



Effect of icosahedral phase on growth behavior of thin oxide film on MgZn₁₂Y_{1.7} alloy via micro arc oxidation

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ABSTRACT

The effect of the icosahedral phase on the growth behavior of the thin oxide film coated on MgZn₁₂Y_{1.7} alloy sample by micro arc oxidation (MAO) was studied. During MAO coating in a phosphate electrolyte with a current density of 25 mA/cm², the responding voltage of the present sample gradually increased as the coating time increased up to 80 s. The surface structure observations indicated that the thin oxide film was prone to be formed more easily on the top of the icosahedral phase than on that of the α-Mg phase matrix in the MgZn₁₂Y_{1.7} alloy sample. This implies that the growth rates of the thin oxide films were different and were also enhanced on the icosahedral phase, which could be explained by the low electrical conductivity of the icosahedral phase itself leading to appreciable micro arcs during MAO coating.

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1. Introduction

In recent years, much attention has been focused on the development of light Mg alloys because of their frequent use in the electronics and automobile industries where weight reduction is most required [1–3]. In spite of their high specific strength, however, Mg alloys are known to be easily corroded in actual conditions, especially in a corrosive environment, due to internal galvanic attack [4–6]. For this reason, it is necessary to protect Mg alloys against corrosive environments. One of the most reliable methods of improving the corrosion-protection properties of Mg alloys is to add metal elements, forming a quasi-crystal phase showing high corrosion resistance. Based on their electrochemical analysis, Shi et al. reported that when the stable icosahedral phase with a quasiperiodic atomic structure was introduced into Mg–Zn alloys, their corrosion protection capability was greatly improved [7]. Nevertheless, in spite of the beneficial effect of the icosahedral phase, a method of overcoming corrosion problem needs to be introduced due to the weak corrosion characteristics of the α-Mg phase which acts as the main matrix in Mg–Zn alloys.

For this purpose, various surface coating methods such as electrochemical plating, anodizing, and micro arc oxidation (MAO) have been applied to form a thin oxide film in order to improve the corrosion resistance [8–11]. The MAO coating is one of the electrochemical surface

treatments that can form an oxide film on various metallic materials by generating local melting with the aid of a micro scale plasma when extremely high voltages are applied to an electrochemical cell [12,13]. Earlier investigations using this process demonstrated that strong passivation films with a micro length scale were formed, depending on the processing variables such as the electrolyte, electrical parameters, and post-treatment [14–17]. There have been numerous reports on the MAO coating of conventional Mg alloys, but few have demonstrated the formation of the oxide film of the Mg–Zn–Y system involving the icosahedral phase during the MAO process. In addition, the growth mechanism of the oxide film has not been elucidated yet. Herein, we investigated the different growth behavior of the α-Mg and icosahedral phases on the Mg–Zn–Y system at the initial stage of MAO coating up to 80 s, in order to provide a better understanding of the variation of the coating characteristics of the present alloy with respect to the coating time.

2. Experimental procedure

The MgZn₁₂Y_{1.7} alloy sample used in this study was prepared by melting high purity 99.9% Mg, 99.9% Zn, and 99.95% Y under a high purity Ar atmosphere in order to avoid the addition of impurities [18]. As shown in Fig. 1, the initial MgZn₁₂Y_{1.7} alloy sample etched in acetone solution consisted of two phases: the primary α-Mg phase as the matrix and the icosahedral phase as a separate eutectic area formed between the α-Mg dendrites [19]. The inset of Fig. 1 displays the selected-area electron diffraction pattern of the icosahedral

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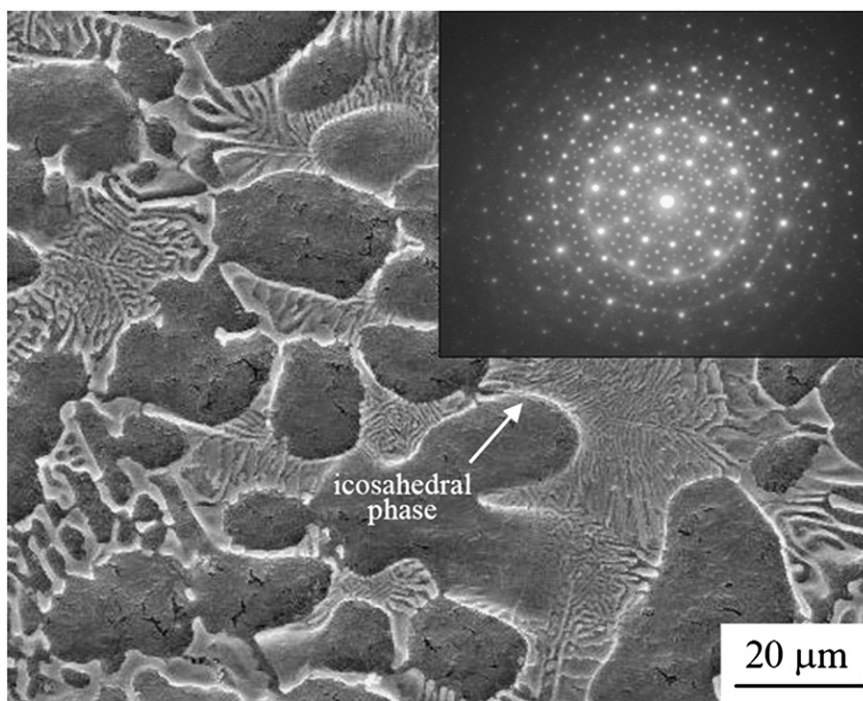


