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Mg-7Gd-5Y-Nd-Zr alloy plate corrosion-resistance property to chloride ion

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Abstract

Rare earth Mg alloy has aroused increasing attention in aviation, spaceflight, war industry application fields; however, its poor corrosion-resistance restricted its wide range of application. For Mg-7Gd-5Y-Nd-Zr extruding plate, the grain orientation and size are different in three planes, which is extruding plane (surface), side plane, and cross-section plane. Microstructure may lead to the variation of corrosion resistant to marine climate environment. The corrosion resistance of chloride ion in three different planes of rare earth Mg plate was studied. The immersion and dynamic potential polarization curves in 3.5 wt. % concentration of sodium chloride solution were used to analysis and compare electrochemical characteristics among the three planes. Optical microscope was employed to observe the microstructure of Mg alloy before and after the chloride ion erosion. The X-ray diffraction was used to determine its corrosion product. The results show that corrosion-resistance properties of the three planes (surface, side and cross section) are different. Pitting corrosion are mainly characteristics and corrosion product is magnesium hydroxide. The different resistant properties of three planes are mainly attributed to different grain size and orientation of the different planes.

Keywords: rare earth magnesium alloy corrosion-resistance to chloride ion grain orientation

Introduction

Due to their low density, high strength and stiffness, dimensional stability, good machining performance, and easy recovery, Mg alloys are regarded as the green and vital structural metallic materials in the 21st century (Song

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Guanglin, 2006). Recent years, magnesium alloys of high strength and heat properties have been obtained by adding rare earth elements. Rare earth magnesium (such as WE43, WE54) have been widely acquired in aerospace fields which need special alloys of high-temperature mechanical properties and high temperature performance. Effect of rare earth elements on corrosion resistance magnesium alloys has obtained increasing concern in order to getting a wider range of applications (Yu Kun et al. 2008). Beijing General Research Institute for Non-ferrous Metals in China has found that Mg–Y alloys with the addition of Y element less than 2.5% heterogeneously corroded in the 3.5% NaCl solution, while Mg–Y alloys with Y more than 2.5% corroded in pitting corrosion(Zhang Kui et al. 2012). The corrosion behaviour of as-cast and extruded Mg−5Y−7Gd−1Nd−0.5Zr alloy in 5% NaCl aqueous solution was also compared (Zhang Kui et al. 2012). Aerospace Research Institute of Materials & Processing Technology in China has found that adding of rare earth elements Gd, Y have significantly improved the corrosion resistance of ZK60 magnesium alloy (Zhang Fan et al. 2012). Central South University has found that adding a small amount of Ce (less than 0.5%) in Mg-9Gd-4Y-1Nd-0.6Zr alloy can make grain refinement, significantly improve corrosion resistance (Yi Jianlong et al.2012). Chongqing University reported research status of magnesium alloy enhanced corrosion resistance of by rare earth (Jiang Xiaojun et al. 2012). Monash University reported that a recent rare earth containing magnesium alloy EV31A was found to be superior resistant to stress corrosion cracking compared with AZ91E under less intense loading of constant load. The superior resistance of EV31A is attributed to a more robust oxide/hydroxide layer (Bharat S. Padekar et al.2013).Universidad Complutense has found that in Nd containing magnesium alloy AM50, formation of Al_2Nd and Al-Mn-Nd intermetallic compounds reduced the volume fraction and modified the morphology of the β-$Mg_{17}Al_{12}$ phase. The addition of Nd improved the corrosion resistance of AM50 due to increased passivity of the surface film and suppression of micro-galvanic couples (R Arrabal et al. 2012).

For extrusion or rolling magnesium alloy thick plate may produce difference of plastic deformation in each direction of plate, leading to the variation of grain size or crystal orientation in various surface. So it is necessary to characterize the corrosion behaviour of different surfaces plate to provide reference for the service of the correct use surface protective. According to Mg-7Gd-5Y-Nd-Zr rare earth magnesium alloy plate, this paper primarily explores corrosion resistance of the different extrusion surfaces.

1. Experimental

Mg-7Gd-5Y-Nd-Zr rare earth magnesium alloy plate supplied by Beijing General Research Institute for Non-ferrous Metals with the chemical composition is shown in table 1.

Samples 1 #, 2 #, 3 # were made from Mg-7gd-5Y-Nd-Zr rare earth magnesium alloy plate, the observation planes corresponding to surface, side and cross section were shown in figure1 (area of work are 1 cm^2). For metallographic characterization, samples were dry ground through successive grade of grit papers from P60 to P1000, then wet ground to P2000, followed by rinsing with isopropyl alcohol in an ultrasonic bath and drying in cold air. The samples were mechanical polished and eroded using 4% nitric acid alcohol.

