is more likely to exist under conditions of high stress and moderate temperatures.

Chapter 2.

EXPERIMENTAL DETAILS.

During the last two decades the problem of intergranular deformation, particularly cavitation, has received increasing attention from investigators of creep deformation. The problem has been approached from two main directions, either on a quantitative basis using high purity metals and alloys in an attempt to evaluate the mechanisms or kinetics of cavitation, or, on a more qualitative basis using commercial metals and alloys in an attempt to determine the effects of metallurgical and external parameters on cavitation behaviour. To this end themajority of tests have employed uniaxial tension as the means of applying a load to the specimen, although tests involving the use of uniaxial compression have been reported in the literature.[71-73] The form, location and degree of cavitation have been determined mainly by conventional metallographic techniques, although X-ray microscopy,[47] electron metallography,[60,99] and density variations[38,57,80] have also been utilised.

During the course of these investigations a number of workers have studied the influence of environment on cavitation behaviour of various metals and alloys. In general a reduction in the degree of cavitation was observed when specimens were deformed in environments from which oxygen had been partially or completely removed, thus indicating a relationship between oxygen and cavitation or the enhancement of cavitation. It has been proposed that this may take the form of the formation of discreet particles by chemical reaction and the subsequent formation of a cavity by grain-boundary sliding, a reduction in the grain-boundary energy thereby making shear of the boundary easier, or stablisation of cavity nuclei by surface condensation of gas atoms or molecules. The main criticism of many of these investigations is that

cavitation behaviour was studied on a qualitative basis and thus no clear indication was obtained as to the extent to which an environment may influence the deformation characteristics of metals and alloys undergoing creep.
It was therefore decided to initiate a programme of work designed to give a quantitative indication of the extent and mode of influence of the environment on cavitation behaviour in metals and alloys.

2. 1. MATERIALS.

2. 1.1. Alloys.

Preliminary investigations of cavitation were carried out on α - brass, the analysis of which is given in Table 1. The results of this investigation indicated that under the conditions required to produce extensive r-type cavitation in the alloy, that is high temperatures and low strain rate, the oxidation rate of the alloy was such that it was extremely difficult to study the behaviour over long periods of time. Consequently it was decided to employ an alloy which was ostensibly oxidation resistant and which did not contain grain-boundary particles. Such an alloy was found in solution-treated 18/8 niobium stainless steel. The alloy has the added advantage of undergoing extensive bulk-grain precipitation of carbide particles without grain-boundary precipitation in the temperature range employed for the investigation. Consequently nucleation of cavities at grain-boundary precipitates could be avoided. The analysis of the alloy employed in the investigation is given in Table 1.

TABLE 1.

Element.	α - brass.	18/8 steel.
C	-	0.048
Si	-	0.570
Mn	0.0008	0.7670

TABLE 1. (contd.)

Element.	α-brass.	18/8 steel.
P	0.0020	0.010
S	-	0.0060
Cr	-	17.410
Ni	-	9.0750
Nb	-	0.760
Ti	-	0.0450
Fe	0.00520	balance
As	0.00110	-
Bi	0.00460	-
Cu	balance	-
Zn	29.386	-

Both alloys were received in the form of half-inch diameter hard drawn bar. Small tensile specimens of the dimensions indicated in figure 11. were machined from this bar stock. The gauge-length diameter was initially machined slightly oversize to allow for a final heavy electro-polish before testing to remove any surface artifacts developed during the heat-treatment.

The specimens were heat-treated in the following manner:

(a) α -brass:

Solution-treated for two hours under argon at 700°C. Water-quenched to room temperature. This treatment was found to produce an equiaxed grain structure of 0.5 millimetre diameter as determined by the line intercept method.

(b) 18/8 stainless steel:

Solution-treated for thirty-six hours at 1300°C in sealed silica tubes containing a partial pressure of argon. The specimens were quenched to room-temperature by breaking the silica tubes under water. Optical and electron metallography indicated that $> 97\%$ of the carbide particles in the initial structure had been taken into solution by this heat-treatment. The micro-structure after the treatment was found to be an equiaxed grain structure of approximately 0.5 millimetre diameter.

2. 1.2. Environment.

As indicated previously, the majority of the literature indicates that oxygen may influence the deformation behaviour of metals or alloys during creep. It was therefore decided to conduct a series of tests under as near identical conditions as experimentally possible in both air and vacuum to allow a direct comparison to be made as to the extent and mode of influence of a gaseous environment, namely nitrogen and oxygen (air), on the deformation behaviour of the alloy. To establish whether any observed influence was due to a 'reaction effect' or due entirely to the presence of a gaseous environment a similar series of tests were conducted with pure argon ($< \lambda$ ppm. O_2, $<$ 5 ppm. N_2) as the environment. If any observed difference in deformation behaviour is due to a 'reaction effect' then no difference in behaviour should be observed between specimens tested in vacuum or argon. Conversely, if the effect is due entirely to the presence of a gaseous environment then no difference in behaviour should be observed between specimens tested in air or argon.

2. 2. APPARATUS.

2. 2.1. Preliminary Work.

The preliminary investigation to establish the optimum conditions for cavitation in the materials under test were carried out on a Hounsfield Tensometer the drive of which had been modified to give a range of crosshead speeds within the range 0.00005 to 5.0 inches per hour. Specimens under test were raised to temperature in a small furnace supported on the slide bars of the tensometer, the temperature of which was controlled to within ± 2C° by means of a proportional controller. The specimens were held in position in the furnace by means of Nimonic split-cup grips and extension rods, figure 12. The temperature of the specimen during the test was measured by a thermocouple attached to the gauge-length. This was found to be within 1.5 C° of the set temperature and to vary by less than 1 C° along the gauge-length.

2. 2.2. Creep Work.

The investigation into the cavitation and mechanical behaviour of the alloy during creep may be subdivided into air experiments and argon and vacuum experiments from the point of view of the apparatus employed.

Tests conducted with air as the surrounding environment were carried out on standard Denison miniature stress-rupture machines (type T47.D.). Temperature control of the furnace was achieved by means of a differential expansion-current limiting device which varied the current in the secondary windings of the furnace. The operating temperature was achieved primarily by a set of primary windings controlled by a Variac, the secondary windings acting only as a means of temperature control in the manner indicated. The temperature control band by this technique was ± 1.5 C°.

The specimen under test was held in position by means of split-grips of the type employed for the hot tensile tests. Specimen temperature was again measured by a thermocouple attached to the gauge-length. Initially a number of thermocouples were employed for this purpose, but experiment showed that the temperature variations along the gauge-length was < 0.5 C° and consequently the number was reduced to one for convenience. Temperature variation at the specimen throughout the test was ± 1 C°.

Extension of the specimen during the test was measured by a spring-loaded dial-gauge moving against the load-arm of the machine. The accuracy of the dial-gauge was estimated at ± 0.00005 inch.

The vacuum and argon environment tests were conducted on a modified. version of the standard stress-rupture machine described previously. The furnace and temperature control unit was replaced by a furnace unit designed to enable a vacuum capsule to be fitted on the test-rig, figures 13 and 14. The capsule consisted assentially of a stainless tube (L) the ends of which were closed by ~~a~~ water-cooled demountable closure plates (C) which supported a vacuum seal designed to provide a dynamic seal between the moving rods and the capsule body. This consisted of a series of 'o' rings and brass discs which were tightened onto the extension rod by means of a screw collar (B). The specimen was supported on the capsule during the test by means of Nimonic split-cup grips. The temperature of the specimen was measured by an Inconel sheathed thermocouple (E) soldered into the closure plate.

The capsule was evacuated from both ends to a working vacuum of 2 X 10^{-5} torr by an Edward's pumping unit, figure 13. Argon environment tests were conducted by introducing gas into the system via a needle valve at the lower evacuation point. The upper evacuation point was connected to a gas wash-bottle containing glycerol through which the gas was pasted. This enabled a small positive pressure to be maintained in the system.

The specimen was raised to the test temperature by means of a Kanthal wound furnace surrounding the capsule. The furnace windings were spaced such that a uniform hot zone of two inches was obtained. Control of the temperature was achieved by a platinum resistance thermometer (K) and a solid state controller. This system achieved a temperature control band width of $< \pm 0.5C^{o}$ at the specimen.

The furnace and capsule were supported on the stress-rupture machine in the conventional manner. Extension of the specimen during the test was again measured by a spring-loaded dial-gauge moving against the lever arm of the creep-machine.

2. 2.3. Electropolishing.

All specimens prior to being deformed were electropolished to remove any surface artifacts developed during the heat-treatment. The conditions employed were as follows:

Two hours in chrome-acetic acid solution at 23 volts. Details of this solution are given elsewhere[101]. This electrolyte was employed in preference to other more rapid polishing electrolytes because of its ability to produce large areas of pit-free surface and the ease of control of the polishing conditions.

A circular stainless steel cathode which completely surrounded the specimen was employed in preference to sheet cathodes in order to obtain uniform polishing over the whole of the specimen surface.

Specimens of the stainless steel for transmission electron microscopy were prepared from thin strips spark-machined from the gauge-length of the creep specimen after test. Prior to electro-polishing each strip was chemically polished to approximately five thousandths of an inch thick using the following solution:

285 Ml/1 glycerol

285 ml/1 100 volume hydrogen peroxide solution

285 ml/1 water

145 ml/1 concentrated hydrochloric acid

The temperature of the solution throughout the thinning process was maintained below 30°C. After chemical thinning specimens for 'thick' thin foil electron microscopy were prepared from the strips by a minature 'Window' technique. The polishing conditions employed were as follows:

Electrolyte: 545 ml/1 Orthophosphoric acid
365 ml/1 Sulphuric acid
90 ml/1 Methanol

Voltage: 7 volts.

Current: 1 amp./ square centimetre.

The strips were polished until several small holes were observed. Small specimens were then cut from the vicinity of the holes for examination. The theory of the 'thick' thin foil technique for observing enclosed cavities is given in the appropriate Experimental Procedure section.

2. 3. EXPERIMENTAL PROCEDURE.

2. 3.1. Preliminary Work.

A preliminary investigation was conducted to determine the conditions required for extensive r-type cavitation in α -brass and 18/8 stainless steel. This was approached from two directions,

(a) determination of the strain-rate at which cavities are formed at a given temperature,

and (b) determination of the temperature at which cavities are formed at a given strain-rate.

The close inter-relationship between these tests enabled the required parameters to be determined from a single series of experiments. Tests were conducted on the α -brass at 100 C° intervals in the range 0°C to 900°C and on the steel at the same temperature intervals in the range 600°C to 1100°C. The strain-rates employed during both series of tests were within the range 0.00005 in./hr. to 0.5 in./hr. increasing by one order of magnitude intervals.

Prior to testing the gauge-length and diameter of each specimen were measured by means of a travelling microscope and micrometer respectively. Throughout the investigation a standard gauge-length of 20 millimetres was employed. As indicated previously, specimens under test were held in position in the furnace by Nimonic split-cup grips and extension rods, the latter being attached to the cross-heads of the tensometer. An indication of the load attained during the test was obtained from the tensometer in the usual manner.

On fracture the ductility of each specimen was determined, the specimen mounted, sectioned, and prepared for metallographic examination. Details of this process are given in the metallographic section.

2. 3.2. Creep Tests.

The results of the preliminary investigations indicated that large r-type cavities were formed in α -brass providing the strain rate was less than 0.01 in./hr. and the temperature in the range 350 to 750°C, and in 18/8 stainless steel at strain-rates less than 0.005 in./hr. and temperatures in the range 700 to 900°C.

As indicated previously the initial results of the creep experiments on α -brass indicated that under the conditions required to obtain extensive cavitation the oxidation rate was far too high for the type of experiment envisaged for this investigation. It was therefore decided to concentrate the investigation entirely on the influence of environment on the cavitation behaviour of 18/8 niobium stablised stainless steel.

As the investigation is primarily concerned with the influence of environment on cavitation behaviour it follows that the test must last a sufficient period of time for diffusion of the constituents of the environment to the centre of the specimen. Calculations based on available data for grain-boundary diffusion of oxygen and nitrogen in[103] γ -iron indicated that this was approximately 1000 hours at 800°C. It was therefore decided that the majority of tests be conducted at this temperature for this period of time. The use of higher temperatures would require modification of both the vacuum capsule and specimen grips before a satisfactory test could be conducted. Lower temperatures, whilst practical from the point of view of the equipment available were considered impracticable from the point of view of the time available for each test.

2. 3.2.1. Air Tests.

A standard gauge-length of twenty millimetres was marked off on each specimen prior to insertion into the test-rig. The temperature of the specimen was raised at approximately 150 C° per hour to the test temperature. This comparatively low rate of heating was employed to avoid thermal shock and possible specimen distortion which are sometimes associated with high rates of heating. The specimen was held at temperature for twenty-four hours before application of the load to allow the system to attain thermal equilibrium. The loads employed during the tests ranged from 2.0 t.p.s.i. to 8.0 t.p.s.i..

Initially the extension of the specimen was recorded every quarter of an hour. After two hours the time interval was extended to one hour and eventually to twelve hours. On failure, or completion of 1000 hours, which ever was the sooner, the specimen was removed from the test-rig and quenched to room temperature. The ductility of the specimen was then measured. The specimen was subsequently mounted, sectioned longitudinally, and prepared for metallographic examination.

A minimum of three tests were conducted at each load employed. A greater number of tests were carried out if the correlation between the results of the three tests was poor.

2. 3.2.2. Vacuum Tests.

Specimen preparation prior to insertion into the test-rig was the same as for the air-test specimens. Loading of the specimen into the vacuum capsule was achieved by inserting the extension rods into the sleeve of the upper closure plate (C), a seal between the two was obtained by means of 'O' rings and brass pressure discs described previously. The whole assembly was then positioned on the vacuum capsule body by means of six thumb screws. The lower closure-plate was sited in a similar manner.

On reaching the working vacuum, 2×10^{-5} torr, the temperature of the specimens was raised to 300 °C and held for approximately an hour to facilitate out-gassing of the system. The specimen temperature was then raised to the test-temperature and held for twenty-four hours before application of the load to enable thermal equilibrium to be attained in the system

The load was applied to the specimen by means of a universal joint attached to the load-arm of the creep-machine. This was employed in preference to a normal unidirectional joint because of its ability to absorb misalignment in the apparatus without straining the specimen. Specimen extension on loading was recorded in the same manner as in the air tests.

On completion of the test the load was removed from the specimen and the system cooled to room-temperature under vacuum. The specimen was then removed and prepared for metallographic examination.

The experimental conditions of the vacuum tests were made as near identical as possible to those of the air tests to enable a direct comparison of the behaviour of the alloy in the two environments to be made. The problem of friction in the extension rod seals was overcome by loading the load-arm of the creep-machine until the extension rods just moved through the seals. Half this load was added to the test load to compensate for the frictional drag in the upper seal during the test.

2. 3.2.3. Argon Tests.

The method of assembly of the test-rig for argon environment tests was identical with that of the vacuum tests. Initially the system was evacuated and flushed with argon at atmospheric pressure. This was repeated a number of times before finally evacuating to a pressure of 2×10^{-5} torr. The temperature of the specimen was then raised to the test temperature in the same manner as in the vacuum tests. On attaining the test temperature argon at a small positive pressure was introduced into the system. The system was held at temperature for twenty-four hours before application of the lead to the specimen to allow it to reach thermal equilibrium.

This procedure was adopted in preference to heating the specimen totally under argon since any 'vapour' due to out-gassing was removed immediately and hence could not contaminate the environment.

After completion of the test the specimen was cooled to room-temperature and prepared for metallographic examination in the manner described previously.

2. 3.3. Metallography.

The metallographic investigation of cavitation in the alloy may readily be divided into optical and electron microscopy. The former was employed primarily to obtain an indication of the size and distribution of the cavities, and the latter to obtain an indication of the morphology of the cavities.

2. 3.3.1. Optical Metallography.

Specimens for optical metallography were mounted in bakelite, sectioned longitudinally, and mechanically polished to 1/4μm. diamond finish in the conventional manner. The time of mechanical polishing was kept to a minimum to reduce the degree of distortion of the cavities. To ensure that the centre-line section of the specimen was being examined the specimen width was carefully measured during the mechanical polishing process. After mechanical polishing each specimen was electro polished in the A_2 Disapol solution at 23 volts for three seconds. This technique of 'shock' electro-polishing was found to remove the work-hardened surface layer without marked distortion of the cavities. After the electro-polish each specimen was electro-etched in 10% Oxalic acid solution at 6 volts for twelve seconds. This again was kept to a minimum to reduce cavity distortion.

A statistical survey of the distribution of cavity size and number was conducted on each specimen by means of a Reichert Projection Microscope fitted with a micrometer stage and a graduated screen. Twenty grain-boundaries which intersected the surface of the specimen were traced from the surface to the centre at a magnification of X 600. The number of true grain-boundaries surveyed in one specimen was in the region of one hundred, a grain-boundary in the context of the survey being composed of four or five successive true grain-boundaries the path of which extended from the surface to the centre of the specimen. A minimum of three specimens were surveyed in this manner producing in all over sixty results per unit depth below the specimen surface. This number of results was considered sufficient to produce an accurate representative mean which took into account the variation in cavitation behaviour with orientation of the grain-boundary to the stress axis. The following parameters were measured:

(a) the number of cavities per unit grain-boundary length,

and (b) the mean size of cavity per unit grain-boundary length.

The unit grain-boundary length employed was 0.166 millimetres, ie. 100 millimetre divided by 600 times magnification. The mean values of these parameters were plotted against distance from the specimen surface. The overall reproducability of these parameters was assessed at ± 10%.

2. 3.3.2. Electron Metallography.

Replica Technique.

Specimens prepared in the manner described for optical metallography were replicated by direct carbon deposition. A thick deposit was employed to facilitate easy removal from the cavitated surface. The carbon replicas were removed by electro-etching in 5% Nital solution at 70 volts followed by immersion of the specimen in distilled water. After washing in 50% nitric acid solution and distilled water the replicas were caught on copper grids, dried, and examined in a J.E.M.6G. electron microscope at 80 Kv..

Scanning Technique.

A number of specimens were removed from the bakelite mounts and fractured by impact. The fractured faces were then examined by conventional metallography for cavities. Little success was achieved due to the small size of the cavities and the short focal length of the objective lens which produced the required magnification. This difficulty was overcome by use of a Cambridge scanning electron microscope. Specimens which had been tested in air and vacuum at 2.0 t.p.s.i. were examined for size and distribution of cavities by this means.

Thin Foil Technique.

The main difficulty of examination of cavities by thin foil electron microscopy is that the diameter of the cavity is usually greater than the thickness of the foil which can be penetrated by the electron beam. This difficulty has been overcome to some extent by Taplin et al[99] who developed a technique of shadowgraph transmission electron microscopy. Basically, the specimen for examination is thinned such that the eletron beam penetrates only where a cavity is enclosed. Thus an outline of the enclosed cavity is produced.

Several specimens were removed from the bakelite mounts and sectioned longitudinally into thin strips by spark machining. These were then thinned by chemical and electro-polishing until it was considered that a section was sufficiently thin for examination by the shadowgraph technique. This section was removed from the strip by cutting with a sharp blade, mounted in a specimen holder and examined in a J.E.M. 6G. electron microscope at 100 Kv.. Details of the polishing solution and conditions employed are given in the Experimental Details - Electro-polishing section.

The main criticism of the technique is that it is difficult to interpret whether an observation is of a totally enclosed cavity or a partially enclosed cavity the morphology of which may have been distorted by polishing.

2. 3.4. Activation Energy Determination.

The activation energies for creep in air and vacuum were determined by a modified version of the temperature change-creep rate change technique originally proposed by Dorn.[102] This technique involves the determination of the minimum creep rate before and after a sudden change in temperature. The activation energy of the process is determined from the equation:

$$\Delta H = R\overset{ln}{\left(\frac{P_1}{P_2}\right)}\cancel{ln}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)^{-1}$$

where P_1 is the minimum creep rate at temperature T_1

P_2 is the minimum creep rate at temperature T_2

If the means of the minimum creep rate of a number of tests at different temperature are plotted in place of P_1 and P_2 then the mean or average activation energy for creep in the alloy may be determined by a graphical change in temperature rather than a physical change.

A number of tests in both air and vacuum were conducted at 700°C and 900°C at a load of 2.0 t.p.s.i.. The use of temperatures above and below the major test temperature enabled an average value of the activation energy at 800°C to be determined. A minimum of three tests were conducted at each temperature, the mean minimum creep rates of which were employed for calculation of the activation energy.

2. 3.5. Gas Analysis.

To assess whether gas had diffused into the specimens during the air test or vice versa during the vacuum and argon tests an oxygen and nitrogen analysis was carried out after each test. A series of specimens were also held at temperature in air for different periods of time to obtain an indication of the rate of diffusion of the gases into the metal.

The oxygen content of the specimens were determined by a vacuum-fusion technique which entailed the melting of a known weight of metal under vacuum in a graphite crucible. Any oxygen present in the specimen as gas or oxide reacts with the carbon of the crucible to produce carbon monoxide. The concentration of carbon monoxide in the evolved gases was then determined by an infra-red absorption spectroscopy technique, and hence the oxygen concentration in the sample.

The nitrogen content was determined by the Kjeldahl technique which is essentially based on the conversion of the nitrogen in the sample into ammonia, the concentration of which is determined by titration, hence the nitrogen concentration in the sample can be calculated.

The difficulty of both techniques of analysis is that they are subject to large experimental errors, particularly when small concentrations are being measured. The inherent errors of the technique are also enhanced by the small size of specimen available for the analysis.

Chapter 3.

RESULTS OF PRELIMINARY WORK.

As the greater proportion of the work in this thesis has been devoted to 18/8 niobium stabilised stainless steel the results of the preliminary investigation employing α-brass will be reported and discussed only in this chapter.

3. 1. Mechanical and Metallographic Examination of α-brass.

The overall effect of variation of strain rate and temperature on the ductility and cavitation behaviour of the alloy appears to follow classical lines, figure 15.

At temperature below 0.4 Tm ($\sim$ 200 C) the alloy failed in a ductile manner at all strain rates. Above this temperature a rapid fall in ductility accompanied by a change in fracture mode from transgranular to intergranular was observed. The degree of the loss of ductility and the form of the intergranular deformation was found to be dependent both on strain rate and on temperature. Thus, whilst no variation in fracture mode with strain rate was found at 0.4 Tm ($\sim$ 200°C), the fracture mode remaining W-type cracking throughout, figure 16, a variation was observed in the ductility of the alloy. This was due to opening of cracks and transgranular plastic deformation at the higher strain rates. At 0.5 Tm ($\sim$ 350°C), on the other hand, both ductility and fracture mode varied with strain rate. The fracture morphology was found to vary from a 'ragged or scalloped-edge' form of W-type cracking at low strain rates, figure 17, to classical sharp outlined W-type cracking at high strain rates. The 'ragged' form of W-type cracking (hereinafter referred to as pseudo-W-type cracking) was associated with a greater loss of ductility than the classical form. The scalloped appearance of this form of cracking suggests that it may be the result of either rapid growth and coalescence of r-type cavities in the plane of the grain-boundary producing W-type cracking of the form postulated by Stiegler et al, or tearing of the boundary between isolated r-type cavities under the influence of the applied shear stress.

At temperatures in the range 0.55 to 0.7 Tm (400 to 600°C) a further fall in ductility at all strain rates was noted. Metallographic examination indicated that at low strain-rates the fracture mechanism was one of growth and coalescence of isolated r-type cavities, figure 18, whilst at high strain rates it took the form of propagation of pseudo-W-type cracks. The strain rate at which the transition from true r-type cavitation to pseudo-W-type cracking occurred was found to be dependent on temperature. Thus at 0.55 Tm (400°C) the transition strain rate was approximately 0.008 whilst at 0.7 Tm (600°C) it was 0.02.

A small increase in ductility was observed in specimens tested at high temperatures, 0.85 Tm (~ 800°C) and low strain rates. Metallographic examination of the fractured specimens showed that extensive grain-boundary migration had taken place under these conditions. This appeared to act as a stress relief mechanism thereby inhibiting cavitation and promoting ductility. At high strain rates fracture by propagation of pseudo-W-type cracks was again observed suggesting that insufficient time was available for stress relief by grain-boundary migration.

3. 1.1. Discussion and Conclusion.

Examination of figure 15, together with the metallographic observations indicates that there exists an optimum range of both temperature and strain rate for failure of α-brass by r-type cavitation. This is illustrated schematically in figure 19. Analysis of the results falling within the r-type cavitation zone indicates that r-type cavities are formed in the alloy at temperatures within the range 350 to 750°C at strain rates less than 0.02. Unfortunately a direct indication of the variation in ductility with temperature at a given strain rate cannot be obtained from these figures. It is possible, however, to obtain a plot of this form by transcribing the plots of figure 15 at a constant strain rate. A typical example of the form of curve obtained is illustrated in figure 20. The curve shows a maximum at temperatures below approximately 0.4 Tm ($\sim 200^{\circ}C$) corresponding to ductile fracture and a minimum corresponding to the development of intergranular cavitation.

The observed change in fracture mode with temperature and strain rate follows the general trend reported in the literature. That is, at low temperatures and high strain rates where stress relief at triple points by plastic deformation is difficult fracture occurs along grain-boundaries lying in the plane of maximum shear stress. In the system investigated this appears to be at approximately 90° to the applied stress axis. The forms of W-type cracking observed in the course of the investigation are typical of those reported by Chang et al[53], figure 3.

Cracking of the morphology of the pseudo-W-type cracking, figure 17, does not appear to have been reported in the literature. Its' appearance, as proposed previously, would suggest that it is the result of either rapid growth of r-type cavities in the plane of the grain-boundary resulting in the formation of W-type cracks by the mechanism proposed by Striegler et al[59] or alternatively tearing of the boundary between isolated cavities under the combined action of the applied stress and grain-boundary shear stress.

Deformation of the alloy under conditions of high temperatures and low strain rates is found to produce failure by growth and coalescence of r-type cavities in boundaries lying at approximately 90° to the applied stress axis. The mechanism of formation of this form of failure, as pointed out in the literature review, is in considerable dispute. Resnick et al[48], and subsequently many other workers, proposed that r-type cavities are nucleated at non-wetting particles lying in the grain-boundary, Gifkins[90], and later Chen et al[91], on the other hand, proposed that nucleation of r-type cavities is the result of fracture of ledges produced by slip-grain-boundary interaction.

Metallographic examination of specimens failed by r-type cavitation showed that many of the cavities and cracks contained an oxide film. It was thought that the film was a product of oxygen diffusion after cavitation and not a prerequisite for cavity nucleation as no discreet oxide particles were observed in grain-boundaries which were not cavitated.

A number of grain-boundaries which did not contain r-type cavities were observed to contain regular shaped serrations, which, in a number of cases, were accompanied by small regular shaped cracks, figure 21. The width of the serrations was found to be approximately 2.5μm and the height 1.5μm. A number of workers[104-107] have shown that the height and width of slip bands in metals and alloys increases with increase in temperature and/or decrease in strain rate. It follows therefore that the serrations observed in the grain-boundaries could be ledges produced by slip-grain-boundary interaction. The height of the serration is unfortunately approximately two orders of magnitude greater than that required for stability in the cavity nucleation models of Gifkins,[90] Chen et al,[91] and McLean.[92] It is possible, however, that the true height of the serration is considerably less than the observed height due to the angle of the grain-boundary to the plane of section.

Theoretical models of r-type cavity nucleation propose that nucleation occurs by fracture at ledge-grain-boundary interfaces under the influence of shear stresses developed at that point by grain-boundary sliding. Growth is thought to occur by either continued grain-boundary sliding or condensation of vacancies. If the former mechanism is correct then plastic flow of material around the ledge interface must take place to maintain material continuity. It follows therefore, that if such plastic flow is restricted stresses of sufficient magnitude to initiate fracture may develop at that point. This is illustrated schematically in figure 22. It is proposed that the cracks observed in figure 21 were formed by such a mechanism.

3. 2. 18/8 Niobium Stabilised Stainless Steel.

The temperature range employed during the preliminary investigation of the fracture behaviour of 18/8 stainless steel was entirely above 0.5 Tm (600°C), consequently no ductile failure was observed, figure 23.

The change in fracture behaviour of the steel with variation in strain rate and temperature was similar to that observed in α-brass. That is, at low strain rates the fracture mode is observed to progress from true-W-type cracking, to pseudo-W-type cracking, and finally to r-type cavitation with increase in temperature. The ductility was observed to decrease rapidly to a minimum and then rise again at a slow rate with change in fracture mode, figure 24. The minimum of the curve was found to correspond to the formation of pseudo-W-type cracking in the temperature range 0.5 to 0.55 Tm ($\sim$ 600 to 700°C) and the rise to the formation of r-type cavities at temperatures above this range. At temperatures above 0.65 Tm ($\sim$ 900°C) extensive grain-boundary precipitation was observed. Precipitation of this form has been shown to produce a denuded zone in the boundary which is capable of undergoing extensive plastic deformation and stress relief processes thus increasing the ductility of the material.[68,69] Final failure was observed to be the growth and coalescence of cavities nucleated at the precipitate particles, figure 25. The nucleation mechanism is possibly of the form proposed by Resnick et al[48], figure 4. At very high temperatures > 0.7 Tm ($> \sim 1000$°C) a further increase in ductility was observed. Metallographic examination indicated that this was due to resolution of some of the precipitated particles thus increasing the ductility of the material by first increasing the degree of plastic deformation which can be accommodated before nucleation of a cavity, and second by reducing the resistance to stress relief by grain-boundary migration.

At high strain rates the fracture form was found to change from true-W-type cracking at low temperatures to pseudo-W-type at high temperatures. The change in fracture morphology was associated with a fall in ductility.

3. 2.1. Discussion and Conclusion.

The results of the preliminary investigation into the cavitation behaviour of 18/8 niobium stabilised stainless steel indicate that failure occurs by r-type cavitation within the temperature range 700 to 900°C providing the strain rate is below 0.005. Because of the possibility of modification of the fracture mechanism at the two extremes of this range and difficulty in construction of apparatus for prolonged tests at the higher end of this range it was decided that the majority of the environmental creep tests be conducted at 800°C. Calculations based on available data for grain-boundary diffusion of oxygen and nitrogen in γ-iron[103] indicate that at 800°C a period of approximately 1000 hours is required for diffusion of these gases to the centre of specimens of the size to be employed in the creep tests. It was therefore decided that the majority of the environmental creep tests be carried out for this period of time.

Chapter 4.

CREEP RUPTURE OF 18/8 NIOBIUM STABILISED STAINLESS STEEL.

The results of the creep tests conducted in air at 800°C are reported graphically in figure 26. Variation in load below approximately 4.0 t.p.s.i. appears to have little affect on the form of the creep curve until the specimen is into the tertiary creep stage. Here the creep rate increases at a greater rate in specimens subjected to the higher loads. This would suggest that the deformation mode is independent of stress during the secondary period, but is stress dependent during the tertiary stage.

Above 4.0 t.p.s.i. a marked increase in both minimum creep rate and ductility with load was observed suggesting that a different deformation mode was operative to that at lower loads.

Variation in temperature was found to exert considerable influence on the form of the creep curve under a given load. A typical example of the form of variation encountered is illustrated by figure 27 which shows the types of curve obtained under a load of 2.0 t.p.s.i.. It can be seen that an increase in temperature brings about an increase in the minimum creep rate, a shorter secondary creep period, greater overall creep rate, and lastly greater creep ductility.

Activation energies determined from these plots by the method described previously give values of 68.5 and 75.8 K.cals./mol. for a temperature decrease and increase respectively, figure 28. It is proposed that the mean value of these, 72.3 K.cals./mol., is the mean value of the activation energy for creep at 800°C, ie. the main test temperature.

4. 1. Optical Metallography.

For convenience the results of the optical metallographic investigation will be reported in three sections, first the investigation into cavitation behaviour at 800°C, second the influence of temperature on the fracture form, and finally, fractography of specimens broken by impact.

The observation made during the mechanical tests that specimens tested at loads in excess of 4.0 t.p.s.i. appeared to behave in a different manner to those tested at lower loads was confirmed by metallographic examination. Examination of specimens tested above 4.0 t.p.s.i. indicated that failure was by the initiation and propagation of W-type cracks. At 8.0 t.p.s.i. these were found to be extensive throughout the specimen section and appeared to be initiated at triple points and to propagate along grain-boundaries perpendicular or near-perpendicular to the applied stress axis, figure 29. Many of the cracks in the bulk of the specimen were observed to have interlinked to produce a single crack several grain-diameters in length. Examination of carefully prepared sections of specimens tested at 6.0 t.p.s.i. showed that although W-type cracking was in evidence at the surface and mid-radius position in the section small 'pits' having the appearance of r-type cavities were observed at the centre of the specimen. Lack of resolution at the high magnifications necessary to observe this feature, > 1500x, prevented definite identification of the 'pits' as r-type cavities or otherwise.

Specimens that had been deformed at loads less than 4.0 t.p.s.i. were found to contain numerous r-type cavities the majority of which lay on boundaries perpendicular or near-perpendicular to the applied stress axis, figure 30. Many of the grain-boundaries were observed to contain cracks the appearance of which suggested that they were the product of growth and coalescence of r-type cavities, figure 31.

The results of the statistical survey of cavity size and number in specimens which had failed by r-type cavitation, figures 32 and 33 indicate that these parameters are sensitive to position in the specimen section. It was found that both are at a maximum at the surface of the specimen and a minimum at the centre. The effect of stress on the magnitude of the parameters appears to be negligible, the spread of the plots for both parameters falling within the experimental error of ± 10%. This suggests that stress, within the range employed, has little or no effect on the number of possible nucleation sites and/or the growth rate of r-type cavities. Surface cracking prevented allocation of a value to the parameters at the subsurface position in the specimen.

