

Tribological study of the AISI316L/Sapphire contact with self-lubricating films of protic ionic liquids

T. Espinosa-Rodríguez^(*), J. Sanes-Molina, M.D. Bermúdez-Olivares

Grupo de Ciencia de Materiales e Ingeniería Metalúrgica, Universidad Politécnica de Cartagena, Cartagena, Spain

ABSTRACT

Ionic liquids have shown an outstanding performance as lubricants in different contacts. Protic ammonium carboxylate ionic liquids (PILs), both neat and as additives in water, are being studied as friction-reducing and wear prevention lubricants in stainless steel-sapphire contacts.

When a PIL was used as additive in water, the high temperature reached at the sliding contact produced the evaporation of water and the formation of a low friction PIL boundary layer.

In the present study, the formation of the PIL boundary layer on AISI316L stainless steel under static conditions is described and its lubricating performance against sapphire balls has been studied. The effect of relative humidity has been studied using a vacuum chamber.

The results described in the present study show a good tribological performance of these thin surface films, in pin-on-disc tests, reducing the running-in period of high friction coefficient, preventing wear and reducing the volume of lubricant with respect to the results obtained when water+1%PIL and neat PIL are used as lubricants.

KEY WORDS: friction, wear, ionic liquids, lubricants.

1.- INTRODUCTION

1.1.- Ionic liquids in tribology

Room temperature ionic liquids (ILs) are fluids composed of ions which are stable in the liquid state at room temperature. ILs present a unique combination of properties, such as nonflammability, a wide electrochemical window, high-thermal stability, wide liquid range, and negligible vapor pressure, which make them useful in a variety of applications.

Among many other applications, ionic liquids have been extensively studied as lubricants and additives for friction reduction and wear protection [1,2], nanophase modifiers [3], electrolytes [4] and as corrosion protection agents either as inhibitors [5], or as precursors of protective surface coatings [6].

By far, the most widely studied ILs belong to the imidazolium family and they can be used either as neat lubricants or as additives of mineral or synthetic oils.

However, for reactive metals such as iron and aluminum-based materials, when the anion contains halides, particularly fluorine, a severe tribocorrosion process may occur, thus increasing friction and wear.

1.2.- Previous studies with protic ionic liquids as lubricants

The most recent reviews on room-temperature ionic liquids also include protic ionic liquids (PILs). The scarce PILs previously used as lubricants contain potentially corrosive groups, with fluorine or sulphur in their composition [7-9].

In the present study, fully organic PILs are used. They are readily available by a quite simple synthetic route as recently described [10]. They can present the advantages of the imidazolium salts without their disadvantages, because they are composed exclusively by C, H, N and O, so no toxic phases will develop and they are not only less corrosive, but they can even show corrosion inhibitor behaviour. The presence of proton donor and acceptor sites in the PILs molecules can build up a hydrogen bonded network which could improve their lubricating performance [11-13].

There exists a large variety of PILs depending on the number of carbon atoms in the chains, the number of hydrogen atoms on the ammonium cation and the number of carboxylate groups in the anion.

Water would be a real eco-lubricant, being cheap, nonflammable, readily available, and with relatively low compressibility. At the same time, some important disadvantages are its poor lubricating performance, corrosiveness, high-melting point, and low-boiling point. Additives must be used in order to minimize these inconveniences. ILs form ordered nanostructures in the liquid state and also in aqueous solution [14] so they can be used as additives.

In a previous work [15], we studied the tribological problem of lubricating a ceramic-metal pair where the extremely high-interface temperatures cause the failure of water or conventional water-based lubricants. In particular, the sapphire-stainless steel contact was selected due to the difficulty to reduce the friction and wear of this contact by using water-based lubricants. The contact was lubricated with water, with the protic ionic liquid bis (2-hydroxyethylammonium) succinate (MSu), and with a 1 wt% solution of MSu in water. Neat water evaporated after the running-in period to give a transition to dry contact. Neat MSu reduced the running-in period, reducing the friction coefficient. The addition of a 1wt% MSu to water not only reduced the running-in period with respect to neat water, but the coefficient of friction showed a marked decrease to ultra-low friction values after water evaporation, because MSu molecules remained as a surface boundary film after the evaporation of water.

