

**Microscopy of glazed layers formed during high temperature sliding wear at 750C**

INMAN, I. A., DATTA, S., DU, H. L., BURNELL-GARY, J. S. and LUO, Q  
<<http://orcid.org/0000-0003-4102-2129>>

Available from Sheffield Hallam University Research Archive (SHURA) at:  
<http://shura.shu.ac.uk/2507/>

---

This document is the author deposited version. You are advised to consult the publisher's version if you wish to cite from it.

**Published version**

INMAN, I. A., DATTA, S., DU, H. L., BURNELL-GARY, J. S. and LUO, Q (2003).  
Microscopy of glazed layers formed during high temperature sliding wear at 750C.  
Wear, 254 (5-6), 461-467.

---

**Copyright and re-use policy**

See <http://shura.shu.ac.uk/information.html>

## **Microscopy of glazed layers formed during high temperature sliding wear at 750 °C**

I.A. Inman<sup>a</sup>, S. Datta<sup>a\*</sup>, H.L. Du<sup>a</sup>, J.S. Burnell-Gray<sup>a</sup>, Q. Luo<sup>b</sup>

<sup>a</sup> Advanced Materials Research Institute, University of Northumbria at Newcastle, E001, Ellison Building, Newcastle upon Tyne NE1 8ST, UK

<sup>b</sup> Materials Research Institute, Sheffield Hallam University, Sheffield S1 1WB, UK

**Abstract:** The evolution of microstructures in the glazed layer formed during high temperature sliding wear of Nimonic 80A against Stellite 6 at 750 °C using a speed of 0.314 ms<sup>-1</sup> under a load of 7N has been investigated using scanning electron microscopy (SEM), energy dispersive analysis by X-ray (EDX), X-ray diffraction (XRD) analysis, scanning tunnelling microscopy (STM) and transmission electron microscopy (TEM). The results indicate the formation of a wear resistant nanostructured glazed layer. The mechanisms responsible for the formation of the nanopolycrystalline glazed layer are discussed.

**Keywords:** High temperature wear; Glaze layer; Oxidation; Superalloy; Nanostructure

## 1. Introduction

High temperature wear is a serious problem in many situations-power generation, transport, materials processing and turbine engines [1-4]. The problem of high temperature wear is accentuated due to faster kinetics of surface oxidation, loss of mechanical hardness and strength of the materials constituting the contacting surfaces and change in adhesion between these surfaces caused by the joint action of temperature and tribological parameters. Efforts have been made to prevent wear using oxidation resistant and thermally stable materials and coatings and materials with preoxidised surfaces [1-5]. However, the conditions associated with the presence of high temperature severely restricts the choice of coatings and materials that can be used to prevent or minimize high temperature wear [1,2].

One of the most elegant methods of generating wear resistant surfaces on coated and uncoated materials is to take advantage of the important events, such as oxidation, debris generation and elemental transfer between the contacting surfaces which accompany the process of high temperature wear [1,2,6]. These events under certain conditions of temperature, pressure and speed lead to the formation of surface glazes on the contacting surfaces which can provide enhanced resistance to further wear [1,2,6]. Although the phenomenon of glaze formation and the general issues relating to wear at elevated temperatures have been studied [1,2,6-10], it is still difficult to predict the precise conditions which promote the formation of glazed surfaces. A step forward would be to gain detailed knowledge of the micro-scale and nano-scale structures of these layers, so that the mechanisms of glaze layer formation can be established. This project on high temperature wear was initiated with this objective in mind. This paper particularly relates to the study of wear at 750 °C.

