Lubrication of Inconel 600 with ionic liquids at high temperature

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ABSTRACT

The friction and wear behavior of Inconel 600 against AISI 52100 steel have been studied in the presence of three ionic liquid (IL) lubricants, two imidazolium derivatives, 1-methyl-3-octylimidazolium tetrafluoroborate (L108) and 1-methyl-3-hexylimidazolium hexafluorophosphate (L-P106), and the quaternary ammonium chloride AMMONEX™ 101 (AM-101), and compared with a mineral base oil at room temperature. The IL lubricants have been studied at high temperature. While the ammonium derivative has been used at 100 and 200 °C, the higher thermal stability of the imidazolium derivatives allows them to be used up to 300 °C. The results show that the imidazolium derivatives are the best lubricants at all temperatures. A temperature increase from 100 to 200 °C reduces wear rates for all ILs due to a transition form abrasive to adhesive wear and formation of a tribolayer on the Inconel wear track. At 300 °C, the hexafluorophosphate derivative produces tribocorrosion attack on the steel ball and severe wear of Inconel 600 due to decomposition of the IL. The wear mechanisms and surface interactions are discussed in terms of IL-metal surface interactions from SEM, EDX and XPS data.

1. Introduction

Ionic liquids (ILs) are non-volatile fluids formed by salts with a melting point lower than room temperature. Many ILs are also non-flammable fluids, with high thermal and chemical stabilities. Their properties can be tailored by varying the side chains attached to the cation and the nature of the anion species, giving rise to numerous families with an increasing number of already implemented or potential technological applications [1–4]. ILs have been studied as lubricants of a series of materials, particularly steel–steel [5–11] and aluminium–steel [12–19] contacts. One of the most promising applications of these new lubricants is their use at high temperatures. Alkylimidazolium tetrafluoroborates have shown good lubricating ability for aluminium–steel contacts at 100 and 200 °C [19]. Previous studies have also shown the potential of ionic liquids in high temperature steel lubrication [20–22].

Imidazolium hexafluorophosphate ILs have shown good lubricating performance and high load carrying capacity under severe conditions, including high vacuum [23]. However, ionic liquids containing this anion are susceptible to decomposition with release of HF and other species by hydrolysis. This process can also take place for other fluorne-containing ILs, however, PF6 IL lubricants have been described to fail at high temperature [21].

Although imidazolium ionic liquids have been the most widely studied family of ionic liquids, some previous results also show promising lubricating performances for other types of ionic liquids such as ammonium derivatives [24].

In the present study, we have selected two imidazolium ILs with tetrafluoroborate and hexafluorophosphate anions, respectively, and a quaternary ammonium chloride to study their lubricating behavior in steel–Inconel 600 contacts. Inconel 600 was selected due to its high temperature and corrosion resistance.

Ionic liquids have previously been studied as lubricants of nickel coatings [25, 26] and chromium coatings [27].

Previous studies [28, 29] on the interaction of Inconel 600 with ILs have shown that IL decomposition takes place after long term immersion tests, although Inconel 600 showed low weight loss. A catalytic mechanism for IL decomposition due to nickel metal atoms has been proposed. When immersion tests are carried out at higher temperatures (>225 °C), Inconel 600 showed localized corrosion.

In the present work we have compared the ILs with a mineral base oil at room temperature. The IL lubricants have also been studied as high temperature lubricants, at 100, 200 or 300 °C, depending on their thermal stability. Wear mechanisms and surface interactions have been related to tribological results.
The results presented here are part of a study on IL-lubrication of high temperature materials such as nickel and titanium [30] alloys.