Therefore, in the present study, the formation of the PIL boundary layer on AISI316L stainless steel under static conditions is described in order to prevent or reduce the running-in period with respect to water and water+1%PIL and to reduce the volume of liquid used when neat PIL is used as lubricant. The lubricating performance of these boundary layers against sapphire balls has been studied. The effect of relative humidity has been studied using a vacuum chamber.

2.- EXPERIMENTAL SECTION

Figure 1 shows the chemical structure of the PIL used in the present work, Di-[bis (2-hydroxyethyl)ammonium] adipate (Dad). This PIL was kindly supplied by Dr. M. Iglesias (currently at the Federal University of Bahia, Brazil) and used as received.

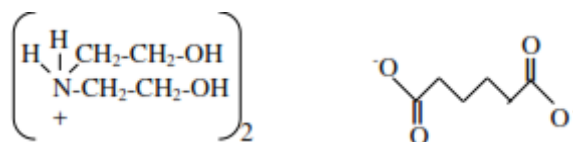


Figure 1. Chemical structure of Di-[bis (2-hydroxyethyl)ammonium] adipate (Dad)

SEM images and EDX analysis were obtained using a Hitachi S3500N scanning electron microscope. Optical micrographs were obtained using a Leica DMRX optical microscope.

For tribological tests, according to ASTM G 99-05 standard, AISI 316L stainless steel (170-220HV) discs (25mm diameter; 5mm thickness; surface roughness $R < 0.1\mu\text{m}$) were tested in a pin-on-disc tribometer (Microtest, Spain) against sapphire balls (Al_2O_3 99%, 0.75mm sphere radius), at room temperature under a normal applied load of 1 N, with a sliding radius of 9 mm, at a sliding velocity of 0.10 ms^{-1} , and a sliding distance of 500 m. Friction coefficients were continuously recorded with sliding distance for each test.

3D surface topography images and volume loss measurements were obtained by means of a Talysurf CLI optical profiler. Wear mechanisms have been studied by optical and electronic microscopy and profilometry.

Mean friction coefficients and wear rates are obtained after at least three tests under the same conditions.

Two kinds of tests have been developed: external lubrication with 0.5ml of neat PIL and water+1%wt PIL added before the tests, and the formation of a PIL boundary layer on AISI316L stainless steel under static conditions.

This PIL boundary layer has been obtained covering the disc surface with the water+1%wt PIL solution and introducing it in a vacuum oven at 60°C during 3 hours, then letting it sit for a day in a desiccator.

3.- RESULTS

3.1.- Tribological performance

Figure 2 compares the friction records for water, water+1%DAd, neat DAd and DAd boundary layer. The results are similar to those obtained for MSu. Water evaporation is necessary to lower friction. The boundary layer shows a lubricating performance even higher than that of the neat PIL:

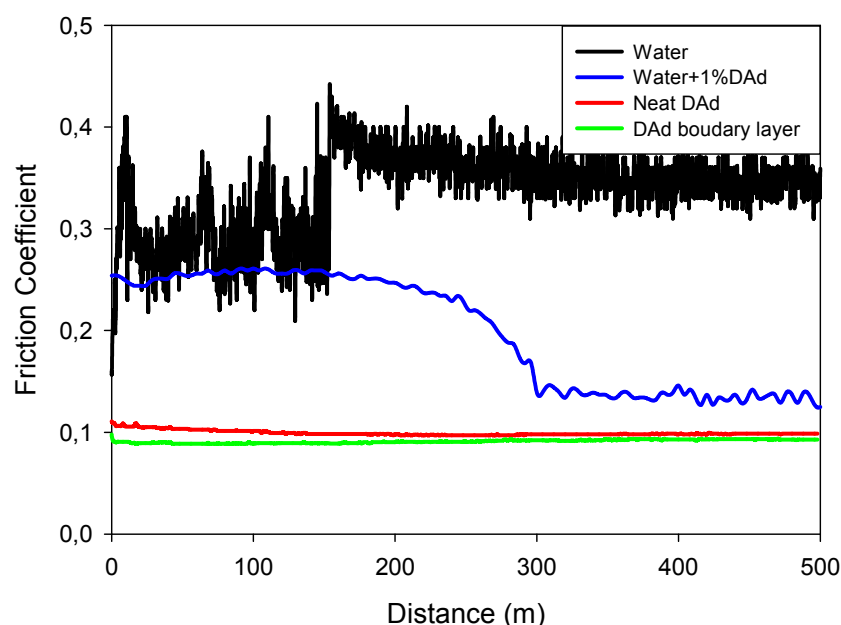
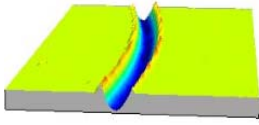

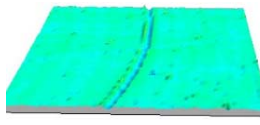





Figure 2. Friction vs. sliding distance for the steel-sapphire contact lubricated with: water (black), water+1%Dad (blue), neat Dad (red) and Dad boundary layer (green).