## 2. Experimental

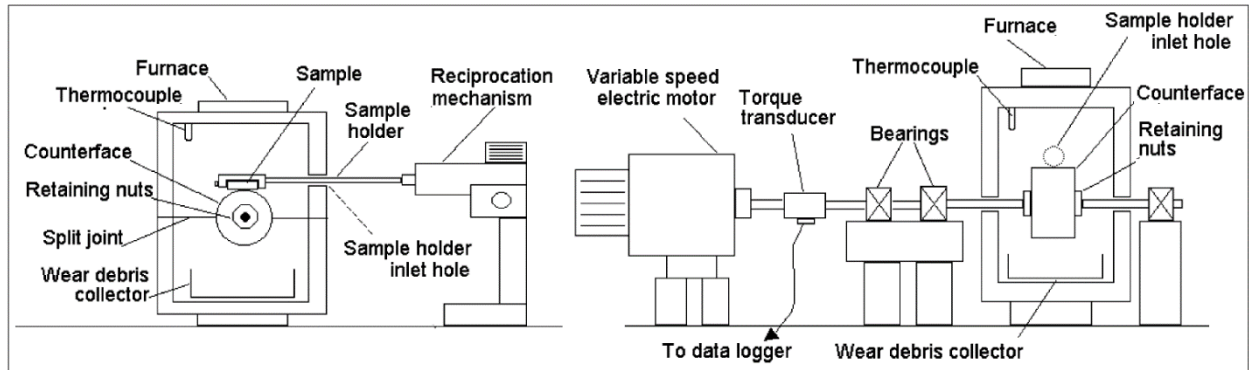
The compositions of materials used for the experimental work are detailed in Table 1.

**Table 1** Nominal compositions of alloys (in wt.%)

	Fe	Ni	Cr	Al	Ti	Mn	W	Co	Si	C
Stellite 6	≤ 2.5	≤ 2.5	27	-	-	1	5	60	1	1
Nimonic 80A	0.7	75.8	19.4	1.4	2.5	-	-	-	0.1	0.08

All high temperature wear tests were carried out on a high temperature reciprocating wear rig in open air, as illustrated in Fig. 1. Details of the high temperature wear machine used have been described previously [1,2]. Basically, the machine was a block-on-cylinder arrangement (the cylinder being the counterface and the block being the sample). A variable speed electric motor rotated the shaft and connected counterface (Stellite 6) of diameter 50 mm and length 50 mm at various speeds. Samples of Nimonic 80A, of dimensions 5mm × 5mm × 45 mm were

held against the counterface using the sample arm in reciprocating motion, with reciprocation at three cycles

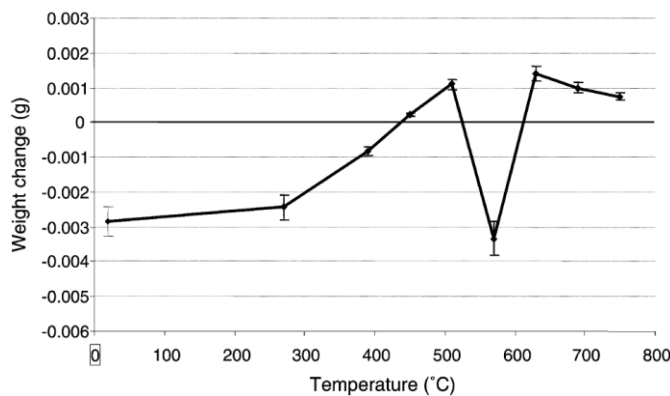


**Fig. 1.** Reciprocating high temperature block-on-cylinder wear rig, as used in the experimental programme.

per minute with a constant stroke of 12 mm. The tests were carried out at a sliding speed of  $0.314\text{ms}^{-1}$  (this being the speed of rotation of the counterface) under a load of 7N at various temperatures. Attention in this paper has been focused on the situation at  $750\text{ }^{\circ}\text{C}$ .

The coefficient of friction data were collected by a Melbourne type TRP-50 torque transducer appropriately connected to the wear rig.

The surface layers produced at  $750\text{ }^{\circ}\text{C}$  were characterized at two levels. The evolution of the microstructures generated was characterised at the micro-scale level using scanning electron microscopy (SEM), energy dispersive analysis by X-ray (EDX) and X-ray diffraction (XRD) analysis. Nano-scale information on the surface layers produced was obtained using mainly transmission electron microscopy(TEM); scanning tunnelling microscope (STM) was used to complement the TEM studies.

