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Electrochemical treatment of aluminium alloy 7075 in aqueous solutions of imidazolium phosphonate and phosphate ionic liquids and scratch resistance of the resultant materials

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ABSTRACT

The abilitiy of 1-ethyl-3-methylimidazolium ethylphosphonate ([ImPhosphonate]) and 1-ethyl-3-methylimidazolium diethylphosphate ([ImPhosphate]) ionic liquids (ILs) to interact with anodized Al7075 T6 aluminium alloy has been studied via electrochemical techniques under different applied potentials, inside and outside the passivation regions. SEM, EDX and XPS analysis have been used to study the composition of the surface coatings. The abrasion resistance after treatment with the ILs has been studied by scratch tests under progressive load, and compared with the performance of the unprotected material and the anodized alloy. While conventional anodization only improves the abrasion resistance of Al7075 in a 30%, the maximum reduction of the penetration depth, 86% with respect to Al7075 and 79% with respect to the anodized alloy, is obtained for the material treated with [ImPhosphonate] at 1 V, in the passivation region. Under these conditions, a phosphorus-containing alumina layer is formed. Applied voltages outside the passivation region for each IL activate the dissolution of the alumina layer and reduce abrasion resistance, not only with respect to the anodized material, but also with respect to the unprotected alloy.

1. Introduction

The use of light alloys such as aluminium, magnesium and titanium alloys has experienced a great expansion due to their good specific properties. However, the wear rate of light alloys tends to be higher than steel for the same tribological conditions. In particular, aluminium alloys present a lower abrasion resistance.

The anodization processes of aluminium have been extensively studied, and some authors have reported on the formation of anodic porous alumina using ionic liquid (ILs) as electrolytes [1–3]. In these studies, several neat imidazolium IL were used as electrolytes for anodization of pure aluminium applying electric potential values of up to 40 V, finding that anion structure strongly affects the ability to form passive layers on the aluminium.

In the case of using fluorine-containing anions [1], a mixed film of Al_2O_3 and AlF_3 was formed. The distribution and proportion of both compounds depends on the pH (pKa) of the electrolyte. Due to the small amount of water that is present in the IL as an impurity, there is a competition between oxide film-formation and film dissolution reactions during the anodic oxidation in the IL. In more acid solutions, at low potentials, anion oxidation reaction together with insertion of decomposed anion occurs, while at higher potential, dissolution of Al_2O_3 and reaction to form AlF_3 occurs.

Salerno et al. [3] used imidazolium IL as additives (0.01–2 wt%) of an oxalic solution to perform the anodization of pure aluminium, assessing that the addition of IL containing BF_4^- anion in a 1:1 M ratio with the oxalic acid increases the growth rate of anodic porous alumina.

For lithium battery applications, aluminium current collectors have shown less corrosion when IL electrolytes were used instead of traditional organic solvents [4–6]. After the application of a 4.2 V potential during 3 h in a solution of IL containing bis[(trifluoromethyl) sulfonyl] amide as the anion, a passivating film of Al-anion compounds was detected in the inner surface of the Al_2O_3/AlF_3 surface layer.

Recently [7–9], the formation of surface films on magnesium alloy by treatment with ionic liquids (ILs) containing P has been studied. Although initial studies confirmed improvement in the corrosion resistance of magnesium alloys due to the formation of a passivating surface film when immersion in phosphonium IL, this surface film used to be heterogeneous and with defects [9]. Time, temperature, water content of IL and alloy microstructure play an important role in the

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Table 1
Chemical structure of the ionic liquids.

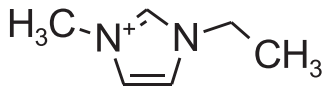
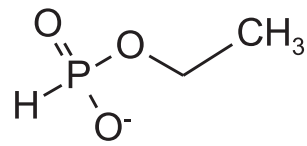
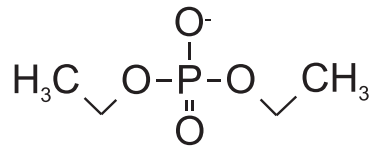
Ionic liquid	Cation	Anions
1-ethyl–3-methylimidazolium ethylphosphonate ([ImPhosphonate])		
1-ethyl–3-methylimidazolium diethylphosphate ([ImPhosphate])		

Table 2
Chemical composition of Al7075 T6.

Element	Si	Fe	Cu	Mn	Mg	Zn	Ti	Cr	Al
Content (wt%)	0.3	0.45	1.5	0.17	2.25	5.5	0.06	0.18	Balance

optimization of the passivation process of the magnesium alloys. In the case of using imidazolium IL with P in the anion [7,8], it has been demonstrated an enhancement of the abrasion and wear resistance of the AZ31B alloy, attributed to the formation of a continuous adhered phosphorus-containing film, mainly composed of magnesium and aluminium phosphates.