All the specimens deformed during the mechanical tests in air were observed to contain cracks in grain-boundaries emerging at the surface of the specimen the appearance of which was found to vary with load. Above approximately 4.0 t.p.s.i. where the fracture mechanism was the propogation of W-type cracks the surface cracks had smooth outlines indicative of failure by shear of the grain-boundary. At stress below this value the surface emergent cracks were observed to have a scalloped appearance indicative of failure by coalescence of r-type cavities, figure 34. This was confirmed by the observation of a number of boundaries which contained 'embryonic' surface cracks in the process of formation by r-type cavity coalescence, figure 35(a) and (b).

A number of the tests conducted at a load of 2.0 t.p.s.i. were interrupted at fractions of the total test time, namely 250, 500, and 750 hours, and metallographically examined. The results of this investigation showed that the r-type cavities first became 'optically resolvable' in surface emergent grain-boundaries and that the point of 'resolvability' in the section moved towards the centre of the specimen with increase in time. That is, the time required for a r-type cavity to be nucleated and grow to a resolvable size increased with increase in distance from the specimen surface. Figure 36 (a) - (e) illustrates the form of the variation observed.

Temperature variation was observed to have considerable influence on the mode of fracture of specimens tested under loads of 2.0 t.p.s.i..

At 700°C cavitation was found to be of the form of small W-type cracks initiated at triple points, figure 37 (a) - (b). The small size of these together with the observation that propogation of cracks along the boundary away from the triple-point was very restricted suggests that crack growth is very difficult at this temperature. The absence of any resolvable r-type cavities, on the other hand, indicates that this mechanism of failure may be more favourable than r-type cavitation under the test conditions.

Cavitation behaviour at 800°C has been extensively reported previously and consequently it will be summarised very briefly at this stage. Fracture at 800°C was observed to occur by the nucleation, growth, and eventually coalescence of r-type cavities, the majority of which lay on grain-boundaries perpendicular or near perpendicular to the stress axis.

Extensive grain-boundary precipitation was observed in specimens tested at a temperature of 900°C. The particles were found to act both as a cavity nuclei and a crack arresting mechanism, as illustrated by figure 38. It can be seen from the photomicrograph that whilst an incoherent particle may nucleate an r-type cavity, its' growth may be restricted by the next particle. This is thought to be due to the particle remaining coherent or semi-coherent with the matrix and hence restricting crack propagation.

Optical fractography, as pointed out previously, gave little information of cavity distribution and morphology due to the short focal length and the narrow depth of field of the objective lens it was necessary to employ to obtain the required magnification. Figure 39 (a)-(b) shows the form of structure observed. As can be seen from the photomicrographs the structure observed does not lend itself readily to interpretation. It is suggested that the large disc-like structure, a number of which are arrowed, are large r-type cavities, and the small almost irresolvable cavities in the metal between the ductile fracture about carbide particles. The distribution of the disc-like structures was found to be fairly general with no preferred orientation.

4. 2. Electron Metallography.

Electron metallography, with the possible exception of scanning electron micro-fractography, cannot give a direct indication of the distribution of cavities in a specimen section. It can, however, show the variation in size and morphology of cavities formed in the metal in a given environment.

4. 2.1. Replica Metallography.

The usefulness of direct carbon replication of polished sections for study of r-type cavity distribution and morphology was found to be very limited owing to a 'keying in' action of the film in the cavities themselves. This resulted in either tearing of the carbon film or folding over to produce an impenetrable area of film on removal from the specimen surface. The technique did, however, show that many of the cavities were lenticular in outline, figure 40 (a) - (d), the major axis of which lay in the plane of the grain-boundary. The dark areas within the outline of the cavity were considered to be an area where the film had folded over.

From the shape of the cavities observed by this technique it may be argued that the major growth direction lies in the plane of the grain-boundary. It must be pointed out, however, that the technique can only give a two dimensional view of a three dimensional parameter, and consequently considerable care must be taken in interpreting the results obtained from it.

4. 2.2. Scanning Electron-Microfractography.

Scanning electron microfractography enabled the fracture surface of specimens broken by impact to be examined at high magnifications without the difficulties associated with optical fractography. The specimens were mounted in the microscope with their axis, ie. the stress axis, parallel to the electron beam. This enabled observations to be made of boundaries which are known to be favourably or unfavourably oriented for cavitation.

Figure 41(a) shows a typical area of the fracture surface, the stress axis of the specimen being perpendicular to the plane of the photomicrograph. It can be seen that cavities are present over the entire surface of all the grain facets with the exception of those inclined at a shallow angle to the stress axis, area A. Examination of such a facet, figure 41(b), showed that r-type cavities were present on the facet only in the vicinity of a grain juncture. This is possibly due to this being a zone of considerable lattice distortion resulting from slip grain-boundary interactions by neighbouring more favourably oriented grains. The apparent absence of r-type cavities elsewhere on the facet could be due to either the grain being unfavourably oriented for cavity nucleation, or alternatively unfavourably oriented for growth. It was difficult to determine which parameter was operative since the expected size of a stable cavity nucleus is less than the size of the cavities due to ductile fracture.

Examination of a typical triple point, figure 41(c) (area B) showed that the majority of cavities on a given facet lie with their major axes parallel suggesting some form of crystallographic relationship. In the region of grain junctures no such crystallographic directionality was observed. This was possibly due, as proposed previously, to the high number of slip systems operative in this zone.

At high magnifications two forms of r-type cavitation were observed depending on the orientation of the grain facet to the stress axis. Grain facets which were inclined at approximately 45° to the stress axis were observed to contain elliptical shaped shallow cavities, figure 47(d), between which existed extensive areas of ductile fracture. The base of each cavity appeared to be deeply striated, the stria being approximately at right angles to the major axis of the cavity. The width of the stria was found to vary between 4-6 μm. Facets which were perpendicular or near perpendicular to the stress axis were found to contain a greater number of cavities than those inclined at shallower angles, figure 41(e). The shape of these was found to be an irregular polyhedron, usually a distorted hexagon in section, the major axis of which lay parallel to one another. Many of the surfaces of the polyhedron were observed to be striated, the stria of neighbouring cavities being parallel. The width of the stria, however, appeared to be less than that observed on cavities formed on lower angle boundaries, 1-3 μm compared with 4-6 μm.

To ascertain whether the areas of small cavities observed between the r-type cavities were due to ductile fracture or cavitation a specimen which had been subjected to the same thermal conditions as the creep test specimens was broken by impact and the fracture face examined, figure 41(f). It can be seen that the fracture contains numerous small cavities due, it is proposed, to fracture about precipitates.

4. 2.3. Thin Foil Electron Metallography.

The preparation of thin foils from creep specimens for transmission electron microscopy has been laboriously tried in this investigation with little success. Transmission electron microscopy should show the structural changes taking place during creep but the areas of interest, namely the grain-boundaries, invariably contain cavities. These cavities made the preparation of thin foils of such areas impossible due to preferential thinning in their vicinity. Examination of this area was found to be possible, however, by the 'thick' thin foil techique developed by Taplin et al.[99]

Typical shadowgraphs obtained by this technique are shown in figure 42 (a) - (d). The profile of the cavities can be seen to be irregular but not to the extent reported by Taplin et al[99] in α -brass and copper. This is thought to be due to the cooling rate from the test temperature being sufficiently slow to allow some annealing of the cavities to take place, Taplin et al[99] have shown this to result in a smooth rounded profile.

The elongation of the cavities observed by this technique confirms the observations made during the fractographic investigation in that the cavities are elongated in the plane of the grain-boundary.

In an attempt to obtain an indication of the morphology of the cavities from these results a series of optical density measurements were taken across the photographic plates. The readings were plotted against position in the profile and a model constructed from the resultant curves. The general shape of the cavity by this technique would appear to be an oblate spheroid, the two major axes of which lay in the plane of the grain-boundary. Figure 43 illustrates the form of model obtained by this technique from figure 42(d).

4. 3. Gas Analysis.

The oxygen and nitrogen contents of the specimens before, during, and after completion of the creep-rupture tests in air are reported in Table 2. It is obvious from the Table that both the oxygen and nitrogen contents of the specimens increase steadily with time at temperature. Over the test period of one thousand hours the oxygen content was found to increase by 117%, that is from 0.006% in the fully solution-treated condition before the test to 0.013% after completion of the test. The corresponding increase in the nitrogen content was from 0.033% to 0.043% respectively, an overall increase of 33%.

Temperature as expected, was found to exert considerable influence on the rate at which the two gases diffused into the steel. Thus at 700°C the oxygen and nitrogen contents increased by 67% and 3% per thousand hours whilst at 900°C the rate was found to have increased by 400% and 46% per thousand hours respectively.

4. 4. Discussion.

Both forms of intergranular creep fracture have been observed in the steel on testing in air. W-type cracking was found to form under conditions of low temperature and/or high stress whilst r-type cavitation was observed at high temperatures and low stresses.

W-type cracking observed during the course of the investigation may be divided into two forms. At high temperatures and high stresses the cracking was found to be of the classical form and to be very extensive throughout the section. At low temperatures and lower stresses, on the other hand, it was confined almost entirely to the triple point.

These observations could be a combined effect of both temperature and stress rather than a single parameter. The requirements for nucleation of a W-type crack are the development of a stress concentration at a triple point by grain-boundary sliding and that this should not be relieved by plastic deformation. For propagation the stress should be sufficiently high to cause shear of the grain-boundary without extensive transgranular deformation. It is thought that both these conditions are satisfied in the high temperature tests, 800°C at stresses $>$ 6.0 t.p.s.i., but that only the first is satisfied in the lower temperature tests, 700°C at 2.0 t.p.s.i.. Hence the failure of cracks nucleated under these conditions to propagate along the grain-boundary.

The observed change in fracture form at a constant stress with increase in temperature would suggest that the mechanism of fracture operative at a given temperature depends on the ability of the material to plastically deform. That is at low temperatures the bulk grain of the material is resistant to plastic deformation and consequently the majority of deformation is concentrated in the grain-boundary. Under such conditions the small degrees of grain-boundary sliding that occur at these temperatures are capable of developing sufficient stress concentrations at triple points to initiate fracture. Propagation of cracks so initiated is thought to occur by the development of stress concentrations at the crack tip by grain-boundary sliding and the applied stress, and propagation of the crack until it is stabilised. Further propagation may then occur by repetition of the cycle.

At high temperatures transgranular deformation can take place giving rise to ledges in the grain-boundary. Cavities are thought to be initiated at these by grain-boundary sliding. Stress concentrations of sufficient magnitude to initiate cracks at triple points are not developed at these temperatures in spite of the increased degrees of grain-boundary sliding due to the high rates of stress relief by plastic deformation.

R-type cavitation has been observed to form in the material at low stresses at 800°C and 900°C. Formation at the latter temperature was found to be associated with the precipitation of carbide particles in the grain-boundary. The mechanism of nucleation would appear to be of the form originally proposed by Resnick et al[48], that is grain-boundary sliding about incoherent or semi-coherent particles. Nucleation of cavities at 800°C has been shown by optical and electron metallography not to be associated with this mechanism. It is thought that the operative process is grain-boundary sliding about ledges.

The observed continued fall in the magnitude of the measured cavitation parameters with increasing distance from the surface of a specimen suggests that either the nucleation mechanism or growth mechanism is sensitive to position in the section. A review of the literature indicates that this may be by one or more of a number of mechanisms. These include the diffusion of reactive gases to form particles in the grain-boundary by chemical reaction, for example internal oxidation, and the subsequent nucleation of a cavity by grain-boundary sliding, the diffusion of gases into ~~an~~ embryonic nuclei thereby stabilising them and promoting growth, and finally reduction of the surface energy of existing cavities by gaseous condensation and thus promoting growth.

All the aforementioned mechanisms involve the diffusion of a gas from the atmosphere surrounding a specimen to the site of an r-type cavity, be it an embryonic nuclei or a stable one. Since diffusion is a time dependent process it follows that the length of the diffusion path is also time dependent. It also follows that if either nucleation or growth are affected by gaseous diffusion then a variation in the degree of cavitation across the specimen section should be observed, and that the degree of cavitiation should be a maximum at the surface and a minimum at the centre of the specimen section. It also follows that the gas content of the specimen should increase with time. The observations made during the course of this work have shown that such variations do exist and growth of r-type cavities is time dependent is illustrated clearly by the advancing front of 'resolvability' of r-type cavities observed in the interrupted tests. It may be argued that the front 'resolvability' of r-type cavities coincides with the gaseous diffusion front, but no direct evidence was obtained from this investigation to substantiate this.

TABLE 2.

Influence of test conditions on the Oxygen and Nitrogen contents of a 18/8 niobium stabilised stainless steel.

Temperature (°C).	Time at Temperature. (hours).	Environment.	Oxygen Content wt. %.	Nitrogen Content wt. %.	Increase in Oxygen Content %½	Increase in Nitrogen Content %.
Bar Stock	-	-	0.006	0.033	-	-
Solution treated	-	-	0.006	0.034	-	3.0
800	250	Air	0.009	0.036	50	5.9
800	500	Air	0.013	0.037	116.5	8.9
800	750	Air	0.014	0.041	133.5	23.5
800	1000	Air	0.015	0.044	150.0	30.0
800	1000	Vacuum	0.006	0.034	0	0
800	1000	Argon	0.007	0.034	16.5	0
900	1000	Air	0.030	0.049	400	46
900	1000	Vacuum	0.008	0.033	33	0
700	1000	Air	0.010	0.035	66.7	3
700	1000	Vacuum	0.006	0.034	0	0

Chapter 5.

CREEP RUPTURE OF 18/8 NIOBIUM STABILISED STAINLESS STEEL IN VACUUM AND ARGON.

It has been established by testing specimens in air that the degree of intergranular cavitation can be correlated with increase in the nitrogen and oxygen contents of the steel. It follows therefore that if the gaseous environment were removed, that is the specimens tested in vacuum, then no variation in degree with position in the specimen section should be observed.

To test the validity of this argument a series of tests were conducted in vacuum under the same conditions of temperature and stress as those in air. To determine whether any difference in cavitation behaviour was due to a 'reaction effect' or due entirely to the presence of a gaseous environment a similar series of tests were conducted in pure argon.

5. 1. Creep Rupture in Vacuum.

Figure 44 shows the form of creep rupture curves obtained on testing the material under various loads at 800°C in vacuum.

Variation in load below approximately 6.0 t.p.s.i. was found to exert little influence on the form of the curve whilst the specimen is undergoing secondary creep. On entering the tertiary stage, however, the creep rate was found to increase rapidly with load. Above 6.0 t.p.s.i. a marked increase in both the minimum creep rate and ductility with load was observed. This rapid change in the form of the creep curve with load would suggest that the deformation mode is stress dependent; that is, at high stresses deformation and eventual fracture occur by a different mechanism to that at low stress levels.

A similar critical condition producing a marked change in the mechanical behaviour was found on varying the temperature at a constant load of 2.0 t.p.s.i. Thus at 700°C and 800°C little difference was observed between the form or magnitude of the two creep curves. At temperatures above this level, however, the material was found to undergo a marked increase in the minimum creep rate and ductility which were accompanied by a decrease in the creep life. The form of the curves obtained from this section of the investigation are illustrated in figure 45.

Activation energies determined from these plots by the method described previously give values of 75.58 K.cals./mol. and 74.98 K.cals./mol. for a temperature increase and decrease respectively. It is proposed that the mean value of these, 75.28 K.cals./mol., is the mean activation energy for creep in vacuum at 800°C, figure 46.

For convenience the results of the optical metallographic examination will be reported in the same sequence as in the air tests, that is first the investigation into cavitiation behaviour at 800°C, second the influence of temperature on the fracture form, and lastly, fractography of specimens broken by impact.

The possible existence of a change in fracture mode with load at 800°C indicated by the mechanical tests was confirmed by the metallographic examination.

Specimens tested at stresses above approximately 6.0 t.p.s.i. were found to have failed by the initiation and propagation of W-type cracks. These were confined mainly to the surface region, although a number of comparatively smaller cracks of the classical form were observed in the bulk of the specimens, figure 47.

Deformation at stresses less than 6.0 t.p.s.i. was found to produce a sparse uniform distribution of r-type cavities throughout the specimen. The majority ~~was~~ were found to lie on grain-boundaries perpendicular or near perpendicular to the applied stress axis, figure 48. With the exception of specimens tested at 6.0 t.p.s.i. no cracks were observed in the specimen sections examined, the cavities remaining as discrete entities throughout. At this stress level a number of small wide surface cracks more indicative of failure by shear rather than coalescence of r-type cavities were found, figure 49.

The statistical survey of the number and size of cavities in specimens which had failed by r-type cavitation indicated that the magnitude of these parameters was little influenced by position in the specimen section, figures 50 and 51. A slight rise both in the number and size of r-type cavities in the region of the surface ~~was~~ were observed. This may be due to there being a greater degree of freedom of movement in surface emergent grain-boundaries compared with those of the interior.

Stress appears from the plots to have little effect on the magnitude of the parameters except in the region of the surface, the spread of the plots for the major portion of the curve falling within the experimental error of ± 10%. This would suggest that under the conditions of the experiments stress has little or no effect on the number of possible nucleation sites And/or the growth of r-type cavities.

With the exception of specimens deformed at or above 6.0 t.p.s.i. no fracture of the surface emergent grain-boundaries was observed. The form of the fracture at 6.0 t.p.s.i., smooth, wide and shallow is more indicative of failure by shear than by growth and coalescence of r-type cavities. It would also suggest that once formed these cracks are rapidly stabilised. At stresses above 6.0 t.p.s.i. fracture appears to be entirely by a mechanism of nucleation of W-type cracks. It is interesting to note in this respect that the surface has the greater propensity for fracture by this mechanism.

Variation in temperature was observed to cause considerable modification of the mode of fracture of specimens stressed at a constant load at 2.0 t.p.s.i..

At 700°C cavitation was found to be of the form of fine W-type cracking confined almost entirely to the triple-point, figure 52. Little or no propagation of the cracks away from the nucleation sites was observed. It would appear therefore that crack propagation at this temperature is extremely difficult. Similarly, the absence of r-type cavitation would suggest that failure by this mechanism was also difficult under the conditions of the experiment.

Cavitation behaviour at 800°C has been reported extensively elsewhere and consequently it will be summarised briefly at this stage.

Fracture at 800°C was observed to occur by the initiation and propagation of r-type cavities primarily along grain-boundaries perpendicular or nearly perpendicular to the applied stress axis.

Extensive grain-boundary migration and precipitation was observed to have taken place in specimens tested at 900°C, figure 53. The grain-boundary migration would appear to have acted as a stress relief mechanism as fracture about precipitates was considerably restricted compared with that observed in specimens tested under similar conditions in air. Final fracture is thought to be the propagation of cavities initiated at the grain-boundary precipitates.

Precipitates both in the matrix and grain-boundary appear to inhibit the extent of migration of the boundary resulting in 'bowing' out of the boundary as shown in figure 54. In this respect grain-boundary precipitates 9/5 appear to be more effective in restricting migration than matrix precipitates.

Optical fractography, as pointed out in the previous section, gave little information of cavity size, morphology, or distribution due to difficulties with the optical system it was necessary to employ to obtain the required magnification. Figure 55 shows the form of structure observed. As can be seen from the photomicrograph no obvious r-type cavities can be seen, the structure being entirely one of cavitation due to ductile fracture about precipitates. Calculations based on the results from the conventional optical metallography indicate that the size of the r-type cavities present in the material are approximately equal to that of the ductile fracture cavities, consequently identification of a r-type cavity on such a fracture surface would be extremely difficult.

5. 2.1. Electron Metallography.

Electron metallography, as indicated previously, is very restricted in the amount of information it can give on cavity distribution. It can, however, give some indication of morphology and size of the cavities.

5. 1.2.1. Replica Metallography.

Considerable difficulty was experienced in removing the deposited carbon film from the specimen surface due to 'keying in' at the cavities themselves. This resulted in either tearing of the film or production of a impenetrable area of film due to folding over.

Cavities observed by this technique were found to be rounded or polyhedral in section, figure 56. It is possible that the observed shape is due to either artificial 'rounding off' during the polishing processes or to sintering of the cavities during the slow cool from the test temperature necessary to maintain the vacuum. This has been shown to produce conditions of sintering in which cavities attain their equilibrium structure, that is a regular polyhedron.

5. 1.2.2. Scanning Electron Micro-Fractography.

Scanning electron microfractography confirmed the results obtained from the optical fractography investigation in that the size of the r-type cavity due to intergranular failure was equal to or less than that of cavities due to ductile fracture about precipitates. Figure 57 shows the form of the structure observed by this technique.

It is obvious from this photomicrograph that identification of an r-type cavity on such a surface is impossible.

5. 1.2.3. Thin Foil Electron Microscopy.

It was thought that the small size of cavity formed in the material under the conditions employed for this section of the investigation would allow foils of the grain-boundary region to be prepared with comparative ease. Unfortunately this was not the case, the material preferentially polished in the region of the cavities and prevented the production of a suitable foil. Consequently the 'thick' thin foil technique was employed to study this region.

Shadowgraphs of cavities obtained by the technique showed them to have a regular outline tending towards an oblate spheroid, figure 58. This is thought to be due to sintering taking place during the slow cooling process to room temperature necessary to maintain the specimen free from oxidation. This phenomenon together with the small size makes it very difficult to draw any conclusions to the true morphology or size of the cavities present in the material.

5. 1.8. Gas Analysis.

Gas analysis before and after testing in vacuum was unable to detect any change either in the nitrogen or the oxygen contents of the specimens. The values obtained were of the same order of magnitude as obtained for the solution-treated material and the 'as-received' bar stock. Table 2 shows the results obtained.

5. 2. Creep Rupture in Argon.

The form of the creep-rupture curves obtained on testing the steel in argon atmosphere at 800°C are illustrated in figure 59. Load would appear from these plots to have little effect on the form of the creep curve until the material has entered the tertiary creep stage. Here the creep rate was found to increase with increase in load.

5. 2.1. Optical Metallography.

Optical metallographic examination of specimens tested in argon were confinced to conducting a statistical survey of r-type cavity size and number by the technique described previously. The results of this survey are illustrated in figures 60 and 61. It is immediately obvious from these plots that the magnitude of the parameters is not very sensitive to position in the specimen section, the majority of the parameters attaining a constant value just below the surface.

Variation in stress appears from the plots to have little effect on the magnitude of the parameters except in the region of the specimen surface where the extent of the deviation increases with stress. At the high stress levels surface cracks were observed. The morphology of the cracks was found to be indicative of failure by growth and coalescence of r-type cavities rather than shear of the boundary under the influence of the applied stress. Cavitation at low stresses was found to be of the form observed in specimens tested in vacuum, that is a uniform distribution of r-type cavities.

5. 2.2. Gas Analysis.

The results of the analysis for the oxygen and nitrogen contents of the steel indicate that the oxygen concentration in the steel increases slightly over a period of one thousand hours. The magnitude of the increase, 16%, is considered to be just outside the experimental error of the technique employed and consequently it is thought that no great significance should be attached to it. The actual oxygen and nitrogen figures obtained from the analysis of the specimens are reported in Table 2.

A possible source of the oxygen is thought to be the argon itself which was stated to have an oxygen content of less than 2 pp.m.. Whilst this is very small in itself it is large compared with that in vacuum of 10^{-5}torr where no increase was detected.

5. 3. Discussion.

It has been shown during the course of this investigation that both W-type and r-type intergranular fracture may occur in specimens tested in vacuum or argon depending on temperature and load.

W-type cracking was found to occur in two forms depending on the temperature and stress. Thus at 600°C cracking was found to be initiated at the surface of specimens and to a lesser extent in the bulk material at loads in excess of 6.0 t.p.s.i.. At 700°C, on the other hand, W-type cracking was initiated as low as 2.0 t.p.s.i.. Propagation of the cracks at this temperature, however, was found to be very limited. The extent of propagation from the triple points was considerably less than that observed in specimens tested in air under similar conditions of temperature and stress, figure 37 c.f. figure 52.

The conditions for the initiation and propagation of a W-type crack in the steel in vacuum or argon should be identical with those for crack formation in air. It follows therefore that any variation in the fracture behaviour of the steel in the different environments must be related to the environment itself. It is not intended to elaborate this argument farther at this stage as it will be discussed at length in the next chapter.

R-type cavities have been observed to form in the material at low stress levels at temperatures in excess of 800°C.

Cavitation at 900°C has been shown to be of the form originally proposed by Resnick et al[48], that is fracture due to grain-boundary sliding about particles. The extent of cavitation would appear limited compared to that in specimens tested in air under the same conditions of temperature and stress. This could be due partially to grain-boundary migration acting as a stress relief mechanism. Migration of the grain-boundary is thought to reduce the stress concentrations around a particle or a growing crack thereby promoting an increase in ductility and fracture life. Pinning of the migrating boundary by particles is thought to prevent total stress relief by this mechanism and consequently failure by propagation of cavities can take place.

Fracture at 800°C has been shown to occur by the coalescence of r-type cavities at stresses below 6.0 t.p.s.i.. The majority of the cavities observed were small and isolated compared with those observed in specimens tested under the same conditions of temperature and stress in air. This would suggest that either the nucleation or growth of r-type cavities in the steel in an argon or vacuum environment is more difficult than in air. This is substantiated to some extent by the failure to observe r-type cavities by fractography and the small size of cavities observed by transmission electron microscopy.

The almost constant number and size of r-type cavities across the specimen section indicates that nucleation and growth must occur at the same rate in all positions in the section. If this argument is valid it follows that all the cavities must be nucleated in a short period of time from one another, say 1-2% of the total creep life, the remainder of the life being composed of cavitation growth and coalescence to produce cracks which eventually precipitate failure.

The slight increase in cavity size and number in the surface region may be readily accounted for if one assumes that the surface emergent grain-boundaries have a greater degree of freedom of movement compared with those of the interior. If this is correct then cavity growth should occur at a greater rate in these regions due to increased grain-boundary sliding and shear of the boundary.

Chapter 6.

GENERAL DISCUSSION AND CONCLUSIONS.

Comparison of the creep curves obtained on testing the steel in the different environments at 800°C, figure 62 (a) - (c), shows that at the stress levels employed in this investigation little difference exists between the creep behaviour in vacuum or argon, but that considerable difference exists between these and the behaviour in air. Specimens tested in air exhibit higher minimum creep rates, higher creep ductilities, and shorter secondary creep periods than corresponding specimens tested in vacuum or argon.

The influence of the environment on the creep behaviour of the steel shown in the form of the creep curves is reflected in the plots depicting the variation of cavitation degree with position in the specimen section, figure 63-65. Very little difference was observed between specimens tested in vacuum and in argon, whilst considerable difference was found between these and the magnitude of cavitation in specimens tested in air under similar experimental conditions. Cavitation in the vacuum and argon environments was uniform throughout the majority of the cross-section with a very slight rise in the degree of cavitation in the surface region. Cavitation in specimens tested in air, on the other hand, was found to be very dependent on the position in the section, cavitation being at a maximum at the surface and at a minimum at the centre of the section.

Figures 66-68 show a series of photomicrographs of the surface, mid-radius, and centre positions of specimens tested under the same conditions of temperature and stress but in different environments. Surface cracking is in evidence at all stress levels in specimens tested in air but only at the highest stresses in those tested in either argon or vacuum. Similarly, comparison of the cavitation behaviour in the mid-radius and centre positions shows that considerable growth and coalescence of r-type cavities has taken place in specimens subjected to an air environment whilst in specimens tested in argon or vacuum the cavities have remained to a great extent as discrete entities.

The influence of the environment on the cavitation behaviour and hence the creep behaviour can be readily illustrated if the difference between the minimum creep rate in air and in vacuum, henceforth to be termed 'environmental factor', is plotted against load, figure 69. The form of the curve would suggest that the influence of environment on the creep behaviour decreases with increase in load. This is thought to be due to a decrease in the contribution of grain-boundary sliding to the total creep deformation with increase in load. That is, as the stress is increased the contribution of grain-boundary deformation, including cavitation, to the overall creep deformation decreases. Hence whilst a difference exists between the degree of cavitation in specimens tested in air and in vacuum at all stress levels the effect of this difference decreases with increase in stress.

Extrapolation of the plots shows that at approximately 7.0 t.p.s.i. the environment has no effect on the creep behaviour of the steel, that is the creep behaviour is the same in air and in vacuum providing the fracture mode remains the same. However, at approximately 6.0. t.p.s.i. a marked change in the direction and magnitude of the 'environmental factor' is observed. Optical metallography has shown this to be due to a change in the fracture mode of specimens tested in air. Below approximately 5.0 t.p.s.i. the fracture mechanism of specimens tested both in air and in vacuum was found to be r-type cavitation. Above this stress level, however, fracture of air tested specimens occurs by the initiation and propagation of W-type cracks. Fracture of specimens in vacuum by this mechanism was not observed except at stress levels considerably greater than 5.0 t.p.s.i.. Plastic deformation accompanying failure by W-type cracking is thought to give rise to the very high creep rates observed in specimens failing by this mechanism. Hence the magnitude of the 'environmental factor' at the transition stress level.

The partial dependence of the creep behaviour and fracture behaviour of the steel on the test environment observed at 800°C was observed to a greater or lesser extent at other temperatures. For example, triple point cracking was observed in all specimens tested at 700°C, but the extent of the propogation was found to be dependent on the test environment. Cracks formed in specimens tested in air were found to have propogated an average distance of half a grain diameter away from the point of initiation whilst those formed in specimens subjected to an argon or a vacuum environment failed to propagate. An indication of this phenomenon can be gained if a comparison is made between figure 37 and figure 52.

The creep behaviour of the steel at this temperature was found to be relatively insensitive to the test environment, little difference existing between the form of the creep curve in air and that in vacuum at the same stress level, figure 70. It is interesting to note that the difference between the increase in the oxygen content of the steel after testing in air and that in vacuum at this temperature is very low compared with that at higher temperatures, 66% : 0% as against 150% : 0% at 800°C, and 400% : 33% at 900°C.

At high temperatures, 900°C, environment was found to exert considerable influence both on the form of the creep curve, figure 72, and on the creep behaviour.

Fracture in all environments was found to occur by the growth and coalescence of r-type cavities initiated at precipitates. Specimens tested in vacuum, however, exhibited higher minimum creep rates, increased creep ductilities, and reduced lives compared with specimens tested in air.

Optical metallography of specimens tested in vacuum at this temperature indicated that the grain-boundaries had undergone considerable migration. No extensive migration was observed in specimens tested in air. It is thought that the grain-boundary migration acted as a stress relief mechanism thereby reducing the degree of grain-boundary deformation and the propensity for cavity nucleation about particles. Hence the observed increase in creep ductility and the minimum creep rate. A reduction in the creep life of the specimens is thought to occur due to the development of a state of 'plastic instability', that is the creep rate of the material increases due to the increase in ductility and the presence of growing cavities until a point is reached at which the system is unable to support the stress fields surrounding the cavities. These then propogate rapidly along the grain-boundaries in a 'brittle' manner to precipitate failure.

Gas analysis has shown a great increase in the oxygen content of specimens tested in air. This was found to be approximately 400%. It is thought on the basis of the work of Shahinian et al[75] that extensive internal oxidation had taken place in the specimen, although no obvious oxide particles were observed in the optical and electron micro-structures. The presence of fine particles formed by internal oxidation have been shown to reduce the extent of grain-boundary migration and hence reducing the creep ductility; and to strengthen both the grain-boundary and the matrix thereby reducing the creep rate and increasing the creep life of the specimen.

That the environment may influence the creep behaviour and the fracture mechanism under a given set of experimental conditions has been established. The similarity of the magnitude of the activation energies for creep in air and in vacuum, 72:15 and 75.28 K.cals./mole. respectively and that for self diffusion of γ -iron, 74.2 K.cals./mole. at 1000°C.[109] would suggest that the mechanism of transgranular creep is not sensitive to the external environment. It follows therefore, that the environment must influence the degree of grain-boundary deformation, namely sliding and cavitation.

The apparent dependence of the cavitation behaviour of the steel on the test environment would suggest that gaseous diffusion into the specimen takes place during the air tests. Analysis of the gas content of the specimen before, during, and after completion of the tests has shown that both oxygen and nitrogen diffuse into the steel throughout the period of the air tests, but not during the vacuum or argon tests. The results of the gas analysis are reported in Table 2.

Thus it has been established that a correlation exists between diffusion of oxygen and nitrogen into the specimen and its cavitation behaviour. It follows, therefore, that any acceptable theory of cavity nucleation and growth must account for this dependence on environment. It must also be able to account for the variation in cavitation behaviour with both temperature and environment.

Fracture at low temperatures, 700°C, is found to occur by the initiation and propagation of W-type cracks. As the temperature is raised the fracture mode changes to r-type cavitation and finally at high temperatures to fracture about grain-boundary particles. Thus three different fracture mechanisms are observed in the same environment depending on the temperature. It follows therefore that three different mechanisms of nucleation and growth all of which may be influenced by the external environment must be operative.

It is proposed to discuss the influence of environment on the three basic fracture mechanisms indicated above separately and to draw general conclusions at the end of the discussion. It is thought that in doing so a clearer indication of the combined influence of temperature and environment on the fracture behaviour of the steel will be obtained than would be if they were discussed as one.

It has been indicated above that the steel shows W-type cracking in creep at 700°C both in air and in vacuum and that propagation of the crack in specimens tested in vacuum is very restricted compared with that in air. If the established theories of W-type cracking are to be accepted then they must be able to explain this phenomenon.

Zener[82] proposed that tensile stress concentrations of sufficient magnitude to initiate fracture are created across grain-boundaries perpendicular to the stress axis unless plastic deformation takes place in the grains at the ends of the grain-boundaries subjected to shear. Many of the simple and more complicated types of crack initiation by this method are shown schematically in figure 8.