Samples immersed by 3.5 wt. % NaCl solution and the corrosion product were rinsed with 20% of CrO3 solution, followed by characterizing the corrosion morphology with scanning electronic microscope (ZEISS EVO18). Phase constitute was analysed by X ray diffraction meters （Rigaku DMAX-RB 12KW） ,Scanning speed 4°/min and scope 0°~90°. The open circuit potential and the polarization curves were obtained in 3.5% NaCl solution using a versatat/Galvanostat Model 273A. A classical three-electrode cell was used with platinum as counter electrode, saturated calomel electrode SCE (0.242 V vs SHE) as reference electrode, and the sample as working electrode. The samples were mounted using epoxy resin and only left an exposed area of 1 cm^2. The lasting time of the open circuit potential test was 300s. The measurements began from the cathode side at a constant voltage scan rate of 0.5mV/s.

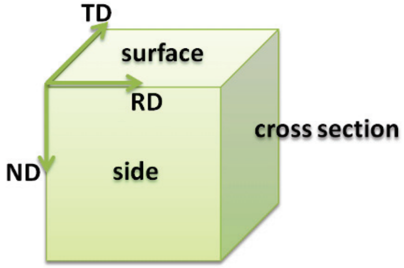

Fig 1 Sample profile schemes

Table 1 the experiment of material chemical composition (wt. %)

element	Gd	Y	Nd	Zr	Al	Si	Cu	Ni	Mn	Mg
Mass fraction (wt. %)	6.5-7.5	4.5-5.7	0.9-1.5	0.4-1.0	0.01	0.01	0.1	0.04	0.1	balance

2. Results and discussion

2.1. Microstructure of samples

Figure 2 shows the microstructure of Mg−7Gd−5Y−Nd−Zr rare earth magnesium alloy. It can be found that the grain of surface and side are fine and uniform, while the grain of cross section reveals larger relatively. Due to the extrusion process and dynamic recrystallization, the surface appears small grains around the big grain, orientation distribution on side plane, and the largest average grain size appears in cross section

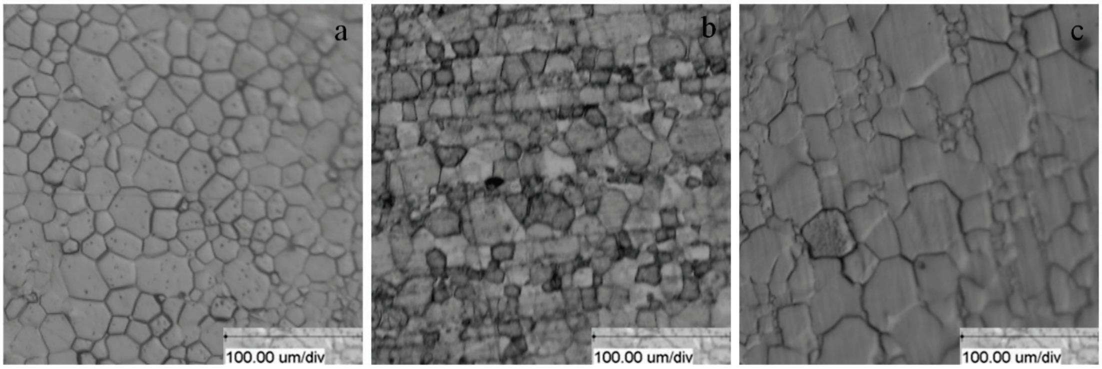

Fig2 Images of Mg-7Gd-5Y-Nd-Zr alloys plate in three planes: (a) surface, (b) side, and (c) cross section

