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

Ian A. Inman

DISSERTATION.COM

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

Copyright © 2003 Ian A. Inman
All rights reserved.

Dissertation.com
Boca Raton, Florida
USA • 2006
Revised November 2008

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

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

A thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy

funded by the EPSRC

School of Engineering and Technology
Northumbria University

November 2003
## Contents

1. **INTRODUCTION**  

2. **LITERATURE REVIEW**  
   2.1 Introduction  
   2.2 Friction  
      2.2.1 Definition of Friction  
      2.2.2 Observed Friction in Real Systems  
      2.2.3 Adhesion  
      2.2.4 Ploughing  
      2.2.5 Combination of Models  
      2.2.6 Complications with the Bowden and Tabor Model  
   2.3 Wear Theory  
      2.3.1 Archard and Hirst – Distinction between Mild and Severe Wear  
      2.3.2 Classification by Mechanism  
   2.4 ‘Two and Three Body’ Wear  
      2.4.1 Overview  
      2.4.2 Surface Films and Preoxidation – Third Body or Not?  
      2.4.3 Behaviour of Particles at the Interface  
      2.4.4 The Effect of Forces of Attraction between Third Bodies  
   2.5 Mild Wear and Mechanisms of Compact Oxide Formation  
      2.5.1 Introduction to Compact Oxides or ‘Glazes’  
      2.5.2 Mechanisms for Generation of Oxide Debris and Compacted Oxide Layer Formation  
      2.5.3 Effects of Environmental Variables  
      2.5.4 Pre treatment of Sliding Surfaces  
      2.5.5 Third Body Interaction in Relation to Compact Oxide Formation  
      2.5.6 Quinn’s Oxidational Wear Model  
   2.6 The Effects of Load and Sliding Speed  
      2.6.1 Early Work  
      2.6.2 Wear of Cobalt Based Alloys  
   2.7 Effect of a Second Phase on Wear  
   2.8 Material Transfer and Mechanical Alloying  
   2.9 Nano-scale Characterisation of Sliding Surfaces  
   2.10 Previous Work within the University of Northumbria  

- i -
### 3. INTRODUCTION TO THE CURRENT INVESTIGATION

### 4. EXPERIMENTAL

#### 4.1 Apparatus and Materials

<table>
<thead>
<tr>
<th>Subsection</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1.1 Apparatus</td>
<td>92</td>
</tr>
<tr>
<td>4.1.2 Materials Used</td>
<td>96</td>
</tr>
</tbody>
</table>

#### 4.2 Wear Testing

<table>
<thead>
<tr>
<th>Subsection</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2.1 Room Temperature to 750°C, at 0.314 m.s$^{-1}$ and 0.905 m.s$^{-1}$</td>
<td>97</td>
</tr>
<tr>
<td>4.2.2 Nimonic 80A versus Stellite 6 – In-depth Studies</td>
<td>99</td>
</tr>
<tr>
<td>4.2.3 Switching off reciprocation – Nimonic 80A versus Incoloy 800HT and Incoloy MA956 versus Incoloy 800HT at 510°C and 0.314 m.s$^{-1}$</td>
<td>100</td>
</tr>
</tbody>
</table>

#### 4.3 Structural Analysis

<table>
<thead>
<tr>
<th>Subsection</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.3.1 Scanning Electron Microscopy with Energy Dispersive Spectroscopy</td>
<td>101</td>
</tr>
<tr>
<td>4.3.2 X-ray Diffraction</td>
<td>101</td>
</tr>
<tr>
<td>4.3.3 Micro-hardness Tests</td>
<td>102</td>
</tr>
<tr>
<td>4.3.4 Nano-hardness Tests</td>
<td>102</td>
</tr>
<tr>
<td>4.3.5 Transmission Electron Microscopy (TEM)</td>
<td>103</td>
</tr>
<tr>
<td>4.3.6 Scanning Tunnelling Microscopy (STM)</td>
<td>103</td>
</tr>
</tbody>
</table>

### 5. RESULTS

#### 5.1 Testing of Nimonic 80A versus Stellite 6 between Room Temperature and 750°C, at 0.314 and 0.905 m.s$^{-1}$

<table>
<thead>
<tr>
<th>Subsection</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1.1 Experimental Observations – Nimonic 80A versus Stellite 6</td>
<td>106</td>
</tr>
<tr>
<td>5.1.2 Optical and SEM Microscopy – Nimonic 80A versus Stellite 6</td>
<td>111</td>
</tr>
<tr>
<td>5.1.3 EDX Analysis – Nimonic 80A versus Stellite 6</td>
<td>120</td>
</tr>
<tr>
<td>5.1.4 Mapping using EDX – Nimonic 80A versus Stellite 6</td>
<td>123</td>
</tr>
<tr>
<td>5.1.5 Autopoint EDX Analysis – Nimonic 80A versus Stellite 6</td>
<td>126</td>
</tr>
<tr>
<td>5.1.6 XRD Analysis – Nimonic 80A versus Stellite 6</td>
<td>126</td>
</tr>
<tr>
<td>5.1.7 Micro-hardness Testing – Nimonic 80A versus Stellite 6</td>
<td>131</td>
</tr>
</tbody>
</table>