Once a crack has been initiated under the correct test conditions at a grain-boundary perpendicular to the stress axis, its propagation, to result in ultimate intergranular fracture, has to occur along both the transverse boundaries and those inclined to the stress axis. Its propagation along an inclined boundary is achieved by shear along the boundary. The energy required for this process is considered to be greater than that for fracture of a transverse boundary.

McLean[70] proposed on the basis of Stroh's equation for brittle fracture that the minimum stress required for the initiation of a crack is given by the equation:

$$\tau_s \geq \left[\frac{12\,\gamma_b\,G}{\pi\,h}\right]^{1/2}$$

where τ_s is the shear stress across the boundary

γ_b is the surface energy per unit area of crack formed in the grain-boundary

G is the shear modulus

h is the length of the sliding boundary.

Smith et al[84], on the other hand, calculated that the minimum stress for nucleation of a crack at the intersection of two shear bands (analogous to triple point cracking) is considerably less than that predicted by this equation. It was also pointed out that if the effective fracture surface energy for crack growth is greater than that for nucleation, then growth is the more difficult process and the crack will only extend with increasing strain in the shearing elements.

On the basis of the results obtained from the experimental work reported in this dissertation it is difficult to ascertain whether nucleation or propagation of the crack is the more difficult process.

From McLean's equation it can be seen that a reduction of the grain-boundary energy, γ_b, would induce a reduction in J_s, that is increase the propensity for nucleation of grain-boundary cracks. Rotherham et al[110] and more recently Hondras[111] have shown that the grain-boundary energy of a metal is reduced by the intergranular diffusion of oxygen. Analysis of the specimens before and after a test has shown that both the oxygen and the nitrogen contents of the steel increase with time of test in air, but remain constant in vacuum and argon. It is therefore proposed that the diffusion of oxygen and nitrogen into the steel during a test in air effectively reduces the grain-boundary energy of the metal. Thus the shear strain necessary to initiate fracture is achieved sooner in specimens tested in air than in specimens tested in an argon or vacuum environment under the same conditions of temperature and stress. Hence cracks will be initiated sooner in specimens subjected to an air environment than in specimens tested in vacuum or argon under the same experimental conditions and, assuming a constant growth rate, will attain a greater size in a given period of time.

Smith et al[84], on the other hand, have pointed out that propagation of the crack may be inhibited if the energy for the creation of a new surface, ie. crack propagation, is greater than that for initiation. However, if the grain-boundary energy is reduced by gaseous diffusion or condensation then crack propagation may readily take place. Thus it is possible that cracks are initiated at the same fraction of the creep life in all environments, but those formed in specimens tested in vacuum or argon fail to propagate due to the energy for propagation being greater than that for nucleation.

It may be concluded that at low temperatures crack initiation and propogation occurs by the same mechanism in all environments, that is the development of tensile stress concentrations at the ends of sliding grain-boundaries. The shear strain necessary to initiate and/or propagate a crack, however, may be reduced by grain-boundary diffusion or condensation of oxygen or nitrogen, thereby promoting intergranular fracture.

As the temperature is raised so the resistance of the bulk-grain material to transgranular deformation is reduced. Consequently the stress concentration conditions for the initiation and propagation of W-type cracks cannot be developed. Failure under these conditions is found to occur by the nucleation, growth, and eventual coalescence of r-type cavities.

Two basic mechanisms have been proposed to account for the nucleation of r-type cavities in metals and alloys. Resnick et al[48], and later many other investigators proposed that cavities are nucleated by sliding of the grain-boundary about incoherent or semi-coherent particles. Whilst this mechanism may be operative in many commercial metals and alloys it cannot be operative in high purity metals and alloys, many of which have been shown to fail by r-type cavitation. No grain-boundary particles have been observed in the system under investigation either by optical or electron metallography, consequently it is considered that this mechanism of nucleation of r-type cavities is not operative in the steel at or below 800°C.

The most accepted mode of nucleation of r-type cavities in pure metals and alloys containing particle-free grain-boundaries is by the interaction of ledges formed by transgranular slip and grain-boundary sliding. This mechanism was first proposed by Gifkins[90] who postulated that ledges could be formed in a grain-boundary by slip accommodation across the boundary. Chen et al[91] proposed a modified form of Gifkins' concept to overcome the criticism that the stress concentrations developed in the model were insufficient to nucleate fracture.

From the literature it would appear that the height of a stable ledge decreases with increase in the bulk-grain strength of the material. Stable heights varying from 20 A° to 100 A° have been quoted. Consequently it was not expected to observe ledges in the steel specimens. Figure 21, however, shows what are thought to be ledges in α-brass immedicatly after fracture.

Both of the mechanisms of cavity nucleation outlined above involve the shearing of two interfaces. It follows therefore that if the energy of the interfaces is reduced by gaseous diffusion then the shear strain necessary to initiate fracture is reduced. Gaseous diffusion, however, is time dependent and consequently cavities are not nucleated simultaneously throughout the cross-section of specimens tested in air, but are nucleated first in the surface region where the grain-boundary energy has been reduced and last at the centre of the section. This hypothesis is substantiated by the photomicrographs of figure 36 which shows that the depth of the 'zone of resolvable cavities' increased with time and gas absorption.

Assuming a constant growth rate it follows that nuclei formed early in the creep life, that is those of the surface region, will attain a greater size in a given period of time than those formed at a later stage of the creep life. Also, since the cavity nuclei are sub-microscopic in size it follows that in a given period of time a greater number of cavities will have attained a resolvable size in the surface region of the specimen compared with the centre. Hence the variation in cavity number observed in the specimen, may be only an apparent variation and not a true represenatation of variation in the number of cavities across the section. The observed variation in size however, figure 32, is considered to be a true phenomenon.

Specimens subjected to an argon or vacuum environment exhibit an almost uniform distribution of cavities indicative of simultaneous nucleation throughout the section. The small size of the cavities formed in specimens subjected to these environments is thought to be due to their formation requiring a greater shear strain than those formed in specimens tested in air under identical conditions of temperature and stress. It follows therefore that the time required to develop the necessary shear strain must be greater in specimens tested in vacuum or argon than in air, and hence the fraction of the total test time available for growth of the cavities is reduced. Assuming that the growth rate is the same in all environments, the observation that cavities formed in specimens tested in argon or vacuum are smaller than those formed in specimens tested under identical conditions in air can thus be accounted for.

The problem of how cavities, once nculeated, may increase in size has been the subject of a great number of investigations. Two mechanisms have received considerable attention in the past decade, these being growth by condensation of vacancies[38,57,86] and growth by continued sliding of the grain-boundary.[21,90,96,97] Because of the conflicting nature of these two theories the evidence for and against each theory will be summarised before the influence of environment on each mechanism is discussed.

Greenwood et al,[57] and later McLean[58] postulated that growth of r-type cavities could occur by condensation of vacancies. Baluffi et al[86] examined the influence of stress on cavity growth using the Nabarro-Herring analysis and derived a critical stress relation for growth of cavities based on the cavity dimensions. Hull et al[38] extended this analysis by assuming that at the temperature of formation of cavities grain-boundary diffusion is the only important diffusion mechanism. A simplified form of Hull et al's expression for cavity growth is as follows:

$$\sigma - P \geq \frac{2\gamma}{r}$$

where σ is the applied stress

P is the hydrostatic stress

γ is the surface energy of the cavity

r is the radius of the cavity.

Hull et al[38] predicted and subsequently demonstrated that under conditions where the effective stress is zero cavities cannot be formed due to an inability of vacancies to diffuse under a hydrostatic stress. Ratcliffe et al[74] subsequently confirmed these results. Unfortunately the equation is valid only if it is assumed that the growth rate of the cavities remains constant and that the number of cavities increases with time. Oliver et al[80] have pointed out that this is unlikely since the area of grain-boundary supplying the vacancies decreases with increase in the number of cavities and the size of the cavities. In addition, Machlin[95] has pointed out that a superimposed hydrostatic pressure will limit the growth of cavities by any mechanism. Finally, Intrater et al[21] have shown that over a wide temperature range the growth of cavities is independent of temperature unlike vacancy diffusion but dependent on the degree of grain-boundary sliding.

From Hull et al's[38] analysis it can be seen that a reduction in the surface energy of the cavity, γ , would induce an increase in the growth rate. Thus cavities growing in grain-boundaries in which gaseous diffusion was taking place would be expected to have a greater rate of growth than those in other boundaries. If this argument is valid it follows that the growth rate of cavities formed in specimens tested in air depends on whether or not the 'gaseous diffusion front' has reached the cavity, the depth of diffusion being time dependent. If all the cavities initially have the same growth rate, assuming simultaneous nucleation throughout the cross-section, then as diffusion occurs the growth rate of cavities in the surface zone is increased by reduction of the surface energy. With time the growth rates of cavities in the remaining section are similarly increased. However, cavities in the surface region will have been growing at the higher growth rate for a longer period of time than those at the centre and consequently will have attained a greater size in a given period of time. Hence the form of the distribution of cavity size observed in the course of this investigation.

In his original hypothesis of cavity nucleation Gifkins postulated that growth occurred by continued grain-boundary sliding after nucleation of the cavity. McLean[97] endorsed this view and showed that cavity growth was possible by a combination of trangranular deformation and continued grain-boundary sliding. Whilst a number of objections based on the form of the cavity produced by this mechanism have been raised[4], cavities of the form postulated by McLean have been observed by a number of investigators[47,60,99,100]. It is considered from the theoretical consideration and photographic evidence published in the literature, that the cavity forms shown in figures 40-42 are of the form postulated by McLean.

Growth of an r-type cavity by grain-boundary sliding requires the creation of a new surface. It follows therefore that if the energy of the new surface were reduced then the shear strain necessary for its creation is also reduced. Hence if the energy of a grain-boundary containing cavities is reduced by gaseous diffusion then cavities may grow at either lower shear strains or at greater rates if the shear strain remains constant. Thus the influence of grain-boundary gaseous diffusion on the cavitation behaviour of a metal or alloy may be two-fold. It may reduce the energy required to create a new surface and thereby reduce the shear strain necessary for its creation, or, alternatively it may reduce the activation energy for sliding thereby increasing the rate of sliding under a given shear strain and hence increase the rate of cavity growth.

If these hypotheses are correct then, following the arguments developed previously, the movement of a 'gaseous diffusion front' across a specimen section would result in a variation of the growth rate of the cavities in the section. In a fixed period of time this would result in a cavity size distribution of the form observed in specimens tested in air, figure 32.

In the absence of grain-boundary energy reduction by gaseous diffusion, for example in specimens subjected to an argon or vacuum environment, the cavity growth rate would be expected to be independent of position in the specimen section. In practice a slight rise in both the size and number of cavities in the region of the surface is observed, figures 50, 51, 60, and 61. This is thought to be due to the grain-boundaries in this region having greater degrees of freedom of movement than those in the interior resulting in increased rates of cavity growth. That is, the slight rise in the rate of cavity growth in the region of the surface of specimens tested in argon or vacuum is due to 'mechanically' increased rates of grain-boundary sliding and not to a reduction of the grain-boundary energy by gaseous diffusion.

Stiegler et al[54] proposed that r-type cavitation and W-type cracking are the results of the same deformation mode. From Hull et al's analysis they obtained a relationship between vacancy flux and the growth of a cavity of the form:

$$j_{gb} \sim \frac{D_{gb}}{KTa}\left(\sigma_n - \frac{2\gamma}{r}\right)$$

where j_{gb} is the vacancy flux into the cavity
D_{gb} is the diffusion coefficient in the grain-boundary
K is Boltzmann's constant
a is the intercavity spacing
T is the temperature in $^{\circ}$K
σ_n is the stress normal to the cavity
γ is the surface energy of the cavity
and r is the radius of the cavity.

If the cavity is to maintain a spherical or polyhedral shape vacancies entering it must be distributed over the surface of the cavity as rapidly as they enter it. If surface diffusion is the predominent mechanism of material transport the surface current or flux of vacancies, j_s, is given by the expression:

$$j_s \sim \frac{D_s \gamma \Omega r}{KT} \cdot \frac{\partial K}{\partial s}$$

where D_s is the surface diffusion coefficient

ν is the number of atoms per unit area

Ω is the atomic volume of the fluxing material

and $\frac{\partial K}{\partial S}$ is the rate of change of radius of curvature with respect to change in position of the surface of the cavity.

Stiegler et al postuated that if j_s was sufficiently high to accommodate all the vacancies entering the cavity then the cavity will maintain a polyhedral shape, figure 41. If the vacancy flux into the cavity is increased then the cavity will grow primarily in the plane of the grain-boundary producing first a lenticular disc, figure 42, and finally W-type cracks. An increase in the vacancy flux into a cavity may be achieved by either increasing the applied stress, σ_n, resulting in an appreciable growth component from dislocation motion and sliding of the grain-boundary or by reduction of the surface energy of the cavity, γ. Reduction of γ by gaseous diffusion would result, from Stiegler et al's analysis, in an increase in the flux of vacancies into the cavity, and also a reduction in the flux distributing the cavities over the cavity surface. Depending on the relative rates of the two growth components growth may be three dimentional, ie. polyhedral shaped cavities showing crystallographic facets, figure 41(e); or pseudo two dimensional, ie. smooth-walled or irregular-walled lenticular disc shaped cavities, figure 42. In the extreme case W-type cracking may be produced.

Temperatures in excess of 800°C were found to induce extensive grain-boundary precipitation of carbide particles. Cavities were observed to be nucleated at the particles in the manner proposed by Resnick et al[48], that is the development of tensile stress concentrations at particles by grain-boundary sliding and the eventual fracture of the particle-matrix interface. It follows that if the energy of the interface is reduced by gaseous diffusion the shear strain necessary to induce fracture is reduced. Hence the formation of a cavity by fracture of a particle-matrix interface may take place more readily in specimens tested in an air environment than those tested in either argon or vacuum under the same conditions of stress. Similarly, once nucleated, the surface energy of the cavity may be reduced by gaseous diffusion resulting in an increased rate of growth.

The general conclusions are as follows:

1. Temperature, at a given strain rate, has considerable influence on the form of failure in a 18/8 niobium stabilised stainless steel. At 700°C fracture occurs by the initiation and propogation of W-type cracks; at 800°C by the initiation, growth, and eventual coalescence of r-type cavities; and finally at temperatures in excess of 900°C by the initiation of cavities at grain-boundary particles, and the propagation of the cavities to precipitate failure.

2. Specimens tested in air at 800°C exhibit higher minimum creep rate, shorter secondary creep periods and higher creep ductilities than specimens subjected to an argon or a vacuum environment under the same conditions of stress.

3. Specimens tested in air exhibit a higher degree of cavitation throughout the cross-section compared with specimens tested in an argon or a vacuum environment under the same conditions of temperature and stress.

4. A continued decrease both in the size and number of cavities from the surface to the centre of the section is observed in specimens tested in air. No such large variation was observed in specimens tested in an argon or in a vacuum environment under the same conditions of temperature and stress.

5. Gas analysis has shown that both the oxygen and nitrogen contents of the steel increase with time of test in air. No such an increase was detected on testing in argon or vacuum.

6. The r-type cavities observed during the course of the work reported in this dissertation are considered to be initiated at grain-boundary ledges since no cavities were observed to be associated with particles at or below 800°C.

7. Little evidence has been obtained to indicate the growth mechanism of r-type cavities either in α-brass or in stainless steel. The general shape of an r-type cavity from the work reported in this dissertation would appear to be an oblate spheroid. On a single grain facet, however, the cavities are elongated in a preferred direction suggesting possible growth by grain-boundary sliding.

8. Gaseous diffusion is considered to reduce the grain-boundary energy of the steel thereby promoting crack initiation and growth. No information has been gained to suggest whether the observed influence of grain-boundary gaseous diffusion on the cavitation behaviour of the steel is due to modification of cavity nucleation rate or modification of cavity growth rate.

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PHOTOMICROGRAPHS.

The stress axes and where applicable the directions of grain-boundary sliding are indicated in the photomicrographs.

Figure 1.

Form of the ideal creep curve.

Figure 2.

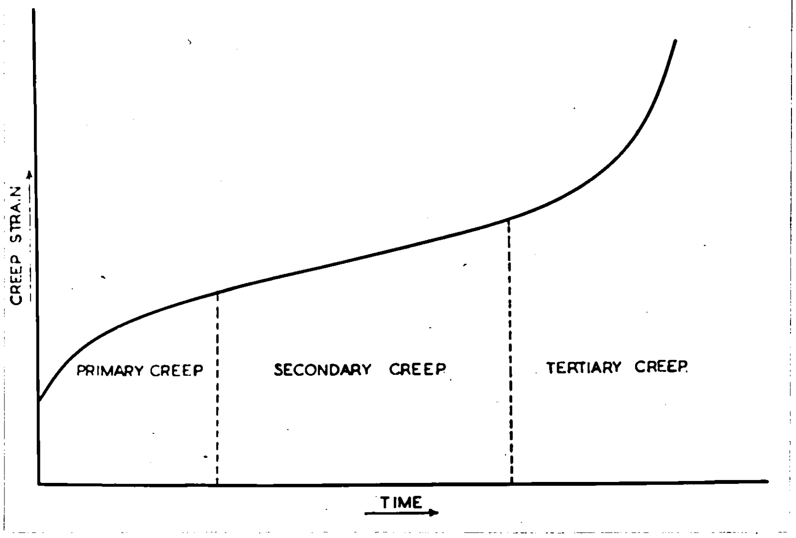
Possible forms of grain-boundary displacement - time curves.

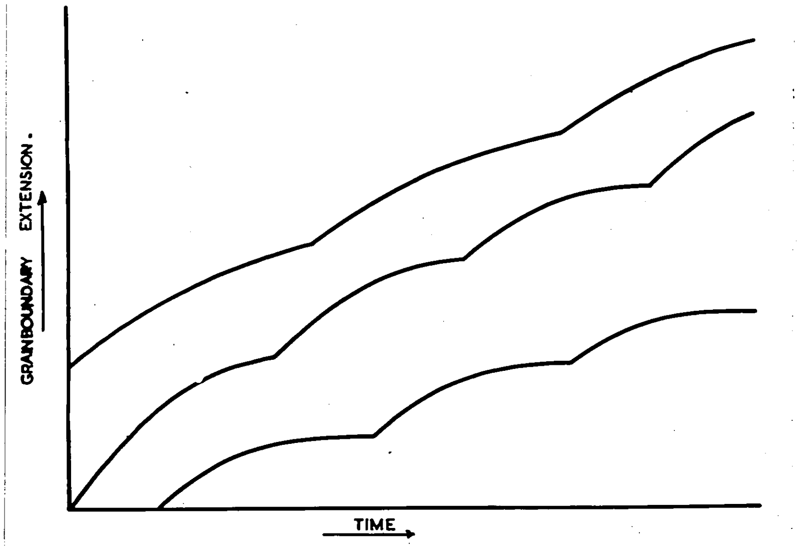
(after Stephens[7]).

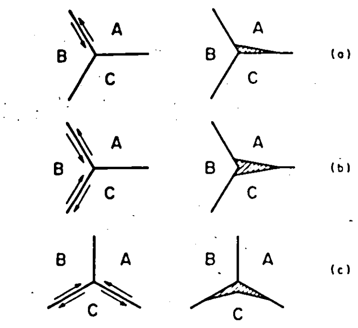
Figure 3.

Nucleation of W-type cracks at grain-boundary triple-points.

(after Chang et al[53]).


CREEP STRAIN
PRIMARY CREEP
SECONDARY CREEP
TERTIARY CREEP
TIME


GRAINBOUNDARY EXTENSION
TIME


A
B
C
(a)
(b)
(c)

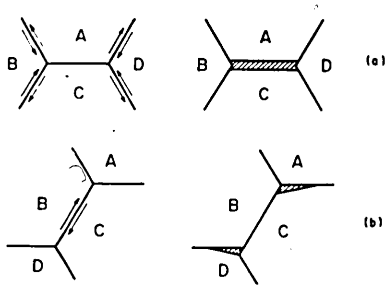

A
B
C
D
(a)
(b)

Figure 4.

Nucleation of cavities by grain-boundary sliding about particles.

(after Resnick et al[48]).

Figure 5.

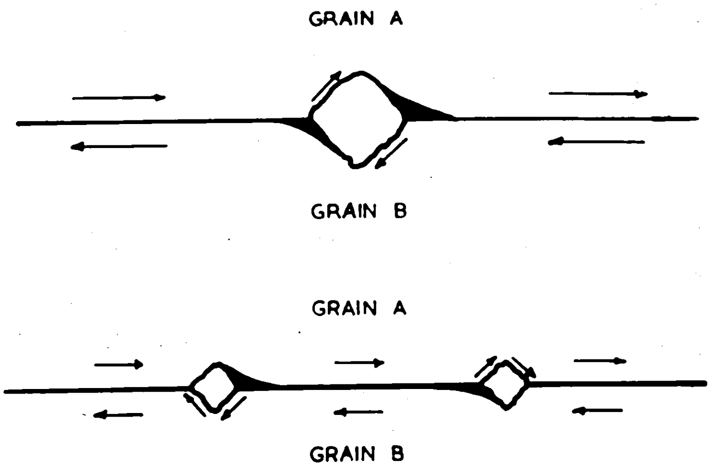
Influence of stress direction after compressive prestrain on cavity formation.

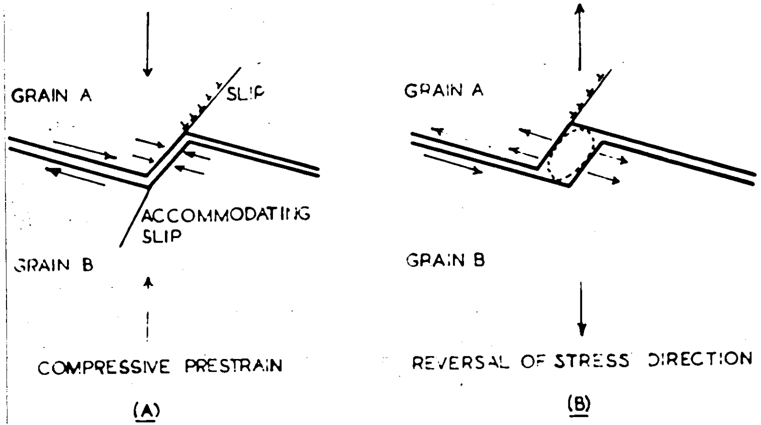
(after Davies et al.[71]).

Figure 6.

Initiation of crack at a grain-boundary.

(after Zener[82]).


GRAIN A
GRAIN B
GRAIN A
GRAIN B


GRAIN A
SLIP
ACCOMMODATING SLIP
GRAIN B
COMPRESSIVE PRESTRAIN
(A)
GRAIN A
GRAIN B
REVERSAL OF STRESS DIRECTION
(B)

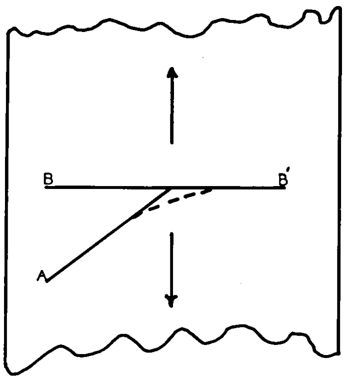

B
B'
A

Figure 7.

Development of W-type cracking from r-type cavitation.

(after Stiegler et al[59]).

Figure 8.

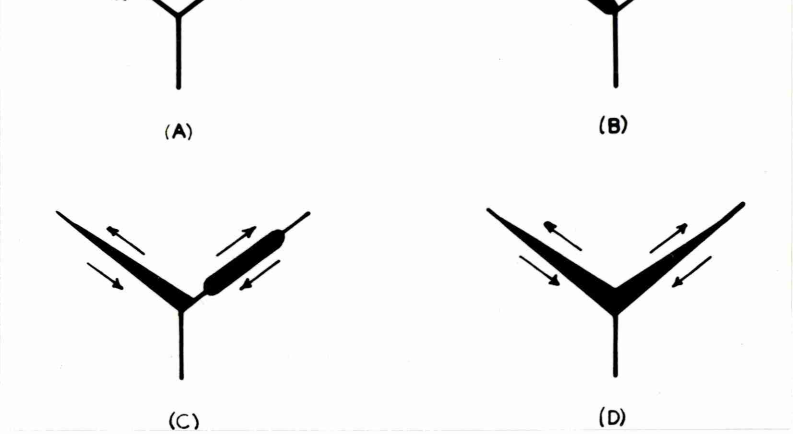
Nucleation of r-type cavities by grain-boundary ledge interaction.

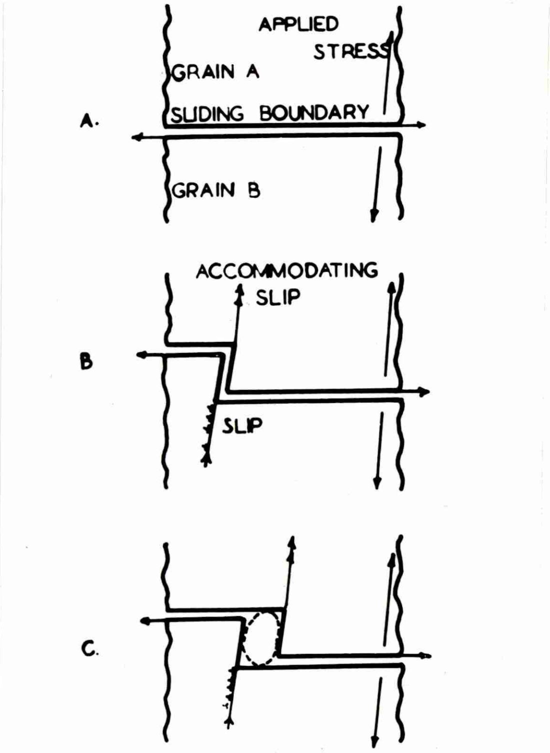
(after Gifkins[90]).

Figure 9.

Influence of the direction of grain-boundary sliding relative to the ledge on r-type cavity nucleation.

(after Davies et al[2]).


(A)
(B)
(C)
(D)


A.
APPLIED STRESS
GRAIN A
SLIDING BOUNDARY
GRAIN B
B
ACCOMMODATING SLIP
SLIP
C.

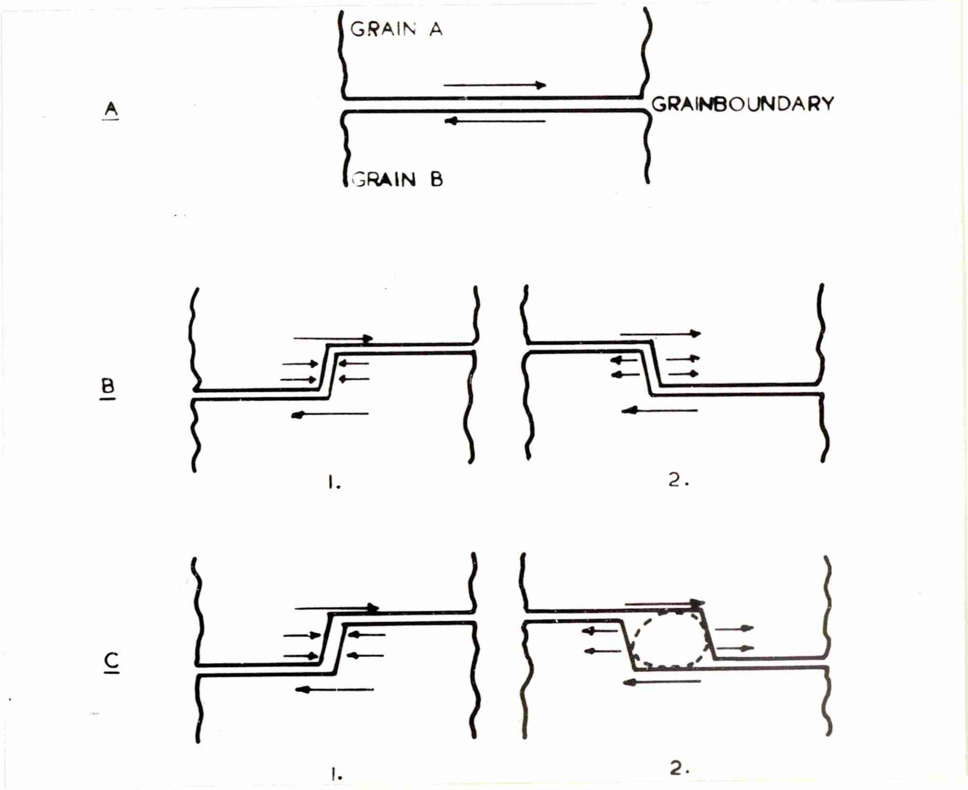

A
GRAIN A
GRAINBOUNDARY
GRAIN B
B
1.
2.
C
1.
2.

Figure 10.

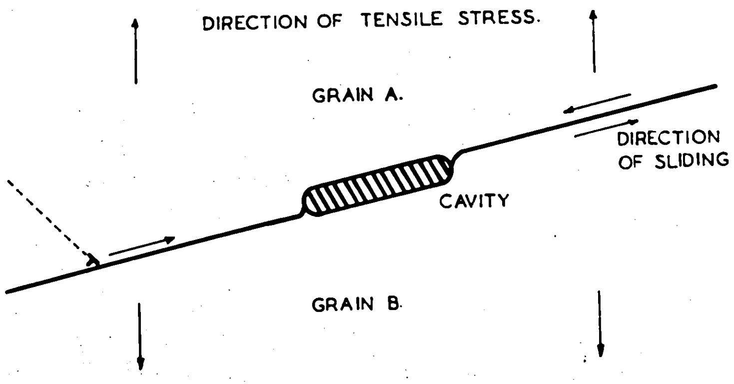
Growth of a r-type cavity by glide of dislocations.
(after McLean et al[97]).

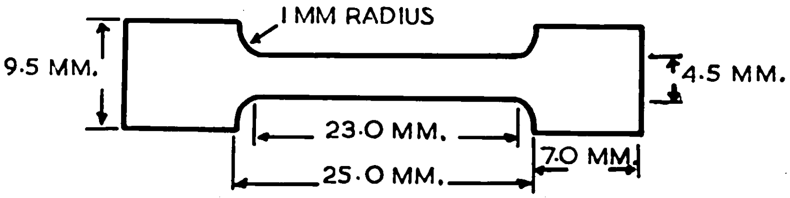
Figure 11.

Form and dimensions of the specimen used throughout the experimental work.

Figure 12.

Specimen mounted in the grips showing the position of the thermocouple.


DIRECTION OF TENSILE STRESS.
GRAIN A.
DIRECTION OF SLIDING
CAVITY
GRAIN B.


1 MM RADIUS
9·5 MM.
4·5 MM.
23·0 MM.
7·0 MM.
25·0 MM.

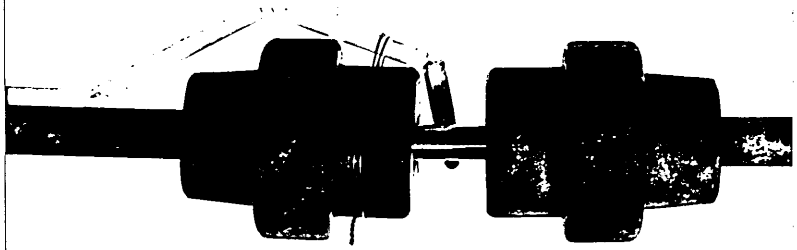
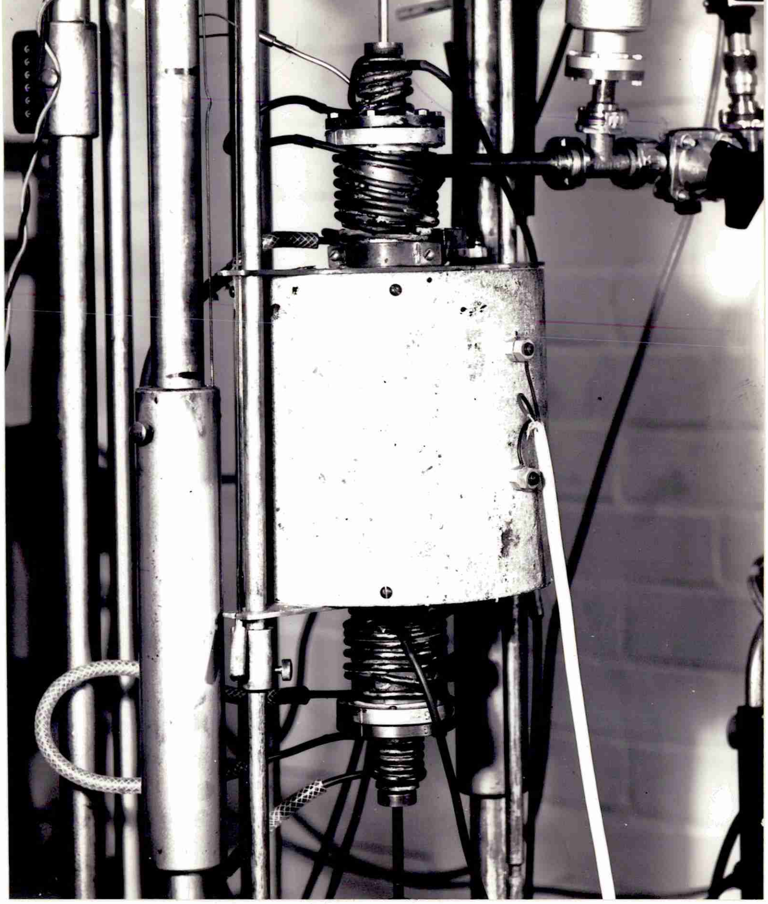


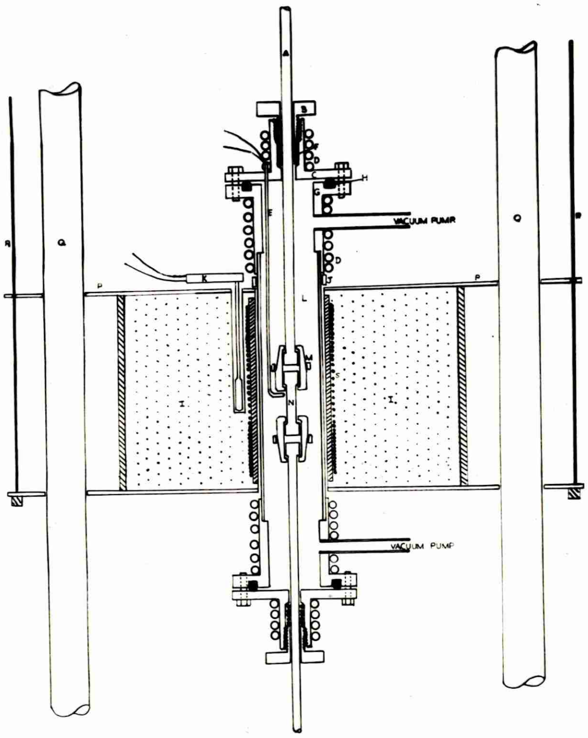
Figure 13.

