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Effects of graphite nano-particle additions on dry sliding behaviour of plasma-electrolytic-oxidation-treated EV31A magnesium alloy against steel in air

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ABSTRACT

This work aims at assessing the PEO (Plasma Electrolytic Oxidation) treatment conditions which may lead to an improved tribological behaviour for the Rare Earth-containing Mg alloy EV31A alloy, which is mainly used in aerospace, military and automotive applications. In particular, we investigated the influence of graphite nanoparticles addition and PEO treatment time (30–90 s) on microstructure, friction/wear and corrosion of layers obtained in phosphate/silicate electrolyte. The addition of graphite was investigated because it may limit the typical high friction of PEO/steel contacts. Since no hazardous additives (such as potassium fluoride) were added to this electrolyte, graphite was investigated also as a possible structure densifier. Dry sliding tests were carried out with a block-on-ring tribometer against AISI 52100 steel. The results showed that the addition of graphite decreased friction and wear, due to the formation of a compact, protective, low-shear transfer layer, consisting of iron oxides (due to mild tribo-oxidation of the countermaterial) and amorphous carbon (from the PEO layer). An intermediate treatment time of 60 s, combined with the addition of graphite, led to the growth of PEO layers with the best combination of thickness, compactness, roughness and microhardness, thus leading to the best tribological behaviour.

1. Introduction

Magnesium alloys offer well-established advantages in terms of specific strength, damping capability and suitability for the casting process. They also display good strength and stiffness at both room and elevated temperatures [1]. Mg alloys are also finding an increasing number of applications in orthopaedic devices such as resorbable implants (which provide temporary support for healing tissues and progressively degrade after fulfilling their function), because their mechanical properties are similar to those of the bone, thus avoiding undesired “stress sheltering” or “stress protection” phenomena [2]. However, these benefits may be offset by problems related to the high corrosion rate in many environments (also applications as resorbable implants may require a careful control of corrosion rate and gas evolution) as well as to the low wear resistance of these alloys. In particular, as regards sliding wear behaviour, magnesium alloys suffer from heavy plastic deformation [3,4], but tribological properties may be improved by surface modification. Among surface modification techniques for magnesium alloys, Plasma Electrolytic Oxidation (PEO), also named Micro-Arc Oxidation (MAO), is a well-established solution for the improvement of wear and corrosion behaviour [5]. PEO/MAO is an electrochemical conversion treatment, mainly applied to aluminium, titanium, magnesium and other valve metals, based on the modification of the growing anodic film by spark/arc micro-discharges, initiated at potentials above the breakdown voltage of the oxide film [6]. Even though the PEO treatment generally improves wear and corrosion resistance, the production of a hard and rough PEO surface layer may lead to an increase of the abrasive component of friction and may induce damage of the countermaterial [5,7,8]. In the particular case of Mg alloys, the increase of coefficient of friction due to the PEO treatment is particularly evident, because untreated Mg alloys tend to display relatively low friction (generally about half as large as those typical for steel-on-steel sliding under similar conditions), due to the hexagonal crystal structure of Mg that permits shearing on the basal planes [4]. Therefore, several papers deal with low-friction modifications of PEO coatings, obtained by incorporation of solid lubricant particles in PEO layers [8–12]. In the case of graphite particles added to PEO layers and grown on pure Al, the addition of graphite particles proved to be

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increasingly beneficial with decreasing particles size [10]. However, in the case of magnesium alloys, there are no published reports, to our knowledge, regarding the addition of graphite particles in the PEO layers, apart from our previous paper on the AZ80 and AZ91 alloys [13]. Therefore, in this work, we report on the influence of graphite nanoparticles and treatment time on microstructure, friction and wear of the PEO-treated EV31A magnesium alloy. Friction and wear tests were carried out against AISI 52100 steel, which is a frequently used reference for dry sliding tests, also in the case of untreated [4] or surface-treated Mg alloys, either by PEO [5,14,15] or by other surface treatments [16]. Moreover, the influence of graphite nanoparticles on corrosion behaviour was evaluated by potentiodynamic polarization tests in 3.5 wt% NaCl.

The Mg alloy investigated in the present work is a Rare Earth (RE) containing alloy, EV31A (Elektron 21®), which is mainly used in military and aerospace applications. Nd and Gd are added in this alloy as main alloying elements, up to 3.1 and 1.7 wt%. respectively. In fact, the addition of RE metals improves both the mechanical properties of Mg alloys and their corrosion resistance [17]. RE alloy additions also have a beneficial effect on the growth rate of the anodic oxide during PEO/MAO treatment [18]. Moreover, EV31A contains Zr because of its grain refining ability and Zn because of its beneficial influence on mechanical properties, as well as on the mitigation of corrosive effects of Fe and Ni impurities [19].

In this work, the PEO treatment was carried out in a phosphate/silicate electrolyte, at relatively high current densities (0.5 A cm^{-2}) and short treatment times (30–90 s). It is worth mentioning that this electrolytic bath is a fluoride-free solution: even though the addition of potassium fluoride to silicate [20] or to silicate-borate [21] solutions improves the compactness of the coating (due to improved electrolyte conductivity, inducing better spark discharge conditions, as well as to modified phase composition of the PEO layer), fluoride-containing industrial wastewaters must be treated because of health and environments risks related to the high affinity towards calcium in living structures. Therefore, in the present work, rather than using electrolyte additives with a detrimental impact on environment and health such as potassium fluoride, we investigated the role of graphite particles, suspended in the aqueous electrolyte, also as possible structure densifiers of the PEO layers (in addition to their lubricating ability).