#### 5.2 In-depth Studies of the Nimonic 80A versus Stellite 6 Wear Pair

<table>
<thead>
<tr>
<th>Subsection</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.2.1 Build up of Glaze with Time – Nimonic 80A versus Stellite 6 at 510°C and 750°C, Sliding Speed 0.314 m.s$^{-1}$</td>
<td>134</td>
</tr>
<tr>
<td>5.2.2 Reversal of Sample and Counterface – Stellite 6 versus Nimonic 80A at 750°C</td>
<td>144</td>
</tr>
<tr>
<td>5.2.3 Substitution of Nimonic 80A with High Purity Nickel Nickel 200™ versus Stellite 6 at 750°C</td>
<td>153</td>
</tr>
</tbody>
</table>
5.3 Testing of Incoloy MA956 versus Stellite 6 between Room Temperature and 750°C, at 0.314 and 0.905 m.s\(^{-1}\)

5.3.1 Experimental Observations – Incoloy MA956 versus Stellite 6 161

5.3.2 Optical and SEM Studies – Incoloy MA956 versus Stellite 6 166

5.3.3 EDX Analysis – Incoloy MA956 versus Stellite 6 174

5.3.4 EDX Mapping – Incoloy MA956 versus Stellite 6 178

5.3.5 Autopoint EDX Analysis – Incoloy MA956 versus Stellite 6 182

5.3.6 XRD Analysis – Incoloy MA956 versus Stellite 6 183

5.3.7 Micro-hardness Testing – Incoloy MA956 versus Stellite 6 187

5.4 Testing of Nimonic 80A versus Incoloy 800HT between Room Temperature and 750°C, at 0.314 and 0.905 m.s\(^{-1}\)

5.4.1 Experimental Observations – Nimonic 80A versus Incoloy 800HT 190

5.4.2 Optical and SEM Morphology – Nimonic 80A versus Incoloy 800HT 196

5.4.3 EDX Analysis – Nimonic 80A versus Incoloy 800HT 204

5.4.4 EDX Mapping – Nimonic 80A versus Incoloy 800HT 206

5.4.5 Autopoint EDX Analysis – Nimonic 80A versus Incoloy 800HT 209

5.4.6 XRD Analysis – Nimonic 80A versus Incoloy 800HT 211

5.4.7 Micro-hardness Testing – Nimonic 80A versus Incoloy 800HT 214

5.4.8 Sliding Without Reciprocation – Nimonic 80A versus Incoloy 800HT, 510°C and 0.314 m.s\(^{-1}\) 219

5.5 Testing of Incoloy MA956 versus Incoloy 800HT between Room Temperature and 750°C, at 0.314 and 0.905 m.s\(^{-1}\)

5.5.1 Experimental Observations – Incoloy MA956 versus Incoloy 800HT 221

5.5.2 Optical and SEM Morphology – Incoloy MA956 versus Incoloy 800HT 229

5.5.3 EDX Analysis – Incoloy MA956 versus Incoloy 800HT 236

5.5.4 EDX Mapping – Incoloy MA956 versus Incoloy 800HT 238

5.5.5 Autopoint EDX Analysis – Incoloy MA956 versus Incoloy 800HT 241

5.5.6 XRD Analysis – Incoloy MA956 versus Incoloy 800HT 245

5.5.7 Micro-hardness Testing – Incoloy MA956 versus Incoloy 800HT 250

5.5.8 Sliding Without Reciprocation – Incoloy MA956 versus Incoloy 800HT, 510°C and 0.314 m.s\(^{-1}\) 254
5.6 In-depth Nano-characterisation – Nimonic 80A versus Stellite 6

5.6.1 Nano-indentation Testing – Nimonic 80A and Incoloy MA956 versus Stellite 6

5.6.2 Nano-scale studies of glaze layers formed on Nimonic 80A samples (slid against a Stellite 6 counterface) at 750°C and 0.314 m.s⁻¹ using TEM and STM