Vacuum system employed for the vacuum and argon tests.

Figure 14.

Schematic representation of the above.





KEY:

A	EXTENSION RODS.	J	SUPPORT COLLAR
B	SCREW COLLAR.	K	PLATINUM RESISTANCE THERMOMETER.
C	CLOSURE PLATE.	L	STAINLESS STEEL VACUUM CAPSULE.
D	WATER COOLING COILS.	M	SPECIMEN GRIPS.
E	SEALED THERMOCOUPLE.	N	SPECIMEN.
F	'O' RING SEALS & PRESSURE DISCS.	P	FURNACE SUPPORTS.
		Q	CREEP M/C. COLUMNS.
G	CAPSULE HEAD.	R	SUPPORT CABLE.
H	'O' RING SEAL.	S	FURNACE WINDING.
I	FURNACE BODY.		

Figure 15.

Variation in ductility with temperature and strain-rate in α -brass.

Figure 16.

W-type cracking in α -brass.

Magnification x 400.

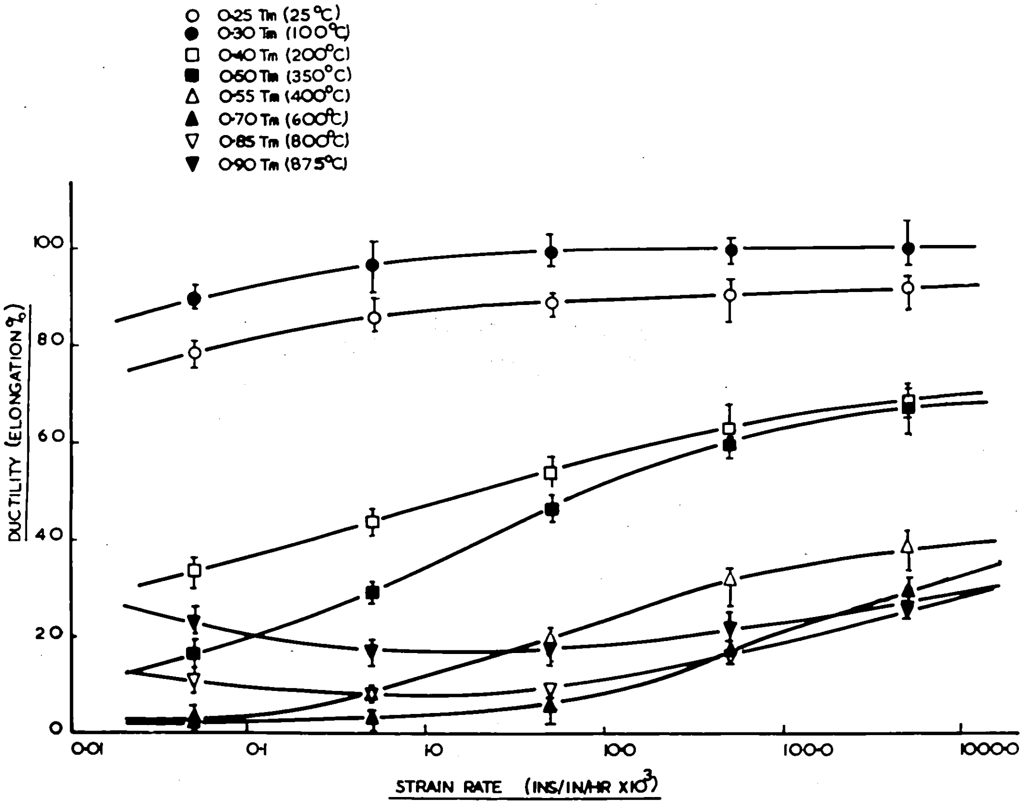

○ 0·25 Tm (25°C)
● 0·30 Tm (100°C)
□ 0·40 Tm (200°C)
■ 0·50 Tm (350°C)
△ 0·55 Tm (400°C)
▲ 0·70 Tm (600°C)
▽ 0·85 Tm (800°C)
▼ 0·90 Tm (875°C)
DUCTILITY (ELONGATION %)
100
80
60
40
20
0
0·01
0·1
1·0
10·0
100·0
1000·0
STRAIN RATE (INS/IN/HR X10^3)

Figure 17.

Pseudo-W-type cracking in α-brass.

Magnification x 400

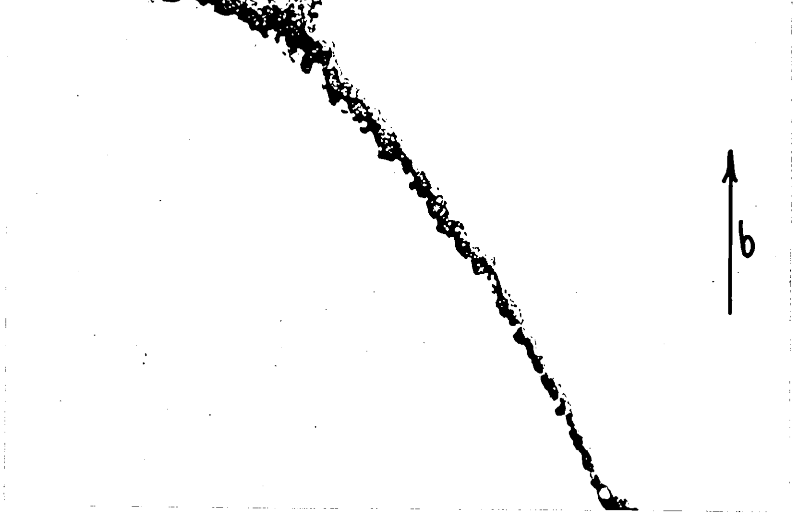
Figure 18.

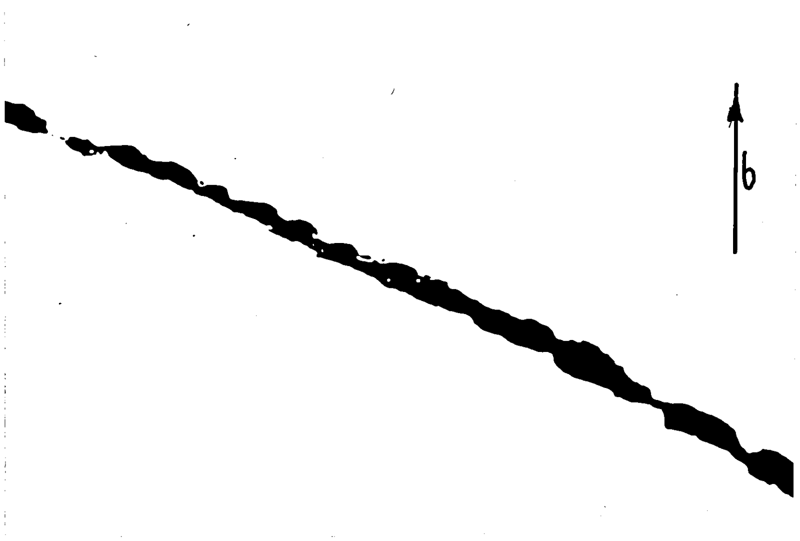
Coalescence of r-type cavities to form continuous grain-boundary cracks in α-brass.

Magnification x 600

Figure 19.

Schematic representation of the Ductility-v-Temperature and Strain-Rate plot for α-brass.


b


b

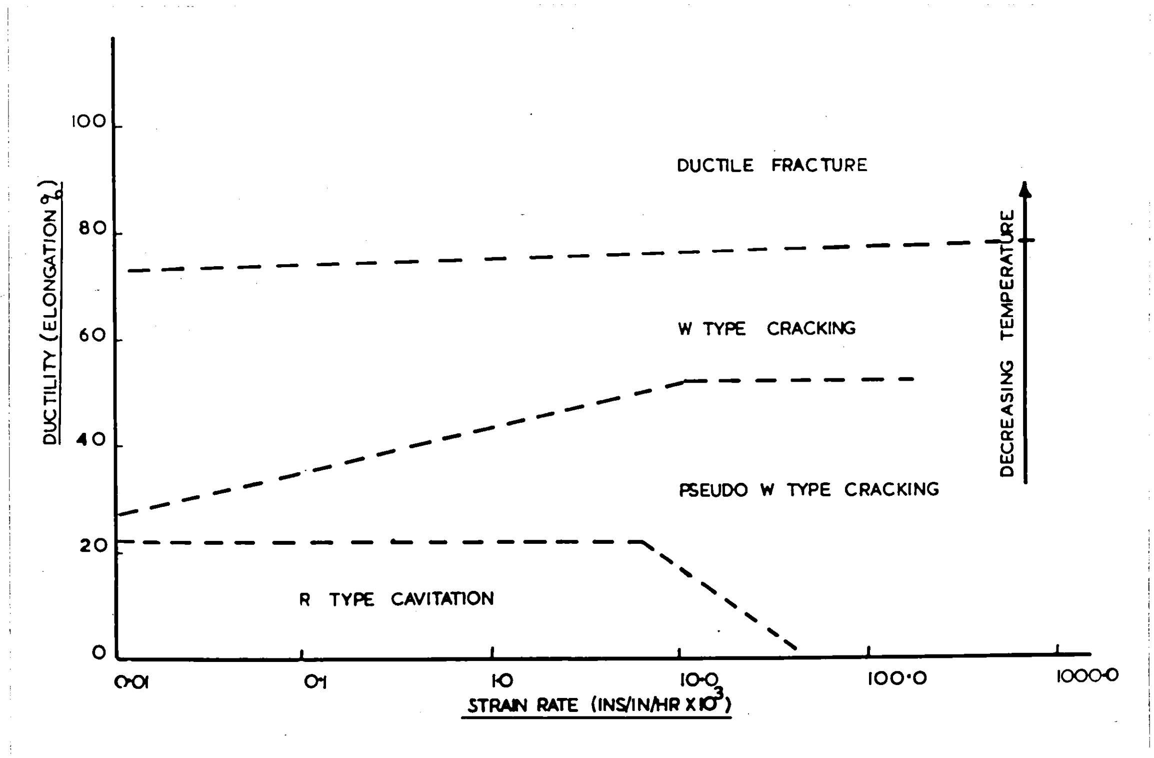

DUCTILITY (ELONGATION %)
100
80
60
40
20
0
DUCTILE FRACTURE
W TYPE CRACKING
PSEUDO W TYPE CRACKING
R TYPE CAVITATION
DECREASING TEMPERATURE
0·01
0·1
1·0
10·0
100·0
1000·0
STRAIN RATE (INS/IN/HR X10³)

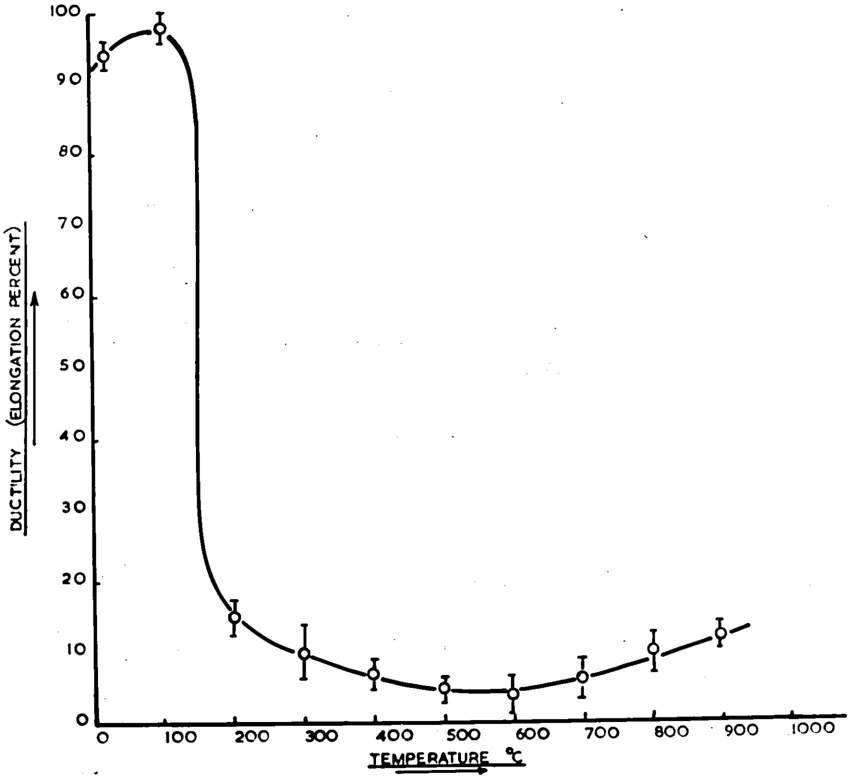
Figure 20.

Variation in the ductility of α -brass with temperature.

Figure 21(a).

Grain-boundary ledges in α -brass.

Magnification x 2000


DUCTILITY (ELONGATION PERCENT)
100
90
80
70
60
50
40
30
20
10
0
0
100
200
300
400
500
600
700
800
900
1000
TEMPERATURE °C


b

Figure 21(b).

Grain-boundary ledges in α-brass.

Magnification x 2000

Figure 22.

Schematic representation of the formation of the ledges shown in the above photomicrograph.


b

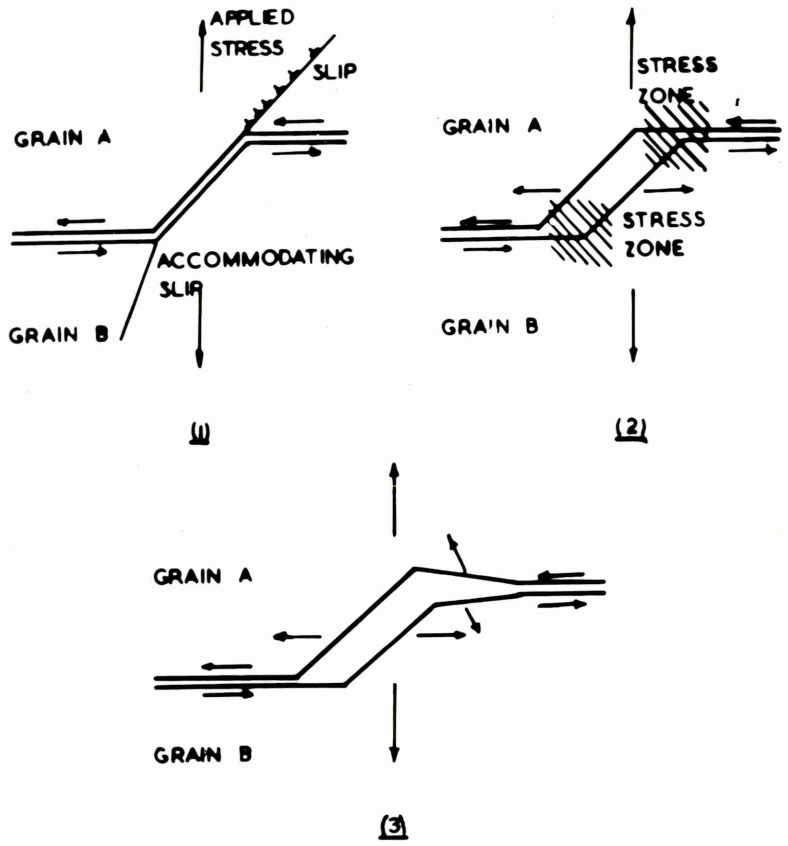
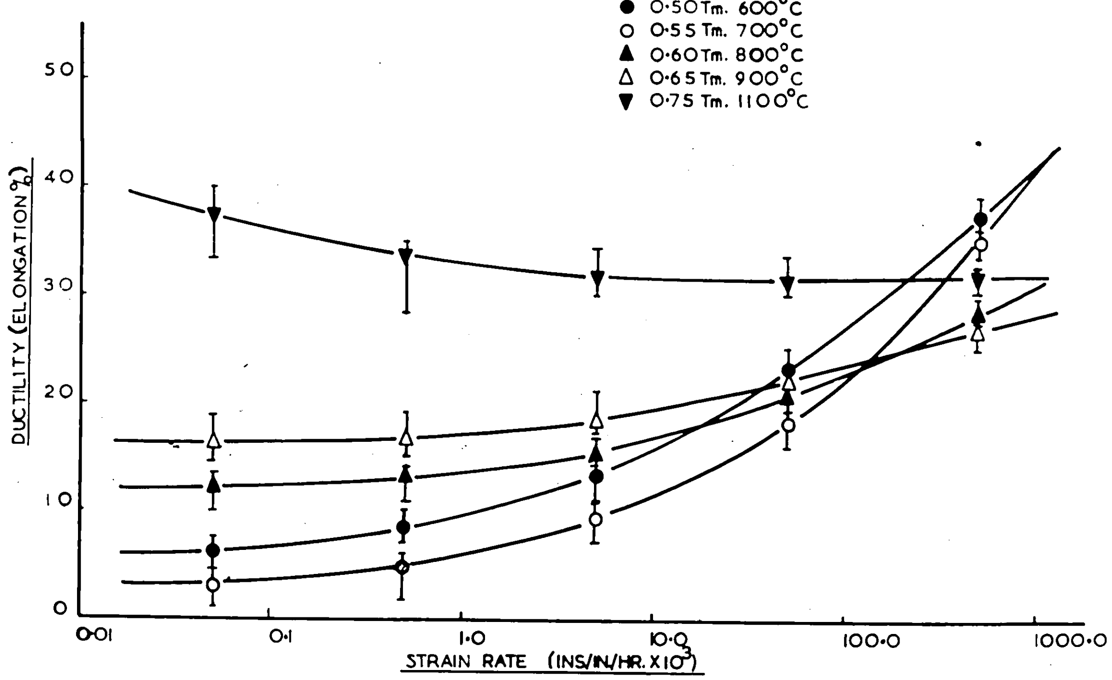

APPLIED
STRESS
SLIP
GRAIN A
ACCOMMODATING
SLIP
GRAIN B
(1)
STRESS
ZONE
GRAIN A
STRESS
ZONE
GRAIN B
(2)
GRAIN A
GRAIN B
(3)

Figure 23.

Variation in the ductility of a 18/8 niobium stabilised stainless steel with temperature and strain-rate.

Figure 24.

Variation of the ductility of a 18/8 niobium stabilised stainless steel with temperature.


● 0·50 Tm. 600°C
○ 0·55 Tm. 700°C
▲ 0·60 Tm. 800°C
△ 0·65 Tm. 900°C
▼ 0·75 Tm. 1100°C
DUCTILITY (ELONGATION %)
50
40
30
20
10
0
0·01
0·1
1·0
10·0
100·0
1000·0
STRAIN RATE (INS/IN/HR. X10^{3})

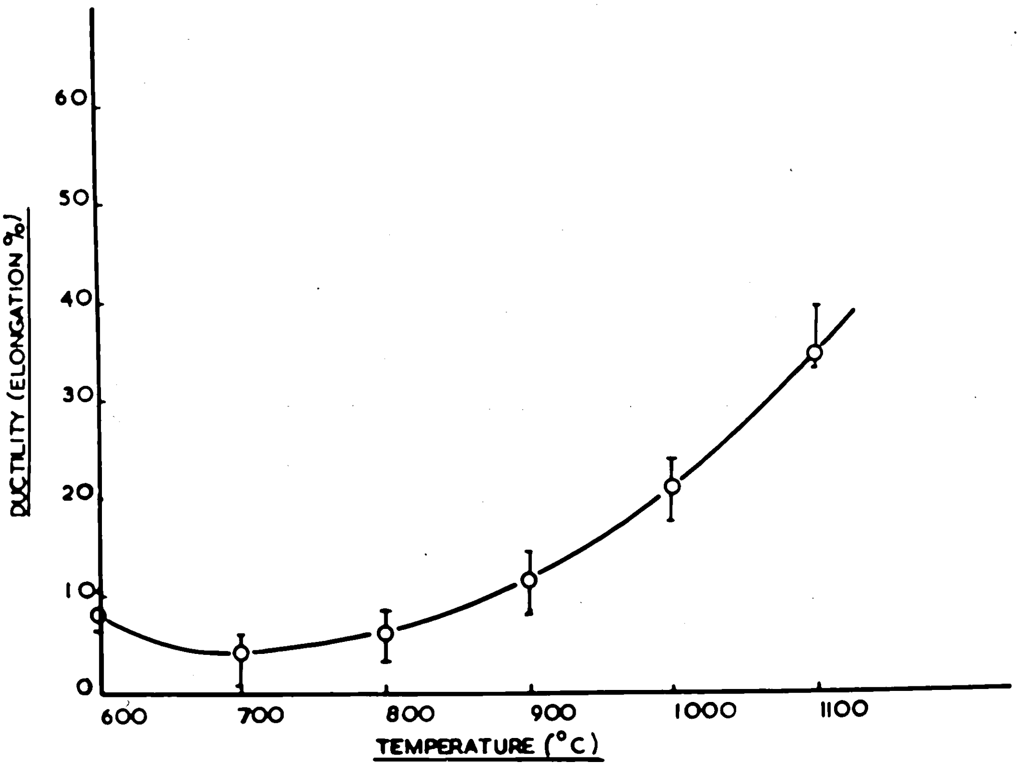

DUCTILITY (ELONGATION %)
60
50
40
30
20
10
0
600
700
800
900
1000
1100
TEMPERATURE (°C)

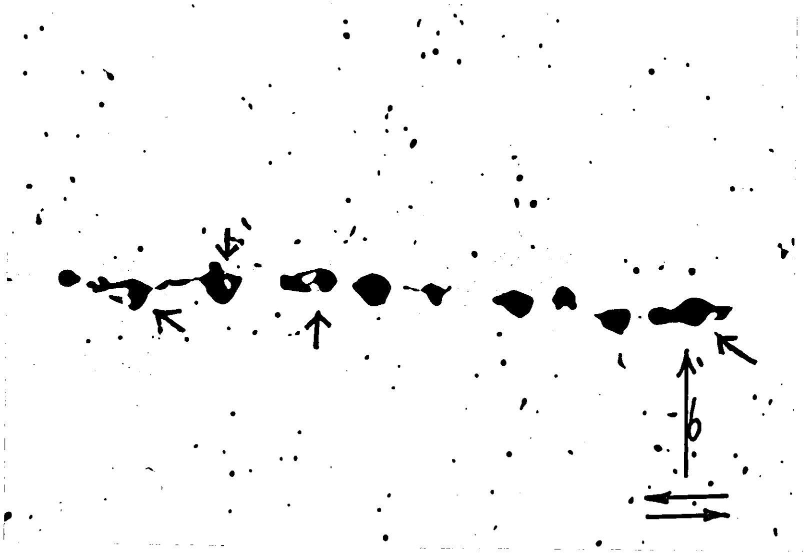
Figure 25.

Cracking about fine grain-boundary particles (arrowed)

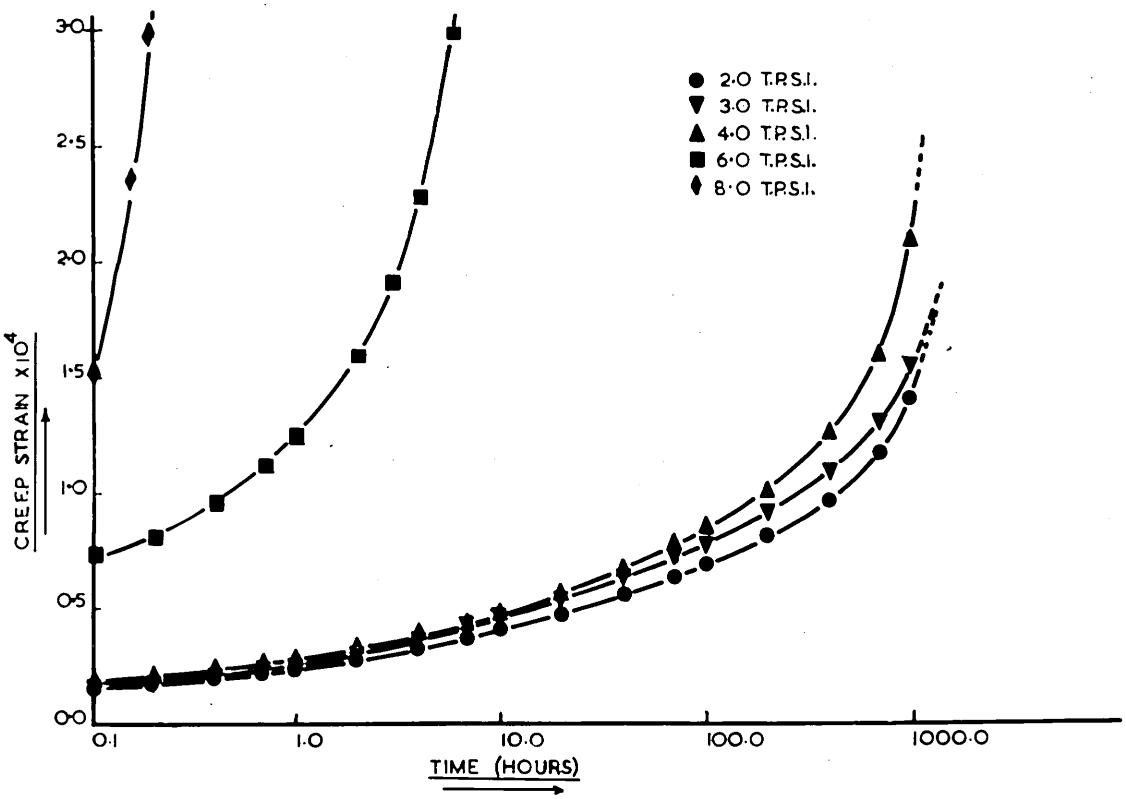
Magnification x 2250

Figure 26.

Creep curve of a 18/8 niobium stabilised stainless steel tested in air.



b



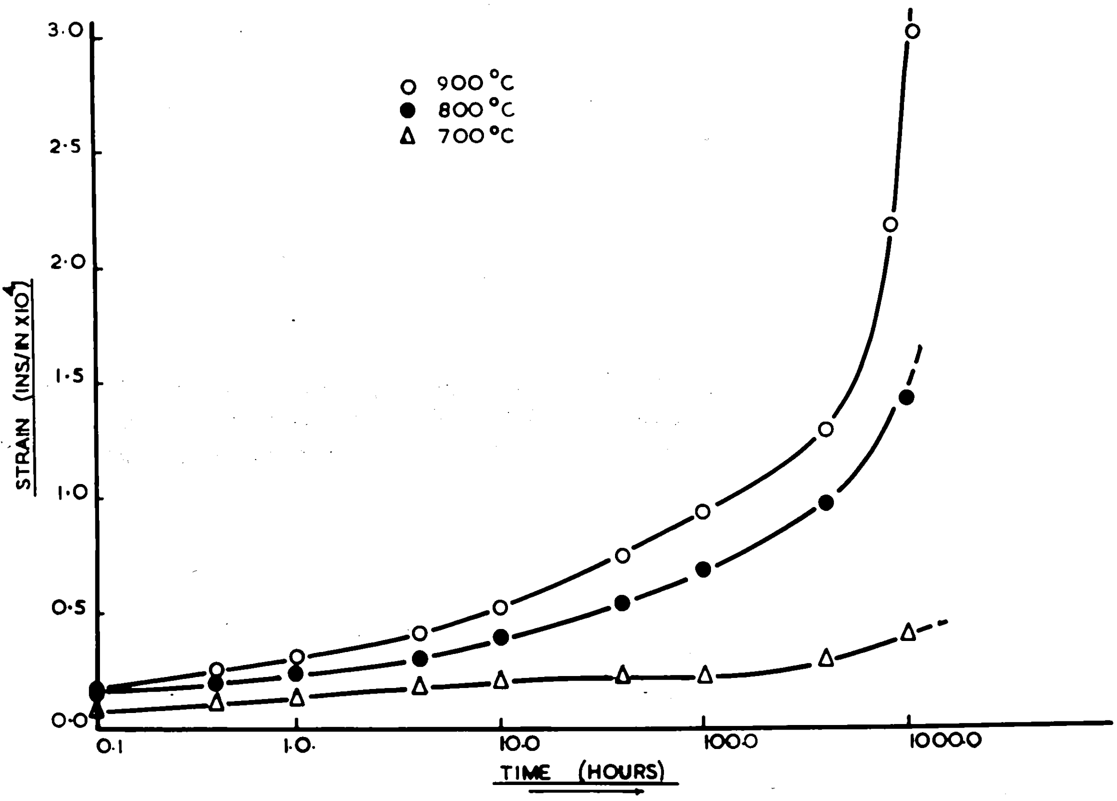
● 2·0 T.P.S.I.
▼ 3·0 T.P.S.I.
▲ 4·0 T.P.S.I.
■ 6·0 T.P.S.I.
♦ 8·0 T.P.S.I.
CREEP STRAIN X10^4
3·0
2·5
2·0
1·5
1·0
0·5
0·0
0·1
1·0
10·0
100·0
1000·0
TIME (HOURS)

Figure 27.

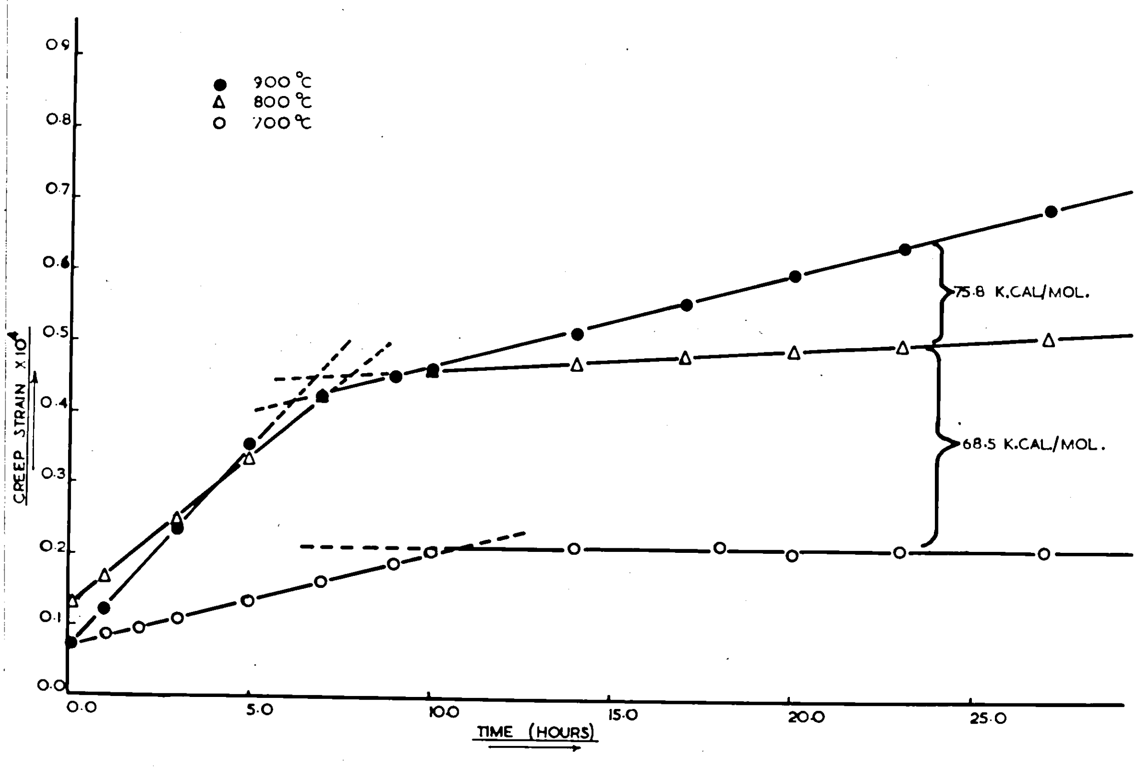
Influence of temperature on the form of the creep curve of a 18/8 niobium stabilised stainless steel tested in air at a stress of 2.0 t.p.s.i..

Figure 28.

Derivation of the activation energy for creep of a 18/8 niobium stabilised stainless steel from the above curves.



○ 900 °C
● 800 °C
Δ 700 °C
STRAIN (INS/IN X10^-4)
3·0
2·5
2·0
1·5
1·0
0·5
0·0
0·1
1·0·
10·0
100·0
1000·0
TIME (HOURS)



● 900 °C
Δ 800 °C
○ 700 °C
CREEP STRAIN X10^-4
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0·0
0·0
5·0
10·0
15·0
20·0
25·0
TIME (HOURS)
75·8 K.CAL/MOL.
68·5 K.CAL/MOL.

Figure 29.

W-type cracking in a specimen of 18/8 niobium stabilised stainless steel tested in air at 800°C and 6.0 t.p.s.i.

Magnification x 20

Figure 30.

