Intermetallics 33 (2013) 120–125

Contents lists available at SciVerse ScienceDirect

Intermetallics

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

Influence of aging treatments on microstructure and electrochemical properties in Mg–8.8Hg–8Ga (wt%) alloy

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ARTICLE INFO

Article history:
Received 31 August 2012
Received in revised form
13 October 2012
Accepted 15 October 2012
Available online 11 November 2012

Keywords:
A. Multiphase intermetallics
B. Corrosion
C. Heat treatment
D. Microstructure
F. Electrochemical characterization

ABSTRACT

All precipitate morphologies in Mg–8.8%Hg–8%Ga alloy for a range of aging temperatures are investigated in detail using SEM, TEM and OM. The results show that $Mg_{21}Ga_5Hg_3$ are the dominant precipitate in Mg–8.8%Hg–8%Ga alloy. $Mg_{21}Ga_5Hg_3$ phase precipitate in dispersed particles. There are few papers focuses on the relationship between the aging behavior and the electrochemical and corrosion properties in Mg–8.8%Hg–8%Ga alloy. This study elaborates on the morphological evolution of $Mg_{21}Ga_5Hg_3$ precipitates as a function of aging time and temperature and investigates the associated second phase morphology-electrochemical and corrosion response. The corrosion behavior of the Mg–8.8%Hg–8%Ga alloy is also discussed.

1. Introduction

Seawater activated batteries were designed by Bell Labs of United States and developed by the General Electric Company. Such batteries provide power for many underwater instruments such as sonobuoys, meteorological radiosondes, underwater defense devices, air-sea rescue equipment and underwater unmanned submerge apparatus [1]. No extra electrolyte is an excellent advantage of such batteries because seawater is the electrolyte. It is useful for weight reduction for batteries and getting higher anode efficiency than lithium or alkaline batteries [2]. Seawater activated batteries can be designed for low and high output power, long-period and short-circle [3]. These batteries rely on the discharge of anode materials in seawater and, therefore, the performance of the anode metals seriously influence the use of seawater batteries, such as corrosion resistance and electrochemical activities [4].

Magnesium alloys are widely used in high energy density batteries and sacrificial anodes due to many advantages, such as rapid activation, low specific mass, low electrode potential and high current capacity [5–7]. As reported commercial magnesium alloys in sacrificial anode, the corrosion and electrochemical properties of the Mg–Al alloys were studied a lot. The corrosion behavior of Mg–Al alloys was influenced greatly by the concentration of Fe impurity [8]. If a lot of MgAl, Mg_2Al_3 and Mg_4Al_3 compounds exist in grain boundary, inter-granular attack occurred and inspired the self-corrosion of magnesium [9]. The existence of twins and increase of grain size accelerated the corrosion of AZ31B alloys [10]. A model of the atmospheric corrosion process of AZ91D was presented, where micro galvanic elements were formed with the a-phase as anode and the eutectic a/β-constituent in the vicinity of the a-phase is the site of the cathodic reactions [11]. The actual specific energy of the Mg–Mn battery is 54 W h kg^{-1} [12]. According to ref [13], the addition of Ce or La produces cathodic intermetallic compounds with RE addition and improved the corrosion resistance of AM60 alloy. The addition of Zn in Mg–Mn alloys refined the grain size and improved the corrosion resistance [14]. But, these investigations demonstrate that the Mg–Al and Mg–Mn anodes have no enough electrochemical activity to produce the huge battery power. The developed magnesium anode materials with high cell voltage are AP65 (Mg–6%Al–5%Pb) [15], Mg–7%Tl–5%Al [5] and Mg–Hg alloys [16]. The specific energy of the seawater battery using Mg–Hg alloys as anode can reach 150 W h kg^{-1}, compared with 30 W h kg^{-1} of lead acid battery. The open potential of Mg–Hg alloys in a 3.5 wt% NaCl solution is −2.0 V (vs.SCE) [17], compared with −1.8 V (vs.SCE) of Mg–6%Al–5%Pb alloys [15]. However, the good results of the Mg anodes obtained in high power seawater battery still meet with problems such as bad deformability, large self-corrosion velocity and low current

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http://dx.doi.org/10.1016/j.intermet.2012.10.007

Table 1
Chemical composition of Mg–8.8%Hg–8%Ga alloy (mass fraction, %).

Hg	Ga	Fe	Ca	Ni	Cu	Mg
7.983	7.952	0.001	0.011	0.012	0.002	Bal.

efficiency [18]. Especially the Cl^- in seawater produces acid environment for the Mg anodes and increases corrosion of the Mg anodes [19].

According to researches [20,21], $Mg_{21}Ga_5Hg_3$ intermetallic compound exist in the Mg–Hg–Ga anodes and its morphology and distribution greatly influence the electrochemical and corrosion properties of the Mg–Hg–Ga anodes. In order to achieve good performance of Mg–Hg–Ga anode, this study will focus on the aging behaviors of Mg–8.8%Hg–8%Ga alloy under different aging conditions and the relationship between the precipitates and the associated electrochemical performance. The corrosion behavior of the Mg–8.8%Hg–8%Ga alloy is also discussed.