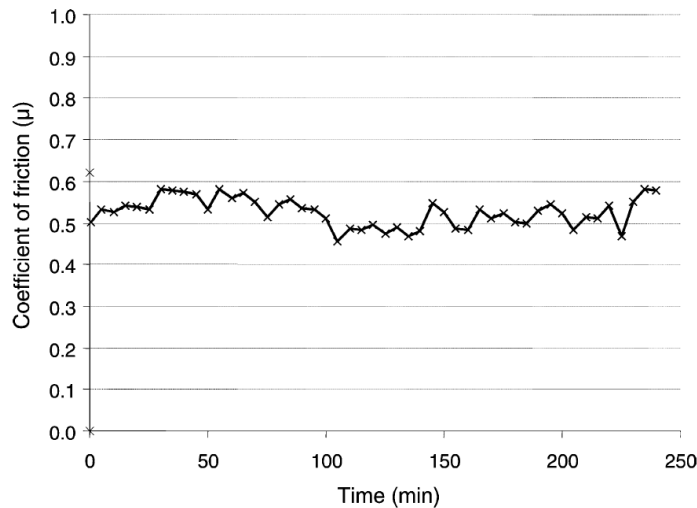


**Fig. 2.** Weight change vs. temperature for Nimonic 80A against Stellite 6 at  $750\text{ }^{\circ}\text{C}$ .

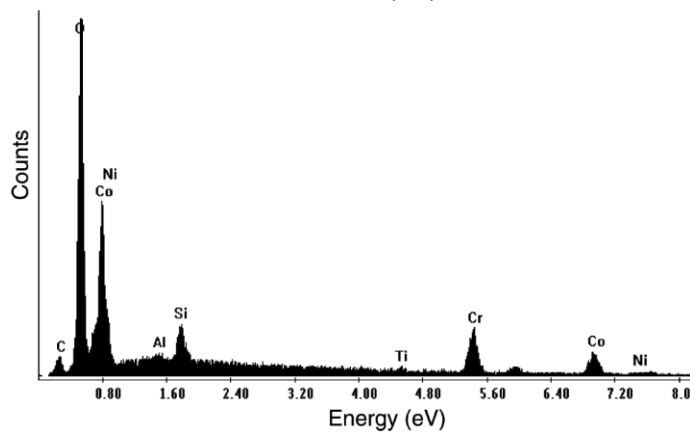
### 3. Results

Fig. 2 displays the wear data on Nimonic 80A / Stellite 6 system as a function of temperature under a load of 7 N at  $0.314\text{ ms}^{-1}$  for total sliding distance of 4522 m. Weight changes were extremely low for all temperatures, with the largest mean change being  $0.002(4)$

g at 270 °C. Slight gains were observed for all test temperatures between 450 and 750 °C, with the maxima in mean values at 510 and 630 °C of 0.001(1) g and 0.001(4) g, respectively. The wear data at a a t