Table 1 shows the specific wear rates of the steel discs for each of the DAd lubricants. Wear tracks on steel and sapphire surfaces are also shown.

Table 1. Specific wear rate, 3D image of the steel disc and optical micrograph of the sapphire ball after tribological tests.

Lubricant	Water+1%DAd	Neat DAd	Dad boundary layer
Specific wear rate (mm ³ /N·m)	3.46x10 ⁻⁵	6.66x10 ⁻⁷	7.54x10 ⁻⁷
Wear track on steel disc			
Wear track on sapphire ball			

Wear rates for neat DAd and for the boundary layer are similar and two orders of magnitude lower than that obtained for water+1%DAd, which produces a very severe wear as can be observed in the SEM micrograph and EDX element maps shown in Figure 3.

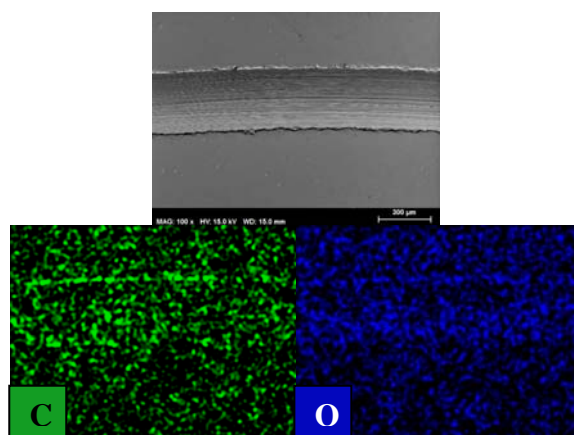


Figure 3. SEM Micrograph and elemental maps of carbon and oxygen inside the wear track of the steel disc after the tribological test with water+1%DAd.

3.2.- Effect of relative moisture

As we have seen in the previous section, the presence of water determines the tribological results. In order to control relative humidity, new tribological test were carried out using DAd boundary layers under different relative humidity (HR) conditions. Figure 4 compares the friction records for the same boundary layer for a 60% and a 30% HR conditions. A 50% decrease in HR produces a 35-40% friction reduction.

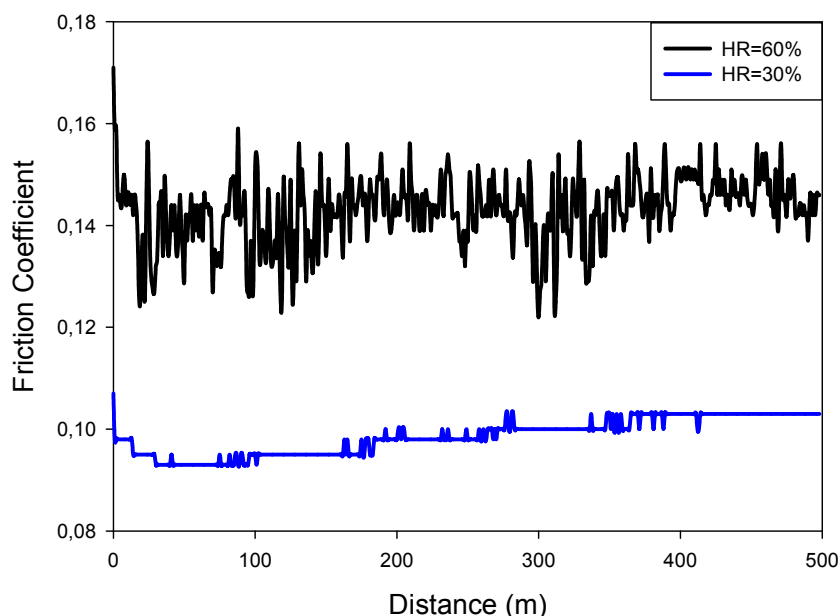


Figure 4. . Friction vs. sliding distance for the steel-sapphire contact lubricated with Dad boundary layer at: HR=60% (black) and HR=30% (blue).