R-type cavitation in a specimen of 18/8 niobium stabilised stainless steel tested in air at 800°C and 2.0 t.p.s.i.

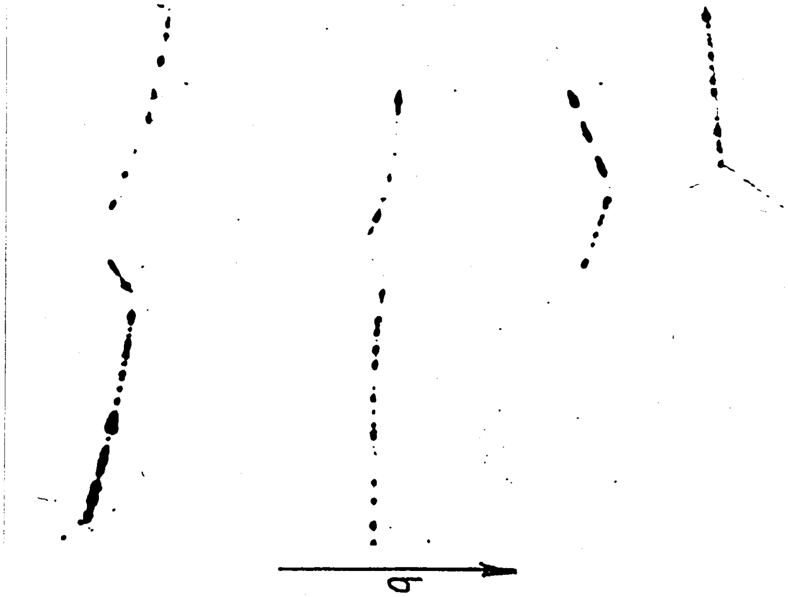
Magnification x 150

Figure 31.

Cracking of a grain-boundary by the growth and coalescence of r-type cavities.

Magnification x 600


b


a

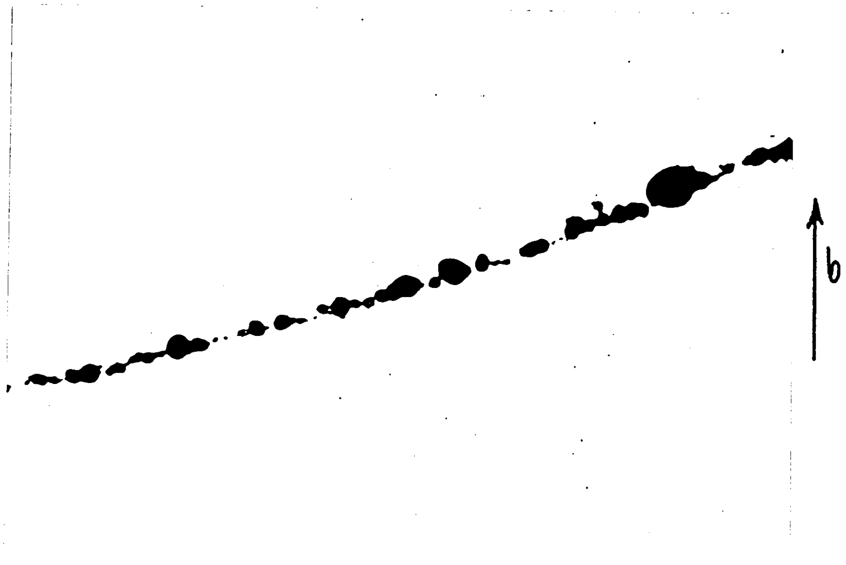
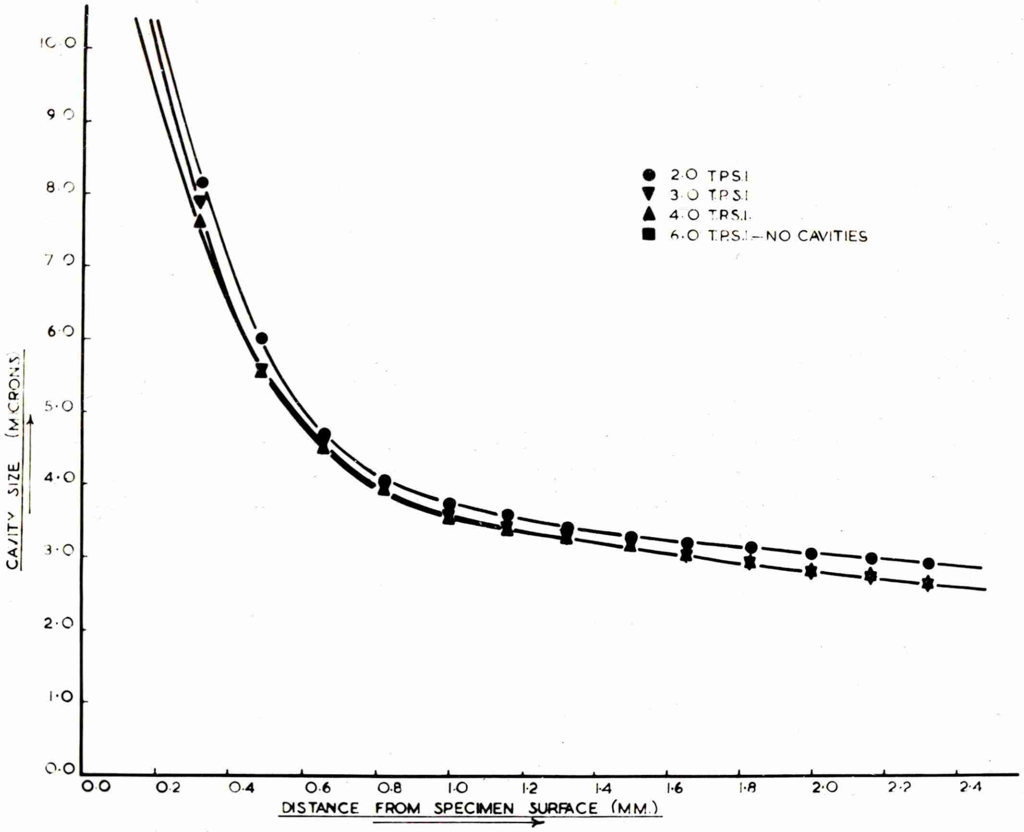

b

Figure 32.

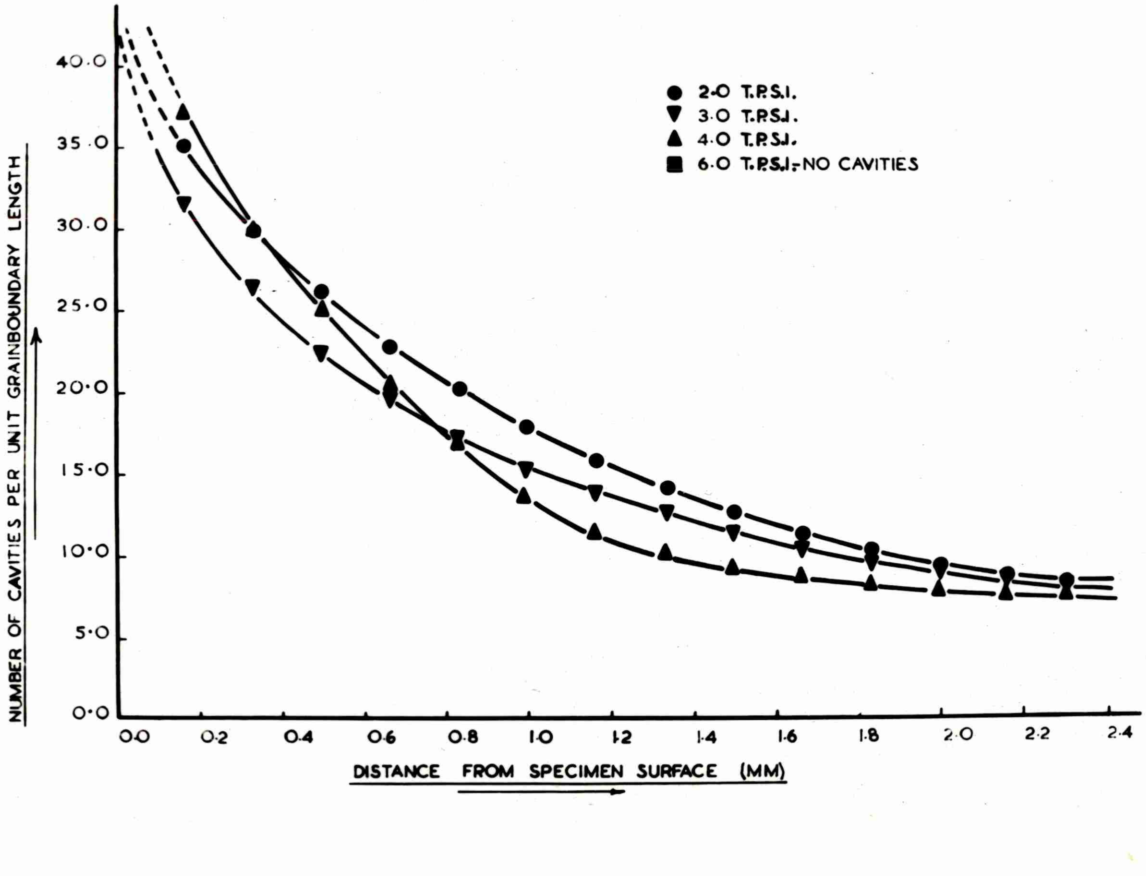
Variation in the size of cavities with distance from the surface in specimens of 18/8 niobium stabilised stainless steel tested in air at 800°C and 2.0 t.p.s.i.

Figure 33.

Variation in the number of cavities with distance from the surface in specimens of 18/8 niobium stabilised stainless steel tested in air at 800°C and 2.0 t.p.s.i.



● 2·0 T.P.S.I.
▼ 3·0 T.P.S.I.
▲ 4·0 T.P.S.I.
■ 6·0 T.P.S.I.–NO CAVITIES
CAVITY SIZE (MICRONS)
10·0
9·0
8·0
7·0
6·0
5·0
4·0
3·0
2·0
1·0
0·0
0.0
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
1·8
2·0
2·2
2·4
DISTANCE FROM SPECIMEN SURFACE (M.M.)



● 2·0 T.P.S.I.
▼ 3·0 T.P.S.I.
▲ 4·0 T.P.S.I.
■ 6·0 T.P.S.I.–NO CAVITIES
NUMBER OF CAVITIES PER UNIT GRAINBOUNDARY LENGTH
40·0
35·0
30·0
25·0
20·0
15·0
10·0
5·0
0·0
0.0
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
1·8
2·0
2·2
2·4
DISTANCE FROM SPECIMEN SURFACE (MM)

Figure 34.

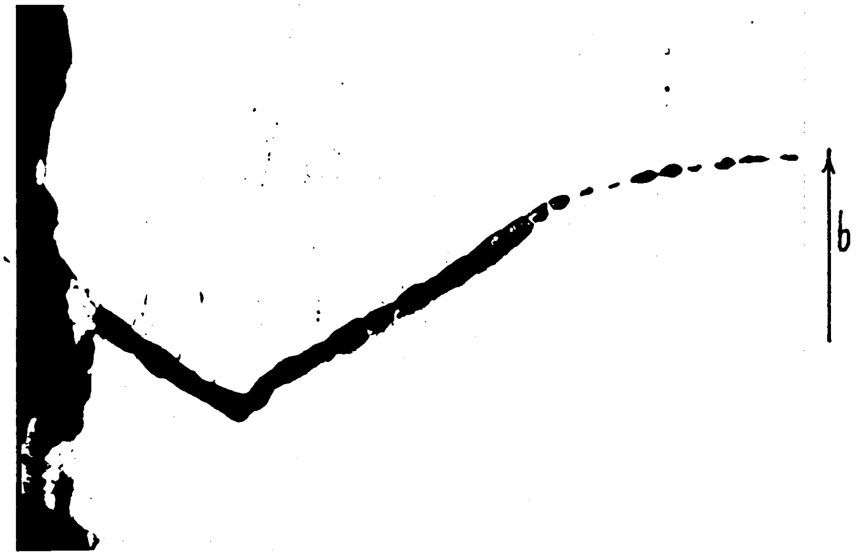
Cracking at the surface of specimens tested in air at 800^{o}C and 2.0 t.p.s.i. due to coalescence of r-type cavities.

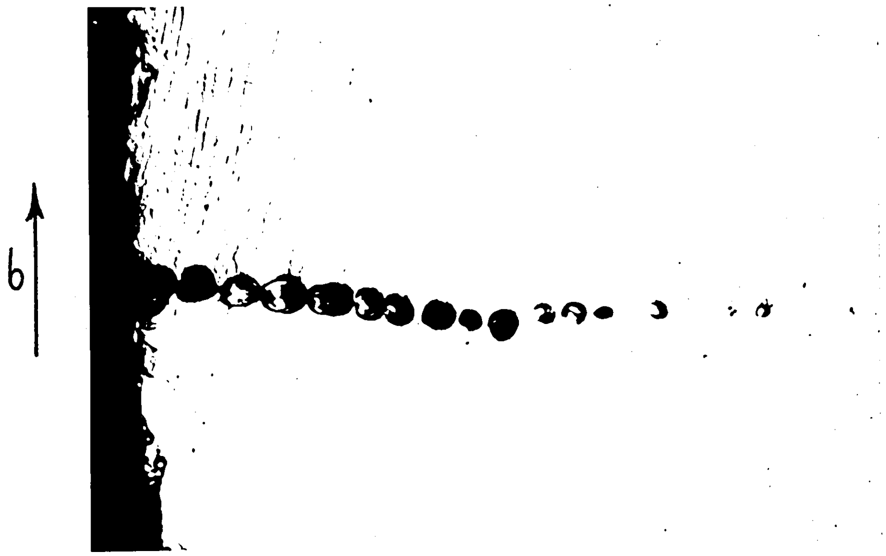
Magnification x 600

Figure 35.

Surface grain-boundaries immedically prior to cracking showing the presence of isolated r-type cavities.

Magnification x 550


b


b

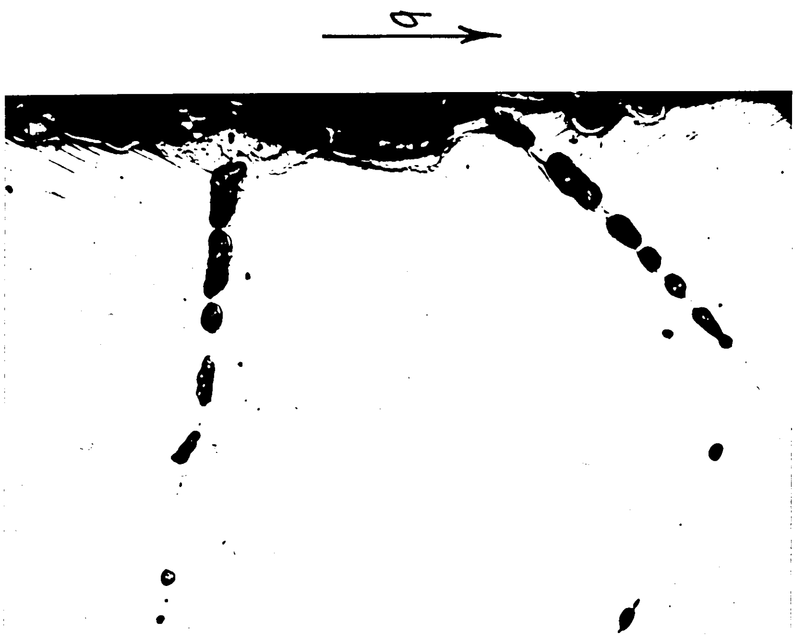
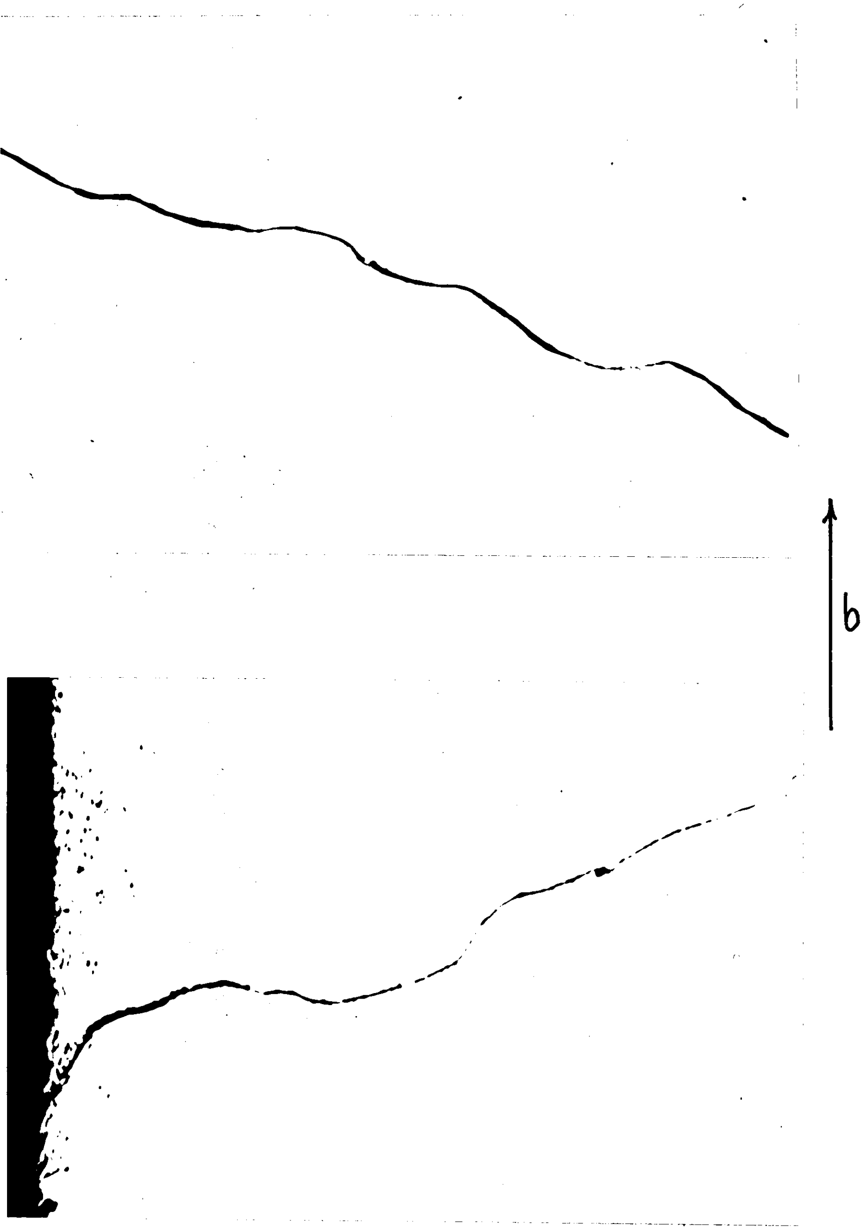

a

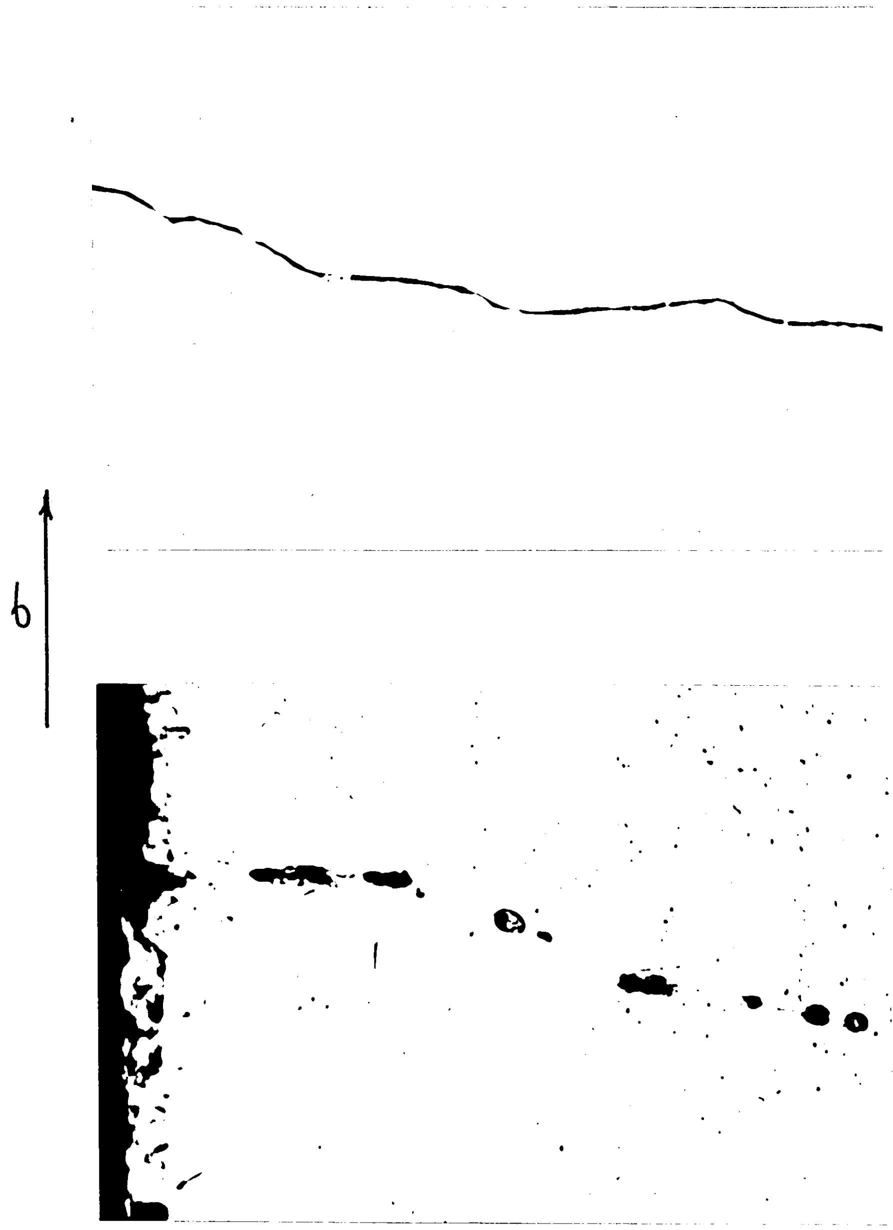
Figure 36.

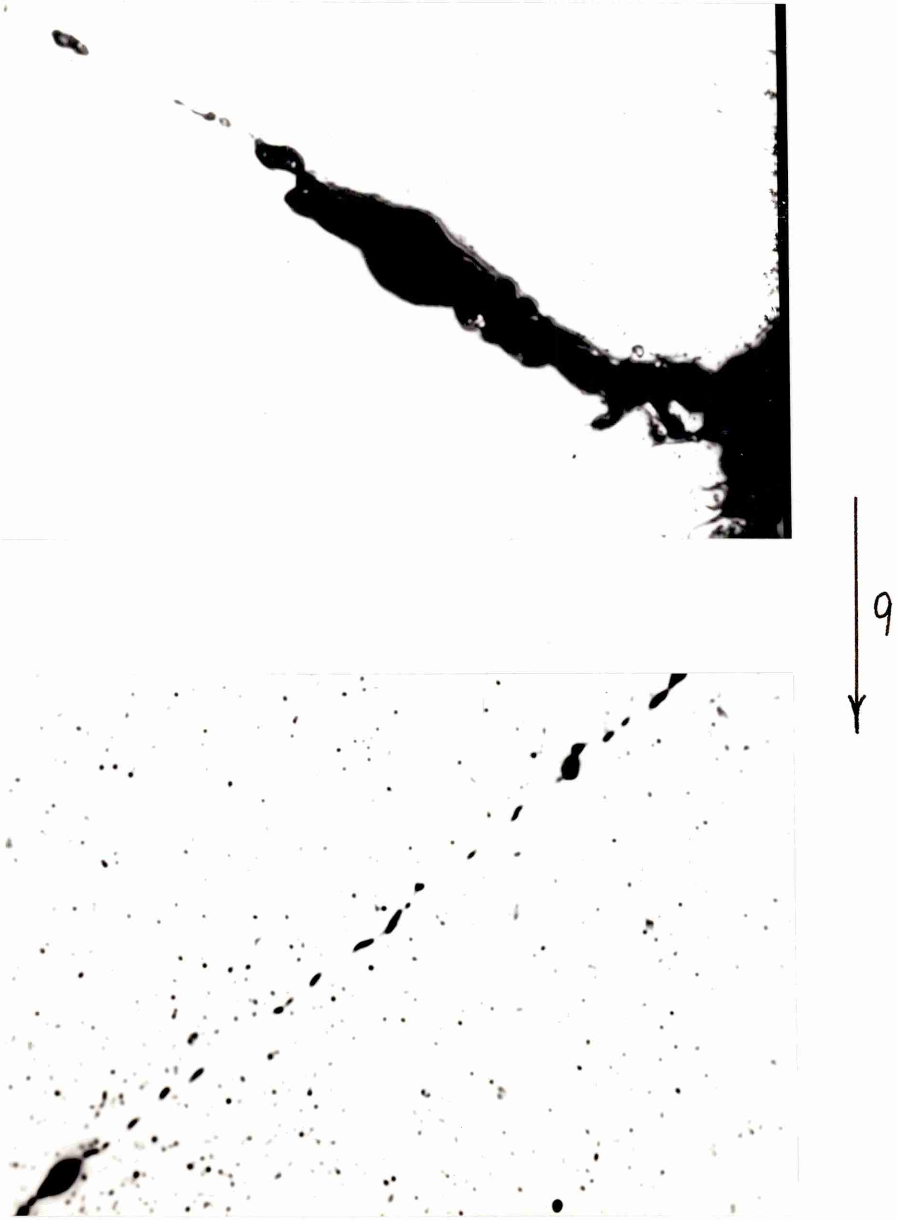
The following are a series of photomicrographs of the surface and centre of specimens tested in air at 800°C and 2.0 t.p.s.i. for

0 hours

250 hours


σ


σ


g


g

Figure 36 (ctnd.)

1000 hours

Magnification x 600

Figure 37.

W-cracks formed in the steel on testing in air at 700°C and 2.0 t.p.s.i.

Magnification x 450


g


g

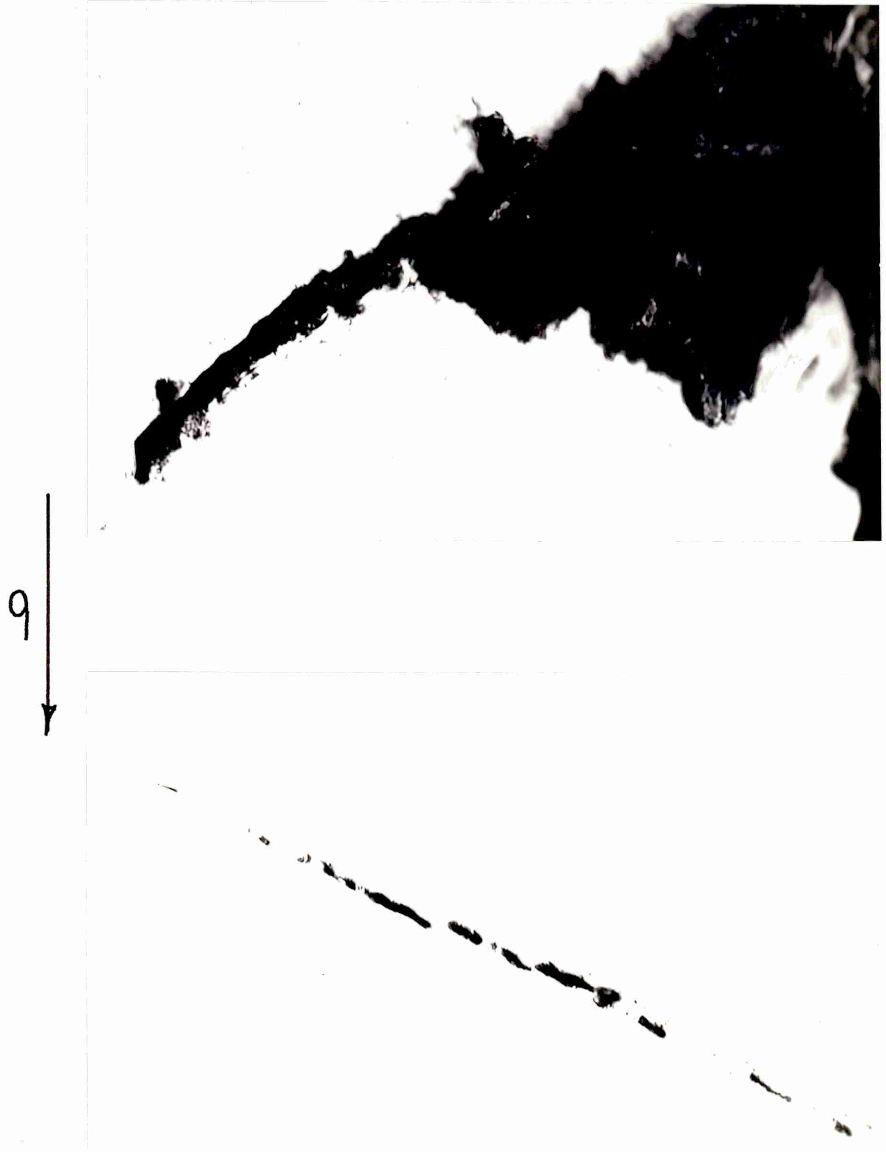

g

Figure 38.

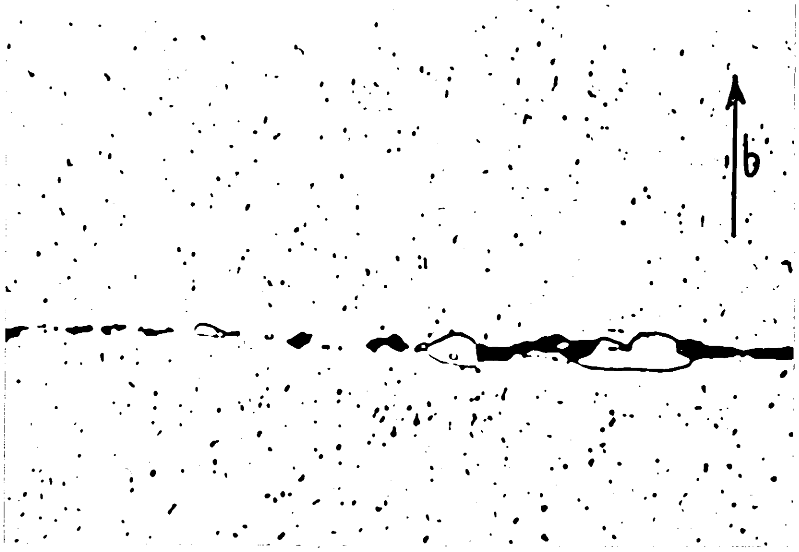
Cracking about grain-boundary particles on testing the steel in air at 900°C and 2.0 t.p.s.i..

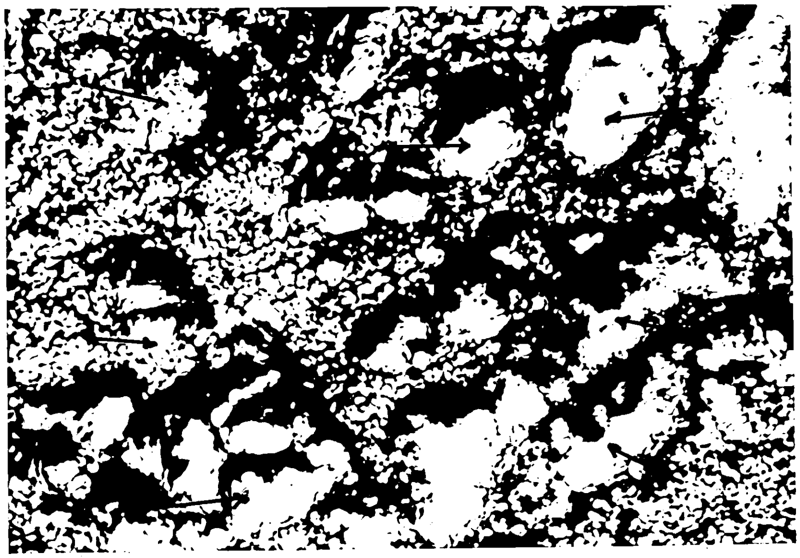
Magnification x 1000

Figure 39.

Optical fractographs showing 'disc-shaped' feature (arrowed).

Magnification x 750


b



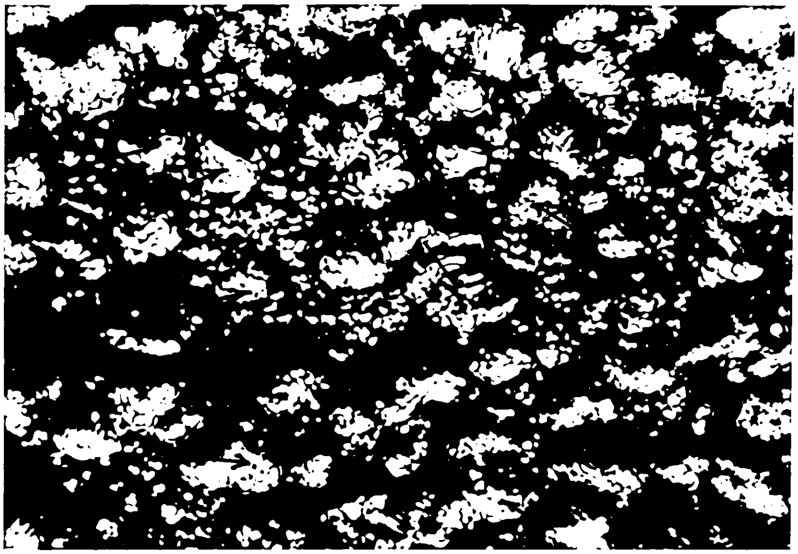


Figure 40. The following are a series of direct carbon replicas of electro-polished and etched sections of test specimens showing lenticular shaped cavities. The specimens were tested in air at 800°C and 2.0 t.p.s.i..