**Fig. 3.** Coefficient of friction vs. time for Nimonic 80A vs. Stellite 6 at 750 °C.



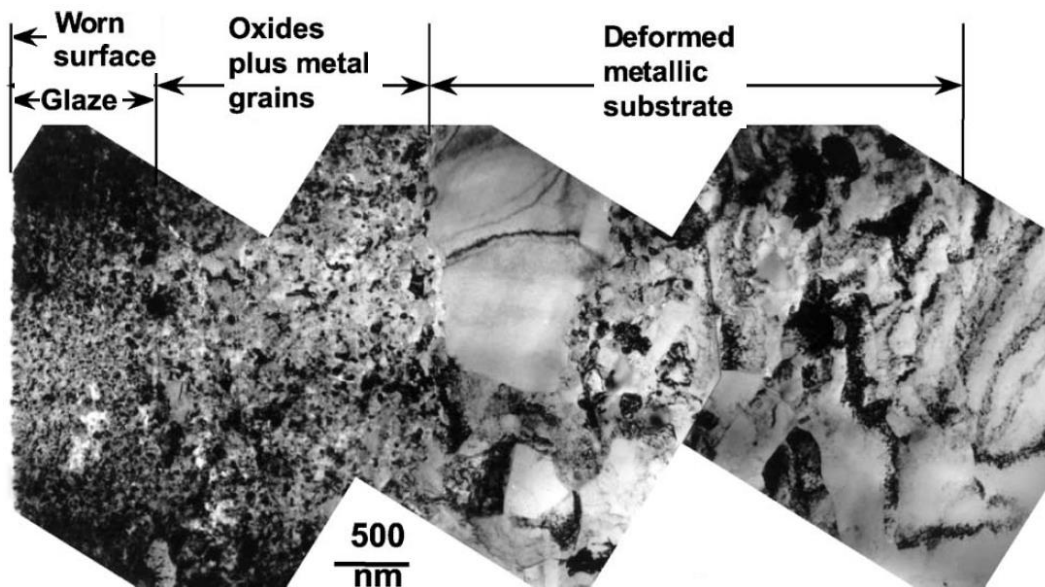
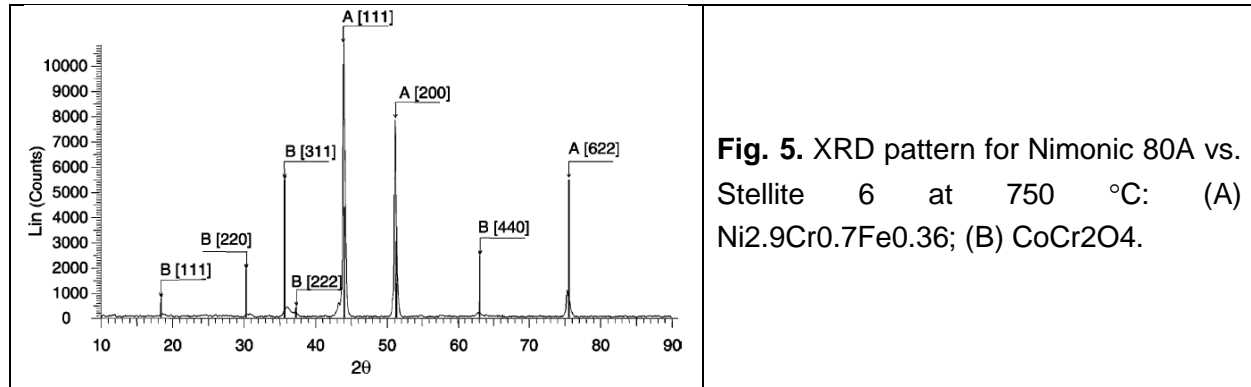
**Fig. 4.** EDX surface spectrum for Nimonic 80A vs. Stellite 6 at 750 °C.

570 °C shows a departure from the general trend. Repeated experiments confirmed the data at 570 °C needing further attention. This paper focuses attention on the situation at 750 °C.

The coefficient of friction values measured during each of the tests showed an initial period of rapid change, before in many cases settling down into a ‘steady state’ situation with reduced variation. The measured friction coefficients in Fig. 3 show no significant changes with time after an initial peak at the very beginning of testing. This indicates that the onset of the formation of a glaze layer was virtually almost immediate giving, the lack of variation indicating a “steady state” in the values of the friction coefficients due to the presence of the glaze on the worn surface.

The spectrum by EDX analysis of the surface generated under sliding wear at 750 °C for 4 h, shown in Fig. 4, reveals the dominant presence of Co, Ni, Cr and O on the glaze surface. Quantification of the results, on average, gives Co = 34.2, Cr = 36.2, Ni = 16.7, Si = 3.8 and Fe = 1.3 (at.%). However, the presence of these elements was also confirmed by TEM EDS which showed some location-to-location variation. The dominant phases identified by XRD included  $\text{CoCr}_2\text{O}_4$  and  $\text{Ni}_{2.9}\text{Cr}_{0.7}\text{Fe}_{0.36}$  (Fig. 5).

