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High-compactness coating grown by plasma electrolytic oxidation on AZ31 magnesium alloy in the solution of silicate–borax

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A B S T R A C T

A ceramic coating was formed on the surface of AZ31 magnesium alloy by plasma electrolytic oxidation (PEO) in the silicate solution with and without borax doped. The composition, morphology, elements and roughness as well as mechanical property of the coating were investigated by X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive X-ray spectrometry (EDS), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and reciprocal-sliding tribometer. The results show that the PEO coating is mainly composed of magnesia. When using borax dope, boron element is permeating into the coating and the boron containing phase exist in the form of amorphous. In addition, the microhardness and compactness of the PEO coating are improved significantly due to doped borax.

1. Introduction

Magnesium alloy as the lightest engineering metal material, owing to its high strength to weight ratio, better electrical conductivity and high thermal conductivity as well as excellent machinability, has been widely used in aerospace, automobile and electronic communication industry [1–4]. However, some difficulties still exist for magnesium and its alloys to obtain extensive applications. The main reason is that the potential of magnesium is the most negative one among engineering metal materials. Therefore, magnesium has very high chemical reaction activity, and easy forms an oxide film on its surface at room temperature, but the oxide film is mainly composed of amorphous magnesia, and it is very easy detached from the substrate during the friction process. This will result in the occurrence of re-oxidation in the shedding position, thus produce oxidation wear [5,6], which limits greatly the applications of magnesium and its alloys in aerospace and other fields. In order to improve the tribological property of magnesium alloy, the surface modification has become an effective way to expand the application of magnesium alloy [7,8]. PEO is a new surface treatment technology developed based on anodic oxidation [9–11]. PEO is also called as micro arc oxidation (MAO) or anodic spark deposition (ASD) [12–14]. During the PEO process, the sample employed as anode was totally immersed in the stainless steel container which was filled with electrolyte, and the stainless steel container was served as the counter electrode. When high voltage is applied between working electrode and cathode, intense plasma electrolytic discharge takes place on the surface of the sample. Under the joint action of high temperature, high voltage and electrochemical reaction, a layer of new PEO coating was formed on the surface of the working electrode [15–17]. The anions in the electrolyte and metallic cations entered the ceramic coating, therefore, the components of ceramic coating changed significantly by high energy. Compared with conventional anodizing treatments, PEO technology can obviously improve the surface properties of magnesium alloys, such as wear resistance [18,19], corrosion resistance, and especially the adhesive force between the coating and the substrate. However, PEO coating is porous, thus the corrosion resistance and the mechanical performance of the coating is not still enough to date [20–22,5,23,24]. In this paper, the ceramic coating with high hardness and compactness has been prepared on the AZ31 magnesium alloy surface by PEO technique. In addition, the composition, morphology, mechanical and tribological properties of the PEO coating and the borax-doped PEO coating were studied, respectively.

2. Experimental

2.1. Preparation of PEO coating

Polished square sample (with dimensions 40 mm × 40 mm × 3 mm) made of AZ31 magnesium alloy (mass fraction: Al 2.5%, Zn 0.8%, balance magnesium) was used as the

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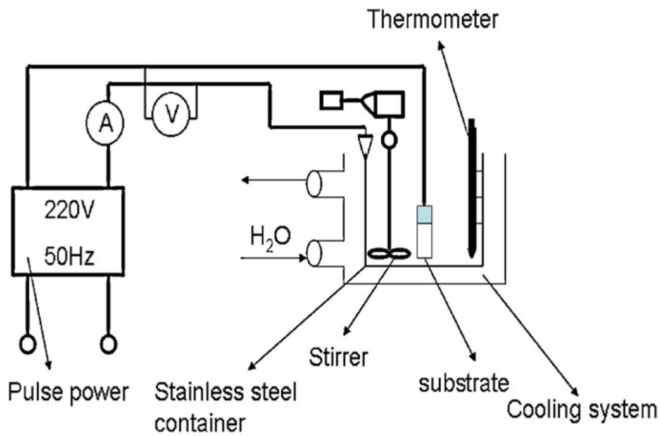

Fig. 1. Schematic diagram of the experimental setup.

substrate material. A homemade pulsed bi-polar electrical source with a power of 5 kW was used for surface treatment of magnesium alloy in a container made of stainless steel. The container was served as the counter electrode and magnesium alloy sample was employed as the anode. The reaction temperature was controlled below 40 °C by a cooling water flow. The electronic power frequency was fixed at 50 Hz. The duty ratios of both pulses were equal to 35%. The PEO electrolyte is mainly composed of sodium silicate (10 g/L) and potassium hydroxide (4 g/L), moreover, the borax doped one is mainly composed of sodium silicate (10 g/L), potassium hydroxide (4 g/L) and borax (3 g/L). The whole PEO process was carried out for 10 min under the current density of 5 A/dm^2. After PEO treatment, the coated samples were washed with water and dried in the air. The experimental setup is shown in Fig. 1.

