

**Compacted Oxide Layer Formation under Conditions of Limited  
Debris Retention at the Wear Interface during High Temperature  
Sliding Wear of Superalloys**

**Ian A. Inman**

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COMPACTED OXIDE LAYER  
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OF LIMITED DEBRIS RETENTION AT  
THE WEAR INTERFACE DURING  
HIGH TEMPERATURE SLIDING  
WEAR OF SUPERALLOYS

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## **DECLARATION**

I hereby declare that:

During the period I have been registered for the degree of Ph.D., for which this thesis is submitted, I have not been a registered candidate for any other award of a university.

Furthermore, I declare that I have attended relevant seminars within the University and presented papers at conferences and relevant meetings on the subject of high temperature wear.

# Compacted Oxide Layer Formation under Conditions of Limited Debris Retention at the Wear Interface during High Temperature Sliding Wear of Superalloys

By Ian A. Inman B.Sc. (Hons.), M.Sc.

## ABSTRACT

For many applications, including power generation, aerospace and the automobile industry, high temperature wear provides serious difficulties where two or more surfaces are able to move relative to one another. It is increasingly the case that with for example, aerospace applications, demands for ever more powerful and efficient engines that thus operate at higher temperatures, conventional lubrication is no longer sufficient to prevent direct contact between metallic surfaces and consequent accelerated wear.

One phenomenon that has been observed to reduce metallic contact and thus high temperature wear and friction is the formation of what are termed 'glazes', essentially layers of compacted oxide wear debris that becomes sintered together to form a low friction wear resistant oxide surface.

This thesis studies the nature of the wear encountered with four different combinations of Superalloys, slid together using a 'block-on-cylinder' configuration developed for accelerated simulation testing of car engine 'valve-on-valve-seat' wear. Predominantly, Nimonic 80A and Incoloy MA956 were used as sample materials and Stellite 6 and Incoloy 800HT were used as counterface materials.

The initial part of this study concentrates on sliding speed – during the current experimental programme, testing was conducted at  $0.314 \text{ m.s}^{-1}$  and  $0.905 \text{ m.s}^{-1}$ , between room temperature and  $750^\circ\text{C}$  – this supplemented previous testing conducted at  $0.654 \text{ m.s}^{-1}$ . When Nimonic 80A was slid against Stellite 6, lowering sliding speed to  $0.314 \text{ m.s}^{-1}$  between  $510^\circ\text{C}$  and  $750^\circ\text{C}$  lead to the formation of wear protective glaze layers consisting of cobalt and chromium oxides from the Stellite 6, whereas at  $0.905 \text{ m.s}^{-1}$  and during previous testing at  $0.654 \text{ m.s}^{-1}$ , only high wear was encountered with debris consisting of nickel and chromium oxides from the Nimonic 80A. When Incoloy MA956 was slid against Stellite 6 at the same sliding speeds and over the same temperature range, a wear protective layer readily formed regardless of sliding speed. However, the sliding speed was observed to affect the relative contributions to the glaze layer from sample and counterface – a shift was observed from largely cobalt and chromium oxides from the Stellite 6 at  $0.314 \text{ m.s}^{-1}$  to largely iron and chromium oxides from the Incoloy MA956 at  $0.905 \text{ m.s}^{-1}$ . Also, the use of a higher sliding speed was noted to promote glaze formation at lower temperature, with glaze appearing at  $450^\circ\text{C}$  for  $0.905 \text{ m.s}^{-1}$ , whereas only severe wear was observed for testing at  $0.654 \text{ m.s}^{-1}$ .

When Incoloy MA956 was worn against Incoloy 800HT, increasing the sliding speed from  $0.314 \text{ m.s}^{-1}$  to  $0.905 \text{ m.s}^{-1}$  had the opposite affect – the beginning of glaze formation was suppressed from  $630^\circ\text{C}$  to  $690^\circ\text{C}$ . Similar results were also observed when Nimonic 80A was slid against Incoloy 800HT, with the beginning of glaze formation suppressed from  $570^\circ\text{C}$  to  $630^\circ\text{C}$ . Thus whether sliding speed promotes or suppresses glaze formation is highly material dependant.

Additionally, both the Incoloy MA956 versus Incoloy 800HT and the Nimonic 80A versus Incoloy 800HT combinations were characterised by high degrees of metallic transfer and especially at room temperature and 270°C, adhesive wear – with Nimonic 80A versus Incoloy 800HT, the level of transfer, mostly from Incoloy 800HT to Nimonic 80A, was observed to increase with increasing sliding speed.