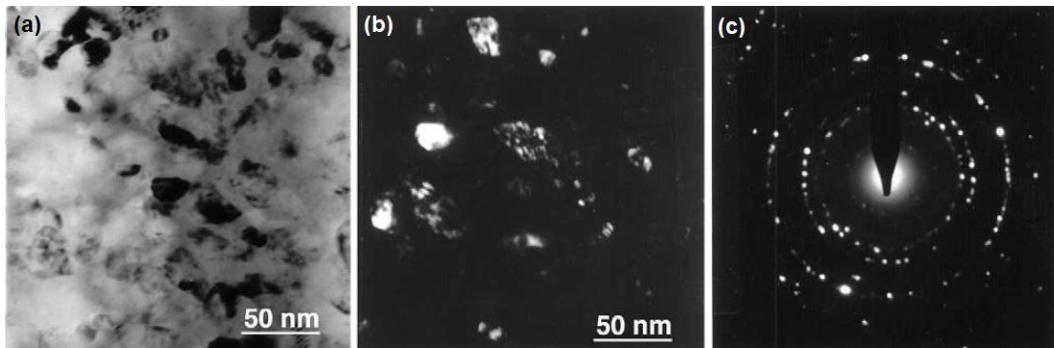
Fig. 6 illustrates a cross-sectional composite transmission electron micrograph of the surface formed during wear test at 750 °C. The micrograph demonstrates the presence of the surface layer (glazed surface), the deformed substrate and the glazed layer/substrate interface. The wear-



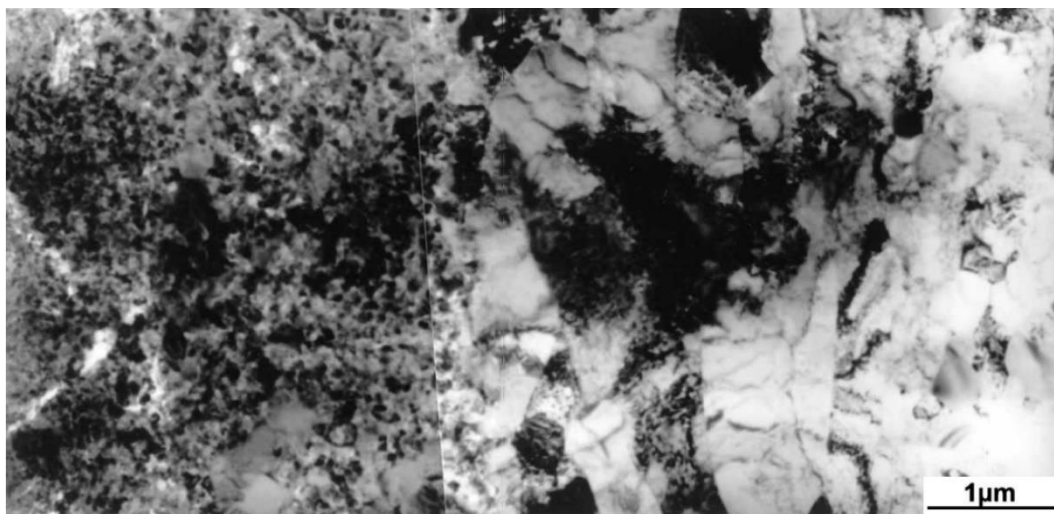
**Fig. 6.** TEM bright field image: wear-induced polycrystalline glaze layer and deformation of substrate.

affected region (total thickness ~3 μm) consisted of three layers—the topmost layer (the glaze layer) showed the presence of uniform grain structure of size 5-15 nm; some of the grains displaying contrast—the dislocation density in this area was low. The interfacial layer consisted of grains of size 10–20 nm and had a higher dislocation density. The layer just beneath the interfacial layer showed sub-surface deformation and the presence of elongated grains. The structure of the glazed layer and the selected area diffraction (SAD) pattern are separately presented in Fig. 7. The SAD pattern consisted of spots arranged in concentric circles indicating the presence of small grains with high angle boundaries, multiple boundaries and large misorientations (formation of misorientated lattice-fragmentation). The poorly defined irregular boundaries indicate non-equilibrium high energy configuration.