2.2. Initiation of corrosion

The corrosion of Mg-7Gd-5Y-Nd-Zr rare earth magnesium alloy plate immersed in the 3.5 wt.% NaCl solution appears as pitting initial (see Figure 3). The corrosion happens rapidly and occurs in the grain boundary by dynamic observing using the optical microscope in situ. Just set the corrosion of the side as an example. The optical microscope pictures of side after 5s, 30s, 90s, 150s immersed in the 3.5 wt. % NaCl solution were shown in Figure 3. We can clearly see that corrosion began to appear in grain boundary which acted as a cathode, H_2 generates and evolutes in the grain boundary, forms bubbles, produces corrosion pit. The micro galvanic couple corrosion reaction is very severe followed by dissolving out a large number of hydrogen. Due to the potential of Mg is inferior to the potential of its alloy elements and second phase. Border impurities and elemental segregation exist as cathode phase form. H_2 generates and evolutes in the grain boundary place. In addition, although the grain of surface and side are fine and grain boundary are more than that in cross section, but grain boundary corrosion won't happen in magnesium alloy theoretically (Xu Bingshe et al. 2007). Therefore surface and side haven’t shown poor corrosion resistance because of more grain boundary. After 9 min from corrosion occurrence, bubbles didn’t occur corrosion nearby the hydrogen region, the grain boundary is clear to be seen, while the grain corrosion away from the hydrogen bubbles is serious. We can indicate that the bubbles play a role for medium transmission obstacle; make the environment inside the bubble mercerization, this will further makes the anode zone pH value reduce, so as to strengthen the micro galvanic couple corrosion process.

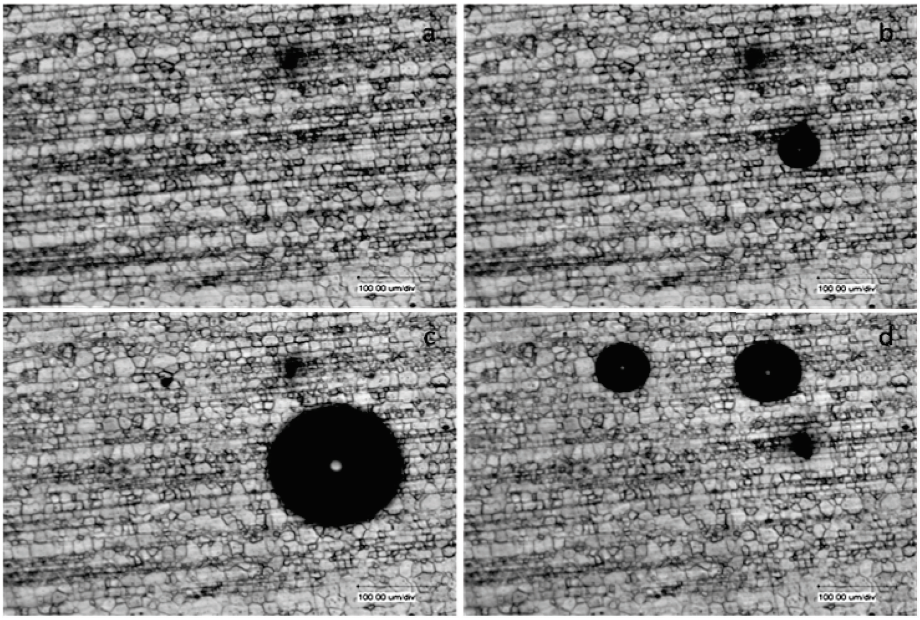

Fig.3 OM images for surface morphologies of Mg-7Gd-5Y-Nd-Zr alloy plate in 3.5 wt. % NaCl solution for :(a) 5s, (b) 30s, (c) 90s, and (d) 150s.

2.3. Corrosion Macro-morphologies

Fig4a, 4b, 4c show the morphology of surface, side and cross section of Mg-7Gd-5Y-Nd-Zr alloy plate immersed in the 3.5 wt. % NaCl solution for 9h. We could claim that the corrosion of the three surfaces in the 3.5 wt. % NaCl solution regards pitting as main type. The corrosion pit is large and deep. The corrosion in side plane is very slight (4b), the corrosion in surface is severe than side, while the corrosion of cross section is much more severe than surface and shows ribbon distribution. Part of the areas in across section has been damaged seriously. The degree of corrosion from light to heavy is in order of side, surface, and cross section. The corrosion hole is large and deep which is shown sharply in the enlarged macro-morphology in Fig4. Figure 5 is the XRD spectrum analysis of Mg-7Gd-5Y-Nd-Zr alloy plate immersed in the 3.5 wt. % NaCl solution for 9h. Magnesium dissolution in aqueous environments proceeds by an electrochemical reaction with water to produce magnesium hydroxide. The oxidation/reduction reacts as follows:

