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Microstructure and electrochemical corrosion behavior of extruded Mg–Al–Pb–La alloy as anode for seawater-activated battery

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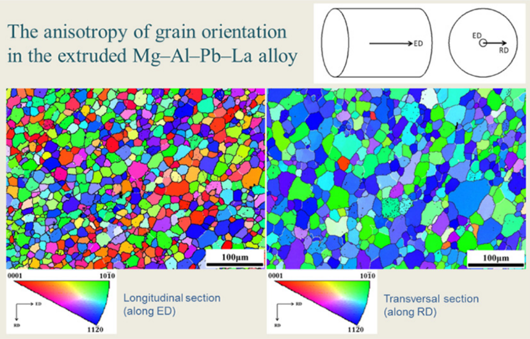
HIGHLIGHTS

- Extrusion improves the discharge activity of Mg–Al–Pb–La alloy.
- The relation between grain orientation and electrochemical corrosion behavior is clarified.
- The extruded Mg-Al-Pb-La alloy is an appropriate anode for seawater-activated battery.

GRAPHICAL ABSTRACT



The anisotropy of corrosion resistance in the extruded Mg–Al–Pb–La alloy is associated with grain orientation. The longitudinal section along extrusion direction (ED) has a high proportion of low-energy (0001) planes and exhibits better corrosion resistance than the transversal section along radial direction (RD).

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ABSTRACT

A seawater-activated battery is a disposable reserve battery that is specifically designed to pollute less due to the absence or relatively less use of heavy metals. Mg–Al–Pb–La alloy is a typical anode material that is used in high-power seawater-activated batteries. In this study, we use microstructure characterization to demonstrate that hot extrusion refines the grains of the alloy and leads to the formation of banded structures composed of the lamellar β-$Al_{11}La_3$ and lump Al—Mn phases. Our electrochemical measurements reveal that the extruded Mg–Al–Pb–La alloy is a promising anode material that exhibits excellent discharge activity and high anodic efficiency at a large current density. Moreover, we also examine the correlation between the grain orientation induced by extrusion and the electrochemical corrosion behavior of Mg–Al–Pb–La alloy. We believe that our results can significantly contribute to the development of seawater-activated batteries.

1. Introduction

Magnesium alloys with high energy density, negative standard electrode potential, and large capacity can serve as anodes for seawater-activated batteries, magnesium-air batteries, dissolved-oxygen batteries, etc. [1–5]. In this backdrop, magnesium-based anodes such as Mg–Hg–Ga, Mg–Al–Pb, and Mg–Al–Tl with high cell voltages have recently been developed [6]. Mg–Al–Pb alloy has been widely used in high-power seawater-activated batteries, particularly the AP65 alloy that has a negative corrosion potential and a nominal composition of Mg-6%Al-5%Pb (wt%) [6].

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A seawater-activated battery is composed of two indispensable parts: a metal anode and a metal chloride cathode made of compounds such as AgCl and CuCl, and such batteries can be used as potential power sources for undersea devices including sonobuoys and electric torpedoes [7,8]. However, magnesium alloys are susceptible to self-corrosion, and the alloy surface is often covered with corrosion products after discharge, which undermines their discharge performance [8–12]. Thus, there is a trade-off between activation and passivation for magnesium. The choice of a suitable magnesium anode significantly impacts the properties of seawater-activated batteries [3,8]. The commonly utilized methods to further improve the properties of magnesium are alloying, plastic deformation, and heat treatment [5,10,12,13].

Rare earth elements (REs) have been found to be suitable candidate elements for alloying with magnesium, since they offer the functionalities of melt purification, lattice distortion, and cathode passivation [12,14,15]. In this regard, Hu et al. [16] reported that the addition of cerium to AP65 alloy led to the refinement of β ($Mg_{17}Al_{12}$) phases and the formation of Al–Ce phases, which significantly enhanced the electrochemical properties of AP65 alloy. Further, Mg–Al–Pb–Ce–Y alloy was found exhibit improved corrosion resistance and discharge performance over those of pure magnesium, AZ31, and Mg–Al–Pb alloys because of the modified microstructures induced by the REs [4]. In addition, lanthanum-containing magnesium alloys such as AE21 and AE42 have been developed as commercial alloys [17]. In this regard, Feng et al. [6] determined that the discharge activity and corrosion resistance of AP65 alloy were enhanced by the addition of lanthanum, which can be mainly attributed to the refined grains and the increasing amount of weak cathodic rare earth phases. Meanwhile, it has been reported that plastic deformation, such as hot extrusion, can significantly change the microstructure of magnesium, exerting an obvious effect on its properties [8,18]. Generally, hot extrusion leads to a deterioration in the corrosion resistance because of the rearranged β ($Mg_{17}Al_{12}$) phases, deformed grains, and increased density of crystal defects, which are strongly supported by many reports [18–20]. However, Jeong et al. [21] found that the corrosion resistance of a Mg-Ca alloy with Ca ≥ 1% was enhanced by extrusion, which was closely related to the effective break-up of Mg_2Ca phases. A similar effect was found by Minárik et al. [17] for an equal channel angular pressed (ECAPed) AZ42 alloy. Moreover, the discharge activity and anodic efficiency of AP65 alloy can be improved via hot extrusion due to the refined grains and uniform grain size according to Wang et al. [8]. It is noting that plastic deformation often gives rise to variations in grain orientation, which in turn has an obvious effect on the electrochemical corrosion behavior of magnesium [7,22,23]. Until recently, however, most reports focused on crystal defects and second phases, and grain orientation has rarely been taken into consideration. It has been reported that grains with basal orientation exhibited better corrosion resistance than those with non-basal orientation for polycrystalline pure magnesium [24]. The rolling surfaces of the rolled AZ31 and AP65 alloys have a much higher proportion of basal crystal planes, and thus, they usually exhibit relatively better corrosion resistance than a cross-sectional surface, owing to the lower surface energy of the basal planes [7,22,24].