The indexed SAD pattern also revealed the presence of oxides of Ni, Cr and Co (indexing not shown here). The dark field images further elaborate on the grain structure of the glazer layer. The occurrence of sub-surface deformation is illustrated in Fig. 8. Dislocations have been observed in the deformed substrate. These dislocations were present as networks inside the



**Fig. 7.** TEM morphological and structural details of glaze layer: (a) bright field image; (b) dark field image; and (c) selected area diffraction.



**Fig. 8.** TEM image showing interface of glaze layer/deformed substrate.

deformed (elongated) grains. It was evidenced that shearing deformation took place in the substrate as a response to the sliding process.

#### 4. Discussion

The present results have clearly indicated the formation of a nano-structured glaze oxide layer during high temperature sliding wear of the system Nimonic 80A/ Stellite 6 at 750 °C using a sliding speed of  $0.314 \text{ ms}^{-1}$  under a load of 7N for a sliding distance of 4522 m. The creation of nano-structures is also confirmed by the STM topography, as shown in Fig. 9. The grain sizes varied from 5 to 10 nm. The thickness of the grains was  $\sim 10 \text{ nm}$ . These results together with the wear data have demonstrated that such a nano-structure surface was extremely effective in

conferring high resistance to wear. The formation of nano-structured surfaces and the effectiveness of such surfaces in conferring improved wear resistance are the two main issues emerging from this work that need consideration and elaboration.

It has been indicated by various authors [10,11] that in many systems surfaces with ultra-fine structure are generated during high temperature sliding wear. Mechanical mixing involving repeated welding, fracturing and re-welding of the debris generated from both contacting surfaces is responsible for the generation of the ultra-fine structured surfaces. However, very few studies have investigated in detail the evolution of microstructures and defect structures generated accompanying the processes of high temperature sliding wear. Detailed TEM studies carried out here allow understanding of the mechanisms of formation of wear resistant nano-structured surfaces.

It is clear from the SEM, XRD and TEM analysis that the initial processes responsible for generating the glazed layer involved: (i) deformation of the surface, (ii) intermixing of the debris generated from the wearing and the counterface surfaces, (iii) oxidation, (iv) further mixing and (v) repeated welding and fracture. These processes were aided by high temperature oxidation and diffusion. The positron annihilation studies confirmed the presence of vacancy cluster consisting of five valences [12].

The next step involves deformation of oxides and generation of dislocations leading to the formation of sub-grains. These sub-grains are then further refined with increasing misorientation giving nano-structured grains with high angle boundaries (a process called “fragmentation”) and non-equilibrium state indicated by poorly defined and irregular grain boundaries. High internal stress is created inside the grains—dislocation density and arrangement depending on the grain size; smaller grains contained fewer dislocations. The process leads to the formation of high energy grain boundaries with a high defect density [13–17].

The superior wear resistance of this nano-structured glaze layer can be ascribed to several factors. The nano-structured glaze layer generated did not suffer Hall-Petch softening, as illustrated in Fig. 10. However, there has also not been a significant degree of work-hardening believed to be associated with the difficulties in generating dislocations in nano-sized grains [18,19]. These two factors together with improved fracture toughness, expected to be conferred by the presence of nano-polycrystalline structure, have made debris generation an inefficient process.

## **5. Summary**

The high temperature sliding wear of Nimonic 80A against Stellite 6 as a counterface alloy allowed the development of a wear resistant nano-structured glaze layer. A process called “fragmentation” involving deformation, generation of dislocations, formation of sub-grains and their increasing refinement causing increasing misorientation, was responsible for the formation of nano-structured grains. The improved wear resistance of such a layer has been attributed to the absence of Hall-Petch softening and the lack of a significant degree of work-hardening and enhanced fracture toughness of the surface.



## **Acknowledgements**

Grateful acknowledgement to the UK Engineering Physics Science Research Council (EPSRC) and British Gas is given for financial support to this project.