6. DISCUSSION

6.1 Nimonic 80A versus Stellite 6

6.1.1 Nimonic 80A versus Stellite 6 between Room Temperature and 750°C, at 0.314 m.s⁻¹

6.1.2 Nimonic 80A versus Stellite 6 between Room Temperature and 750°C, at 0.905 m.s⁻¹

6.1.3 Wear Map for Nimonic 80A versus Stellite 6

6.1.4 Elimination of Alloying Elements – Nickel 200™ versus Stellite 6 at 750°C

6.2 Incoloy MA956 versus Stellite 6

6.2.1 Incoloy MA956 versus Stellite 6 between Room Temperature and 750°C, at 0.314 m.s⁻¹

6.2.2 Incoloy MA956 versus Stellite 6 between Room Temperature and 750°C, at 0.905 m.s⁻¹

6.2.3 Wear Map for Incoloy MA956 versus Stellite 6

6.3 Nimonic 80A versus Incoloy 800HT

6.3.1 Nimonic 80A versus Incoloy 800HT between Room Temperature and 750°C, at 0.314 m.s⁻¹

6.3.2 Nimonic 80A versus Incoloy 800HT between Room Temperature and 750°C, at 0.905 m.s⁻¹

6.3.3 Wear Map for Nimonic 80A versus Incoloy 800HT

6.4 Incoloy MA956 versus Incoloy 800HT

6.4.1 Incoloy MA956 versus Incoloy 800HT between Room Temperature and 750°C, at 0.314 m.s⁻¹

6.4.2 Incoloy MA956 versus Incoloy 800HT between Room Temperature and 750°C, at 0.905 m.s⁻¹

6.4.3 Wear Map for Incoloy MA956 versus Incoloy 800HT

6.5 Nano-scale Studies of High Temperature Wear – Nimonic 80A / Stellite 6 at 750°C and 0.314 m.s⁻¹

6.5.1 Nano-hardness of Glaze Layers – Nimonic 80A versus Stellite 6 and Incoloy MA956 versus Stellite 6

6.5.2 Nano-scale Characterisation of Glaze Layers – Nimonic 80A / Stellite 6 at 0.314 m.s⁻¹ and 750°C
7. SUMMARY

7.1 Effect of Sliding Speed between Room Temperature and 750°C

7.1.1 Nimonic 80A versus Stellite 6
7.1.2 Incoloy MA956 versus Stellite 6
7.1.3 Nimonic 80A versus Incoloy 800HT
7.1.4 Incoloy MA956 versus Incoloy 800HT

7.2 In-depth and Nano-scale Studies of Nimonic 80A Samples worn against Stellite 6 at 750°C and 0.314 m.s⁻¹

7.2.1 Nano-hardness of Glaze Layers – Nimonic 80A versus Stellite 6 and Incoloy MA956 versus Stellite 6
7.2.2 Nano-scale Characterisation of Glaze Layers – Nimonic 80A / Stellite 6 at 0.314 m.s⁻¹ and 750°C

8. RECOMMENDATIONS FOR FURTHER WORK

REFERENCES

APPENDIX 1: Related Articles and Contacting the Author

(not an official part of the thesis)

A1.1 Contacting the Author
A1.2 Articles Directly Related to the Current Study
A1.3 Other Related Work
### List of Tables

| Table 2.1: | Quinn’s comparison of the various classifications of wear | 19 |
| Table 2.2: | Wear data for standard and alternatively processed superalloys | 21 |
| Table 2.3: | Wear rates of case hardened steels before and after implantation of oxygen ions, 400 m sliding distance | 52 |
| Table 2.4: | Wear rates of case hardened steels before and after implantation of oxygen ions, 100 m sliding distance | 52 |
| Table 4.1: | Standard conditions used in wear rig operation, unless stated elsewhere | 95 |
| Table 4.2: | Main wear pairs used during testing | 96 |
| Table 4.3: | Nominal compositions of alloys in wt% | 96 |
| Table 4.5: | Sliding times and equivalent distances for timed tests of Nimonic 80A versus Stellite 6 | 100 |
| Table 4.6: | Key specifications for Hysitron Triboindenter used for nano-indentation tests | 104 |
| Table 4.7: | Nominal load parameters used for nano-indentation tests on Nimonic 80A samples slid against Stellite 6 at 510°C and 750°C, also Incoloy MA956 samples slid against Stellite 6 at 750°C | 104 |
| Table 5.1: | Hardness data for glaze and undeformed substrate, Nimonic 80A versus Stellite 6 slid at 750°C | 134 |
| Table 5.2: | Hardness data for glaze, for a Stellite 6 sample slid against a Nimonic 80A counterface at 0.314 m.s⁻¹ and 750°C | 151 |
| Table 5.3: | Hardness data for glaze and undeformed substrate – Nickel 200TM versus Stellite 6 slid at 750°C | 160 |
| Table 5.4: | Hardness data for glaze and undeformed substrate, Incoloy MA956 versus Stellite 6 slid at 750°C | 188 |
| Table 5.5: | Hardness data for transfer layers between room temperature and 570°C, Nimonic 80A versus Incoloy 800HT | 217 |
| Table 5.6: | Hardness data for glaze and undeformed substrate, Nimonic 80A versus Incoloy 800HT slid at 750°C | 218 |
| Table 5.7: | Hardness data for transfer layers at room temperature and 270°C, Incoloy MA956 versus Incoloy 800HT | 252 |
| Table 5.8: | Hardness data for glaze and undeformed substrate, Incoloy MA956 versus Incoloy 800HT slid at 750°C | 252 |
| Table 5.9: | Nano-indentation data for glaze layers formed on Incoloy MA956 at 750°C, also Nimonic 80A at 510°C and 750°C when slid against Stellite 6 | 259 |
| Table 5.10: | Selected Area Diffraction (SAD) indexing data for glaze layer, produced by wear of Nimonic 80A versus Stellite 6 | 262 |
**Table 6.1:** Free energies of formation for key oxides at 727°C formed under conditions of static oxidation

