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Scripta Materialia 56 (2007) 597–600
Scripta MATERIALIA
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Converting hcp Mg–Al–Zn alloy into bcc Mg–Li–Al–Zn alloy by electrolytic deposition and diffusion of reduced lithium atoms in a molten salt electrolyte LiCl–KCl

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Received 15 September 2006; revised 11 December 2006; accepted 18 December 2006
Available online 11 January 2007

A body-centered cubic (bcc) Mg–12Li–9Al–1Zn (wt.%) alloy was fabricated in air by electrolysis from LiCl–KCl molten salt at 500 °C. Electrolytic deposition of Li atoms on cathode (Mg–Al–Zn alloy) and diffusion of the Li atoms formed the bcc Mg–Li–Al–Zn alloy with 12 wt.% Li and only 0.264 wt.% K. Low K concentration in the bcc Mg alloy strip after the electrolysis process resulted from 47% atomic size misfit between K and Mg atoms and low solubility of K in Mg matrix.

Keywords: Mg–Li alloy; Electrolysis; Deposition; Diffusion; hcp → bcc

Magnesium alloys have the lowest density (1.74 g cm^{-3}) of all metallic constructional materials [1]. The alloys are attractive for use in fuel economical vehicles [2]. However, Mg alloys exhibit poor formability at room temperature, which limits their use because, among other reasons, their crystal structures are hexagonal close-packed (hcp). Adding over 10.3 wt.% lithium transforms the hcp structure of the magnesium to a body-centered cubic (bcc) lattice, substantially increasing the ductility of the alloy and reducing its density [3,4]. Adding Al increases the strength of Mg–Li alloys [5–7]. Mg–Li and Mg–Li–Al alloy thin foils can be used as anodic materials in magnesium battery systems [8,9]. The standard way to produce Mg–Li based alloys is vacuum metallurgical technique, using argon gas [7,8,10,11]. A high-frequency electric induction furnace that is mounted in a vacuum chamber is typically required [7]. Mg–Li and Mg–Li–Al ingots then undergo heavy hot and cold rolling into thin sheets or foils [10,11]. Although a vacuum-based metallurgical process for Mg–Li alloys has been developed [7,8,10,11], little is known about fabricating a bcc Mg–Li–Al alloy strip in air [12]. This work aims to form a Mg–Li–Al–Zn alloy strip (2.3 mm thick) in air, rather than by vacuum metallurgy. In this study, electrolysis was performed at 500 °C to convert a 2 mm-thick hcp Mg alloy to bcc Mg alloy, and the rolling of the Mg–Li–Al–Zn alloy strip was examined. The tensile properties of the rolled-strip were reported.

The molten LiCl–KCl salt was electrolyzed in air at 500 °C. The electrolyte was a mixture of 45 wt.% LiCl and 55 wt.% KCl. AZ91 Mg–Al–Zn alloy was used as a cathode material, with composition 8.8 wt.% Al, 0.65 wt.% Zn, 0.18 wt.% Mn, 0.01 wt.% Si, 0.0017 wt.% Fe, 0.0021 wt.% Cu, 0.0006 wt.% Ni, 0.003 wt.% Na and 0.004 wt.% K. The cathodic strip sample was 2 mm thick, 25 mm wide and 90 mm long. A graphite bar was adopted as the anode. Figure 1 schematically depicts the configuration of the electrolytic cell. The following three-step electrolysis was performed, using a DC power supply unit, which applied a current to the electrolytic cell. First, the electrolysis current was set to 3 A (~3.88 V) for 1 h. Then, the current was maintained at 2 A (~3.75 V) for another 1 h. The current was then reduced to 1 A (~3.65 V) to complete the final electrolysis for 20 min. X-ray diffraction analysis was performed using Cu Kα radiation at 40 kV at a scanning speed of 1° min^{-1} to identify the bcc crystal structure of Mg alloy. The fully charged strip sample was expanded to a thickness of 2.7 mm and a width of 27 mm, since Li diffused into the Mg matrix. The chemical composition of the Mg–Li–Al–Zn alloy specimens was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The 2.7 mm-thick

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doi:10.1016/j.scriptamat.2006.12.017

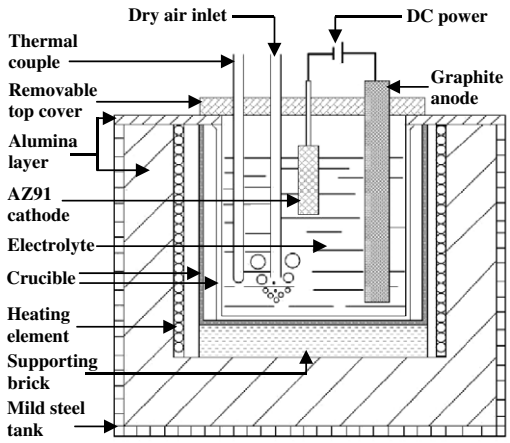

Figure 1. Schematic of the electrolytic cell used in this study.

strip sample was machined to a thickness of 2.3 mm. Each strip was homogenized in a vacuum furnace at 350 °C for 5 h and then furnace-cooled, before it was rolled. The rolling reduction per pass was about 0.2 mm. During the rolling process, the specimens underwent five rolling passes followed by a short annealing treatment at 150 °C for 20 min, until an Mg–Li–Al–Zn foil with a thickness of 0.2 mm was obtained. The total rolling reduction ratio was 91.3%. Some of the Mg alloy foils were annealed at 150 °C for 30 min. Tensile specimens of the rolled foil with a gauge length of 25 mm and a gauge width of 6 mm were machined. Uniaxial tensile tests in the rolling direction were conducted, using initial strain rates of 10^{-3}, 10^{-2} and 10^{-1} s^{-1}.