2. Experimental details

The mineral oil (MO) used has been described elsewhere [31] and is an additive-free paraffinic (62.1%)–naphtenic (30.2%) oil (viscosity 112.5 cSt at 40 °C, viscosity index 95; total sulfur content 1.06%) manufactured by Repsol-YPF (Spain). Ionic liquids (Fig. 1) L-108 and L-P106 (purity >97%) were commercially available from Fluka Chemie (Germany). Ionic liquid AMMOENG\textsuperscript{TM} 101 (AM-101) (purity >95%) (Fig. 1) was supplied by Solvent Innovation (Germany). Inconel 600 (74.8%Ni; 15.0%Cr; 8.9%Fe; 0.22%Si; 0.25%Ti; 0.16%Al; 0.07%C) disks (20 mm diameter; 10 mm thickness; hardness 156 HV; \( R_a \approx 0.2 \mu m \)) were tested against AISI 52100 (1.52%Cr; 0.95%C; 0.33%Mn; 0.25%Si; hardness 848 HV; roughness \( R_a \approx 0.01 \) ) steel balls (0.8 mm sphere radius), in the presence of 1 ml of the lubricants. Tribological tests according to ASTM G-99-05 were carried out in air under a load of 2.45 N with a sliding speed of 0.15 ms\(^{-1}\) and for a sliding distance of 850 m using a pin-on-disk tribometer equipped with an oven (Microtest, Spain; Fig. 2) [19]. Unless otherwise stated, all test samples were cleaned with acetonitrile, acetone and n-hexane and dried in air. Friction coefficients were continuously recorded with sliding distance for each test. Volume loss from Inconel 600 disks was determined by image analysis using a Leica DMRX optical microscope with an Optimas image analyzer, from wear track width mean values after at least 12 measures along the wear scars with standard deviation lower than 3%. When plastic deformation and accumulation of material at the edges of the wear track are observed, wear rates have been confirmed by contact profilometry measurements with an ALPA-SM profilometer. The final wear rates are average values from the results of measurements along at least three wear tracks obtained under the same set of experimental conditions.

Thermal-oxidative stability of the lubricants (Table 1) was determined by thermogravimetric analysis (TGA), with a Shimadzu TGA-50 equipment in air atmosphere, between 25 and 800 °C, at a heating rate of 10 °C min\(^{-1}\).

<table>
<thead>
<tr>
<th>Lubricant</th>
<th>Temperature (°C)</th>
<th>Onset</th>
<th>50% weight loss</th>
<th>Endset</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mineral oil MO</td>
<td>263.1</td>
<td>300.3</td>
<td>339.5</td>
<td></td>
</tr>
<tr>
<td>AM-101</td>
<td>219.1</td>
<td>236.2</td>
<td>336.4</td>
<td></td>
</tr>
<tr>
<td>L-108</td>
<td>370.9</td>
<td>400.6</td>
<td>436.2</td>
<td></td>
</tr>
<tr>
<td>L-P106</td>
<td>322.0</td>
<td>355.3</td>
<td>393.0</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3a shows friction coefficients and wear rates for Inconel 600 disks sliding against AISI 52100 pins lubricated with MO, AM-101, L-108 and L-P106 at room temperature. The performance of the quaternary ammonium AM-101 is very similar to that of the mineral base oil (MO), while both imidazolium ILs reduce friction (with a maximum reduction of a 48% for L-P106 with respect to MO) and wear rates, with a maximum reduction of more than one order of magnitude in the case of L-108.

Fig. 4 shows wear track profiles at room temperature illustrating the change from the very severe wear in the presence of MO (Fig. 4a), with plastic deformation at the edges of the wear track and abrasion grooves inside it, to the mild surface damage on Inconel 600 when L-108 is used as lubricant (Fig. 4b). Severe abrasion is also observed for L-P106 (Fig. 4c).

3. Results and discussion

3.1. Thermal stability of the neat lubricants

From the point of view of practical application, one of the relevant characteristics of the lubricants is their thermal stability. The weight loss determined by TGA (Table 1) shows that imidazolium ILs L-108 and L-P106 are highly stable compared with the ammonium IL AM-101 and with the mineral base oil (MO). In a previous study [19], we have shown that the higher thermal stability of L-108 with respect to MO is maintained even when the lubricants are heated at 150 °C for 8 hours. This high thermal stability of ionic liquids is one of the factors that could make them good candidates for high temperature lubrication.