**Table 6.2:** Summary of mean micro-hardness values for glaze and deformed substrate for Nimonic 80A and Incoloy MA956 versus Stellite 6 at 750°C

**Table 6.3:** Mean hardness values for glaze and deformed substrate for Nimonic 80A versus Incoloy 800HT at 750°C

**Table 6.4:** Mean hardness values for glaze and deformed substrate for Incoloy MA956 versus Incoloy 800HT

**Table 6.5:** Mean nano-hardness and modulus values for glaze – Nimonic 80A / Stellite 6 (510°C and 750°C) and Incoloy MA956 / Stellite 6 (750°C)
List of Figures

Figure 2.1: Modes of relative motion – sliding and rolling 5
Figure 2.2: Coulomb’s model for sliding friction 7
Figure 2.3: Deformation during sliding, represented by the ploughing of the flat surface of a softer material by a rigid cone of harder material 12
Figure 2.4: Wear surfaces produced during the sliding of Incoloy MA956 against Incoloy 800HT at 270°C and 750°C 15
Figure 2.5: Variation in wear rate with sliding speed at 20, 300 and 400°C in air and also 300°C in pure oxygen for α/β brass sliding against steel 15
Figure 2.6: Experimental Data from Archard and Hirst’s Work on Like-on-Like Sliding at 1.8 m.s⁻¹ 17
Figure 2.7: Archard and Hirst’s Experimental Data 18
Figure 2.8: Variation of ‘normalised’ wear rates of Al 12.3 wt. % Si alloy slid against Cu, Cu 4.6% Al and Cu 7.5% Al 22
Figure 2.9: The three models of abrasive wear 23
Figure 2.10: Abrasive wear as a result of an idealised cone sliding across a flat surface 28
Figure 2.11: Wear particle formation by shear deformation of voids 28
Figure 2.12: Idealised cell showing relative dimensions, from plan, side and end structures of cells in the wear surface 29
Figure 2.13: Effectiveness of wear reduction on S45C plain carbon steel due to the introduction of Fe₂O₃ particles 32
Figure 2.14: Mechanisms of possible movement of particles during sliding of particulate materials 37
Figure 2.15: Variation of coefficient of friction and wear rate of Fe 4.9%Cr with oxygen partial pressure during like on like sliding at 20°C 45
Figure 2.16: Variation of wear and coefficient of friction as a function of relative humidity 48
Figure 2.17: Effects of pre oxidation and pre sliding on wear of S45C at 20°C 49
Figure 2.18: ‘Modified’ version of Jiang’s diagrammatic representation of sliding wear processes at various temperatures 56
Figure 2.19: Oxygen transport between oxide plateaux and cracks in the oxides 62
Figure 2.20: Variation in wear rate with sliding speed at 20, 300 and 400°C in air and also 300°C in pure oxygen for α/β brass sliding against steel 66
Figure 2.21: Effect of sliding speed on wear rate / load – 0.52% carbon steel

Figure 2.22: Effect of sliding speed on wear rate of Al 12.3 wt. % Si versus various counterface materials

Figure 2.23: Wear transition map for steels showing regions of mild and severe wear – sliding conditions corresponding to different types of wear transitions observed are also indicated

Figure 2.24: Variation in wear rate with sliding speed and load for the rubbing of laser clad Stellite 6 pins with AISI 4340 steel disks

Figure 2.25: Binary phase diagram for cobalt and chromium, showing the transition temperature for 27% chromium

Figure 2.26: Identification of grain boundary carbides by changes in distribution of cobalt and chromium in the Stellite 6 substrate

Figure 4.1: Reciprocating high temperature block on cylinder wear rig, as used in the experimental programme

Figure 4.2: Wear rig furnace, showing sample arm (with sample), shaft and counterface in position for testing

Figure 4.3: Typical samples used for wear tests

Figure 4.4: Loading profile for nano-indentation tests conducted on glaze layers

Figure 5.1: Effect of temperature on weight change and wear rate – Nimonic 80A versus Stellite 6

Figure 5.2: Temperature versus coefficient of friction – Nimonic 80A versus Stellite 6

Figure 5.3: Sample wear scar optical images – Nimonic 80A / Stellite 6, 0.314 m.s⁻¹

Figure 5.4: Sample wear scar optical images – Nimonic 80A / Stellite 6, 0.905 m.s⁻¹