Fig. 1. Initial microstructure of $\text{MgZn}_{12}\text{Y}_{1.7}$ alloy sample used in this study. Inset indicates the selected area diffraction pattern of the icosahedral phase.

phase. The present pattern contained a five-fold symmetry of the diffraction spots which was known to be typical for the icosahedral phase [20,21]. Prior to the MAO coating, the samples were cut into $25 \times 20 \times 2$ mm plates, polished with #1000 SiC papers, rinsed with distilled water, and ultrasonically cleaned in ethanol. The MAO coating process was carried out using a 20 kW power supply, an acrylic-vessel container with a sample holder and a cathode composed of stainless steel mesh whose distance from the anode was 50 mm in the alkaline electrolyte consisting of 0.09 M KOH + 0.05 M KF + 0.01 M $\text{K}_4\text{P}_2\text{O}_7$. The applied current density was held at 25 mA/cm^2 for 80 s. The surface and cross-sectional images of the MAO-treated samples were obtained using field-emission scanning electron microscopy (FE-SEM, HITACHI S-4800) operated at an accelerating voltage of 15 kV. An energy dispersive X-ray spectroscopy (EDS, AMETEK Genesis APEX2) equipped in FE-SEM was also used to inspect the distribution of the chemical elements in the MAO-coated samples. The elemental mapping was performed on the area of $20 \times 20 \mu\text{m}$ in sample. The constituent phases in the MAO-coated samples were observed by X-ray diffraction (XRD, RIGAKU D/MAX-2500/PC) operating at voltage of 40 kV. The chemical compounds present in the oxide film were detected by X-ray photoelectron spectroscopy (XPS, VG microtech ESCA 2000) with monochromatic Al K α (1486.6 eV) X-ray source, beam size of $400 \mu\text{m}$ diameter and a 90° take-off angle.

3. Results and discussion

The surface structure and oxide formation on the $\text{MgZn}_{12}\text{Y}_{1.7}$ alloy sample processed by MAO coating for coating times of up to 80 s are shown in Fig. 2. As shown in Fig. 2(a), the surface morphology of the sample coated for 40 s was nearly the same as that of the initial sample (Fig. 1), due to the short immersion time of the sample within the electrolyte during MAO coating, where the responding voltage was around ~ 128 V. In this study, the breakdown voltage, starting from which the micro arcs started to appear, was observed to be ~ 150 V. Thus, no appreciable oxide nodules were detected. When the responding voltage exceeded ~ 176 V, the oxide nodules and micro pores caused by the micro arcs appeared mainly on top of the

icosahedral phase region, as shown in Fig. 2(b). It is known that when the current density is initially imparted, abundant oxygen bubbles are electrochemically produced at the interface between the electrolyte and the anode substrate, resulting in the formation of a very thin passivation film. As the coating time increases, however, the strong electric field between the anode substrate and the passivation film reaches a critical point, beyond which the passivation film is broken, due to the impact and/or tunneling ionization and, therefore, oxide nodules are readily formed by electrochemical reactions assisted by micro arcs. As a result, the oxide formation on top of the icosahedral phase is different from that found on the α -Mg phase, since the electrical conductivity of the icosahedral phase is forty times lower than that of the α -Mg phase, leading to the preferential occurrence of noticeable micro arcs on the icosahedral phase during MAO coating, particularly in the case of Mg alloys containing Zn–Y elements [22]. At a responding voltage of ~ 214 V, micro arcs were produced and thermal ionization also occurred. It was clear that, in terms of the oxide formation, there was a significant difference between the α -Mg and icosahedral phases of the MAO-coated $\text{MgZn}_{12}\text{Y}_{1.7}$ alloy sample as shown in Fig. 2(c). In addition, the average size of the micro pores in the thin oxide film formed on the icosahedral phase was larger than that on the α -Mg phase.

To examine the growth behavior of the thin oxide films on the two different phases in $\text{MgZn}_{12}\text{Y}_{1.7}$ alloy as a function of the coating time, the cross-sectional images of the present samples were obtained, as shown in Fig. 3, and Table 1 lists their thickness values obtained from Fig. 3. The white area in Fig. 3 is the icosahedral phase, while the dark area indicates the α -Mg phase. Fig. 3(a) displays the cross-sectional image of the sample coated for 40 s, revealing that, regardless of the constituent phases in the $\text{MgZn}_{12}\text{Y}_{1.7}$ alloy, the presence of thin oxide films formed by micro arcs was barely detected. At a coating time of 60 s, a thin oxide film appeared on the icosahedral phase, as shown in Fig. 3(b). The thickness values of the oxide films on the α -Mg and icosahedral phases were measured to be ~ 0.5 and $\sim 1.0 \mu\text{m}$, respectively. When the coating time reached 80 s, the entire sample surface was fully covered with the oxide film, as shown in Fig. 3(c). This different growth behavior was attributed to the difference in the electrical resistivity of

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