3.2. Friction coefficients and wear rates at variable temperature

Fig. 3a shows friction coefficients and wear rates for Inconel 600 disks sliding against AISI 52100 pins lubricated with MO, AM-101, L-108 and L-P106 at room temperature. The performance of the quaternary ammonium AM-101 is very similar to that of the mineral base oil (MO), while both imidazolium ILs reduce friction (with a maximum reduction of a 48% for L-P106 with respect to MO) and wear rates, with a maximum reduction of more than one order of magnitude in the case of L-108.

Fig. 4 shows wear track profiles at room temperature illustrating the change from the very severe wear in the presence of MO (Fig. 4a), with plastic deformation at the edges of the wear track and abrasion grooves inside it, to the mild surface damage on Inconel 600 when L-108 is used as lubricant (Fig. 4b). Severe abrasion is also observed for L-P106 (Fig. 4c).
When the three IL lubricants are compared at 100 and 200 °C (Figs. 3b and c), L-108 shows the highest friction reducing ability (Fig. 3b) while the lowest wear rates are obtained for the L-P106 hexafluorophosphate derivative (Fig. 3c).

It is interesting to notice that, in all cases, wear rates at 200 °C are lower than those at 100 °C. Studies [33] on the dry wear resistance of nickel alloys at high temperature have shown that wear rates can decrease under increasing temperature due to the formation of smooth oxide layers. The wear reduction observed here is related to changes in wear mechanisms and surface interactions which give rise to the formation of tribolayers, as will be discussed in the next section.

Finally, the more thermally stable ILs were tested at 300 °C, where friction and wear reach maximum values (Figs. 3b and c). Friction coefficients at 300 °C (Fig. 3b) are similar for both L-108 and L-P106, but the wear rate increase from 200 to 300 °C is particularly pronounced for the hexafluorophosphate L-P106 (Fig. 3c). In fact, at 300 °C, L-P106 is close to its weight loss onset temperature (Table 1).

### 3.3. Wear mechanisms and surface interactions

#### 3.3.1. EDX results

We have seen that AM-101 shows a poor lubricating performance at room temperature, with friction and wear values similar to those of MO. Fig. 5 shows the wear tracks on Inconel 600 and AISI 52100 steel balls after lubrication with AM-101 as a function of temperature. At room temperature (Figs. 5a and d), a severe abrasion mechanism takes place causing surface damage on both materials. At 100 °C (Figs. 5b and e), the predominantly abrasive mechanism is also present. In contrast, at 200 °C (Figs. 5c and f), an adhesive mechanism appears, with plastic deformation both on the Inconel wear track and on the steel ball. These observations could be explained by the thermal softening of the materials and could account for the wear rate decrease at 200 °C (Fig. 3c) due to smoothing of the asperities on the steel surface, which now appears covered by a plastically deformed layer. The EDX spectra
for Inconel wear track (Fig. 5c) and steel ball (Fig. 5f) show neither material transfer, nor tribochemical interaction with the AM-101 II lubricant.

Fig. 6 shows wear tracks on Inconel 600 for L-108 as a function of temperature. The strong increase from 25 to 100 °C (Fig. 3c) is in agreement with the smooth surface observed at room temperature (Fig. 6a) and the severely damaged surface by abrasion at 100 °C (Fig. 6b). In contrast, the wear track at 200 °C (Fig. 6c) appears partially covered by a smooth tribolayer. The EDX analysis (Fig. 6c) of this tribolayer corresponds to the base Inconel 600 alloy.

The more adhesive component of the wear mechanism at 200 °C can be confirmed by observation of the steel surface. Fig. 7 shows SEM micrographs and Ni transfer layers on the steel ball at 100 °C (Fig. 7a) and 200 °C (Fig. 7b). Although this is not a quantitative technique, the abrasion marks appear to be reduced and the area covered by the transfer layer increased as the temperature increases, thus reducing the asperities on the steel surface and preventing the direct steel–Inconel contact.