2. Materials and methods

The Mg alloy EV31A, treated by Plasma Electrolytic Oxidation (PEO), was provided by Magnesium Elektron® as sand-cast plates, in the T6 condition. Small bars ($5 \times 5 \times 80$ mm^3) were cut from plates. The standard T6 heat treatment consists of the following steps: solutioning at 520 °C for 8 h, quenching in 70 °C water, aging at 200 °C for 16 h. The chemical composition of the EV31A alloy is reported in Table 1.

Before PEO treatment, the EV31A samples were polished by standard metallographic techniques and then degreased in ultrasonicated acetone. The fluoride-free PEO electrolyte was an alkaline solution with 50 g L^{-1} of $Na_5P_3O_{10}$, 50 g L^{-1} of Na_2SiO_3, 40 g L^{-1} of NaOH in deionised water. The absence of fluorides salts in the electrolyte was compensated by slightly increasing the anodizing cell voltage, as demonstrated by Da Forno and Bestetti [22]. Graphite nanoparticles (average size < 100 nm, supplied by Sigma-Aldrich, product number 633100), were dispersed in acetone before their addition to the electrolyte by using sodium dodecyl sulphate (0.5 g L^{-1}) as surfactant. The concentration of graphite nanoparticles was 3 g L^{-1} for all the samples obtained at different treatment times (as listed in Table 2). Actually, as proved by investigations reported in a previous work [13], graphite nanoparticles tend to form micrometric-sized agglomerates. The plasma electrolytic oxidation process was carried out in DC mode using a TDK-Lambda DC power supply of 400 V/8 A capacity. During the treatment, the sample worked as the anode, whilst the cathode was a steel mesh. The electrolyte was magnetically stirred during the treatment and maintained at room temperature by a cooling bath. The PEO treatments were performed by maintaining a constant current of 0.5 A cm^{-2} and allowing voltage variations. The treated samples and treatment conditions are summarised in Table 2.

Table 2
Samples and PEO treatment conditions.

Substrate	*Sample name*	*PEO treatment time (s)*	*Graphite nanoparticles*
EV31A	60 s	60	–
	30 s + C	30	3 g L^{-1}
	60 s + C	60	3 g L^{-1}
	90 s + C	90	3 g L^{-1}

2.1. Microstructural and mechanical characterization

Microstructural characterization of the untreated EV31A alloy was carried out by standard metallographic techniques. Etching with Picral (4 vol% Picric Acid in Ethanol) or acetic Picral (5 mL Acetic Acid, 6 g Picric Acid, 10 mL Water, 100 mL Ethanol) was performed to highlight grain structure and precipitates inside the grains of the EV31A Mg alloy. Surface and cross-sectional observations of the PEO-treated specimens were carried out by scanning electron microscopy (SEM, Zeiss EVO 50) in low vacuum mode.

The phase constitution of the PEO layers was determined by X-ray diffraction (XRD), performing θ–2θ scans from 20° to 90° with a 0.05 step size and a 5 s dwell time, by a Siemens D500 X-ray diffractometer with a Ni-filtered Cu-Kα radiation source (λ = 0.15405 nm), operated at 40 kV and 30 mA.

Raman spectra were recorded by a Renishaw InVia micro-spectrometer, coupled with a Leica DMLM microscope, using the 50 mW Ar^+ laser (wavelength: 514.5 nm) as excitation source and employing low laser powers to avoid sample degradation (full power 50 mW, reduced with different filters). The laser was focused on spots of about 2 µm diameter.

XPS analysis were run on a Perkin-Elmer Φ5600ci spectrometer using standard Al K_α radiation (1486.6 eV) working at 250 W. The working pressure was $< 5 \cdot 10^{-8}$ Pa. The spectrometer was calibrated by assuming the binding energy (BE) of the $Au4f_{7/2}$ line at 83.9 eV with respect to the Fermi level. The standard deviation for the BE values was 0.15 eV. The reported BE were corrected for the charging effects, assigning, in the outer layers where contamination carbon is still present, to the C1s line of carbon the BE value of 284.6 eV [23]. Survey scans (187.85 pass energy, 1 eV/step, 25 ms per step) were obtained in the 0 – 1300 eV range. The atomic composition, after a Shirley type background subtraction [24], was evaluated using sensitivity factors supplied by Perkin [25]. The assignments of the peaks were carried out by using the values reported in the reference handbook [25], in the NIST XPS Database [26].

Topographic measurements were carried out on coating free

Table 1
Chemical composition (wt%) of EV31A (*ORE = other rare earths); ORE concentration refers to the total of cerium, lanthanum and praseodymium, as specified by the SAE AMS 4429 A standard.

Nd	*Gd*	*Zr*	*Zn*	*Fe*	*Ni*	*Cu*	*Si*	*Ag*	**ORE*	*Mg*
2.8	1.3	0.56	0.29	0.003	< 0.0010	< 0.008	< 0.01	< 0.1	< 0.14	Bal.