$$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2\uparrow \quad (1)$$

$$\text{Oxidation: } Mg \rightarrow Mg^{2+} + 2e^- \quad (2)$$

$$\text{Reduction: } 2H_2O + 2e^- \rightarrow H_2\uparrow + 2OH^- \quad (3)$$

Corrosion products are mainly $Mg(OH)_2$ (Song Guanglin, 2006). Figure 6 is the XRD spectrum analysis results of the three different planes of Mg-7Gd-5Y-Nd-Zr rare earth magnesium alloy compared with the standard XRD spectrum of magnesium. Diffraction peak strength of different crystal planes in cross section shows slight difference with the standard magnesium (PDF#35-0821). Meanwhile, the diffraction peak of [0 0 0 2] and [2 -1 -1 9] crystal planes in surface is lower than that of standard magnesium, while the diffraction peak of [2 -1 -1 0] and [1 1 -2 0] crystal planes in surface is higher than that of standard magnesium. It is evident that the crystal plane diffraction in side shows serious difference with that of standard magnesium. In detail, the counts number of [0 0 0 2] and [2 -1 -1 9] crystal planes in side are higher than that of standard magnesium, the counts number of [2 -1 -1 0] and [1 1 -2 0] crystal planes in side are higher than that of standard magnesium. According to the result, it is obvious that the different grain orientation lead to the different corrosion resistance. Compared with standard magnesium, there are differential left movement of the diffraction peak position of different diffraction planes in the plate planes. According to Bragg Equation, the decreasing of diffraction angle could attribute to the increasing of interplanar spacing. We could conclude that there is tensile stress in the three planes (Michael T. Hutchings et al. 2005). The relation between tensile stress and corrosion resistance is worth to be further studied.

Bragg equation: $\lambda=2d\sin\theta$ *(4)*

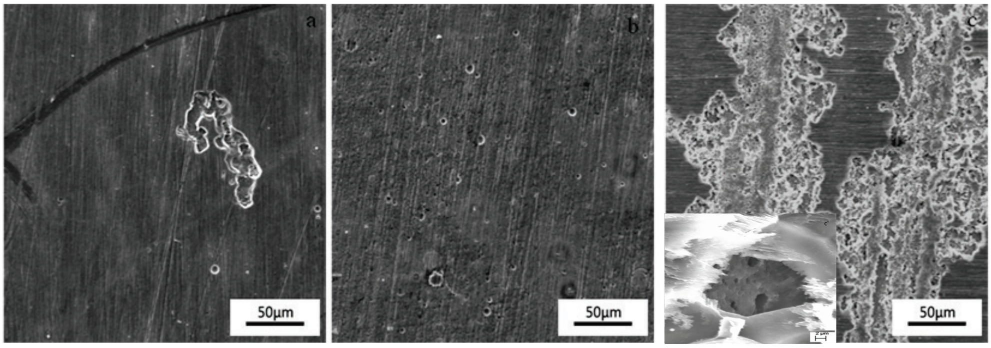

Fig.4 SEM images for surface morphologies of Mg-7Gd-5Y-Nd-Zr alloy plate in3.5 wt. % NaCl solution for 9 h:(a),surface, (b) side, and (c) cross section ,(c') is the partial magnified detail of cross section

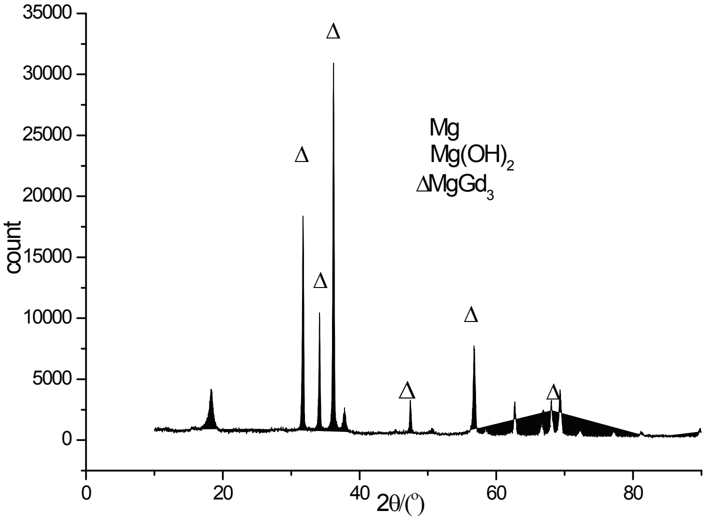

Fig 5 XRD result of Mg-7Gd-5Y-Nd-Zr rare earth magnesium alloys plate in 3.5 wt. % NaCl solution for 9 h