Magnifications x 10,000
x 14,500 and 20,000
respectively.

Figure 41.

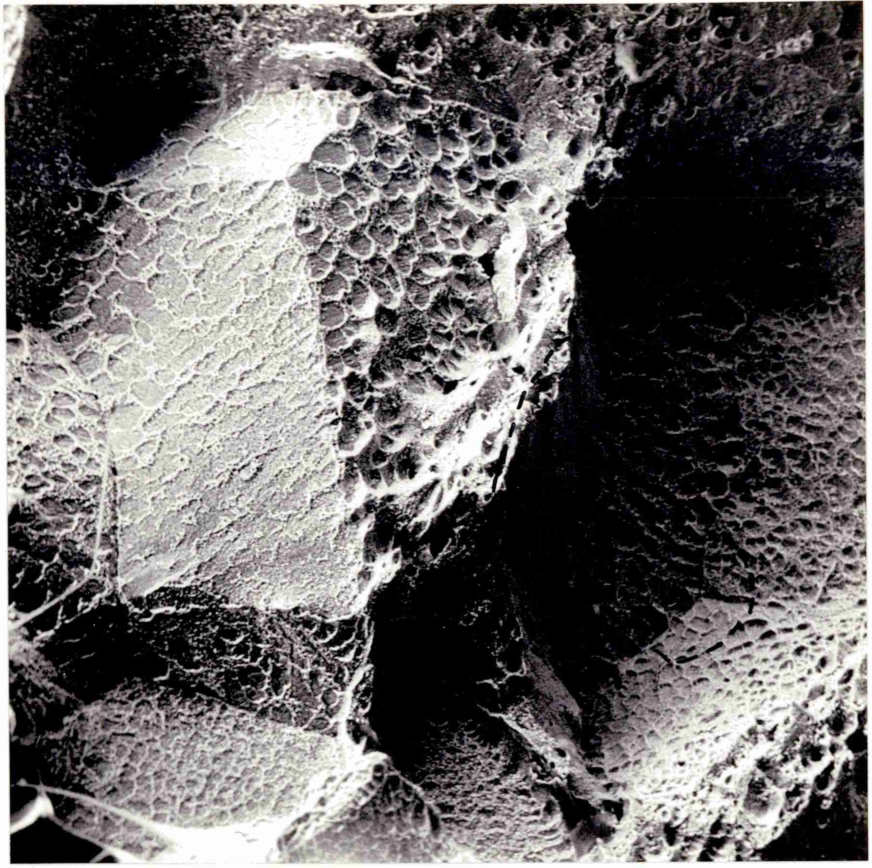
The following are a series of electron microfractographs of specimens tested in air at 800°C and 2.0 t.p.s.i. and broken by impact.

(a) General fracture surface structure showing a uniform distribution of cavities. The stress axis of the specimen is approximately perpendicular to the plane of the photomicrograph.

Magnification x 130

(b) High magnification view of area (A) in photomicrograph (a) showing the absence of cavities on grain facets at low angles to the stress axis.

Magnification x 700



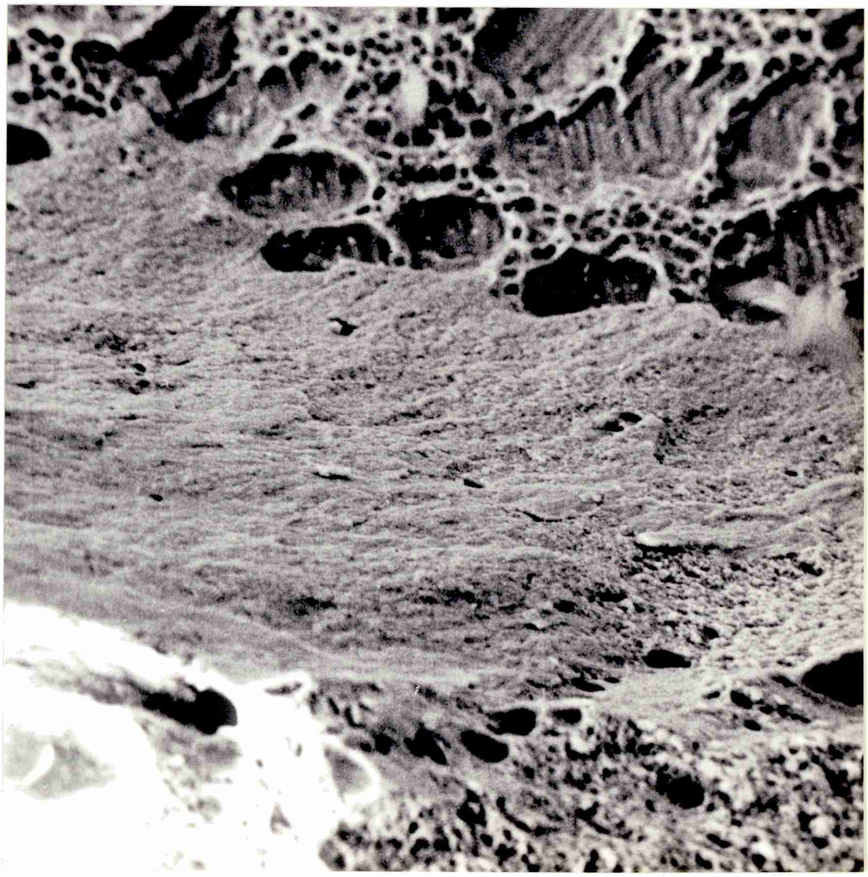


Figure 41 (ctnd).

(c) High magnification view of a triple-point, area (B) in photomicrograph.

(a) Note that whilst the majority of the major axes of the cavities lie parallel to one another on a given facet, they are of random orientation at the grain facet junctures and are not continuous from one grain facet to another.

Magnification x 800

(d) Grain facet lying at approximately 45° to the applied stress axis.

Note their shallow lenticular disc-like shape and the presence of ductile fracture porosity between the cavities.

Magnification x 800

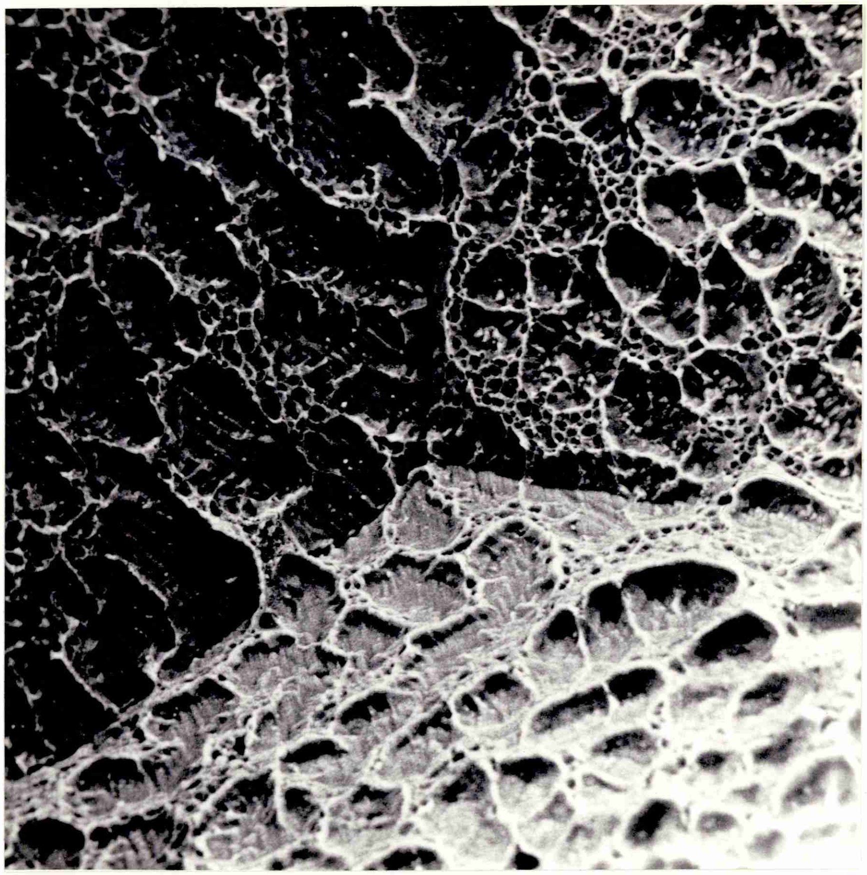


Figure 41 (ctnd.)

(e) Grain facet lying at approximately 90° to the applied stress axis.

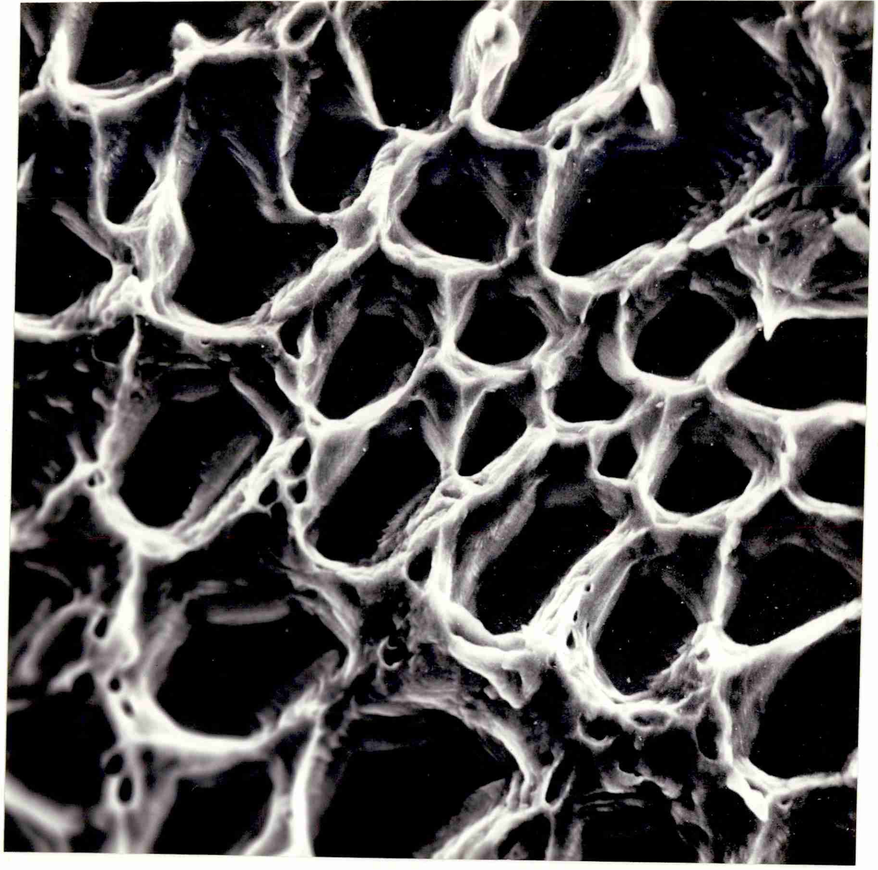
Note the faceted polyhedral shape and the absence of extensive inter-cavity ductile fracture cf. facets oriented at 45° to the applied stress axis, photomicrograph (d).

Magnification x 1400

(f) Surface of a specimen subjected to the same thermal history as the creep specimens and broken by impact.

Note the fine porosity or cavitiation due, it is thought, to ductile fracture about precipitates.

Magnification x 1650



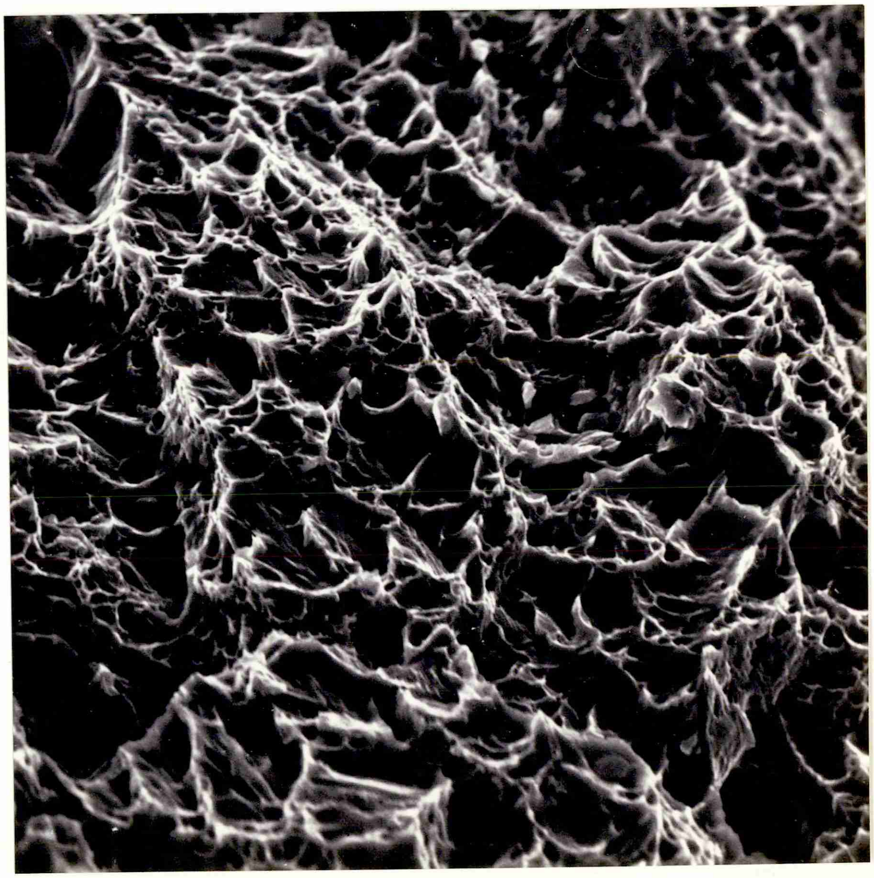


Figure 42.

The following are a series of transmission electron micrographs of foils containing cavities. The foils were prepared by the 'thick& thin foil technique.

Magnifications x 116,000 x 150,000 and x 45,000 respectively.

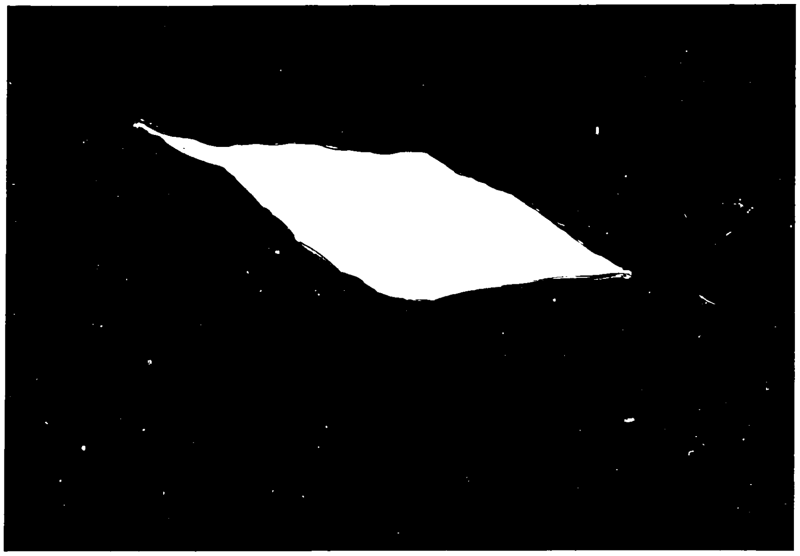


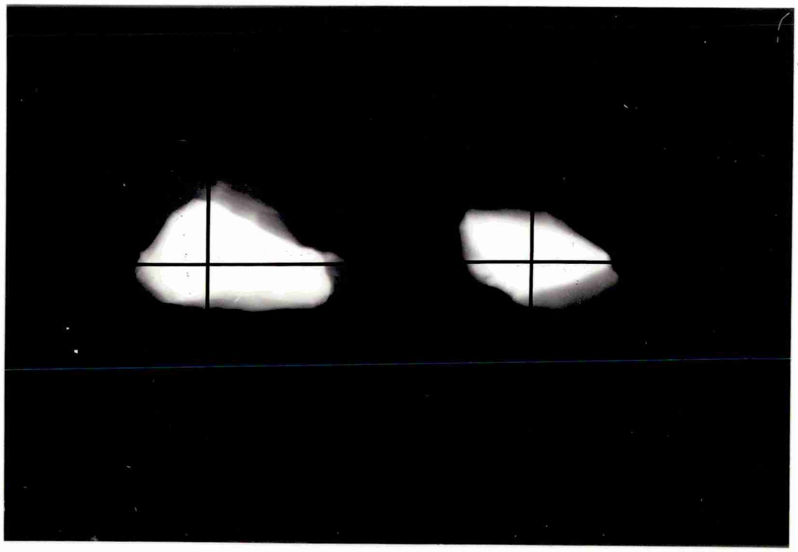
Figure 42 (ctnd.)

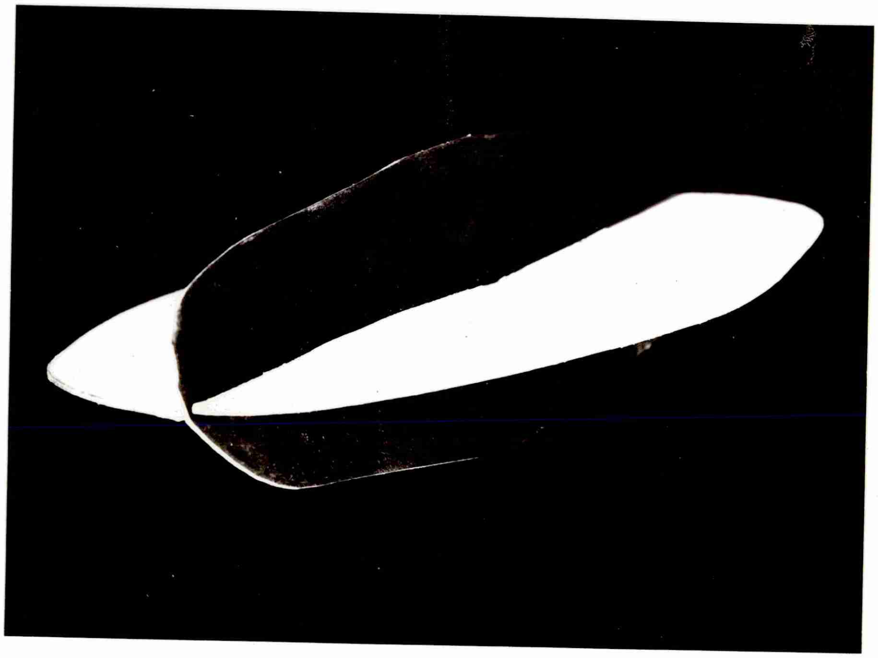
Cavities as observed by the 'thick' thin foil technique.

Magnification x 40,000

Figure 43.

Model of a cavity produced by optical density measurements across the eletron-micrograph shown above. The lines of the scan are as indicated on the photomicrograph.





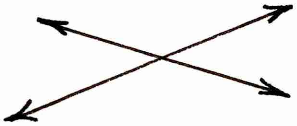
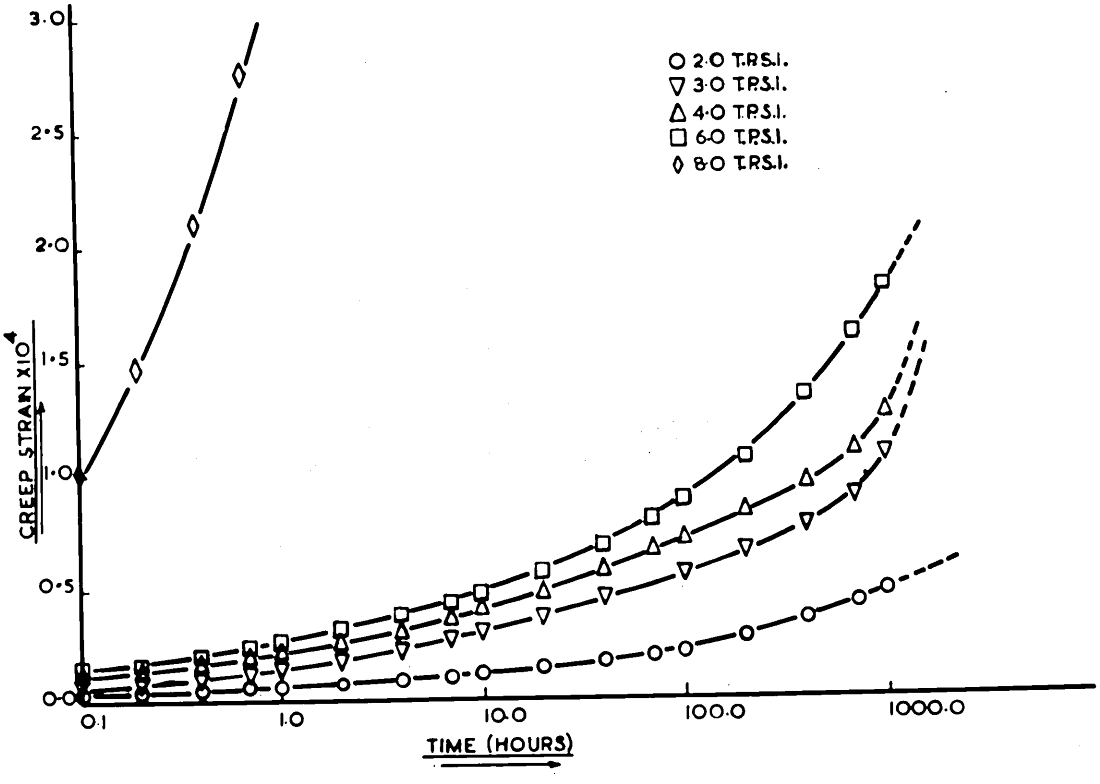


Figure 44.

Creep curves of a 18/8 niobium stabilised stainless steel tested in vacuum at 800°C.

Figure 45.

Influence of temperature on the form of the creep curve of a 18/8 niobium stabilised stainless steel at 2.0 t.p.s.i. in vacuum.


3·0
2·5
2·0
1·5
1·0
0·5
0·0
CREEP STRAIN X10⁴
0·1
1.0
10.0
100.0
1000.0
TIME (HOURS)
○ 2·0 T.P.S.I.
▽ 3·0 T.P.S.I.
△ 4·0 T.P.S.I.
□ 6·0 T.P.S.I.
◊ 8·0 T.P.S.I.

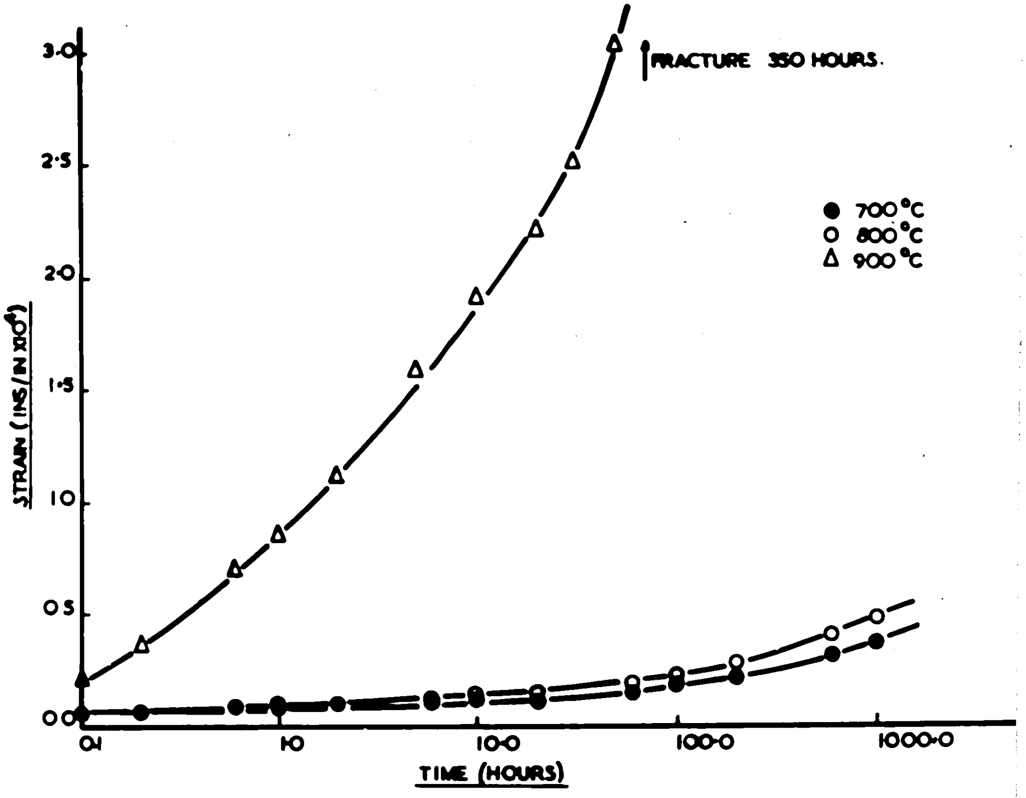

3·0
2·5
2·0
1·5
1.0
0.5
0.0
STRAIN (INS/IN X10⁴)
0·1
1·0
10·0
100·0
1000·0
TIME (HOURS)
FRACTURE 350 HOURS.
● 700°C
○ 800°C
△ 900°C

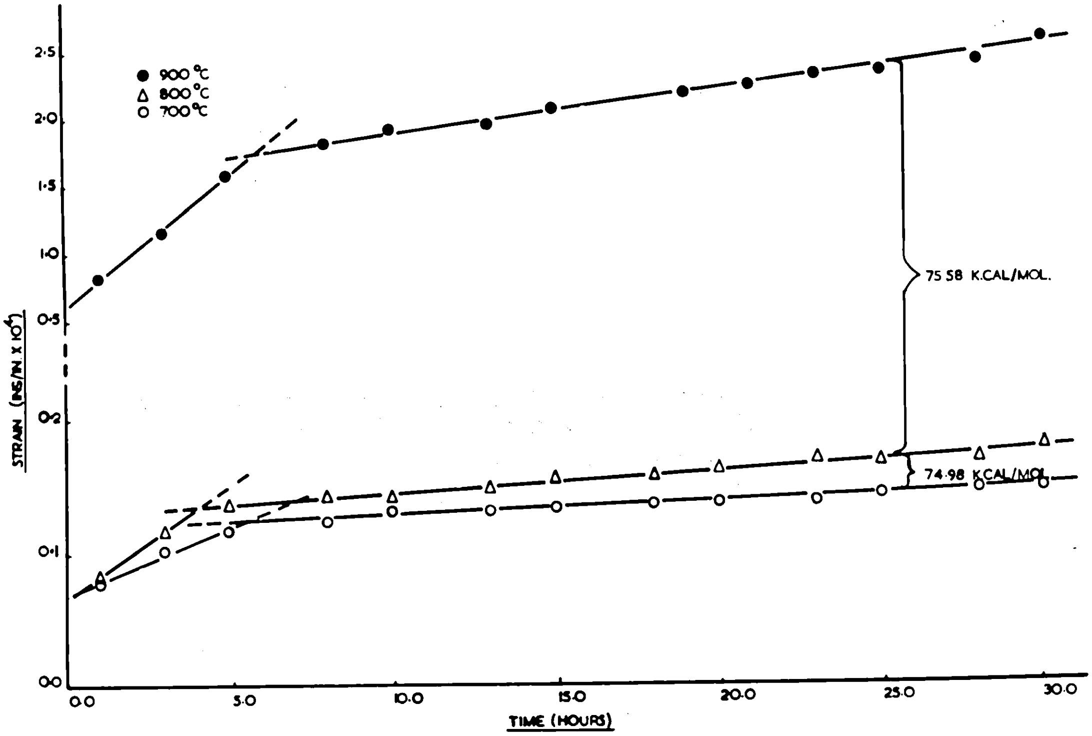
Figure 46.

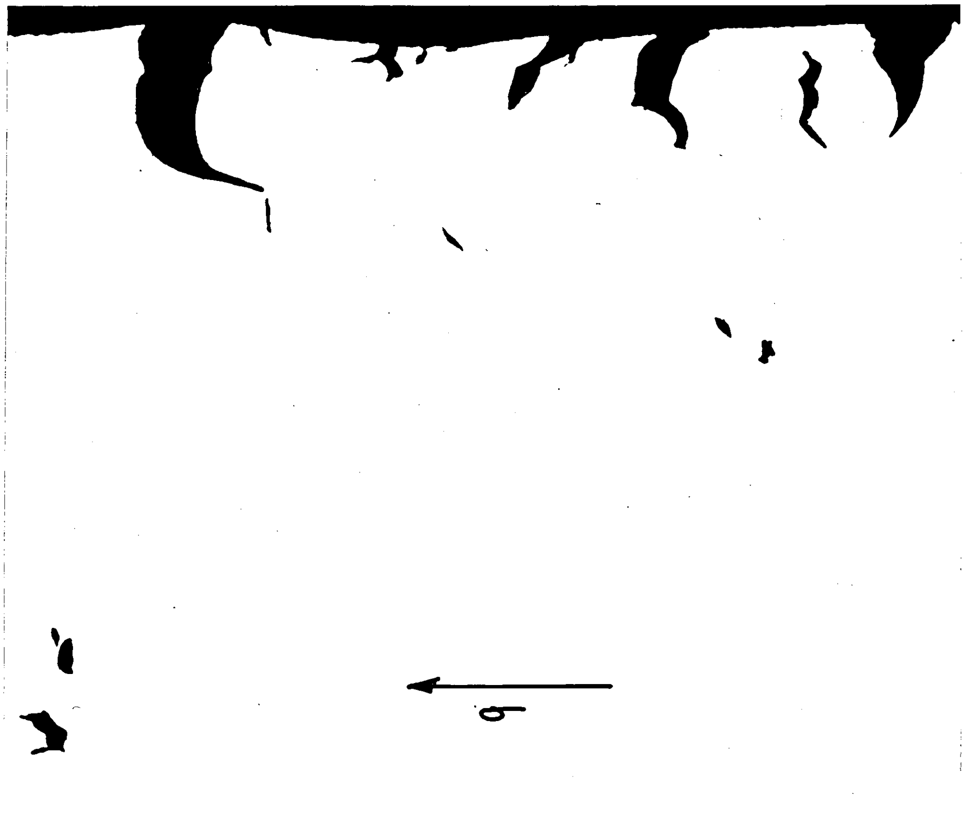
Derivation of the activation energy for creep of a 18/8 niobium stabilised stainless steel at 800°C and 2.0 t.p.s.i. in vacuum from the above curves.

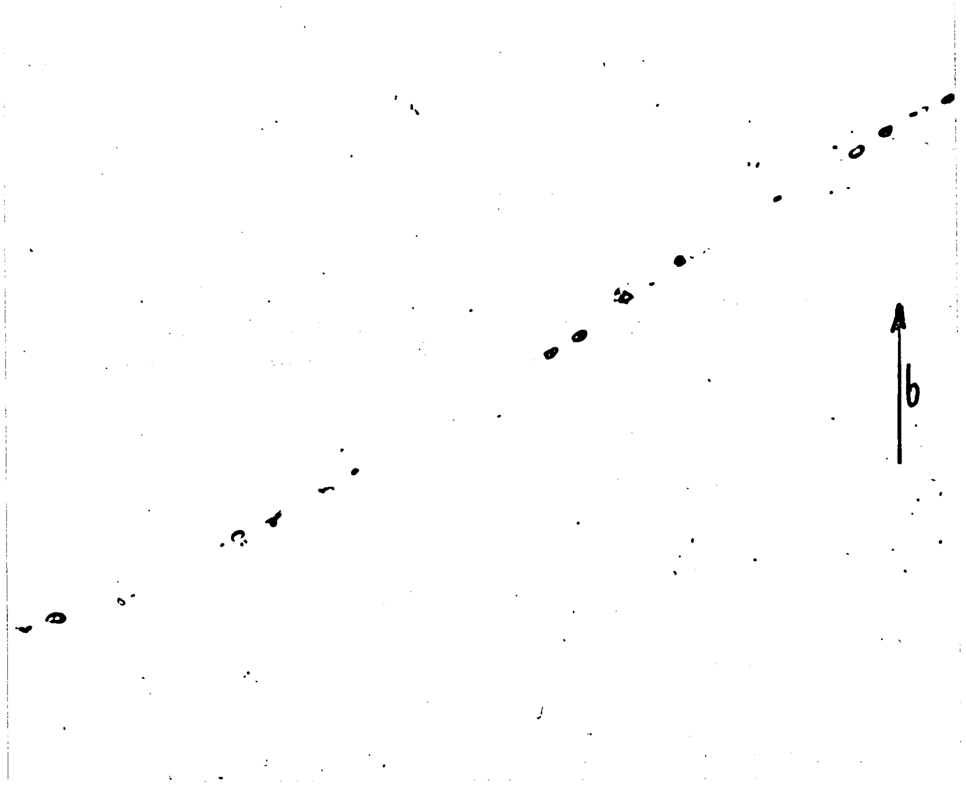
Figure 47.

W-type cracking in the steel on testing in vacuum at 800°C and 6.0 t.p.s.i. Cf. that in air, figure 29.