2. Experimental

Mg–Hg master alloys were first melted in a sealed iron tube filled with argon, as described in a previous paper [16]. Then the Mg–Hg alloys, Mg and Ga with 99.99% purity were melted in a muffle furnace. The chemical composition of the Mg–8.8%Hg–8% Ga alloy (seen in Table 1) was determined by ESA (Energy Spectrum Analysis) and atomic absorption spectrum analysis. Homogenization of the specimens was carried out at 773 K for 24 h. Aging treatment was designed according to the DSC (Differential Scanning Calorimetry) measurements, which were performed with a NETZSCH DSC 200 F3 and the heating up ratio is 30 k min^{-1}. Fig. 1 shows the DSC curve of the Mg–8.8%Hg–8%Ga alloy. It can be seen that there is an exothermic peak at 416 K. For determining the precipitate phase, the specimens were aged at 423 K, 473 K and 523 K for 2 h–96 h.

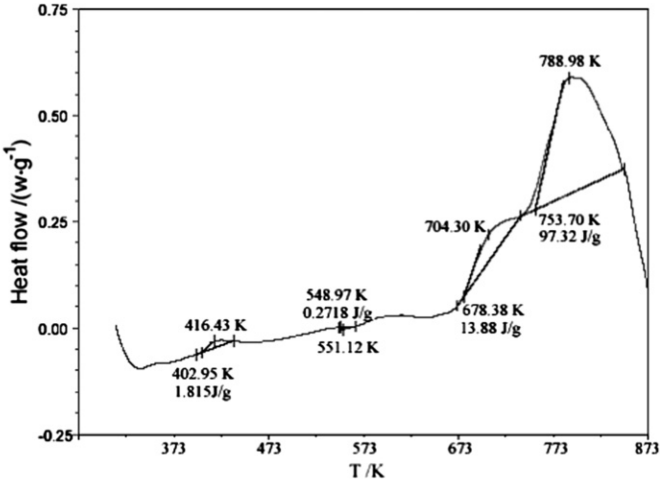

Fig. 1. DSC curves of the Mg–8.8%Hg–8%Ga alloy.

Microstructure and corroded surface of the specimens were observed using SEM, TEM (Transmission Electron Microscope) and OM (Optical Microscope). SEM observation was carried out using KYKY-2800 and TEM observation was carried out using Tecnai G2 20 ST. The specimens for TEM observation were polished to 0.08 mm with emery paper and ion milled with RES 101. The corrosion product was determined by XRD with a Rigaku D/Max 2500 V diffractometer with Cu Kα radiation.

Potentiodynamic and galvanostatic experiments were performed with a Potentiostat–Galvanostat (Model 263A) in a 3.5% (mass fraction) NaCl solution. The scanning rate of potentiodynamic measurement is 5 mV s^{-1} and the anodic current density in the galvanostatic test is 180 mA cm^{-2}. The specimens were polished with emery paper and buffed to a mirror finish. Each of them was sealed with epoxy resin except for an exposed surface of 10 mm × 10 mm submitted to the electrochemical tests in a three-electrode cell. A platinum sheet was used as the auxiliary electrode and a saturated calomel electrode (SCE) with a standard electrode potential of 0.2412 V (SHE) was used as the reference electrode.

3. Results and discussion

3.1. Microstructures of Mg–8.8%Hg–8%Ga alloy in different conditions

Fig. 2 shows the microstructures of (a) cast alloy and (b) homogenized alloy. The cast Mg–8.8%Hg–8%Ga alloy has intergranular compounds with high Hg and Ga contents according to ESA measurements. The specimen aging at 773 K for 24 h has homogenized microstructure and no residual intermetallic compounds at the grain boundaries.

Fig. 3 shows the TEM images of the Mg–8.8%Hg–8%Ga alloys after different aging treatments. As seen in Fig. 3 (a), no second phase exists in homogenized specimen. Fig. 3 also reveals only the dispersed particles are precipitated during different aging treatments. The size of the dispersed precipitates increased from 10 nm to 20 nm when the aging time increased from 2 h to 96 h and increased from 5 nm to 20 nm when the aging temperature increased from 423 K to 523 K. From Fig. 3 (b–f), it can be observed that the number density of the dispersed precipitates increased

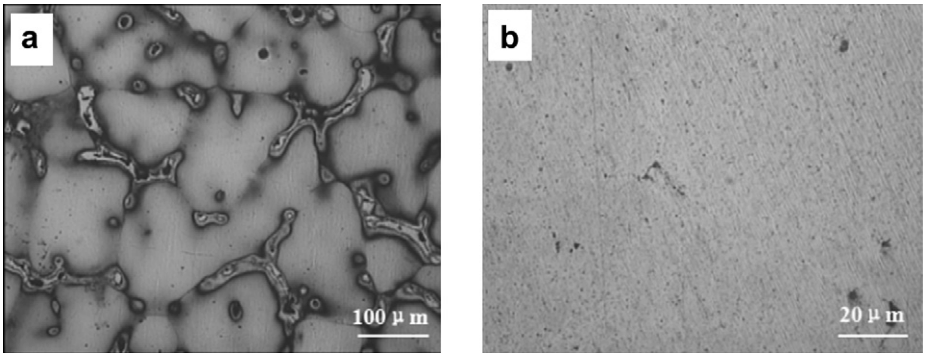

Fig. 2. Microstructures of the Mg–8.8%Hg–8%Ga alloy: (a) cast; and (b) solid solution.