Figure 5.5: SEM micrographs for Nimonic 80A versus Stellite 6 – wear surface

Figure 5.6: SEM micrographs for Nimonic 80A versus Stellite 6 showing change in wear scar morphology between 510°C and 690°C at 0.905 m.s⁻¹ / 4,522 m

Figure 5.7: SEM micrographs for Nimonic 80A versus Stellite 6 – debris

Figure 5.8: Counterface wear scar optical images – Nimonic 80A / Stellite 6, 0.314 m.s⁻¹

Figure 5.9: Counterface wear scar optical images – Nimonic 80A / Stellite 6, 0.905 m.s⁻¹

Figure 5.10: EDX data – variation of composition of loose debris and glaze layers (Nimonic 80A vs. Stellite 6), room temperature to 750°C, 0.314 m.s⁻¹

Figure 5.11: EDX data – variation of composition of loose debris (Nimonic 80A vs. Stellite 6), 570°C to 750°C, 0.905 m.s⁻¹
Figure 5.12: Cross sectional EDX element maps for Nimonic 80A worn against Stellite 6 subsequent to wear at 0.314 m.s⁻¹

Figure 5.13: Data from Autopoint EDX analysis for Nimonic 80A slid against Stellite 6 at a sliding speed of 0.314 m.s⁻¹ and a temperature of 750°C

Figure 5.14: XRD data – Nimonic 80A versus Stellite 6 at 0.314 m.s⁻¹

Figure 5.15: XRD data – Nimonic 80A versus Stellite 6 at 0.905 m.s⁻¹

Figure 5.16: Glancing Angle XRD data – Nimonic 80A versus Stellite 6 at 0.314 m.s⁻¹

Figure 5.17: Subsurface layer hardness for samples slid at 0.314 and 0.905 m.s⁻¹, Nimonic 80A versus Stellite 6

Figure 5.18: Change in weight and wear rate with time for Nimonic 80A versus Stellite 6 at 510°C, 630°C and 750°C

Figure 5.19: Change in coefficient of friction with sliding distance for Nimonic 80A versus Stellite 6 at 510°C and 750°C

Figure 5.20: Glaze build up with time for Nimonic 80A versus Stellite 6 – optical

Figure 5.21: Glaze build up with time for Nimonic 80A versus Stellite 6 – SEM low resolution images (X300)

Figure 5.22: Glaze build up with time for Nimonic 80A versus Stellite 6 – SEM high resolution images (X3.0K)

Figure 5.23: XRD data – Nimonic 80A versus Stellite 6 at 0.314 m.s⁻¹ / 510°C

Figure 5.24: XRD data – Nimonic 80A versus Stellite 6 at 0.314 m.s⁻¹ / 750°C

Figure 5.25: Weight change and wear rate versus sliding speed for Stellite 6 as the sample material worn against a Nimonic 80A counterface at 750°C

Figure 5.26: Coefficient of friction versus temperature – Stellite 6 vs. Nimonic 80A

Figure 5.27: Compacted oxide produced on Stellite 6 samples slid against a Nimonic 80A counterface at different sliding speeds – optical images

Figure 5.28: Compacted oxide produced on Stellite 6 samples slid against a Nimonic 80A counterface at 0.314 m.s⁻¹ and 0.905 m.s⁻¹ – SEM images

Figure 5.29: Backscatter image of the side profile of a Stellite 6 sample

Figure 5.30: Variation in hardness with increasing distance from the sliding surface for both the cobalt rich matrix and the carbide precipitates in Stellite 6 slid against a Nimonic 80A counterface at 750°C

