Vacuum 141 (2017) 144–151

Contents lists available at ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

Effect of Si addition on microstructure and properties of magnesium alloys with high Al and Zn contents

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ARTICLE INFO

Article history:
Received 23 February 2017
Received in revised form
31 March 2017
Accepted 3 April 2017
Available online 4 April 2017

Keywords:
Degradable magnesium alloys
Microstructure
Mechanical properties
Corrosion behavior

ABSTRACT

In order to assess the possibility of using magnesium alloys with high Al and Zn contents as degradable fracturing balls, the effects of Si addition on microstructures, mechanical properties and degradable behavior of Mg-17Al-5Zn (mass.%) alloy were investigated. The results show that the minor Si addition can refine α-Mg matrix and modify Mg_2Si particles. With the increase of Si content, the yield strength of the alloys initially increases and reaches to the maximum 309 MPa in alloy containing 0.5 wt % Si. The degradable corrosion rate exhibits an inverse trend and reaches the maximum in alloy containing 3 wt % Si with 0.46 mm/day at 298 K and 5.39 mm/day at 366 K, respectively.

1. Introduction

Due to the overall superior properties, including low-density, high specific stiffness, improved damping, electromagnetic shielding capacities, recycling potential and good castability, magnesium alloys are widely used in aerospace, automobile, and electronic industries [1,2]. However, the poor corrosion resistance limits their industrial applications [3,4]. To overcome this, much research has been conducted aiming at improving the corrosion resistance of magnesium alloys [5,6]. In contrary, during the past few years, their readily corrodible characteristic feature has made the utilization of magnesium alloys possible in some areas, such as degradable fracturing ball applied to the oil industry. Multistage hydraulic fracturing is considered necessarily for economically efficient production in the oil industry. During the oil production, the degradable fracturing balls are usually used. One main advantage of using the degradable fracturing balls is to eliminate the lost production. High bearing strength and degradation rate are the two most important performance requirements for candidate materials used in the fracturing balls areas [7].

So far, alloying has been the widely used strategy to improve the strength of magnesium alloys [8–11]. On the other hand, some alloying elements in magnesium alloys were found to be able to increase the corrosion rate through the precipitation of galvanic-corrosion-acceleration second phases [10,12]. It has been shown that the strength and corrosion rate of as-cast magnesium alloys can be significantly enhanced by increasing the contents of Al (13–25 wt %) and Zn (2–15 wt %) [10]. Adding 5 wt % Cu also makes Mg-17Al-3Zn alloy have a good combination of mechanical properties and degradation rate, mainly due to the modification of the amount, morphology and distribution of β-$Mg_{17}Al_{12}$ and T-MgAl-CuZn phases [12]. Yuan and the coworkers reported [11] that appropriate silicon addition can increase the strength and toughness of Mg-Al-Zn alloys at elevated temperature, due to the precipitating of Mg_2Si particles. Lisitsyn et al. [13]. expected that the volume fraction and morphology of Mg_2Si particles have a significant influence on the corrosion properties of Mg-Zn-Mn-Si-Ca alloys. Dargusch and the coworkers [14] also reported that the morphology of the Mg_2Si phase in die-cast Mg-Al-Si alloys is a function of the silicon content, and creep rates at 100 h decreases with increasing silicon content.

As a result of low density (1.99×10^3 kg/m^3) and thermal expansion coefficient (7.5×10^{-6} K^{-1}), and high hardness (460 $HV_{0.3}$), elastic modulus (120 GPa), and melting temperature (1358 K), Mg_2Si particles often act as an excellent heat-resistant strengthening phase to improve the mechanical properties of light metals [9]. However, because of the eutectic reaction, Mg_2Si

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http://dx.doi.org/10.1016/j.vacuum.2017.04.005
0042-207X/

compounds in Mg-Al alloys prone to forming undesirable coarse Chinese script, which greatly deteriorates the mechanical properties. To overcome this, a few studies have been focusing on the morphological modification (size, shape and distribution) of Mg_2Si particles by alloying minor elements, including Sb, Y, Ca, and P, and optimizing ingot metallurgy (by adding KBF_4 or K_2TiF_6) or heat-treatment technology [8,9,15,16]. In addition to improving the strength of alloys, Mg_2Si particles also exhibit complicated corrosion behavior in Al and Mg alloys. For example, Mg_2Si particles are stable in solutions of pH 8 to 14 and undergo selective magnesium dissolution in solutions with pH 7 and lower in AA6061 aluminum alloy [17,18]. It is also found that Mg_2Si is cathodic with respect to AS31 magnesium alloys for whole range of tested pH, conversely, anodic to aluminum alloys AA6360 and AA7075 in the acidic and neutral solutions, but cathodic in alkaline conditions [19]. Compared to Al alloys [19,20], the investigations on the effects of Si or Mg_2Si on the mechanical and corrosion properties of Mg alloys, i.e., Mg-Al-Zn, are rather limited.

The current research will contribute to a better understanding of the Si-effects on the microstructures, mechanical properties and corrosion behavior of as-cast Mg-Al-Zn alloys containing high Al and Zn contents. To achieve this, Mg-17Al-5Zn alloys with various amount of Si were fabricated. Their microstructure, mechanical and corrosion properties were characterized using different methods.