Studies on the interaction between ILs and aluminium alloys are limited [10,11]. As far as we are aware, only one previous study [11] attempted the electrochemical etching of AA5083 aluminium alloys, instead of pure aluminium, with ILs. A 2-step anodic treatment with a phosphonium IL as the electrolyte was used, demonstrating the prevalence of an electrochemical etching process.

No previous studies on the effect of electrochemical treating with ILs on the tribological behaviour of aluminium alloys have been reported. The present study was recently presented at a conference [12].

2. Experimental

1-ethyl-3-methylimidazolium ethylphosphonate [ImPhosphonate] and 1-ethyl-3-methylimidazolium diethylphosphate [ImPhosphate] ionic liquids (Table 1) (purity > 98%) were commercially available from Solvionic (France) and used in 20 wt% aqueous solutions, with pH values of 6.6 for [ImPhosphonate] and 3.5 for [ImPhosphate].

Aluminium alloy 7075 T6 was purchased from Alu-Stock S.A. in the form of a 50 mm diameter rod, the elemental composition is listed in Table 2.

Test specimens were machined and cut to a shape of 40 mm diameter and 5 mm thickness. Before the electrochemical tests, aluminium samples were polished to a mean surface roughness (Ra) of 0.15 ± 0.03 µm, measured by a RT ALPA-SM contact profiler, then rinsed in deionized water and isopropanol, dried with air and put in a PTFE minicell [8].

Anodized Al7075 was obtained using a two electrode configuration for the anodic polarization (Fig. 1a), with a Pt wire as the counterpart. A constant voltage of 14 V was applied during 1 h using a solution of 18 wt% of H_2SO_4 in water as electrolyte. The voltage was applied with DC Power Supply SM10010 and data were recorded with a Keysight 34465 Digital Multimeter. The thickness of the Al_2O_3 layer was measured by a coating thickness measuring system QNix 7500, with an average value of 30 ± 5 µm.

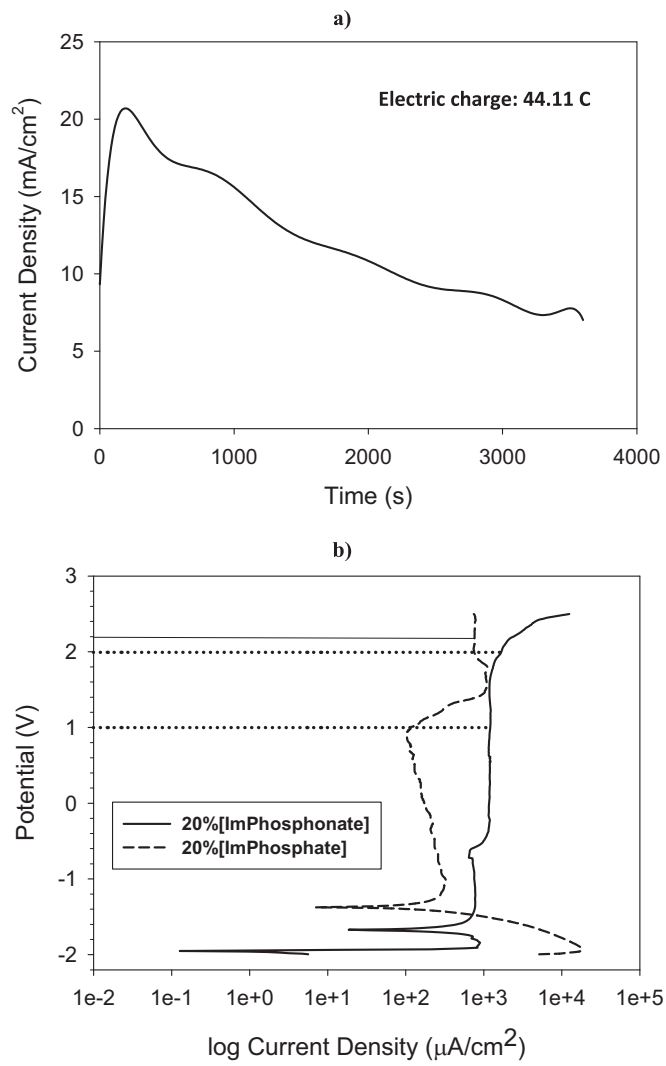


Fig. 1. a) Current density evolution for anodic polarization of Al 7075 T6 in 18 wt% H_2SO_4. Constant Potential of 14 V; b) Potentiondynamic polarization tests for anodized Al7075 in 20 wt% solutions of ILs showing the selected voltages.

Following anodization, the samples were treated by chronoamperometry method. Chronoamperometry tests were performed using a

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