Figure 5.31: Compacted oxide produced on a Nimonic 80A counterface slid against Stellite 6 samples at 0.314 m.s⁻¹ and 0.905 m.s⁻¹
Figure 5.32: Weight change and wear rate versus sliding speed for Nickel 200TM versus Stellite 6 at 0.314 m.s⁻¹ and 0.905 m.s⁻¹ 155
Figure 5.33: Friction data for Nickel 200TM versus Stellite 6 at 0.314 and 0.905 m.s⁻¹ 156
Figure 5.34: Comparison of wear scars produced by wear of Nimonic 80A versus Stellite 6 and Nickel 200TM versus Stellite 6 156
Figure 5.35: SEM images of Nickel 200TM samples slid against a Stellite 6 counterface at 0.314 and 0.905 m.s⁻¹ 158
Figure 5.36: XRD Plots for glaze from Nickel 200TM versus Stellite 6 159
Figure 5.37: Subsurface layer hardness for samples slid at 0.314 and 0.905 m.s⁻¹, Nickel 200TM versus Stellite 6, 750°C 160
Figure 5.38: Effect of temperature on weight change and wear rate – Incoloy MA956 versus Stellite 6 164
Figure 5.39: Coefficient of friction versus temperature – Incoloy MA956 vs. Stellite 6 165
Figure 5.40: Sample wear scar optical images – Incoloy MA956 / Stellite 6, 0.314 m.s⁻¹ 168
Figure 5.41: Sample wear scar optical images – Incoloy MA956 / Stellite 6, 0.905 m.s⁻¹ 169
Figure 5.42: SEM micrographs for Incoloy MA956 versus Stellite 6 – wear surface 170
Figure 5.43: SEM micrographs for Incoloy MA956 versus Stellite 6 – debris 171
Figure 5.44: Counterface wear scar optical images – Incoloy MA956 / Stellite 6, 0.314 m.s⁻¹ 172
Figure 5.45: Counterface wear scar optical images – Incoloy MA956 / Stellite 6, 0.905 m.s⁻¹ 172
Figure 5.46: EDX data – variation of composition of loose debris and glaze layers (Incoloy MA956 vs. Stellite 6), room temperature to 750°C, 0.314 m.s⁻¹ 177
Figure 5.47: EDX Data – variation of composition of glaze layers (Incoloy MA956 vs. Stellite 6), 510°C to 750°C, 0.905 m.s⁻¹ 177
Figure 5.48: Cross sectional EDX element maps for Incoloy MA956 worn against Stellite 6 subsequent to wear at 0.314 m.s⁻¹ 179
Figure 5.49: Cross sectional EDX element maps for Incoloy MA956 worn against Stellite 6 subsequent to wear at 0.905 m.s⁻¹ 180
Figure 5.50: Data from Autopoint EDX analysis for Incoloy MA956 slid against Stellite 6 at sliding speeds of 0.314 and 0.905 m.s⁻¹ and 750°C 181
Figure 5.51: XRD for Incoloy MA956 versus Stellite 6 – 0.314 m.s⁻¹ 184
Figure 5.52: XRD for Incoloy MA956 versus Stellite 6 – 0.905 m.s⁻¹ 185
Figure 5.53: Glancing Angle XRD for Incoloy MA956 versus Stellite 6 – 0.314 m.s\(^{-1}\)

Figure 5.54: Subsurface layer hardness for samples slid at 0.314 and 0.905 m.s\(^{-1}\), Incoloy MA956 versus Stellite 6

Figure 5.55: Effect of temperature on weight change and wear rate – Nimonic 80A versus Incoloy 800HT

Figure 5.56: Temperature versus coefficient of friction for Nimonic 80A versus Incoloy 800HT

Figure 5.57: Distance to transition in coefficient of friction from high variability (severe wear) to low variability (mild wear) at 630°C, 690°C and 750°C – Nimonic 80A versus Incoloy 800HT at 0.905 m.s\(^{-1}\)

Figure 5.58: Optical images for Nimonic 80A versus Incoloy 800HT at 0.314 m.s\(^{-1}\)

Figure 5.59: Optical Images for Nimonic 80A versus Incoloy 800HT at 0.905 m.s\(^{-1}\)

Figure 5.60: SEM micrographs for Nimonic 80A versus Incoloy 800HT – wear surface

Figure 5.61: SEM micrographs for Nimonic 80A versus Incoloy 800HT – debris

Figure 5.62: Counterface wear scar optical images – Nimonic 80A / Incoloy 800HT, 0.314 m.s\(^{-1}\)

Figure 5.63: Counterface wear scar optical images – Nimonic 80A / Incoloy 800HT, 0.905 m.s\(^{-1}\)

Figure 5.64: Cross sectional EDX element maps for Nimonic 80A worn against Incoloy 800HT subsequent to wear at 0.314 m.s\(^{-1}\)

Figure 5.65: Cross sectional EDX element maps for Nimonic 80A worn against Incoloy 800HT subsequent to wear at 0.905 m.s\(^{-1}\)

Figure 5.66: Data from Autopoint EDX analysis for Nimonic 80A versus Incoloy 800HT at sliding speeds of 0.314 and 0.905 m.s\(^{-1}\) and 750°C

Figure 5.67: XRD for Nimonic 80A versus Incoloy 800HT at 0.314 m.s\(^{-1}\)

Figure 5.68: XRD for Nimonic 80A versus Incoloy 800HT at 0.905 m.s\(^{-1}\)

Figure 5.69: Glancing Angle XRD for Nimonic 80A vs. Incoloy 800HT at 0.314 m.s\(^{-1}\)

Figure 5.70: Subsurface layer hardness for samples slid at 0.314 and 0.905 m.s\(^{-1}\), Nimonic 80A versus Incoloy 800HT