2. Experimental

Mg-Al-Zn-Si alloys as listed in Table 1 were prepared by vacuum melting commercial pure Mg (99.9 wt %), aluminum (99.6 wt %), and zinc (99.2 wt %) and Al-20Si master alloy. Melting was carried out in a steel crucible. The casting temperature was set at 983 K. The produce billets are 70 mm in diameter and 150 mm in length.

Microstructure and phase compositions were characterized using optical microscope (OM, LEICA MEF4A/M) and scanning electron microscope (SEM, Nava Nano SEM 230) equipped with energy dispersive spectroscope (EDS, OXFORD). X-ray diffraction (XRD, Rigaku D/max 2550 PC using Cu Kα) analysis was carried out to identify the main phases of the investigated alloys. All specimens for the microstructural characterization were cut from the same positions on the billets, i.e. at about 15 mm from the bottom of billets and ground through 2000 grit SiC paper and polished with 0.5 μm alumina suspension followed by chemical etching using a solution of 4 vol % nitric acid + ethyl alcohol.

Cylinder compression specimens (Φ7 × 12 mm) were cut by electric spark machining from the casting ingots and room temperature compression tests were performed using an Instron universal testing machine (Instron 3369) with a crosshead speed of 1 mm/min. Prior to compression test, all faces of compression specimens were ground through 600-grit SiC paper. The mechanical results reported in this study are the mean values of three specimens.

The corrosion behavior of the alloys was investigated using immersion testing and polarization measurements. Small cylindrical specimens of Φ17 × 10 mm were molded into epoxy resin with only one side exposed as a working surface for immersion corrosion tests. These specimens were ground through 2000-grit SiC paper and polished using 0.5 μm colloidal alumina suspension. Prior to immersed corrosion tests, each epoxy-prepared sample was weighed. Because the fracturing ball is degraded in fracturing fluid whose effective constituent is 3 mass % potassium chloride (KCl) solution [10,21,22], the immersion corrosion tests were carried out in 500 ml beakers filled with 3 mass % KCl solution prepared in the HXS-H (constant temperature water box) to simulate the degradation process [10,12,21,22]. Two different temperatures, 298 K and 366 K, were used [10,12,21,22]. The specimens were removed from the solution after the immersion for 11 h and ultrasonically cleaned for 5 min in a mixture solution of AgNO3 (3.3 g/L) and CrO3 (66 g/L) to eliminate corrosion products [10,12]. Eventually, these specimens were dried and weighed again after being rinsed in distilled water. According to the actual weight loss of specimens, the average corrosion rates, by neglecting the weight loss of the mounting epoxy, were calculated using the following equation [12]:

$$V = 240\left[M_0 - M^t\right]/[\rho \times A \times t] \quad (1)$$

where M_0 and M^t is the initial weight [g] and the weight after the corrosion treatment for t h, respectively; t is the immersion corrosion time [h] and A is the sample area [cm^2] exposed to the solution, for this study, t is 11 h, A is 1.54 cm^2; ρ is the metal density [g/cm^3].

The polarization measurements were carried out in a corrosion cell containing 500 ml of 3 mass % KCl using a standard three electrode configuration: the sample as the working electrode with an about 0.5 cm^2 exposed surface and saturated calomel electrode as the reference electrode with a platinum electrode as counter. Prior to each test, specimens were ground with 2000-grit SiC paper and polished with 0.5 μm colloidal alumina suspension. The potentiodynamic polarization tests were measured using the CHI660C electrochemical test equipment at 298 K and 366 K. Polarization was started after the open circuit potential kept in a steady state potential. The polarization scan rates were 1 mv/s and 0.2 mv/s at 298 K [3,23], and 1 mv/s at 366 K. The electrochemical tests were conducted at least three times to confirm a good reproducibility.

In order to clearly distinguish the corrosion morphology of the Mg-Al-Zn-Si alloys after polarization measurement, the corrosion product covering on the surface of sample was removed using $AgNO_3$ (3.3 g/L) and CrO_3 (66 g/L) solution, and the corresponding corrosion morphologies were observed using SEM equipped with EDS.

Table 1
The nominal compositions of testing alloys (weight %).

Alloys	Al	Zn	Si	Mg
Alloy 1	17	5	0	Balance
Alloy 2	17	5	0.25	Balance
Alloy 3	17	5	0.5	Balance
Alloy 4	17	5	1	Balance
Alloy 5	17	5	2	Balance
Alloy 6	17	5	3	Balance

3. Results and discussion

3.1. Microstructure

Fig. 1 shows the XRD patterns of investigated alloys. The Mg-17Al-5Zn alloy is mainly composed of the α-Mg and β-$Mg_{17}Al_{12}$ phases. Due to the variations of interplanar spacing resulting from the solution of Al or Zn, the diffraction peaks of α-Mg and β-$Mg_{17}Al_{12}$ appear slightly offset ($2\theta < 0.3^\circ$). However, some new diffraction peaks corresponding to the Mg_2Si intermetallic compounds appear in the patterns of the Si-containing alloys (alloys 3, 4 and 6), which confirms the in-situ reaction of Si with Mg matrix to form fine Mg_2Si particles. In-situ Mg_2Si particles could be attributed to the comparatively low solid solubility (0.003 at. %) of Si in Mg and the high electronegativity difference between Si and Mg [8]. Moreover, higher-intensity Mg_2Si diffraction peaks appear with the increase of Si from 0.5 to 3 wt % indicating the generation of