Also important is to examine the morphology and composition of wear debris. As can be seen in Fig. 8, wear debris particles at 200 °C contain metallic oxides and no metallic chips removed by abrasion are observed.

If we examine now the ball surface (Fig. 9a) and wear track (Fig. 9b) at 300 °C for L-108, an extensive plastic deformation takes place on Inconel 600 which was not observed at lower temperatures (Fig. 8) and is in agreement with thermal softening at this high temperature.

When the wear tracks on Inconel 600 are observed (Fig. 10) after lubrication with L-P106, wear mechanism changes with temperature similar to those described for L-108 are observed; that is, very mild damage at room temperature (Fig. 10a), severe abrasion at 100 °C (Fig. 10b) and the presence of a tribolayer at 200 °C (Fig. 10c). However, in this case, the EDX spectrum of the tribolayer at 200 °C (Fig. 10c) shows not only oxide, but also the presence of phosphorus and fluorine from the hexafluorophosphate anion. The superposition of the spectra shown in Fig. 11 allows a better appreciation of the composition changes with temperature inside the wear track. This shows that a tribochemical process has taken place. In this case, the reaction products form a protective layer on the Inconel 600 surface.

When the steel ball surface is observed after the test at 300 °C in the presence of L-P106, Fig. 12a shows the presence of L-P106 drops on the steel surface and severe surface degradation on the contact zone. Fig. 12b shows the presence of fluorine and phosphorus on the contact zone, in agreement with a tribocorrosion process. Under these conditions, a very severe damage on Inconel 600 is also observed, with crack propagation and fracture (Fig. 12c) and removal of large metallic flakes (Fig. 12d).

This result is in agreement with previous observations [21] for steel–steel lubrication at high temperature, where PF$_6$ ILs failed at 300 °C.

3.3.2. XPS results

Table 2 shows the XPS binding energies on Inconel 600 after the tests with L-P106 at 100, 200 and 300 °C, and with L-108 at 300 °C.
At 100 °C, the binding energies found inside the Inconel 600 wear track after lubrication with L-P106 (Table 2) show peaks assignable to Ni 2p$_{3/2}$ of metallic Ni (852.3 eV), Fe 2p$_{3/2}$ of iron metal (707.6 eV) and to nickel and chromium oxides (854.4 and 577.5 eV, respectively). This is in agreement with the EDS spectrum (Fig. 10b) and shows that no tribocorrosion reactions have taken place between the metals and the L-P106 lubricant at this temperature.

Fig. 6. SEM micrographs of the wear tracks on Inconel 600 lubricated with L-108: (a) 25 °C; (b) 100 °C; (c) 200 °C, with EDX spectrum of the selected zone.

Fig. 7. SEM micrographs and Ni elemental maps of AISI 52100 steel balls after lubrication with L-108: (a) 100 °C; (b) 200 °C.
At 200 °C, XPS (Table 2) results for L-P106 lubricated Inconel 600 are similar inside and outside the wear track (around 2 mm outside the wear edge) with the significant difference of the presence of a F1s peak at 685.8 eV inside the wear track and the absence of it outside the wear track. This shows that the wear reduction observed at 200 °C could be related to surface interactions between Inconel 600 and L-P106, although no extensive decomposition of the IL has apparently taken place.

The EDX spectrum (Fig. 10c) had shown the presence of fluorine and phosphorus in the region of the wear track covered by the tribolayer at 200 °C. The fact that XPS shows no phosphorus inside the wear track shows that the tribolayer is non-uniform.

At 300 °C, Inconel 600 shows the presence of fluorine, phosphorus and nitrogen inside the wear track (Table 2). The new P 2p peaks at 133.8 and 135.3 eV are assignable to phosphates and adsorbed L-P106, respectively, while the N1s binding energy at 400.4 eV could be due to nitrogen oxidation [7]. These phosphorus and nitrogen peaks are not observed outside the wear track (Table 2), and show that decomposition of L-P106 has taken place at the contact zone.