Figure 5.71: Optical and SEM images of sample surfaces on sliding without reciprocation – Nimonic 80A versus Incoloy 800HT at 510°C and 0.314 m.s\(^{-1}\)
| Figure 5.72: | Coefficient of friction versus sliding distance for Nimonic 80A versus Incoloy 800HT at 510°C and 0.314 m.s\(^{-1}\) without reciprocation | 221 |
| Figure 5.73: | Effect of temperature on weight change and wear rate – Incoloy MA956 vs. Incoloy 800HT | 224 |
| Figure 5.74: | Temperature versus coefficient of friction for Incoloy MA956 versus Incoloy 800HT | 225 |
| Figure 5.75: | Distance to transition in coefficient of friction from high variability (severe wear) to low variability (mild wear) at 630°C, 690°C and 750°C – Incoloy MA956 versus Incoloy 800HT at 0.314 m.s\(^{-1}\) and 0.905 m.s\(^{-1}\) | 226 |
| Figure 5.76: | Optical Images for Incoloy MA956 versus Incoloy 800HT at 0.314 m.s\(^{-1}\) | 230 |
| Figure 5.77: | Optical Images for Incoloy MA956 versus Incoloy 800HT at 0.905 m.s\(^{-1}\) | 231 |
| Figure 5.78: | SEM micrographs for Incoloy MA956 versus Incoloy 800HT – wear surfaces | 232 |
| Figure 5.79: | SEM micrographs for Incoloy MA956 versus Incoloy 800HT – debris | 233 |
| Figure 5.80: | Counterface wear scar optical images – Incoloy MA956 / Incoloy 800HT, 0.314 m.s\(^{-1}\) | 234 |
| Figure 5.81: | Counterface wear scar optical images – Incoloy MA956 / Incoloy 800HT, 0.905 m.s\(^{-1}\) | 234 |
| Figure 5.82: | Cross sectional EDX element maps for Incoloy MA956 worn against Incoloy 800HT subsequent to wear at 0.314 m.s\(^{-1}\) | 239 |
| Figure 5.83: | Cross sectional EDX element maps for Incoloy MA956 worn against Incoloy 800HT subsequent to wear at 0.905 m.s\(^{-1}\) | 240 |
| Figure 5.84: | Data from Autopoint EDX analysis for Incoloy MA956 versus Incoloy 800HT at sliding speeds of 0.314 and 0.905 m.s\(^{-1}\) and 750°C | 243 |
| Figure 5.85: | XRD for Incoloy MA956 versus Incoloy 800HT – 0.314 m.s\(^{-1}\) | 246 |
| Figure 5.86: | XRD for Incoloy MA956 versus Incoloy 800HT – 0.905 m.s\(^{-1}\) | 248 |
| Figure 5.87: | Subsurface layer hardness for samples slid at 0.314 and 0.905 m.s\(^{-1}\), Incoloy MA956 versus Incoloy 800HT | 253 |
| Figure 5.88: | Optical and SEM images of sample surfaces on sliding without reciprocation – Incoloy MA956 versus Incoloy 800HT at 510°C and 0.314 m.s\(^{-1}\) | 255 |
| Figure 5.89: | Coefficient of friction versus sliding distance for Incoloy MA956 versus Incoloy 800HT at 510°C and 0.314 m.s\(^{-1}\) without reciprocation | 256 |
| Figure 5.90: | TEM bright field image showing wear induced polycrystalline glaze layer and deformation of Nimonic 80A substrate | 261 |
Figure 5.91: TEM morphological and structural details of glaze layer on Nimonic 80A

Figure 5.92: TEM-EDS patterns for glaze and Nimonic 80A substrate

Figure 5.93: TEM image showing interface of glaze layer / deformed Nimonic 80A substrate

Figure 5.94: STM surface line profile results on glaze layer formed on Nimonic 80A

Figure 6.1: Wear processes for Nimonic 80A versus Stellite 6 from room temperature to 750°C at 0.314 m.s\(^{-1}\)

Figure 6.2: Mean Knoop hardness (hot hardness, 50 g load, 12 s dwell time) from room temperature to 510°C, with wear regimes with respect to temperature identified for the Nimonic 80A / Stellite 6 and Incoloy MA956 / Stellite 6 systems

Figure 6.3: Wear processes for Nimonic 80A versus Stellite 6 from room temperature to 750°C at 0.905 m.s\(^{-1}\)

Figure 6.4: Wear map for Nimonic 80A versus Stellite 6

Figure 6.5: Wear processes for Nickel 200\(^\text{TM}\) slid against a Stellite 6 counterface at 750°C, for 0.314 and 0.905 m.s\(^{-1}\)

Figure 6.6: Wear processes for Incoloy MA956 versus Stellite 6 from room temperature to 750°C at 0.314 m.s\(^{-1}\)

Figure 6.7: Wear processes for Incoloy MA956 versus Stellite 6 from room temperature to 750°C at 0.905 m.s\(^{-1}\)

Figure 6.8: Wear map for Incoloy MA956 versus Stellite 6

Figure 6.9: Wear processes for Nimonic 80A versus Incoloy 800HT from room temperature to 750°C at 0.314 m.s\(^{-1}\)

Figure 6.10: Layers formed on Nimonic 80A sample and Incoloy 800HT counterface at 750°C and 0.314 m.s\(^{-1}\)