Magnification x 20


● 900 °C
△ 800 °C
○ 700 °C
75 58 K.CAL/MOL.
74·98 K.CAL/MOL.
STRAIN (INS/IN x 10⁴)
2·5
2·0
1·5
1·0
0·5
0·2
0·1
0·0
0·0
5·0
10·0
15·0
20·0
25·0
30·0
TIME (HOURS)


σ


b

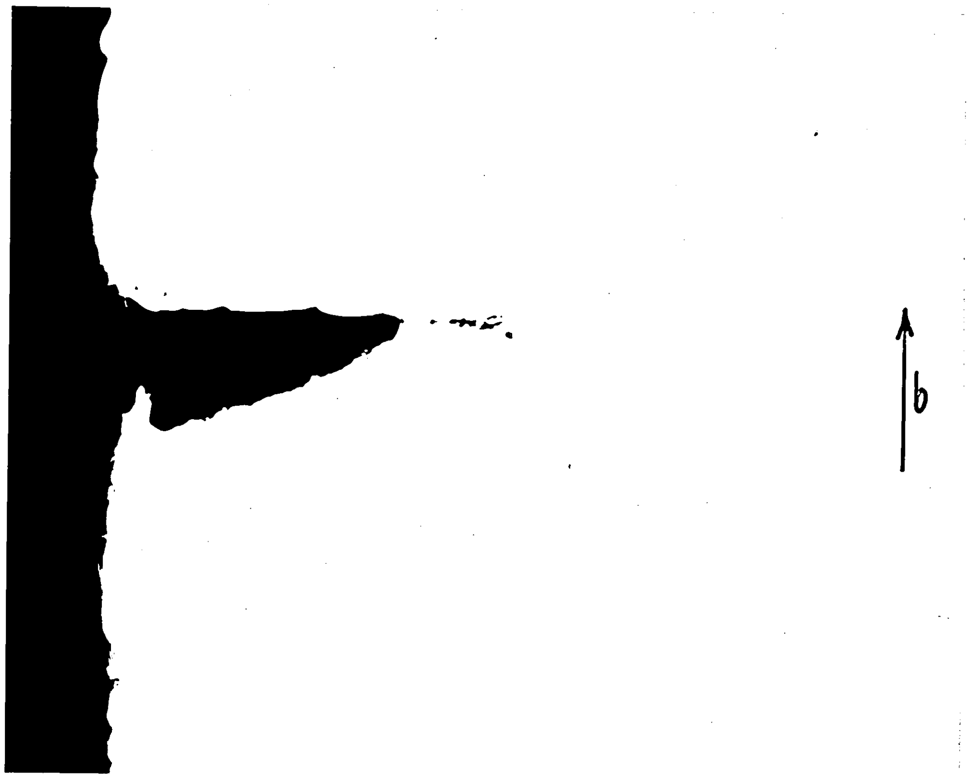

b

Figure 48.

R-type cavitation formed in the steel on testing in vacuum at 800°C and 2.0 t.p.s.i.

Magnification x 600

Figure 49.

Stabilised surface cracking on testing the steel in vacuum at 800°C and 6.0 t.p.s.i..

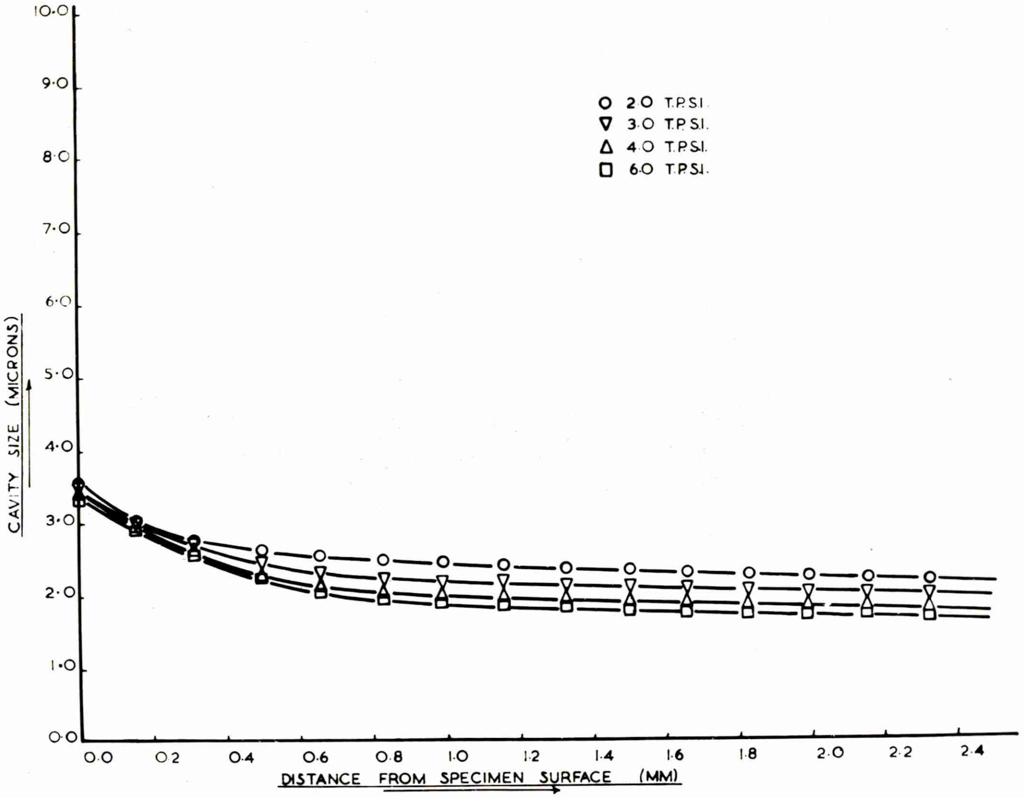
Magnification x 600

Figure 50.

Variation in the size of r-type cavities with distance from the surface in specimens of a 18/8 niobium stabilised stainless steel tested in vacuum at 800°C.

Figure 51.

Variation in the number of r-type cavities with distance from the surface in specimens of a 18/8 niobium stabilised stainless steel tested in vacuum at 800°C.


10·0
9·0
8·0
7·0
6·0
5·0
4·0
3·0
2·0
1·0
0·0
CAVITY SIZE (MICRONS)
○ 2·0 T.P.S.I.
▽ 3·0 T.P.S.I.
△ 4·0 T.P.S.I.
□ 6·0 T.P.S.I.
0·0
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
1·8
2·0
2·2
2·4
DISTANCE FROM SPECIMEN SURFACE (MM)

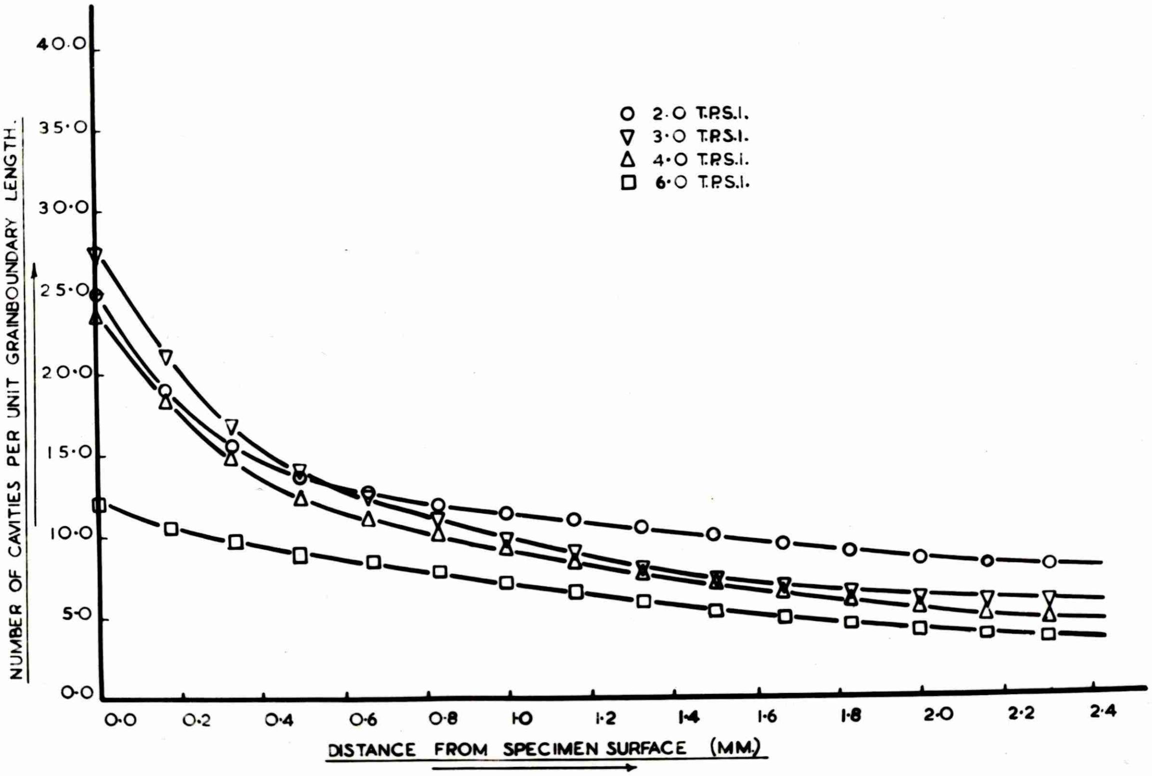

40·0
35·0
30·0
25·0
20·0
15·0
10·0
5·0
0·0
NUMBER OF CAVITIES PER UNIT GRAINBOUNDARY LENGTH.
○ 2·0 T.P.S.I.
▽ 3·0 T.P.S.I.
△ 4·0 T.P.S.I.
□ 6·0 T.P.S.I.
0·0
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
1·8
2·0
2·2
2·4
DISTANCE FROM SPECIMEN SURFACE (MM.)

Figure 52.

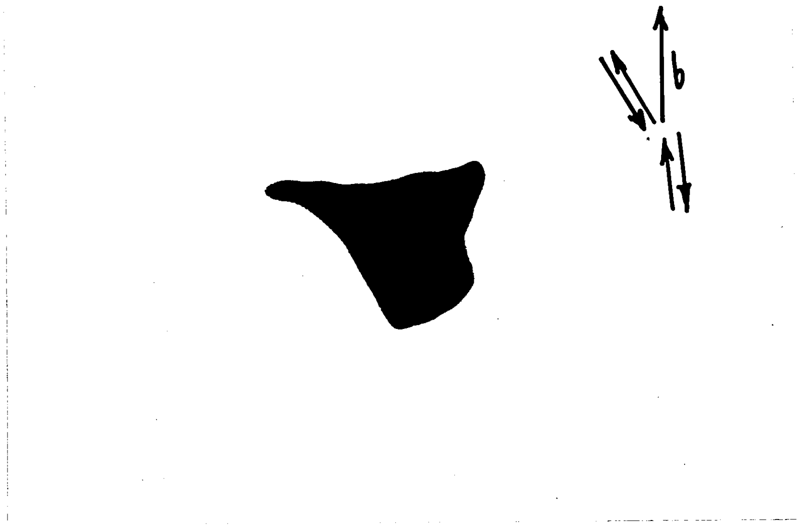
W-type cracking at triple points in the steel on testing in vacuum at 700°C and 2.0 t.p.s.i. Note the restriction of crack propogation compared with that in air, figure 37.

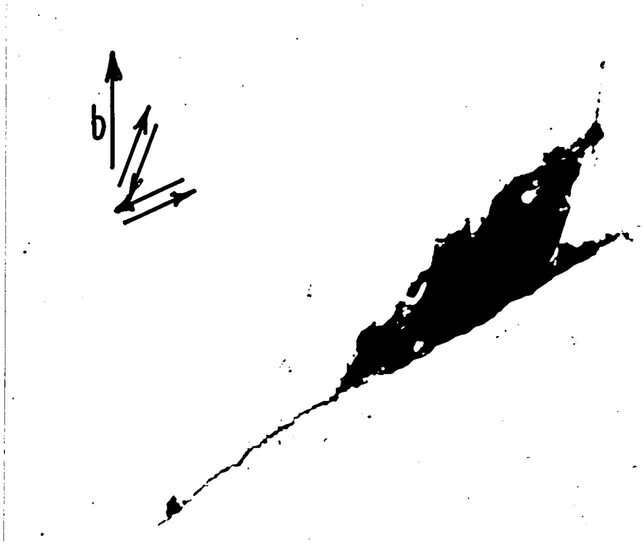
Magnification x 800 and x 6500 respectively.

Figure 53.

General structure of the steel on testing in vacuum at 900°C and 2.0 t.p.s.i. showing directional grain-boundary migration.

Magnification x 150


b


b

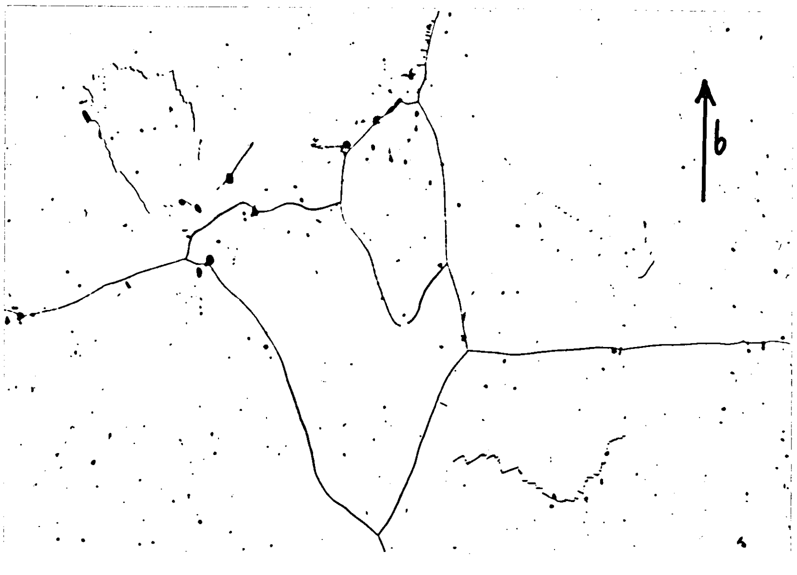

b

Figure 54.

High magnification photomicrograph of grain-boundary migration in the steel at 900°C showing bowing out of the boundary between particles.

Magnification x 400

Figure 55.

Optical fractograph showing the absence of any feature resembling r-type cavitation. The fine porosity is considered to be due to ductile fracture about precipitates.

Magnification x 900

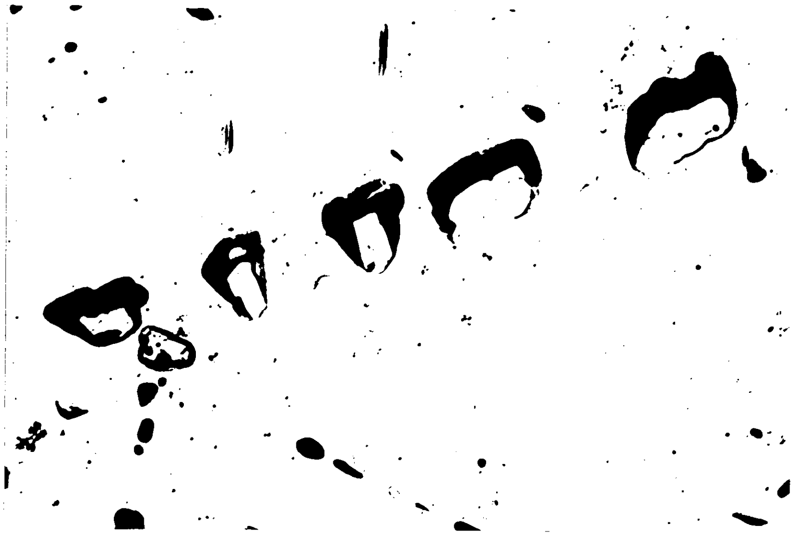

g

Figure 56.

The following are a series of direct carbon replicas of electro-polished and etched section of test specimens showing 'rounding' of the cavities.

The specimens were tested in vacuum at 800°C and 2.0 t.p.s.i.

Magnification x 14,000
12,500 and x 18,000
respectively.



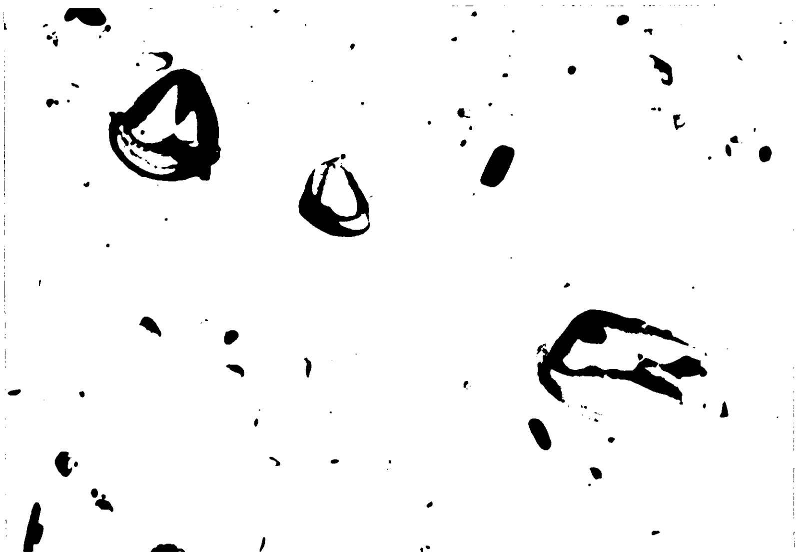


Figure 57.

Electron-micro-fractograph of a specimen tested in vacuum at 800°C and 2.0 t.p.s.i.

Magnification x 1500

Figure 58.

Transmission electron-micrographs of cavities formed in specimens of the steel tested in vacuum.

Magnifications x 10,000
and x 175,000 respectively

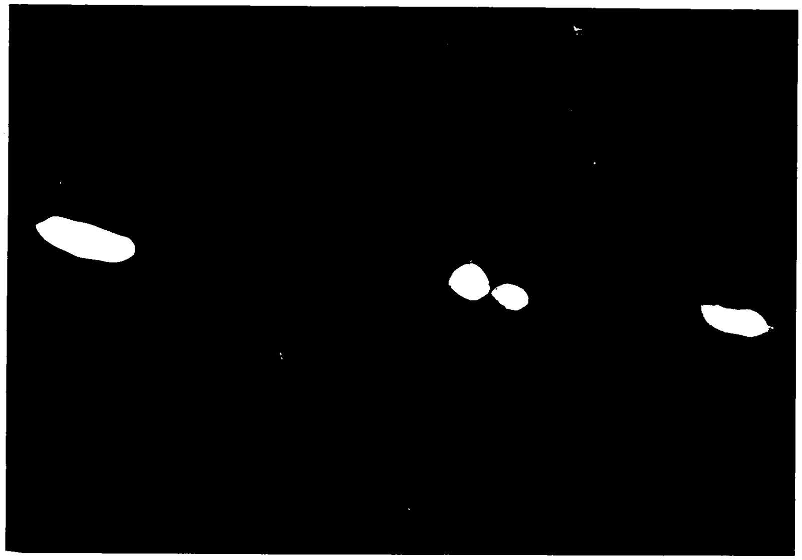
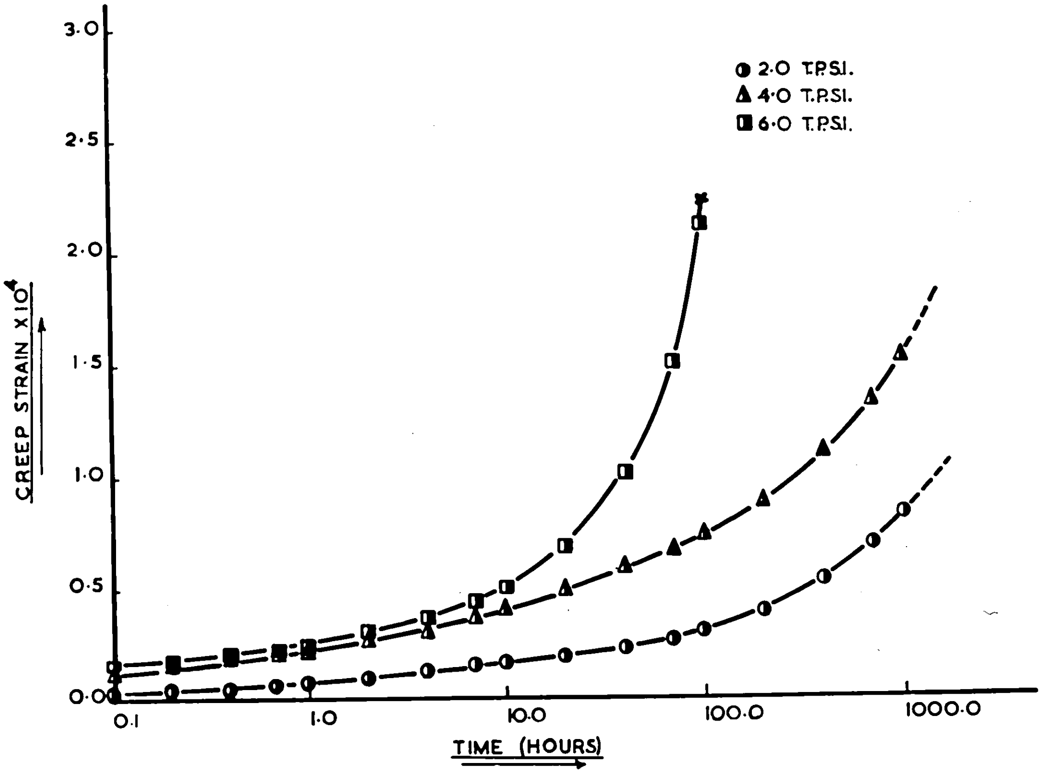


Figure 59.

Creep curves of a 18/8 niobium stabilised stainless steel tested in argon at 800°C.



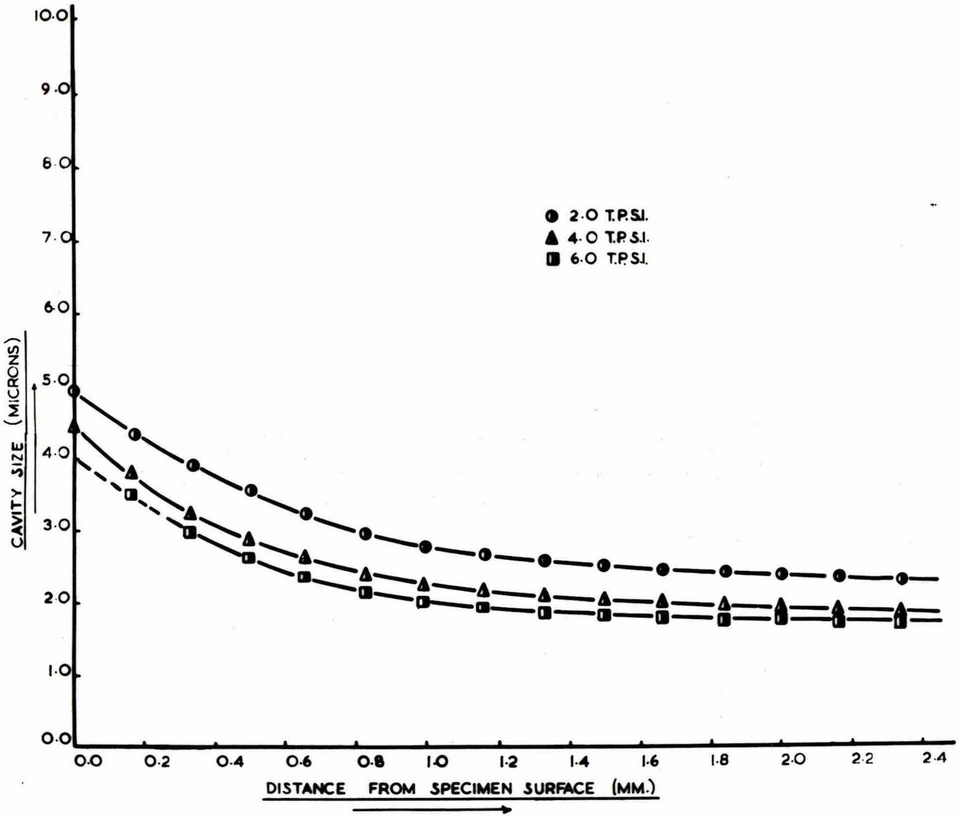
3·0
2·5
2·0
1·5
1·0
0·5
0·0
CREEP STRAIN X10⁴
0·1
1·0
10·0
100·0
1000·0
TIME (HOURS)
◐ 2·0 T.P.S.I.
▲ 4·0 T.P.S.I.
◨ 6·0 T.P.S.I.

Figure 60.

Variation in the size of r-type cavities with distance from the surface in specimens of a 18/8 niobium stabilised stainless steel tested in argon at 800°C.

Figure 61.

Variation in the number of r-type cavities with distance from the surface in specimens of a 18/8 niobium stabilised stainless steel tested in argon at 800°C.


10·0
9·0
8·0
7·0
6·0
5·0
4·0
3·0
2·0
1·0
0·0
CAVITY SIZE (MICRONS)
● 2·0 T.P.S.I.
▲ 4·0 T.P.S.I.
■ 6·0 T.P.S.I.
0·0
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
1·8
2·0
2·2
2·4
DISTANCE FROM SPECIMEN SURFACE (MM.)

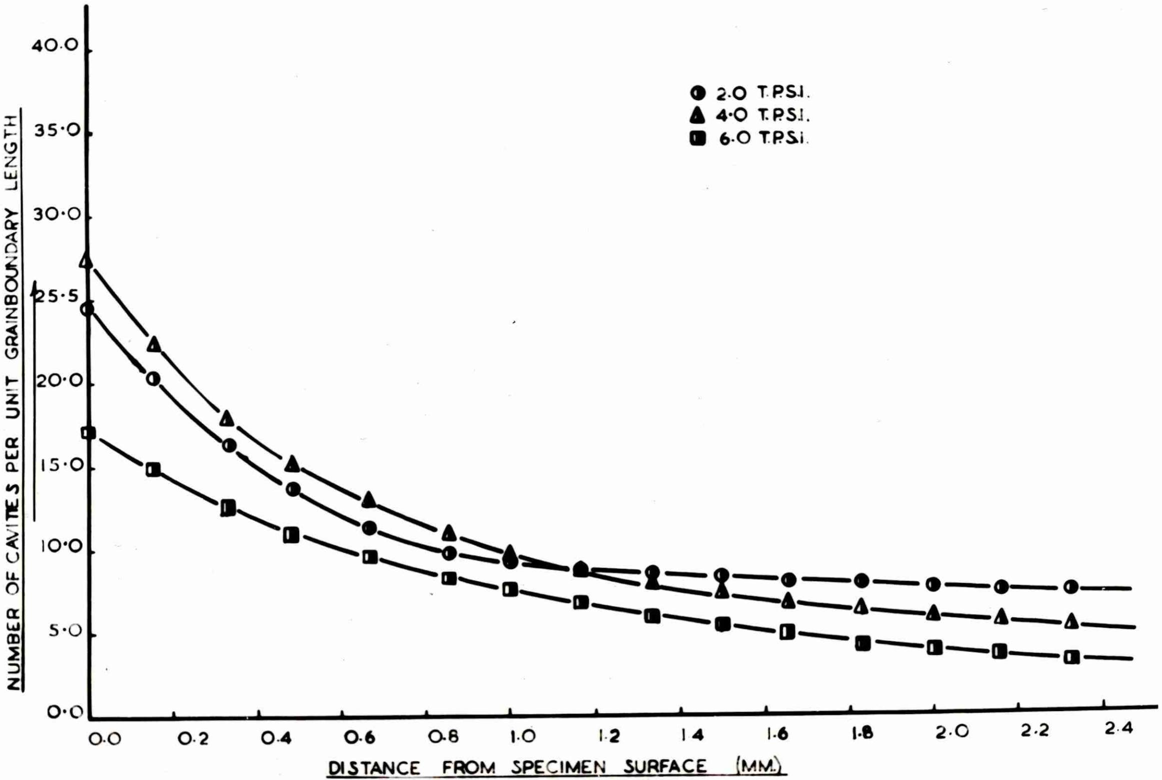
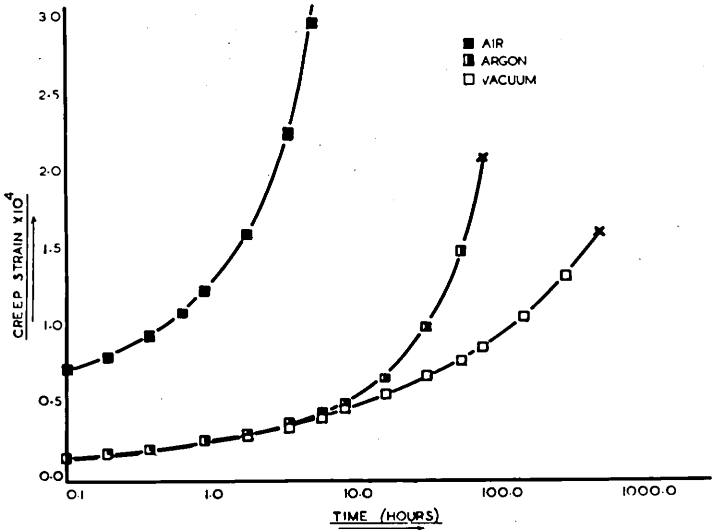
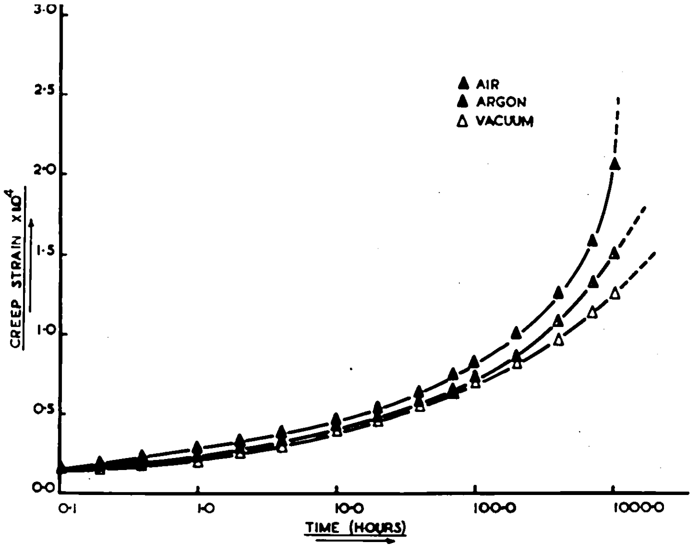
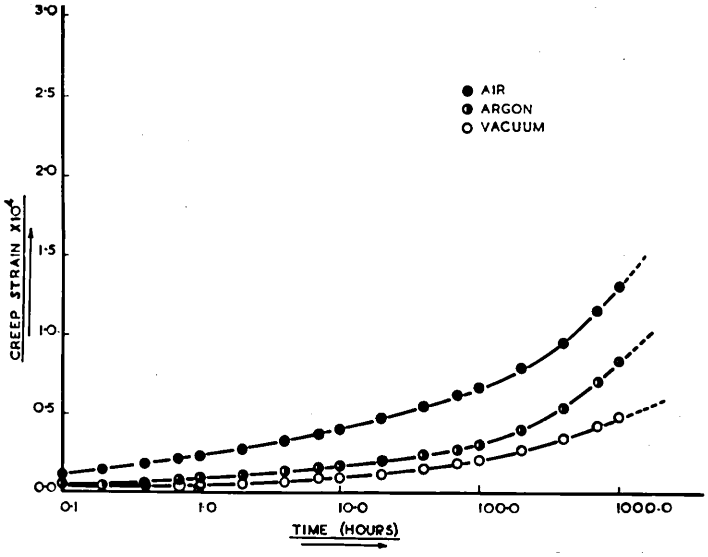

40·0
35·0
30·0
25·5
20·0
15·0
10·0
5·0
0·0
NUMBER OF CAVITES PER UNIT GRAINBOUNDARY LENGTH
● 2·0 T.P.S.I.
▲ 4·0 T.P.S.I.
■ 6·0 T.P.S.I.
0·0
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
1·8
2·0
2·2
2·4
DISTANCE FROM SPECIMEN SURFACE (MM.)

Figure 62.

Comparison of the creep curves of a 18/8 niobium stabilised stainless steel tested in air, argon, and vacuum at 800°C and 6.0, 4.0, and 2.0 t.p.s.i. respectively.