## **References**

- [1] P.D. Wood, The effect of the counterface on the wear resistance of certain alloys at room temperature and 750 °C, Ph.D. Thesis, University of Northumbria, UK, 1997.
- [2] S. Rose, Studies of the high temperature tribological behaviour of some superalloys, Ph.D. Thesis, University of Northumbria, UK, 2000.
- [3] F.H. Stott, D.S. Lin, G.C. Wood, The structure and mechanism of formation of the “glaze” oxide layers produced on nickel-based alloys during wear at high temperatures, *Corrosion Sci.* 13 (1973) 449–469.
- [4] M. Johnson, P. Moorhouse, J.R. Nicholls, DTI Industry Valve Project, 1990, pp. 61–68.
- [5] F.H. Stott, J. Glascott, G.C. Wood, Factors affecting the progressive development of wear-protective oxides on iron-base alloys during sliding at elevated temperatures, *Wear* 97 (1984) 93–106.
- [6] M.G. Gee, N.M. Jennett, High resolution characterisation of tribochemical films on alumina, *Wear* 193 (1995) 133–145.
- [7] P.D. Wood, P.K. Datta, J.S. Burnell-Gray, N. Wood, Investigation into the high temperature wear properties of alloys contacting against different counterfaces, *Mater. Sci. Forum* 251–254 (1997) 467–474.
- [8] A. Wisbey, C.M. Ward-Close, Wear resistant surfaces on high temperature titanium alloy and titanium aluminide by diffusion bonding, *Mater. Sci. Technol.* 13 (1997) 349–355.
- [9] J. Jiang, F.H. Stott, M.M. Stack, The effect of partial pressure of oxygen on the tribological behaviour of a nickel-based alloy, N80A, at elevated temperatures, *Wear* 203–204 (1997) 615–625.
- [10] X.Y. Li, K.N. Tandon, Microstructural characterization of mechanically mixed layer and wear debris in sliding wear of an Al alloy and an Al based composite, *Wear* 245 (2000) 148–161.
- [11] S. Datta, I.A. Inman, H.L. Du, Q. Luo, Microscopy of glazed layers formed during high temperature wear, in: *Proceedings of the Invited Talk at the Institute of Materials, Tribology Meeting, London, November 2001.*
- [12] P.K. Datta, H.L. Du, E. Kuzmann, Near surface structural changes of glaze layers formed during high temperature sliding wear, to be published.
- [13] H. Gleiter, Nanocrystalline materials, *Prog. Mater. Sci.* 33 (1989) 223–315.
- [14] R.Z. Valiev, R.K. Islamgaliev, I.V. Alexandrov, Bulk nanostructured materials from severe plastic deformation, *Prog. Mater. Sci.* 45 (2000) 103–189.
- [15] T.C. Lowe, R.Z. Valiev, Producing nanoscale microstructures through severe plastic deformation, *JOM* 52 (2000) 27–28.

[16] A.K. Ghosh, W. Huang, Severe deformation based progress for grain subdivision and resulting microstructures, in: T.C. Lowe, R.Z. Valiev (Eds.), *Investigations and Applications of Severe Plastic Deformation*, Kluwer Academic Publishers, Dordrecht, 2000, pp. 29–36.

[17] R.S. Mishra, S.X. McFadden, A.K. Mukherjee, Analysis of tensile superplasticity in nanomaterials, *Mater. Sci. Forum* 304–306 (1999) 31–38.

[18] R.S. Mishra, A.K. Mukherjee, Superplasticity in nanomaterials, in: A.K. Ghosh, T.R. Bieler (Eds.), *Superplasticity and Superplastic Forming*, TMS, Warrendale, 1998, pp. 109–116.

[19] R.S. Mishra, S.X. McFadden, A.K. Mukherjee, Tensile superplasticity in nanocrystalline materials produced by severe plastic deformation, in: T.C. Lowe, R.Z. Valiev (Eds.), *Investigations and Applications of Severe Plastic Deformation*, Kluwer Academic Publishers, Dordrecht, 1994, pp. 231–240.