The higher thermal stability of L-108 could prevent this tribocorrosion process, although surface interactions are shown by the presence of some iron fluoride [34] inside the wear track (Table 2).

4. Conclusions

The tribological performance of the Inconel 600-AISI 52100 pair has been studied in the presence of room-temperature 1-methyl-3-octylimidazolium tetrafluoroborate (L108), 1-methyl-3-octylimidazolium hexafluorophosphate (L-P106) and quatern-

![Fig. 8. Inconel 600 wear debris morphology and composition after lubrication with L-108 at 200 °C.](image)

![Fig. 10. SEM micrographs and EDX spectra of the selected regions inside the wear tracks on Inconel 600 after lubrication with L-P106: (a) 25 °C; (b) 100 °C; (c) 200 °C.](image)

![Fig. 9. SEM micrographs of: (a) steel ball surface and (b) Inconel 600 wear track after lubrication with L-108 at 300 °C.](image)
ary ammonium chloride AMMOENG™ 101 (AM-101) ionic liquids with reactive fluorine-containing and chloride anions, respectively.

Inconel 600 gives high friction coefficients and wear rates when lubricated with mineral oil or ammonium chloride ionic liquid AM-101 at room temperature.

From 25 to 200 °C, the imidazolium tetrafluoroborate (L-108) and hexafluorophosphate (L-P106) ILs show better lubricating performance than the ammonium derivative.

At 200 °C, all IL lubricants give lower wear rates than at 100 °C, particularly in the case of L-P106, due to the formation of a tribolayer containing fluorine and phosphorus from the hexafluorophosphate anion.

A transition to very severe wear is observed at 300 °C due to thermal softening and plastic deformation. In the case of L-P106, severe corrosion of the steel ball is observed at 300 °C, while the formation of phosphates and nitrogen oxides inside the Inconel

<table>
<thead>
<tr>
<th>IL</th>
<th>Sample</th>
<th>O</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
<th>F</th>
<th>P</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-P106</td>
<td>Wear track (100 °C)</td>
<td>531.1</td>
<td>852.3</td>
<td>577.5</td>
<td>707.6</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>532.1</td>
<td>854.4</td>
<td>577.0</td>
<td>709.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Wear track (200 °C)</td>
<td>529.6</td>
<td>852.6</td>
<td>577.0</td>
<td>709.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Outside the wear track</td>
<td>533.3</td>
<td>535.6</td>
<td>536.7</td>
<td>712.4</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>(200 °C)</td>
<td></td>
<td>577.0</td>
<td>712.4</td>
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<td></td>
<td>Wear track (300 °C)</td>
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<td>709.6</td>
<td></td>
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<tr>
<td></td>
<td>Outside the wear track</td>
<td>531.4</td>
<td>533.4</td>
<td>533.4</td>
<td>713.4</td>
<td></td>
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<td></td>
<td>(300 °C)</td>
<td></td>
<td>578.5</td>
<td>713.4</td>
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<tr>
<td>L-108</td>
<td>Wear track (300 °C)</td>
<td>529.7</td>
<td>852.4</td>
<td>573.9</td>
<td>710.9</td>
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<tr>
<td></td>
<td>Outside the wear track</td>
<td>531.9</td>
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<td>713.9</td>
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<tr>
<td></td>
<td>(300 °C)</td>
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<td>573.9</td>
<td>713.9</td>
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</table>

Fig. 11. Superposition of the EDX spectra after lubrication with L-P106 at 100 °C (dark gray) and at 200 °C (light gray).

Fig. 12. Lubrication with L-P106 at 300 °C: (a) SEM micrograph of the steel ball after the test (before cleaning); (b) EDX spectrum of the selected zone in the SEM micrograph of the ball (after cleaning); (c) wear track on Inconel 600; (d) wear debris.
600 wear track indicates that IL decomposition and tribochemical reactions have taken place at the steel–Inconel 600 contact. The lower wear rate obtained for the tetrafluoroborate derivative L-108 at 300 °C could be due to its higher thermal stability and lower tribochemical reactivity.

Acknowledgments

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References