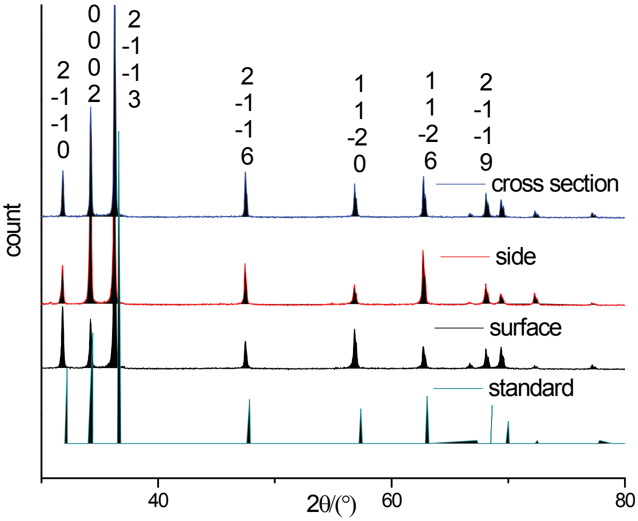

Fig 6 XRD result of the three different planes of Mg-7Gd-5Y-Nd-Zr rare earth magnesium alloys compared with standard magnesium.

2.4. Polarization curves

It is evident that these samples have different polarization curve shapes in the tested solution. Corrosion potentials (*Ecorr*) and corrosion current densities (*Icorr*) of the samples, obtained from the polarization curves, were illustrated in Fig.7. It is obvious that *Ecorr* of side is much higher than that of surface and cross section. There is higher *Ecorr* in surface than that in cross section. These observations demonstrate that the corrosion tendentiousness of Mg-7Gd-5Y-Nd-Zr rare earth magnesium alloy plate in 3.5 wt.% NaCl solution orderly is: cross section > side > surface, i.e., the property of the corrosion resistance in order is: side > surface > cross section. The polarization curves of side and cross section show that the work electrode planes have occurred passivation. This phenomenon was possible caused by the formation of passive film along with the dissolution of magnesium (Song Guanglin, 2006)

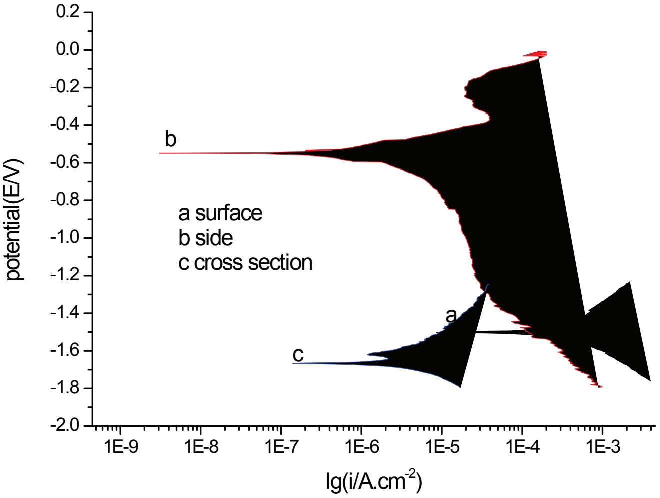

Fig.7 Polarization curves of Mg-7Gd-5Y-Nd-Zr rare earth magnesium alloy plate in 3.5 wt. % NaCl solution r: (a) surface, (b) side, (c) cross section

Through the above analysis, it is clear that *Ecorr* of this rare earth Mg alloy is higher than that of pure Mg with E_{corr} (vs SCE) −1.790 V (Yu Kun et al. 2008). Research shows that the corrosion behaviour is one of the critical properties in the application of Mg alloys and can be generally improved by the addition of RE elements (Neubert, V et al. 2007, Liu Yaohui et al. 2010, Song Guangling et al. 2010, and Tang Guoyi et al. 2010). During the extrusion process, the large deformation, dynamic recovery and recrystallization process of surface and side result in the preferable organization uniformity, decreasing of grain boundary segregation, the uniform distribution of solid soluble in matrix elements, decreasing of the potential difference in matrix everywhere. And then, it is indicated that the fine grain microstructure have more grain boundary, the second phase distribute along the grain boundary in general, the continuous and uniform distribution of second phase could play a significant role in preventing the further expansion of corrosion(Xu Bingshe et al. 2007). Therefore, the corrosion resistance of surface and side is better than that of cross section.

3. Conclusions

(1) Pitting is the main corrosion mode in the 3.5 wt. % NaCl solution for the Mg-7Gd-5Y-Nd-Zr extrusion plate and corrosion products are mainly Mg (OH)$_2$

(2) The corrosion rate exist difference in three planes of extrusion plate. The property of the corrosion resistance in order is: side > surface > cross section.

(3) The different resistant rate of three planes are mainly attributed to different grain size ,orientation and residual stress of the different planes

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