2.2. Structure and performance analysis of PEO coating

The crystalline phase of the coating was studied by the X-ray diffraction (XRD) with a Cu Kα source, and the surface morphology was observed on a scanning electron microscopy (SEM; Hitachi S-570). In addition, the composition of the prepared coating was determined through the energy dispersive X-ray spectrometry (EDS) and X-ray photoelectron spectroscopy (XPS; PHI 5700 ESCA System,USA) with an Al Kα source (1486.6 eV). The digital Instruments Nanoscope III atomic force microscope (AFM) was applied to analyze the surface structure of the obtained coating, and the root mean square roughness was calculated and the effect of borax-

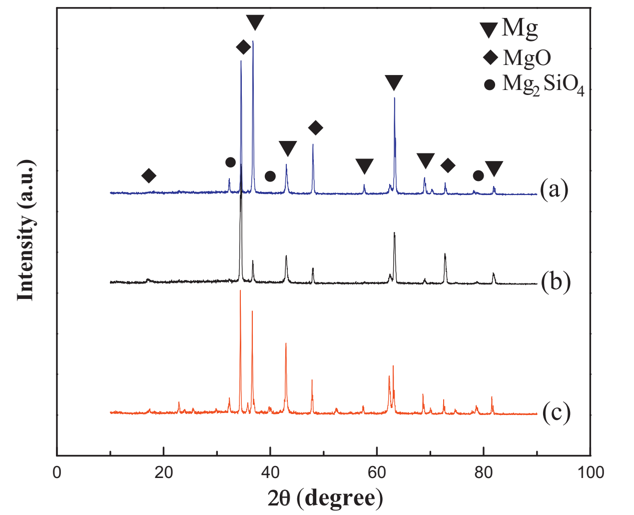

Fig. 2. XRD patterns of the samples of (a) PEO coating, (b) magnesium alloy substrate and (c) borax doped PEO coating.

doped on the surface morphology of the coating was investigated [25]. Nano-indentation measurement system was used to evaluate the hardness of PEO coating, and the elastic modulus and hardness values were derived from the load-displacement curves according to the method used by Oliver and Pharr [26]. The friction coefficient of the PEO coating was tested by a reciprocal-sliding tribometer (Center for Tribology, HIT, China). The unlubricated sliding was performed with the load of 5 N at the sliding speed of 50 mm/s and sliding amplitude of 20 mm at the ambient temperature and humidity. A computer connected to the tester recorded the friction coefficient curves. The test methods and conditions of the wear rate may reference to our previous reports [27].

3. Result and discussion

3.1. Phase and element composition of the PEO coating

Fig. 2 shows the X-ray diffraction patterns of the samples of (a) the PEO coating, (b) magnesium alloy substrate and (c) the borax doped PEO coating. As compared with the PEO coating of (a), the borax doped PEO coating has no obviously change in the crystalline phase, and the prepared coatings are mainly composed of crystalline magnesia phase. Unexpectedly, it can be noticed in Fig. 2(c) that no peak associated with crystalline boron appears

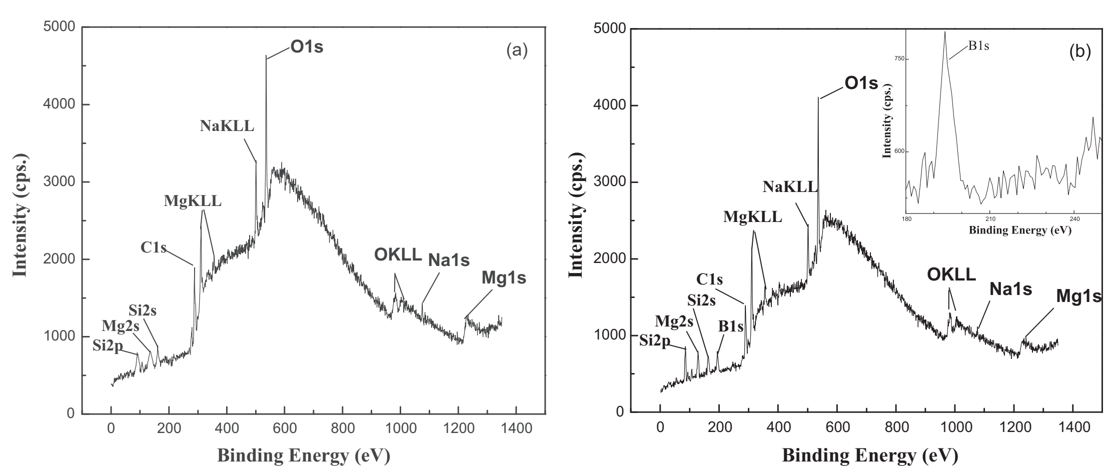

Fig. 3. XPS spectra of (a) PEO coating and (b) borax doped PEO coating.