4.- CONCLUSIONS

New self-lubricating stainless steel surfaces have been obtained by controlled water evaporation from 1wt.% solutions of PILs in water.

The new boundary layers present a tribological performance similar to that of the neat PILs, under low relative humidity conditions, to prevent water absorption.

ACKNOWLEDGEMENTS

The authors wish to express their gratitude to the Ministerio de Economía y Competitividad (MINECO, Spain) (MAT2011-23162 and MAT2014-55384-P) for financial support. T. Espinosa is grateful to the Ministerio de Educación, Cultura y Deporte (MECD, Spain) for a research Grant (AP2010-3485).

REFERENCES

- [1] I. Minami, Ionic liquids in tribology. *Molecules*, 14 (2009) 2286-2305.
- [2] M.D. Bermúdez, A.E. Jiménez, J. Sanes, F.J. Carrión, Ionic Liquids as Advanced Lubricant Fluids. *Molecules* 14 (2009) 2888-2908.
- [3] N. Saurín, J. Sanes, M.D. Bermúdez, Effect of graphene and ionic liquid additives on the tribological performance of epoxy resin. *Tribol. Lett.* 56 (2014) 133-142.
- [4] M. Galinski, A. Lewandowski, I. Stepniak, Ionic liquid as electrolytes. *Electrochim. Acta* 51 (2006) 5567-5580.
- [5] T. Tüken, F. Demir, N. Kicir, G. Sigircik, M. Erbil, Inhibition effect of 1-ethyl-3-methylimidazolium dicyanamide against steel corrosion. *Corros. Sci.* 59 (2012) 110-118.
- [6] T. Espinosa, A.E. Jiménez, G. Martínez-Nicolás, J. Sanes, M.D. Bermúdez, Abrasion resistance of magnesium alloys with surface films generated from phosphonate imidazolium ionic liquids. *Appl. Surf. Sci.* 320 (2014) 267-273.
- [7] T.L. Greaves, C.J. Drummond, Protic ionic liquids: properties and applications. *Chemical Reviews* 108 (2008) 206-237.

- [8] C.A. Angell, Y. Ansari, Z.F. Zhao, Ionic liquids: past, present and future. *Faraday Discussions* 154 (2012) 9–27.
- [9] T.L. Greaves, D.F. Kennedy, A. Weerawardena, N.M.K Tse, N.M.K.; N. Kirby, C.J. Drummond, Nanostructured protic ionic liquids retain nanoscale features in aqueous solution while precursor bronsted acids and bases exhibit different behavior. *Journal of Physical Chemistry B* 115 (2011) 2055–2066.
- [10] V.H. Alvarez, S. Mattedi, M. Martin-Pastor, M. Aznar, M. Iglesias, Synthesis and thermophysical properties of two new protic long-chain ionic liquids with the oleate anion. *Fluid Phase Equilibria* 299 (2010) 42–50.
- [11] R.A. Asencio, E.D. Cranston, R. Atkin, M.W. Rutland, Ionic liquid nanotribology: stiction suppression and surface induced shear thinning. *Langmuir* 28 (2012) 9967–9976.
- [12] T. Espinosa, J. Sanes, A.E. Jiménez, M.D. Bermúdez, Surface interactions, corrosion processes and lubricating performance of protic and aprotic ionic liquids with OFHC copper. *Appl. Surf. Sci.*, 273 (2013) 578-597.
- [13] T. Espinosa, J. Sanes, A.E. Jiménez, M.D. Bermúdez, Protic ammonium carboxylate ionic liquid lubricants of OFHC copper. *Wear* 303 (2013) 495–509.
- [14] J. Łuczak, J. Hupka, J. Thoming, C. Jungnickel, Self-organization of imidazolium ionic liquids in aqueous solution. *Colloids Surfaces. A. Physicochem Eng. Asp.* 329 (2008) 125–133.
- [15] T. Espinosa, M. Jiménez, J. Sanes, A.E. Jiménez, M. Iglesias, M.D. Bermúdez, Ultralow friction with a protic ionic liquid boundary film at the water-lubricated sapphire-stainless steel interface. *Tribol. Lett.* 53 (2014) 1-9.