Figure 6.11: Wear scar cross section on Incoloy 800HT counterface worn against a Nimonic 80A sample – 0.314 m.s\(^{-1}\) and 0.905 m.s\(^{-1}\)

Figure 6.12: Wear processes for Nimonic 80A versus Incoloy 800HT from room temperature to 750°C at 0.905 m.s\(^{-1}\)

Figure 6.13: Distance to transition in coefficient of friction from high variability (severe wear) to low variability (mild wear) at 630°C, 690°C and 750°C – Nimonic 80A versus Incoloy 800HT at 0.905 m.s\(^{-1}\)

Figure 6.14: Layers formed on Nimonic 80A sample and Incoloy 800HT counterface at 750°C and 0.905 m.s\(^{-1}\)

Figure 6.15: Wear map for Nimonic 80A versus Incoloy 800HT

Figure 6.16: Distance to transition in coefficient of friction from high variability (severe wear) to low variability (mild wear) at 630°C, 690°C and 750°C – Incoloy MA956 versus Incoloy 800HT at 0.314 m.s\(^{-1}\) and 0.905 m.s\(^{-1}\)
Figure 6.17: Wear processes for Incoloy MA956 versus Incoloy 800HT from room temperature to 750°C at 0.314 m.s^{-1} 303
Figure 6.18: Layers formed on Incoloy MA956 sample and Incoloy 800HT counterface at 750°C and 0.314 m.s^{-1} 304
Figure 6.19: Wear scar cross section on Incoloy 800HT counterface worn against an Incoloy MA956 sample – 0.314 m.s^{-1} and 0.905 m.s^{-1} 305
Figure 6.20: Wear processes for Incoloy MA956 versus Incoloy 80HT from room temperature to 750°C at 0.905 m.s^{-1} 308
Figure 6.21: Layers formed on Incoloy MA956 sample and Incoloy 800HT counterface at 750°C and 0.905 m.s^{-1} 309
Figure 6.22: Wear map for Incoloy MA956 versus Incoloy 800HT 312
Figure 6.23: STM imaging of compacted oxide glaze formed during sliding wear of Nimonic 80A against Stellite 6 314
Figure 6.24: Surface and sub surface layer micro-hardness for Nimonic 80A samples slid against Stellite 6 at 0.314 m.s^{-1} and 750°C 316
ACKNOWLEDGEMENTS

I would like to thank Prof. Santu Datta and Dr. Jim Burnell-Gray, my supervisors, for their help, advice and encouragement with this thesis.

I also wish to take the opportunity to thank other staff and research students within the Advanced Materials Research Institute and the School of Engineering, Science and Technology for all the help and assistance given. In particular, I wish the thank Bob Best for assistance and help with Scanning Electron Microscopy and Energy Dispersive X-Ray, and Ed Lancely, Clive Hartis and John Bagnall for help in the day-to-day running of this project.

Many thanks must be made also to my parents and friends who had to listen to all my tales of woe whilst I completed the write-up of this thesis. I also wish to pass on my gratitude to Sunderland Association Football Club where I am a season ticket holder; my trips to the Stadium of Light for football matches were at times the only break I had from my doctoral work.

I also wish to thank the EPSRC for their funding of this project.
This copy of this thesis has been supplied on condition that anyone who consults it is understood that its copyright rests with the author. No quotation from the thesis and no information derived from it may be published without the author’s prior written permission.
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 m.s\(^{-1}\) and 0.905 m.s\(^{-1}\), between room temperature and 750°C – this supplemented previous testing conducted at 0.654 m.s\(^{-1}\). When Nimonic 80A was slid against Stellite 6, lowering sliding speed to 0.314 m.s\(^{-1}\) between 510°C and 750°C lead to the formation of wear protective glaze layers consisting of cobalt and chromium oxides from the Stellite 6, whereas at 0.905 m.s\(^{-1}\) and during previous testing at 0.654 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 m.s\(^{-1}\) to largely iron and chromium oxides from the Incoloy MA956 at 0.905 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°C for 0.905 m.s\(^{-1}\), whereas only severe wear was observed for testing at 0.654 m.s\(^{-1}\).

When Incoloy MA956 was worn against Incoloy 800HT, increasing the sliding speed from 0.314 m.s\(^{-1}\) to 0.905 m.s\(^{-1}\) had the opposite affect – the beginning of glaze formation was suppressed from 630°C to 690°C. Similar results were also observed when Nimonic 80A was slid against Incoloy 800HT, with the beginning of glaze formation suppressed from 570°C to 630°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\(^{-1}\) 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\(^{-1}\), but also at 0.905 m.s\(^{-1}\) – this was due to the elimination of chromium oxide (in the form of Cr\(_2\)O\(_3\)) 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\(^{-1}\) 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\(^{-1}\) 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 nano-polycrystalline 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 “glazed” layer on one or both surfaces, which minimises and can almost completely eliminate subsequent wear.