

Abrasion resistance of magnesium alloys with surface films generated from phosphonate imidazolium ionic liquids



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ABSTRACT

Surface films formed by treatment with the ionic liquids (ILs) 1,3-dimethylimidazolium methylphosphonate (LMP101), 1-ethyl-3-methylimidazolium methylphosphonate (LMP102) and 1-ethyl-3-methylimidazolium ethylphosphonate (LEP102) on magnesium alloys have been studied. The abrasion resistance of the coated alloys was studied by microscratching under progressively increasing load, and compared with that of the uncoated materials. Abrasion-protective phosphorus-containing films are generated on AZ31B, with an order of abrasion resistance as a function of the IL of LEP102 > LMP101 > LMP102, with a reduction in penetration depth of a 67% for the sample treated with LEP102 with respect to the uncovered alloy. This is attributed to the formation of a continuous adhered phosphorus-containing film. In contrast, the abrasion resistance of EZ33A alloy is not improved due to the presence of the less reactive Zn-rich phase at the grain boundaries, which prevents the formation of a continuous protective layer. The results are discussed from contact angles, SEM–EDX and XPS analysis.

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1. Introduction

Light metal alloys, such as aluminum, titanium and magnesium based alloys, have been the object of numerous research efforts in order to overcome their major disadvantages with respect to conventional ferrous alloys, that is, their poor tribological performance and, in the case of magnesium alloys, their very poor corrosion resistance.

Phosphonate-containing coatings deposited on AZ31B magnesium alloy have shown an improved corrosion protection performance [1] due to the strong chemical bonding of phosphonate groups to the magnesium substrate. Alkylphosphonate self-assembled films have been developed [2] as degradation reducing and biocompatibility enhancing agents for magnesium alloys for biodegradable implants, where the phosphonate groups show mono-, bi- and tridentate bonding modes with the magnesium alloy surface.

Phosphonate self-assembled monolayers have been shown to improve the tribological performance of aluminum [3] and copper [4] surfaces.

Among many other applications, ionic liquids (ILs) have been extensively studied as lubricants for friction reduction and wear protection [5–15], and as corrosion protection agents either as inhibitors [16–27], or as precursors of protective surface coatings [28–30]. Corrosion protective layers have been developed on magnesium alloys by immersion in ILs and, in most cases, by using electrochemical methods [31–40].

In particular, surface interactions and film formation by ILs on magnesium metal and magnesium alloys, and their corrosion protection performance, have been thoroughly studied by MacFarlane, Forsyth et al. [41]. The most widely studied ILs for corrosion protection coatings have been trihexyl(tetradecyl)phosphonium derivatives with different fluorine or phosphorus-containing anions.

Immersion tests of AZ31 magnesium alloy in the ionic liquid trihexyl(tetradecyl) phosphonium bis(trifluoromethanesulfonyl) amide have shown the formation of a multilayered film, with a thin outer layer of IL-derived species [42]. In the same way, when the AZ31 magnesium alloy was studied under cyclic voltammetry in the ionic liquid tri(hexyl)tetradecylphosphonium-bis 2,4,4-trimethylpentylphosphinate, a phosphorus rich outer layer was formed on a magnesium oxide and hydroxide underlying film [34].

ILs have also shown good tribological performance as lubricants or lubricant additives in aluminum or titanium alloys in sliding systems against metal or ceramic materials [5–15,43–50]. However, even the best lubricants fail to prevent severe wear of magnesium

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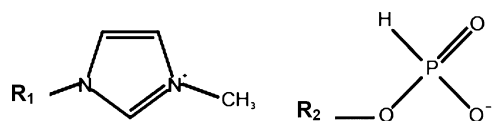


Fig. 1. Chemical structure of phosphonate ILs. [$R_1=R_2=CH_3-$ (LMP101); $R_1=CH_3-CH_2-$, $R_2=CH_3-$ (LMP102); $R_1=CH_3-CH_2-$, $R_2=CH_3-CH_2-$ (LEP102)].

alloys, which need to be protected by surface films for tribological applications [51].

There are no precedents of the use of ILs in surface film formation for the wear protection of magnesium alloys. In the present work, we have studied the ability of three phosphonate imidazolium ILs to create surface layers on two magnesium alloys, in order to improve their abrasion resistance.