In our study, we prepared Mg–Al–Pb–La alloy to analyze the effects of hot extrusion on the alloy's microstructure and electrochemical corrosion behavior. In addition, we especially examined the effects of crystal orientation, grain defect, and second phase in detail.

2. Experimental detail

2.1. Materials preparation

Mg-6%Al-5%Pb-1%La (wt%) alloy (referred to as AP65-La) was prepared by melting and casting using an induction furnace under the protection of an argon atmosphere at 750 °C. The alloying elements (Al, Zn, and Pb) were added in the form of pure metals (99.99 wt%), while other elements such as Mn and La were added via intermediate alloys, i.e., Al-15%Mn and Mg-30%La (wt%). Next, the molten metal was poured into an iron mold with a diameter of 120 mm under the protection of sulfur powder. Table 1 lists the chemical composition of AP65-La alloy as analyzed with inductively coupled plasma atomic emission spectrometry. Next, progressive solution treatments at 330 °C for 16 h and then 420 °C for 2 h were performed for the as-cast AP65-La alloy followed by water quenching. The as-quenched AP65-La alloy was preheated at 450 °C for 18 h. Subsequently, it was extruded into a rod with a diameter of 40 mm at an extrusion speed of 3 m min^{-1} and an extrusion ratio of 9:1. Thereafter, the extruded alloy was air cooled.

Table 1
Chemical composition of the as-quenched AP65-La alloy (wt%).

Element	Al	Pb	La	Zn	Mn	Fe	S	P	Mg
Content	5.600	4.760	0.910	0.540	0.089	0.006	0.003	0.001	Bal.

2.2. Microstructure characterization

Optical microscopy, scanning electron microscopy (SEM), electron probe microanalyses (EPMA), and electron backscatter diffraction (EBSD) were employed to characterize the microstructures of AP65-La alloys before and after extrusion. The longitudinal section along the extrusion direction (ED) and the transversal section along the radial direction (RD) of the extruded alloy are shown in Fig. 1.

The specimens used for metallographic observations were ground with SiC abrasive paper followed by diamond polishing, and then etched in a solution consisting of 3 g picric acid, 2.5 mL acetic acid, 50 mL ethanol, and 5 mL distilled water. The average grain sizes of the alloys were evaluated by means of the linear intercept method using Nano Measurer 1.2 software. The number of grains taken into account was 200 before and after extrusion, respectively. The EBSD was carried out under SEM condition, and the thin foils used for EBSD observation were pared down to 500 μm with an electron discharge cutter, and then ground to a thickness of 70 μm with SiC abrasive paper. Finally, the thin foils were ion-milled with ion incident angle of 3° using an ion beam thinner to remove the surface stress layer. The corrosion morphologies after cleaning of the corrosion products were monitored after 72 h of immersion in 3.5 wt% NaCl aqueous solution. The 3.5 wt% NaCl solution was prepared with analytical grade chemicals and distilled water to simulate seawater [7,8].

2.3. Weight loss measurements

The specimens used for weight loss measurements were ground and weighed using a digital balance with the precision of 0.1 mg to obtain the original weight. Next, the specimens were immersed in 3.5 wt% NaCl solution for 72 h at (25 ± 1)°C. Finally, the specimens were cleaned with chromic acid, dried by hot air flow, and reweighed to obtain the weight loss and weight loss rate.

2.4. Electrochemical measurements

The corrosion behavior at the open-circuit potential (OCP) and the discharge performance of AP65-La alloys before and after extrusion

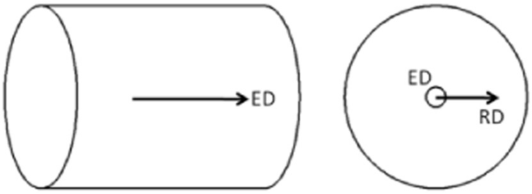

Fig. 1. Sampling directions in the extruded AP65-La alloy. The ED is extrusion direction and the RD is radial direction, respectively.