Applied Surface Science 405 (2017) 529–539

Contents lists available at ScienceDirect

Applied Surface Science

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

Global and local investigations of the electrochemical behavior the T6 heat treated Mg–Zn–RE magnesium alloy thixo-cast

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ARTICLE INFO

Article history:
Received 6 October 2016
Received in revised form 22 January 2017
Accepted 9 February 2017
Available online 14 February 2017

Keywords:
Magnesium alloy
Rare earth elements
EIS
Pitting corrosion
Microcapillary
Thixoforming

ABSTRACT

The influence of semi-solid metal processing (SSM called also as thixoforming) of ZE41A magnesium alloy on the electrochemical behavior in 0.1 M NaCl solution was investigated. To describe the corrosion behavior of ZE41A alloy, the electrochemical measurements were conducted in global and local scale for two types of specimens: (1) ingot-feedstock, (2) specimen after thixoforming and T6 treatment. The heat treatment and thixoforming significantly improved mechanical properties of ZE41A alloy. The global corrosion potential is slightly higher for treated sample what is related to the presence of Zr–Zn nanoparticles distributed in solid solution. The corrosion behavior differences between feedstock and thixo-cast after T6 samples are also visible in local scale, what has been revealed by using microcapillary technique. However there is no improvement in corrosion behavior after treatment. Corrosion morphology of the treated sample indicate higher susceptibility to pitting and filiform corrosion. Corrosion rate is also slightly higher.

1. Introduction

Magnesium and its alloys have the lowest density among the currently known construction materials therefore, they are increasingly being used in many branches of industry. Moreover, the magnesium alloys are treated as material of twenty first century and the interest in these alloys still rising due to their environmental friendliness, dimensional stability, good heat dissipation, good electro-magnetic shield and quite good mechanical properties [1–4]. Unfortunately high chemical activity and poor corrosion resistance of magnesium alloys greatly limit their applications in industry [5]. Thus, the study of the corrosion mechanisms and improving the anti-corrosion properties of magnesium alloys are an important element for their applications in the future.

The microstructure plays a significant role in corrosion processes of magnesium alloys what has been widely studied and described [6–22]. It is well known that casting methods and the type of the heat treatments performed on magnesium alloys have influence on their microstructure and mechanical properties [21–23]. Likewise, the corrosion behavior of magnesium alloys depends on their microstructure i.e. the presence of various phases, precipitates, eutectic [5–8,10–12,15,17,18,20,23–25]. Moreover, the type of heat treatment performed on the magnesium alloys determine their electrochemical behavior [24,28]. In some works it has been shown that β-$Mg_{17}Al_{12}$ plays a dual role in the corrosion resistance of AZ91 alloy [10,12]. The corrosion potential of β-$Mg_{17}Al_{12}$ has been found to be more positive than that of the α-magnesium, which may accelerate the galvanic corrosion of magnesium alloy. On the other hand, if β-$Mg_{17}Al_{12}$ phase forms of a continuous network, the corrosion propagation in the matrix is hinder [8,10,12,15]. The corrosion measurements performed at the microscale have revealed that places containing the β-$Mg_{17}Al_{12}$ and AlMn phases exhibit the highest corrosion resistance [26]. The corrosion behavior of the eutectic has been studied in H_3PO_4 buffered solution [18]. It has been revealed that the eutectic acts as an anodic barrier in the absence of Cl^- ions at pH 7, but at pH 11 this effect disappeared. In solution containing the ClO_4^- ions the eutectic was more susceptible to pitting corrosion than the matrix α-Mg [27].

The chemical composition of magnesium alloys has significant influence on their corrosion resistance and mechanical properties. The presence of Zn in the magnesium alloys increases of their

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http://dx.doi.org/10.1016/j.apsusc.2017.02.076
0169-4332/

Table 1
Chemical composition of studied ZE41A magnesium alloy.

	wt.%	at.%
Mg	94.16	98.06
Zn	4.0	1.55
Re	1.3	0.24
Zr	0.53	0.14

strength and corrosion resistance. It must be noted that the high concentration of Zn creates the secondary phases, which lead to galvanic corrosion processes resulting from the potential difference between the matrix and secondary phase particles [29]. Zirconium is added to the magnesium alloys in order to the grain refining of the casting structure [30,31]. Unique efficiency of Zr as grain refiner resulting from good matching of the crystallographic network of the Zr and Mg elements as well as limited zirconium solubility in liquid magnesium (about 0.45 wt.%). On the other hand, the addition of rare earth elements to magnesium alloys leads to improvement of castability of these alloys, decreasing of the grain size and improve the strength at elevated temperatures and increase the resistance to corrosion [32,33].