2. Experimental

ILs (Fig. 1) with purity >98% were commercially available from Solvionic (France) and used as received. Magnesium alloys AZ31B (3%Al; 1%Zn; 0.6%Mn; 0.1%Si; Mg balance; hardness 57 HV) and EZ33A (2.5–4%Ce; 2–3%Zn; 0.4–1%Zr; 0.1%Cu;

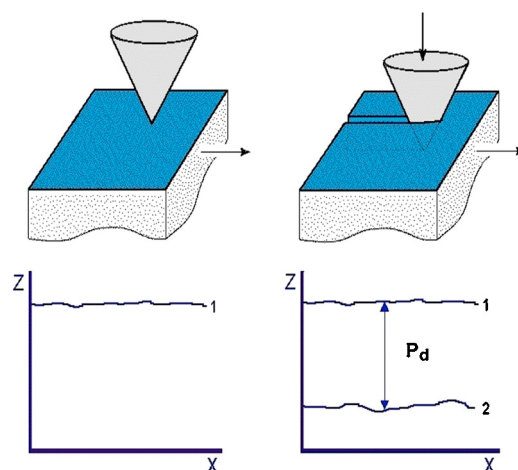


Fig. 2. Scheme of the abrasion scratch test (P_d = penetration depth).

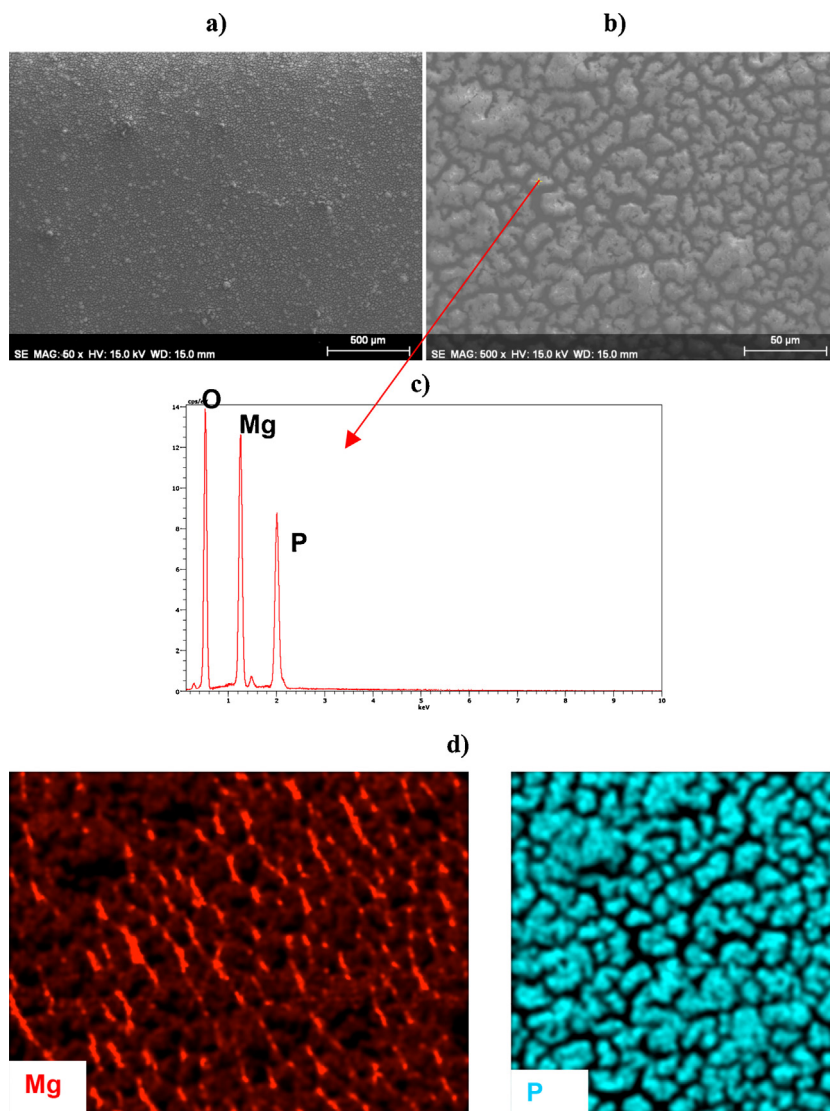


Fig. 3. Surface layer on AZ31B after being covered by LMP101: (a) low and (b) high magnification SEM micrographs; (c) EDX spectrum of the surface coating; (d) magnesium and phosphorus element maps.

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