Further experimental studies concentrating on the sliding of Nimonic 80A versus Stellite 6 at 0.314 m.s<sup>-1</sup> and 750°C, indicated extremely rapid formation of glaze from Stellite 6-sourced debris – this consisted of an initial transfer of material from the harder Stellite 6 to the softer Nimonic 80A, followed by the steady development of a wear resistant glaze layer. The reversal of sample and counterface whilst varying sliding speed demonstrated that direction of transfer was more strongly influenced by material than configuration (i.e. which material was sample and which material was counterface). Finally, the substitution of Nimonic 80A with high purity nickel promoted the formation of glaze at not just 0.314 m.s<sup>-1</sup>, but also at 0.905 m.s<sup>-1</sup> – this was due to the elimination of chromium oxide (in the form of Cr<sub>2</sub>O<sub>3</sub>) from the predominantly nickel oxide (NiO) debris. This result, however, raises a number of queries yet to be answered. Firstly, why were nickel and chromium together readily able to form an oxide glaze with Nimonic 80A worn against Incoloy 800HT, but not so readily with Nimonic 80A worn against Stellite 6? Secondly, why did chromium readily form an oxide glaze with cobalt at 0.314 m.s<sup>-1</sup> with the Nimonic 80A versus Stellite 6 combination, but not so readily with nickel at higher sliding speed?

Finally, nano-characterisation studies were carried out on the glaze layers formed on Nimonic 80A samples slid against Stellite 6 at 0.314 m.s<sup>-1</sup> and 750°C. These glaze layers were shown to have a nano-scale grain structure, with a grain size of as little as 5 to 15 nm at the very surface of the glaze. A likely route of formation was established, starting with deformation of the surface, intermixing of debris from sample and counterface, oxidation of debris, further mixing and repeated welding and fracture – these processes are aided by high temperature oxidation and diffusion. The grain size is then refined by the formation of sub-grains, accompanied by increasing mis-orientation to give nano-structured grains - a non-equilibrium state results, with poorly defined and irregular grain boundaries. The presence of a nanopolycrystalline structure implies improved fracture toughness. However, the disorganised nature of the glaze layer suggests the production of a glaze is, overall, an inefficient process.

Analysis was performed using optical microscopy, SEM, EDX, EDX mapping and Autopoint, XRD, Glancing Angle XRD and extensive micro-hardness testing. Some preliminary nano-hardness testing was also carried out, that suggested glaze hardness levels not too far removed from bulk theoretical hardness values for chromium oxide and indicating low porosity and high levels of sintering within the glaze layers. Nano-characterisation studies were carried out using TEM and STM.

## 1. INTRODUCTION

Wear is an unavoidable and a potentially serious problem in all areas of engineering. Under normal conditions, good design practice along with appropriate materials selection and the use of an appropriate coating or lubricant system, may be sufficient to minimise wear of interacting surfaces or components to an acceptable level.

However, high temperature wear, particularly above 400°C, poses a problem in that protection by the use of lubricants is not available – the temperature capabilities of most hydrocarbon- or silicone-based lubricants are limited to 200°C and even solid lubricants such as molybdenum disulphide can only survive to at most 400°C. Thus for applications ranging from valve-on-valve seat wear in an internal combustion engine to turbines in aerospace and power generation, alternative approaches are required. Suitable materials are selected on the basis of their high temperature environmental resistance, and physical and mechanical properties – excellent chemical and oxidational resistance, high temperature strength and creep resistance are thus paramount. For these reasons, superalloy materials such as Nimonic 80A are popular for such applications. However, such properties do not always guarantee immunity against high temperature wear.

Coatings, pre-oxidation and surface modification of alloys can also give a greater degree of protection, especially during the extremely damaging ‘run-in’ period. However, the lifetime of the modified surfaces can be limited and once the underlying, unmodified material is exposed, wear rates are often very similar to the unprotected material from this point on. In addition to this, there is with time an increasing demand for greater operational efficiency and thus higher operational temperatures in aerospace applications and power generation. In such cases, traditional methods of surface protection are becoming less effective. An alternative approach would be to produce an in-situ surface layer, assisted by the events occurring during the wear process.

High temperature wear arises from and involves the simultaneous occurrence of two degradation processes – i) environmental interaction with faster kinetics and ii) damage due to wear – both processes taking place at the contacting surfaces under load. However, these two degradation processes can be used with benefits to generate a