■ AIR
◧ ARGON
□ VACUUM
CREEP STRAIN X10^4
3.0
2·5
2·0
1·5
1·0
0·5
0·0
0·1
1·0
10·0
100·0
1000·0
TIME (HOURS)


▲ AIR
▲ ARGON
△ VACUUM
CREEP STRAIN X10^4
3·0
2·5
2·0
1·5
1·0
0·5
0·0
0·1
1·0
10·0
100·0
1000·0
TIME (HOURS)

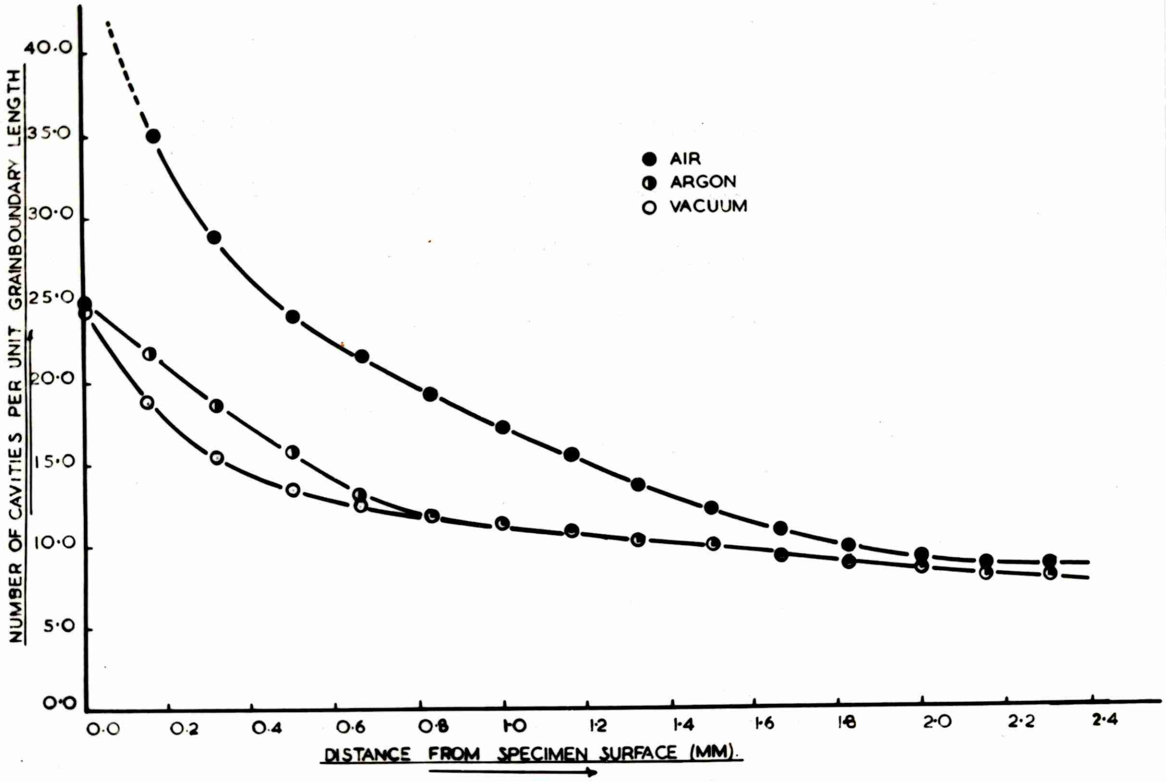

● AIR
◑ ARGON
○ VACUUM
CREEP STRAIN X10^4
3·0
2·5
2·0
1·5
1·0
0·5
0·0
0·1
1·0
10·0
100·0
1000·0
TIME (HOURS)

The following plots are comparisons of the variation in r-type cavity size and number with distance from the surface in specimens of a 18/8 niobium stabilised stainless steel tested at 800°C in environments of air, argon, and vacuum.

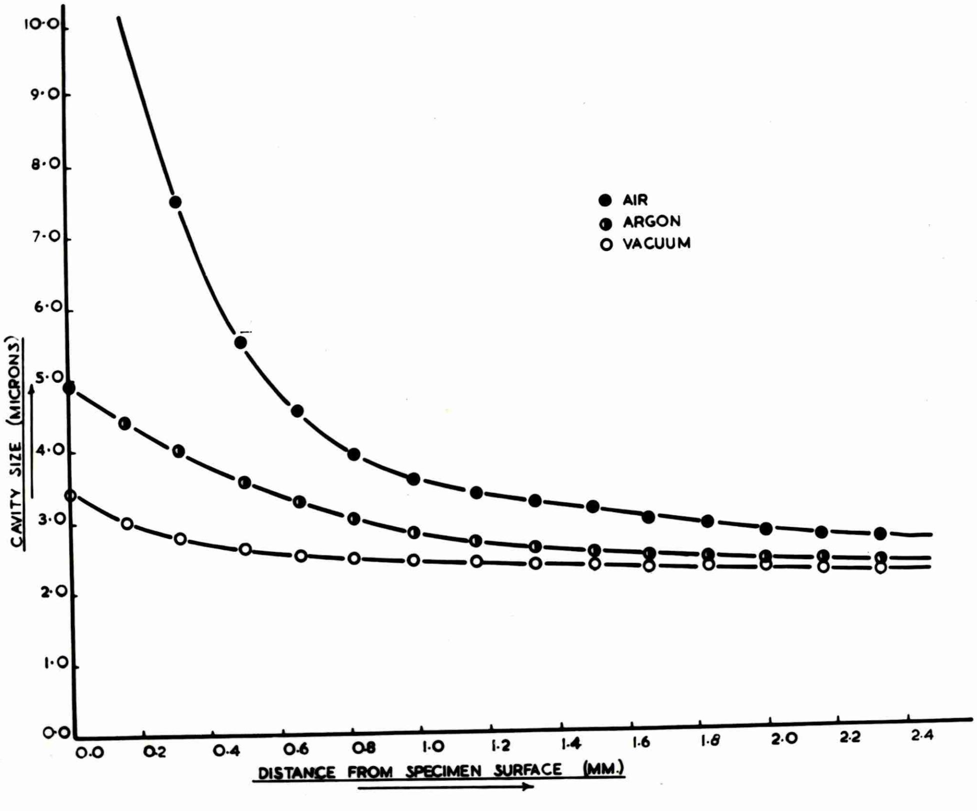
Figure 63.

Temperature 800°C.

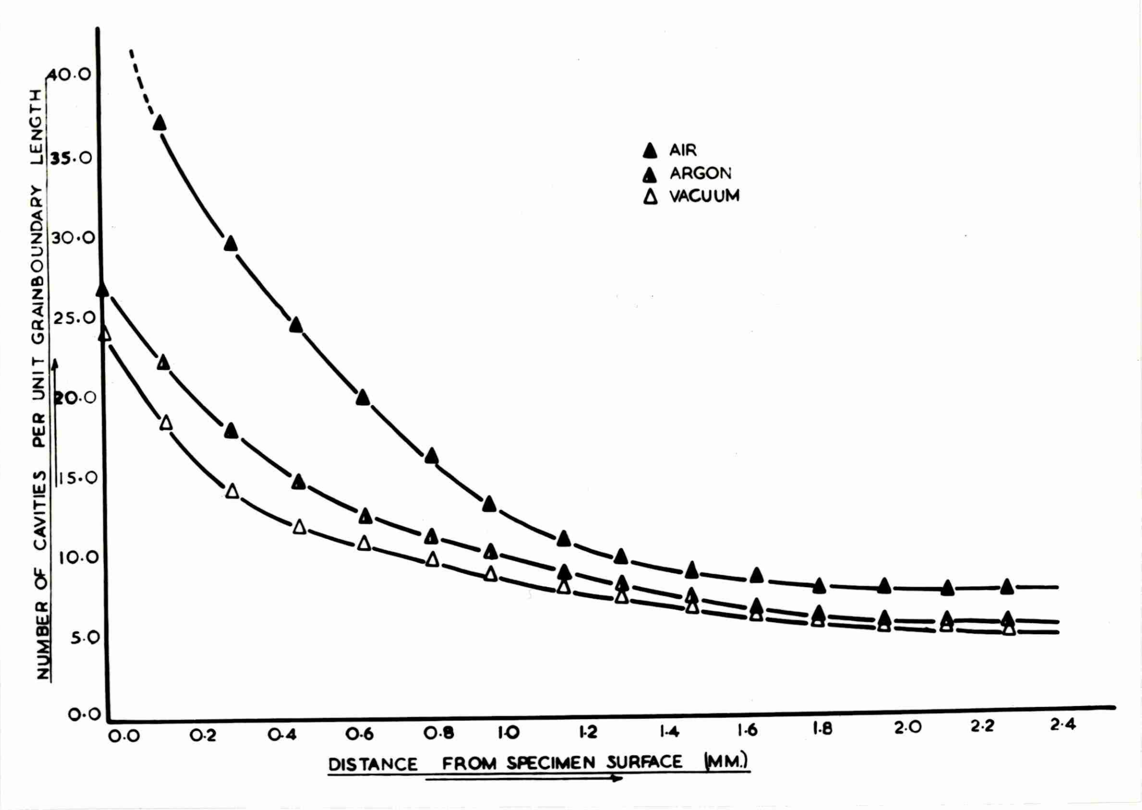
Stress 2.0 t.p.s.i.



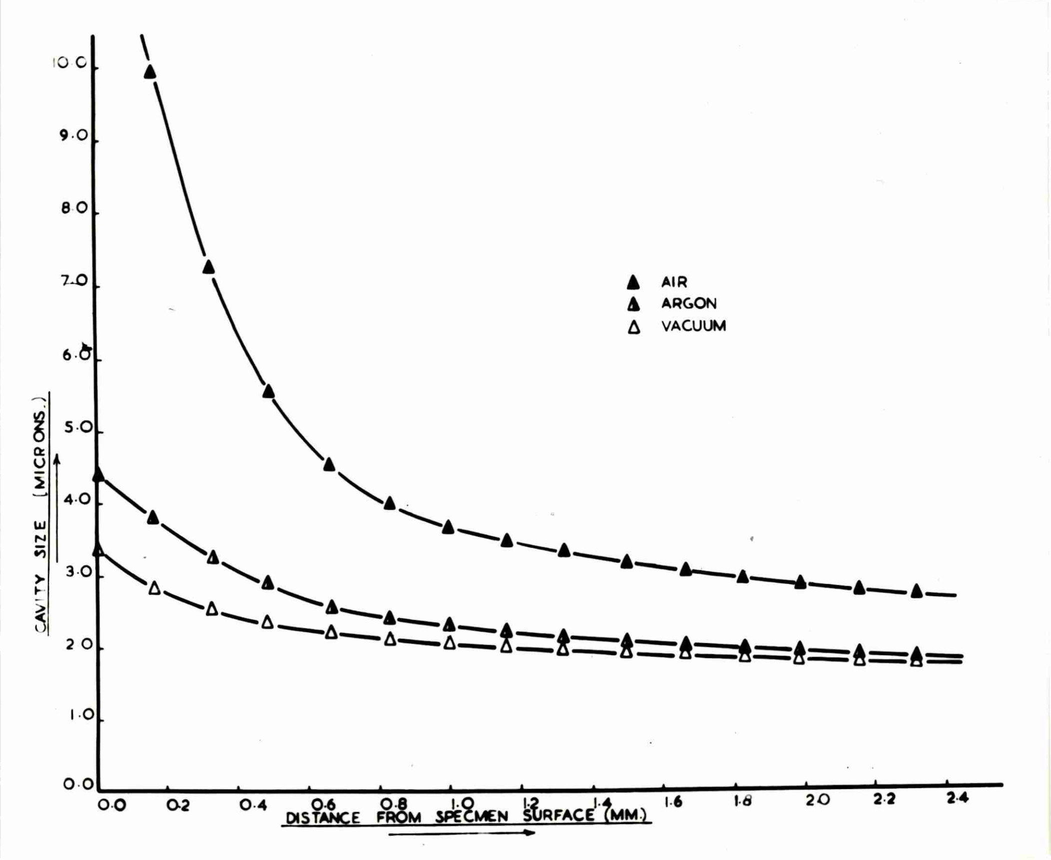
NUMBER OF CAVITIES PER UNIT GRAINBOUNDARY LENGTH
0·0
5·0
10·0
15·0
20·0
25·0
30·0
35·0
40·0
● AIR
◐ ARGON
○ VACUUM
0·0
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
1·8
2·0
2·2
2·4
DISTANCE FROM SPECIMEN SURFACE (MM).



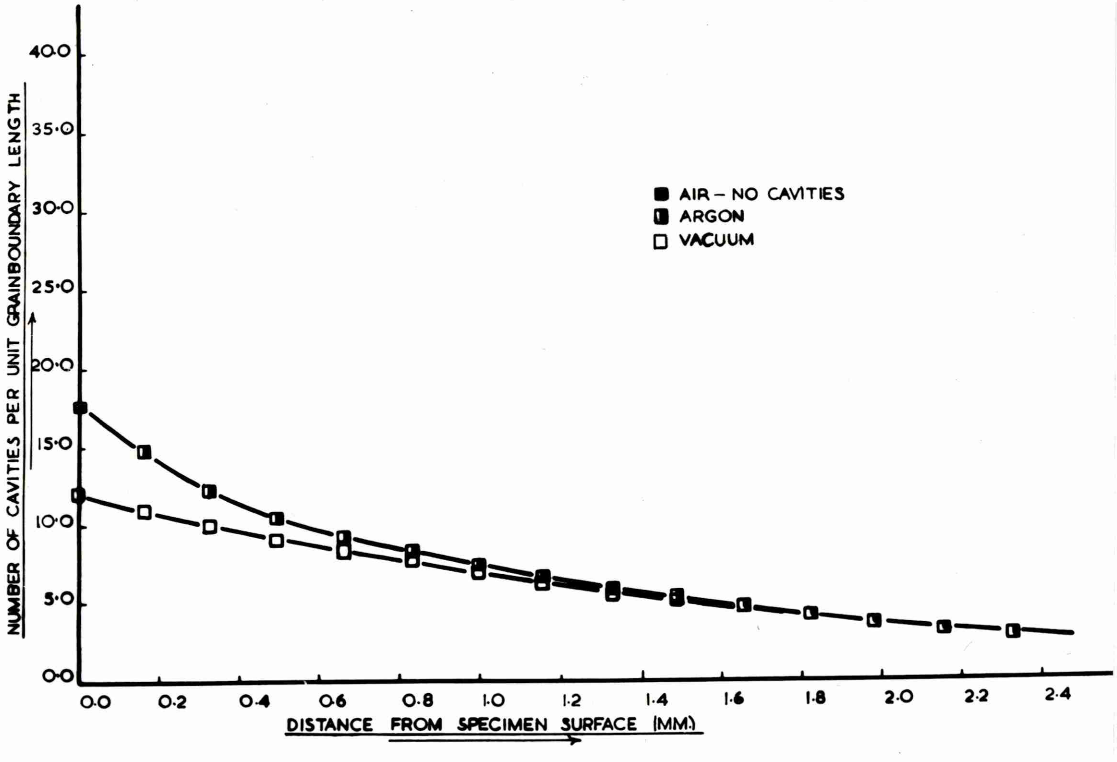
CAVITY SIZE (MICRONS)
0·0
1·0
2·0
3·0
4·0
5·0
6·0
7·0
8·0
9·0
10·0
● AIR
◐ ARGON
○ VACUUM
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
DISTANCE FROM SPECIMEN SURFACE (MM.)

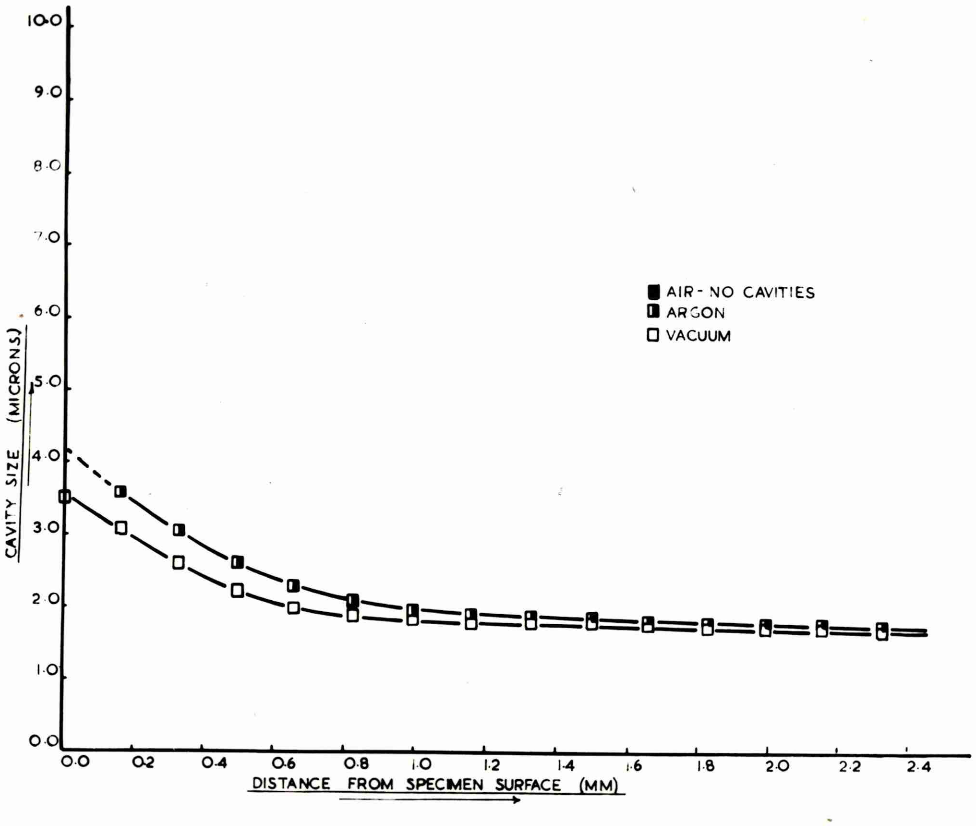


▲ AIR
▲ ARGON
△ VACUUM
NUMBER OF CAVITIES PER UNIT GRAINBOUNDARY LENGTH
40.0
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0.0
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
DISTANCE FROM SPECIMEN SURFACE (MM.)



▲ AIR
▲ ARGON
△ VACUUM
CAVITY SIZE (MICRONS.)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
DISTANCE FROM SPECMEN SURFACE (MM.)


■ AIR – NO CAVITIES
◧ ARGON
□ VACUUM
NUMBER OF CAVITIES PER UNIT GRAINBOUNDARY LENGTH
40·0
35·0
30·0
25·0
20·0
15·0
10·0
5·0
0·0
0·0
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
1·8
2·0
2·2
2·4
DISTANCE FROM SPECIMEN SURFACE (MM)

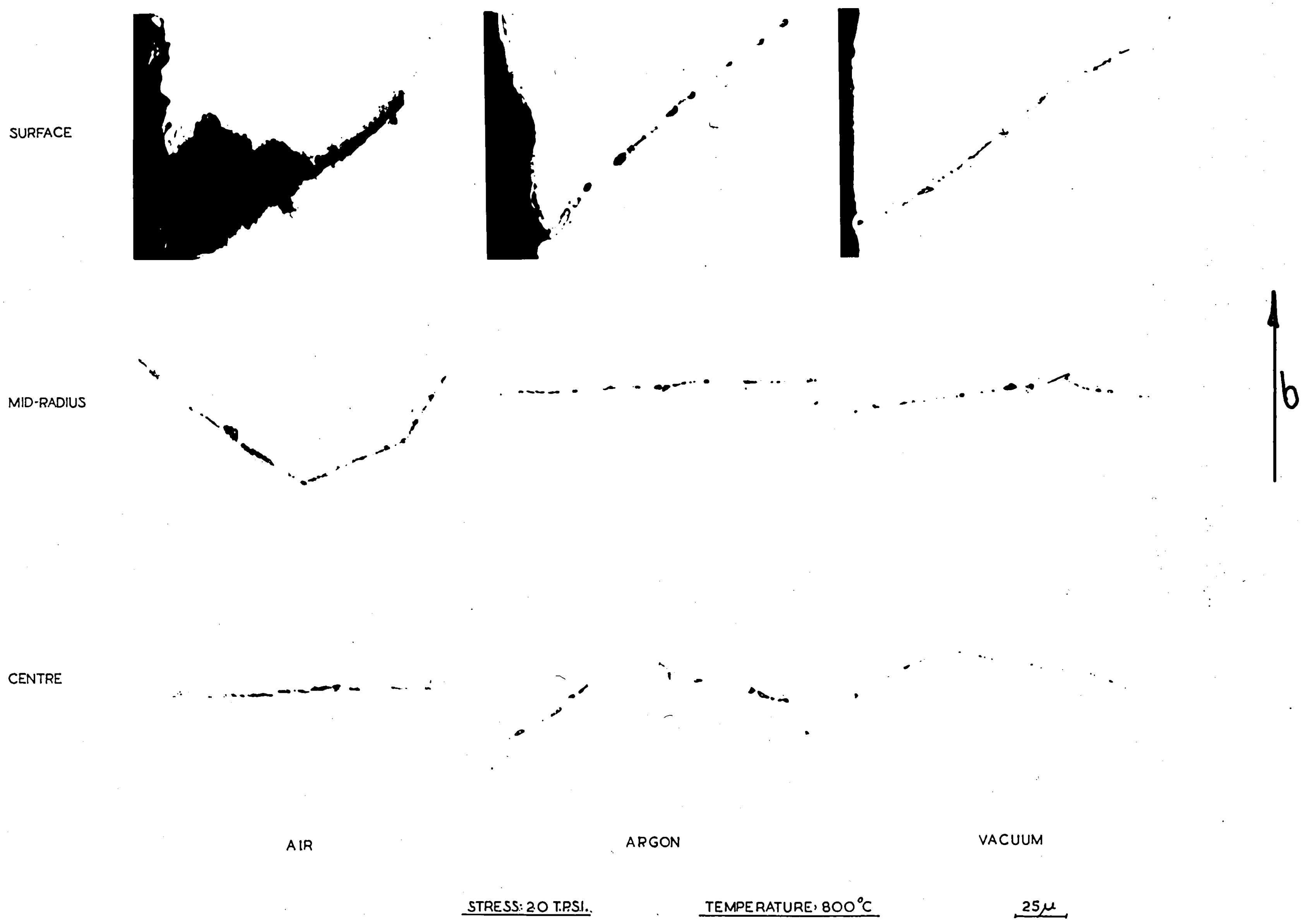

■ AIR – NO CAVITIES
◧ ARGON
□ VACUUM
CAVITY SIZE (MICRONS)
10·0
9·0
8·0
7·0
6·0
5·0
4·0
3·0
2·0
1·0
0·0
0·0
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
1·8
2·0
2·2
2·4
DISTANCE FROM SPECIMEN SURFACE (MM)

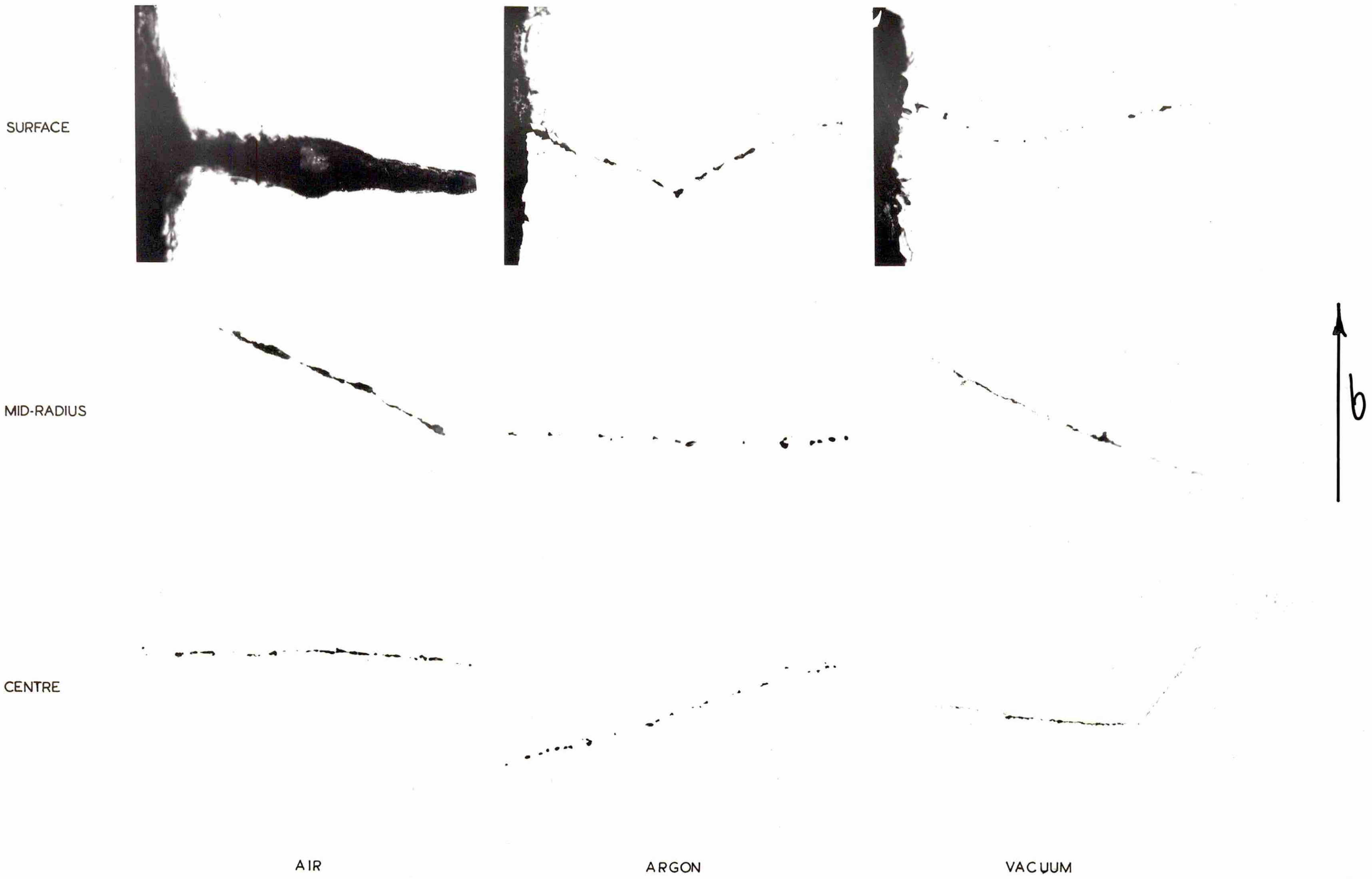
The following three figures are composite photomicrographs showing the degree of cavitation at the surface, mid-radius, and centre position in specimens of 18/8 niobium stabilised stainless steel tested at 800°C.

Figure 66.

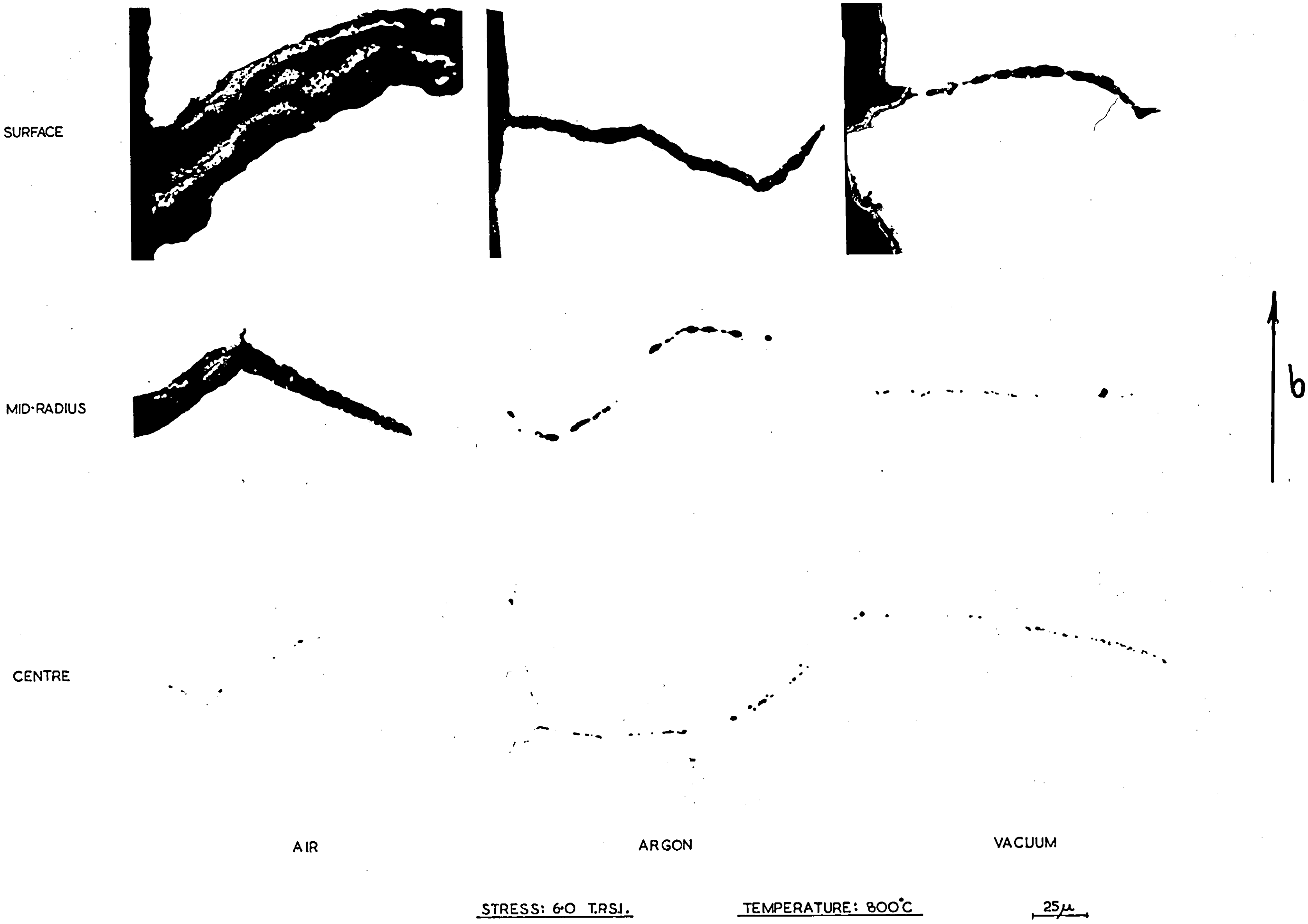
Temperature 800°C.

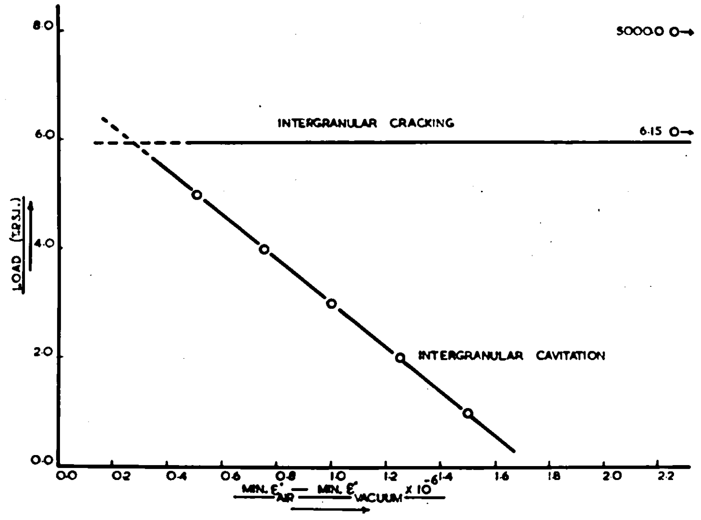
Stress 2.0 t.p.s.i.

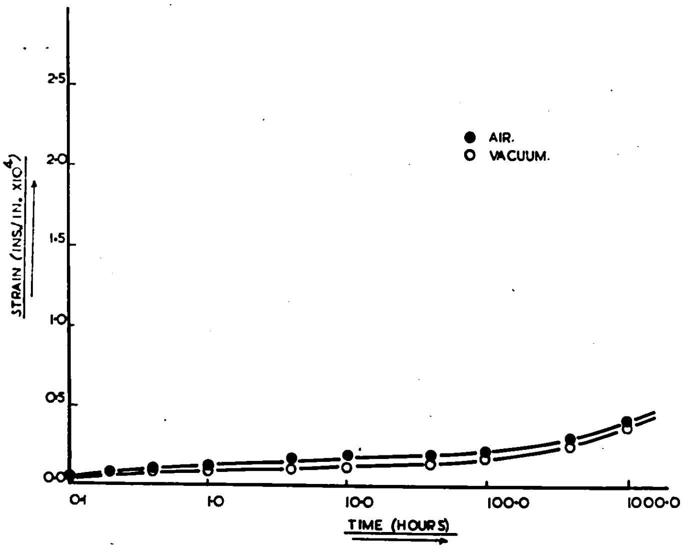

SURFACE
MID-RADIUS
CENTRE
AIR
ARGON
VACUUM
STRESS: 2O T.P.S.I.
TEMPERATURE: 800°C
25μ
b

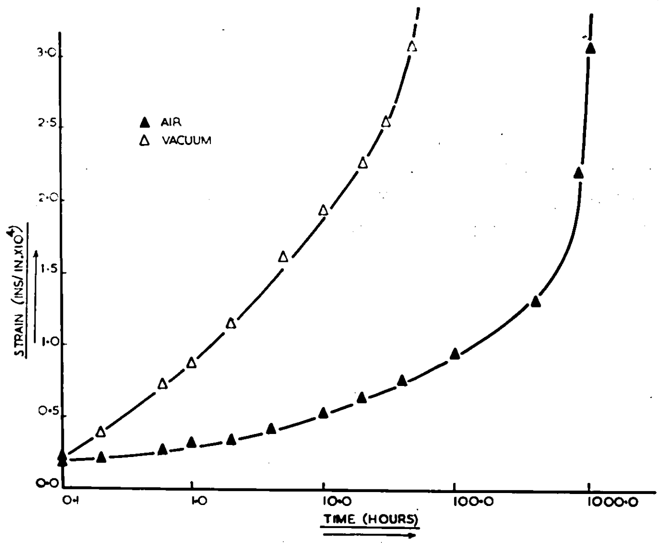


STRESS: 4·0 T.P.S.I. TEMPERATURE: 800°C. 25 μ


SURFACE
MID-RADIUS
CENTRE
AIR
ARGON
VACUUM
b
STRESS: 6·0 T.P.S.I.
TEMPERATURE: 800°C
25μ


8.0
6.0
4.0
2.0
0.0
LOAD (T.P.S.I.)
5000.0 O→
INTERGRANULAR CRACKING
6.15 O→
INTERGRANULAR CAVITATION
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
MIN. ε' AIR — MIN. ε' VACUUM x 10⁻⁶


2.5
2.0
1.5
1.0
0.5
0.0
STRAIN (INS/IN. X10⁴)
● AIR.
O VACUUM.
0.1
1.0
10.0
100.0
1000.0
TIME (HOURS)


3.0
2.5
2.0
1.5
1.0
0.5
0.0
STRAIN (INS/IN.X10⁴)
▲ AIR
△ VACUUM
0.1
1.0
10.0
100.0
1000.0
TIME (HOURS)