Figure 2(a) presents the optical microstructure of the as-cast AZ91 alloy sample (the cathodic material (before electrolysis)). The interdendritic network structure among the α-Mg dendrites comprised eutectic α-Mg and $Mg_{17}Al_{12}$, as indicated by the arrows in Figure 2(a). Figure 2(b) shows the X-ray spectrum of the AZ91 cast alloy. Sharp hcp magnesium peaks and $Mg_{17}Al_{12}$ peaks were identified. Part of the sample was changed to bcc Mg when the first electrolysis step was completed, as indicated in Figure 3(a). Figure 3(b) displays the optical microstructure of the Mg–Li–Al–Zn alloy strip after the three-step electrolysis was carried out. Figure 3(c) presents the result of the XRD analysis of the Mg–Li–Al–Zn strip. Sharp bcc Mg and relatively weak AlLi diffraction peaks were observed. No X-ray intensity peaks from hcp structure and the $Mg_{17}Al_{12}$ β phase were detected (Fig. 3(c)). Thus, after the three-step electrolysis procedures, the original matrix of hcp structure was converted into a bcc crystal structure. Lithium, potassium and sodium in the Mg–Li–Al–Zn alloy sample were detected by ICP-AES. The results indicated that the as-electrolyzed sample contained 11.9 wt.% lithium, 0.264 wt.% potassium and 0.012 wt.% sodium, as well as the original Al and Zn of the alloy. The as-electrolyzed strip was homogenized at 350 °C for 5 h and then furnace-cooled, before being rolled. The as-rolled bcc Mg alloy foil was 0.2 mm thick, 80 mm wide and 173 mm long. Figure 4(a) displays the

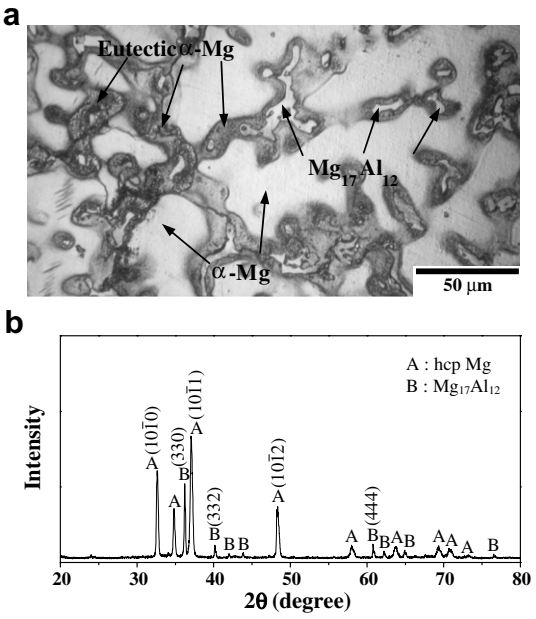

Figure 2. (a) Optical micrograph of AZ91 alloy (the cathodic material (before electrolysis)), in cross-sectional view; (b) XRD pattern of the AZ91 alloy.

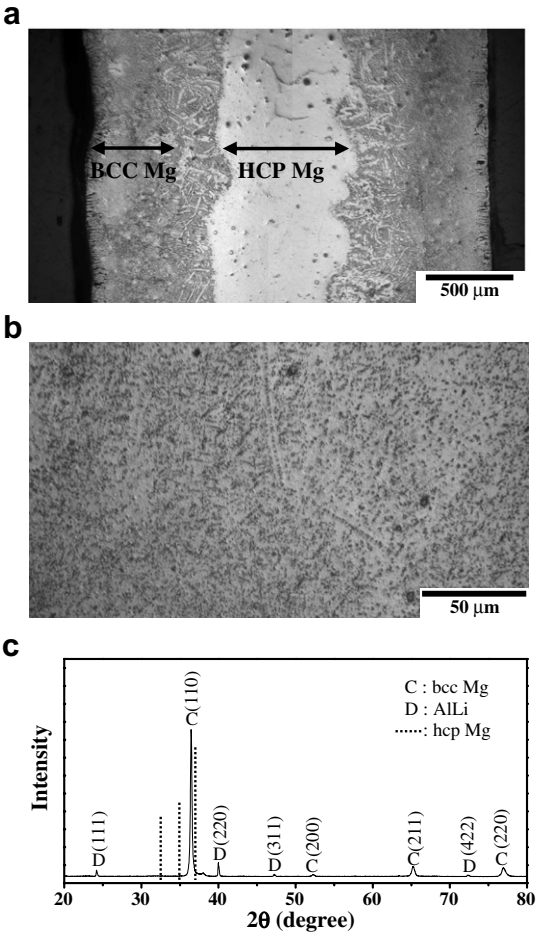

Figure 3. Cross-sectional microstructure: (a) after the first step electrolysis; (b) optical micrograph of the Mg–Li–Al–Zn strip, being fully charged by Li; (c) XRD pattern of the Mg–Li–Al–Zn strip.