There are many types of the shaping (casting, rolling, extrusion) and modifying (work hardening, heat treatment) of metals and alloys. During these processes it is possible to obtain a material of desired shape and a suitable microstructure which affects the properties of the component. Semi-solid metal processing (SSM) – is the shaping of metal components in the semi-solid state, which utilizes thixotropic behavior of metal suspension containing 15–80% of liquid phase. It is possible when the microstructure consists of globular grains surrounded by a uniformly distributed liquid phase [34]. Alloys could be shaped in this way at much smaller forces than during forging or rolling. A further intensive research led to the development of two methods of forming: rheoforming (directly from the liquid state during the solidification) or thixoforming (after heating from the solid state to semi-solid state) [35]. The essential step in all technologies of net-shape forming that explore the semi-solid processing concept is generation of globular morphologies within an alloy microstructure [36]. It is well established that SIMA (Strain Induce Melting Activated) [37], resulting in residual strain stored in a billet during hot deformation in solid state, is the effective way of generating globular morphologies upon subsequent partial re-melting. SIMA concept includes rolling [38], extrusion [39] and severe plastic deformation with a particular example of ECAP.

In this paper the electrochemical behavior of ZE41A magnesium alloy (Mg–Zn–Zr–rare earth elements (RE)) has been described after the thixoforming process (semi-solid metal processing – SSM) and heat treatment what improved the mechanical properties of the alloy. ZE41A magnesium alloy have found applications in aeronautical industry because of its good mechanical properties, very good weldability and castability [40]. The corrosion behavior of two specimens of ZE41A alloy: 1/ingot (as-cast) and 2/specimen of ZE41A alloy after thixoforming process and T6 heat treatment proceeded by microstructure refining process (by ECAP – Equal Channel Angular Pressing; 2 passes) has been studied.

2. Experimental procedure

2.1. Preparation of samples – thixoforming process and HT characterization

ZE41A magnesium alloy ingot, supplied by Electron Magnesium UK, with chemical composition presented in Table 1 was used in the present study (denoted as *ingot*).

The ZE41 ingot was subsequently hot rolled at 350 °C with a thickness reduction of 50% using the quarto-duo DW4-L rolling mill. As the next step, the blank with dimensions was cut into samples of 25 mm × 25 mm × 80 mm and processed by ECAP at 250 °C. Using vertical press for semi-solid metal processing, the ECAP-ed billet was then thixoformed at 630 °C, which corresponds 25% of liquid fraction (further sample was assigned as *T6 thixo-cast*). In order to improve the mechanical properties of ZE41A thixo-cast specimen has been attend T6 heat treatment consisting of saturation at 520 °C for 8 h and aging at 180 °C for 50 h. Before microstructural and electrochemical investigations both ingot and T6 thixo-cast samples were mechanically grinded with emery papers, polished using diamond pastes and smoothed with a colloidal silica suspension. Next, the specimens were cleaned in ethanol and dried in air.

2.2. Surface observations and analysis

Light micorscope (Nikon Eclipse L100) was used for the optical observations of the surface of ZE41A magnesium alloy. SEM (JEOL 7600 F instrument) equipped with an energy dispersive X-ray spectrometer (EDS) was used to observe the surface with high resolution and to estimate the atomic percentage of the chemical elements in local scale. Tecnai G2 F20 (200 kV) TEM microscope equipped with high-angle annular dark field scanning transmission electron microscopy detector (HAADF-STEM) and energy dispersive X-ray (EDS) EDAX allowed to perform bright filed observation, electron diffractions and chemical elements analysis (points and maps) of the ZE41A specimens. TEM specimens have been prepared by twin-jet electropolishing (Tenupol-5) using a solution of 10.6 g lithium chloride LiCl, 22.32 g magnesium perchlorate $Mg(ClO_4)_2$, 1000 ml methanol, and 200 ml 2-butoxy-ethanol at −40 °C and 80 V. Afterwards, the oxide layer has been removed from the specimen surface using Leica EM RES101 Ion Beam Milling System. Identification of phases present in the ZE41A alloy has been done by XRD using Philips PW 1840 X-ray diffractometer with Co Kα radiation (λ = 1.78896 Å).

2.3. Electrochemical measurements methodology

Corrosion behavior of ZE41A alloy has been studied at the global scale by means of a classical electrochemical three electrode system [41,42]. In this system the platinum plate was used as a counter electrode, Ag/AgCl (3 M KCl) as a reference electrode and ZE41 magnesium alloy was a working electrode. The surface of the specimen used for this measurements was about 0.5 cm^2. In order to study the electrochemical behavior of single phase (matrix, precipitate, etc.) the Electrochemical Microcell Technique (EMT) was employed. This technique allows to perform the electrochemical measurements at the microscale and it is powerful method to study local corrosion phenomenas on the metal surface [43–46]. Microsystem consists of a glass micro-capillary that is filled with electrolyte (Fig. 1a). The micro-capillary tip was sealed to the specimen surface with a layer of silicon rubber. The microcell (connected with capillary) was mounted on a microscope for precise positioning of the micro-capillary on the surface (Fig. 1b). The diameter of the capillary tip was in the range of 50 μm. The counter electrode was a platinum wire, and the reference electrode was a Ag/AgCl (3 M KCl).

In order to obtain the characteristics of the local corrosion behavior of ZE41A alloy, local OCP and LSV curves need to be repeated few times. This allows to observe a trend in local electrochemical behavior, which may be varied because of non-homogeneous structure (with presence of intermetallic phases, eutectics, etc.). Moreover, there are other factors, which affect the electrochemical response of this type of metallic alloys (the size of precipitates, crystallographic orientation, defects in the structure) [24,25,41,46].