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Corrosion Behavior of As-Cast Binary Mg-Dy Alloys

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Abstract: The addition of rare earth elements (REE) is an effective way to improve the corrosion properties of magnesium alloys. Dysprosium has a very high solubility in Mg (25.3 wt.% at 561 °C) and could therefore be a promising alloying element for Mg based implants. In this study, four binary Mg-xDy (x=5, 10, 15 and 20 in wt.%) alloys were prepared by permanent mould direct chill casting. Microstructure and Dy distribution were investigated using optical microscope and EDX analysis. Corrosion rate was measured with hydrogen evolution method and corrosion morphology was observed after immersion for different time in 0.9 wt% NaCl solution with optical and SEM. The results show that with the increase of Dy, the amount of Dy in Mg matrix and area of Dy segregation are both increased. At the same time, the amount of second phase is also increased. Filiform corrosion is reduced while pitting corrosion is increased with the increment of Dy. As a result, lowest corrosion rate is obtained at Mg-10Dy alloy.

Introduction

Magnesium alloys are being increasingly used in automotive, aerospace and electronic industries due to their low density, adequate strength–weight ratio and excellent castability. Moreover, the use of Mg alloys as biodegradable implants has attracted much attention [1]. However, the poor corrosion properties of Mg alloys are currently limiting their applications [2].

For the Mg-Al system it was shown that alloying with rare earth elements (REE), such as Ce, La, Nd or Ho, is an effective way to improve the corrosion resistance [3-7]. This improvement is due to the following effects: i) REE containing phases can tie up impurities such as iron [3]; ii) the amount, size, shape and distribution of second phases are altered by the addition of REE [5, 7]; iii) REE are oxidized and incorporated into the corrosion film during corrosion [4, 5, 7]. However, corrosion rates of Mg-REE (REE = Ce, La, Nd) binary alloys systematically increase in NaCl solution with increasing volume of intermetallics [8]. It was also found that the corrosion rate increases in NaCl solution in yttrium-containing alloys (Y, from 2 to 7wt.%) due to an increase in second phase formation [9].

From the above discussion it can be concluded that REE may have multiple effects influencing corrosion resistance of Mg. Corrosion resistance should be improved by a reduction of second phase formation by addition of REE. From this point of view, REE with high solubility could be a good choice. Therefore, Dy was selected due to its high solubility of 25.3 wt.% at the eutectic temperature and because in vitro cytotoxicity studies showed low toxicity of this element [10]. In this work binary Mg-Dy alloys were investigated to determine the influence of different amounts of Dy on the corrosion properties.

Experimental procedures

Permanent mould direct chill casting [11] was used to prepare the alloys. High-purity Mg was molten in a mild steel crucible under a protective atmosphere (Ar + 2 % SF_6). Pure Dy was added at a melt temperature of 720 ^{o}C in amounts of 5, 10, 15 and 20 wt.%. The melt was stirred for 30 min at 200 rpm. The size of ingot was 6 cm×12 cm×20 cm. The chemical compositions of the alloys were analyzed using inductively coupled plasma–optical emission spectroscopy ICPOES (Spectroflame, Spectro, Kleve, Germany), as listed in table 1. Microstructure and corrosion morphology were investigated using a Reichert-Jung MeF3 optical microscope with a digital camera attachment and a Zeiss Ultra 55 (Carl Zeiss GmbH, Oberkochen, Germany) scanning electron microscopy (SEM) equipped with energy dispersive X-ray analysis (EDX).

The hydrogen evolution measurement was carried out by immersion tests in standard eudiometer set-ups with a total volume of 400 ml and a resolution of 5 ml. The tests were performed in 0.9 wt. % NaCl solution at room temperature. The specimens with dimensions of 10 mm × 10 mm × 10 mm were prepared by grinding each side with 2400 grid emery paper and degreasing the surfaces with ethanol prior to corrosion testing. Three samples were used for each alloy. In order to investigate the corrosion process of Mg-Dy alloys, corrosion morphology of Mg-Dy alloys at different immersion time was studied. The corrosion products were removed using chromic acid (180g/l) for 20 min immersion at room temperature.

Results and discussion

Fig. 1 illustrates the microstructure of Mg-Dy alloys. Areas of Dy segregation are found in all the alloys and it increases with the increment in Dy content. In Mg-5Dy alloy, only very few and small second phase was found. With increasing the Dy content, the number and size of second phases increases. Table 2 shows the distribution of Dy in Mg-Dy alloys, analyzed by EDX. Since the type of phase in four Mg-Dy alloys is the same, the analysis for the composition of phase was done only in Mg-20Dy alloy. The results indicate a correlation of the Dy content in the matrix to the amount of Dy in the alloys. Dy content in matrix is about half of the Dy content in alloys.

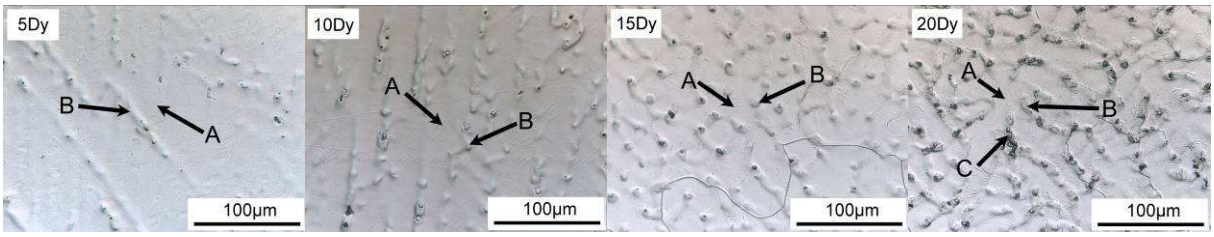

Fig. 1 Optical microstructure of Mg-Dy alloys, A: matrix, B: segregation area, C: intermetallic phases

Table 1 Chemical composition of alloys [wt. %].

Alloy	Dy	Fe	Ni	Cu	Mg
Mg-5Dy	4.5	0.025	<0.01	<0.01	Bal.
Mg-10Dy	8.7	0.033	<0.01	<0.01	Bal.
Mg-15Dy	13.1	0.023	<0.01	<0.01	Bal.
Mg-20Dy	18.9	0.043	<0.01	<0.01	Bal.

Table 2: Dy distribution in Mg-Dy alloys [wt. %]

alloys	Matrix (A)	Segregation area (B)	Phase (C)
Mg-5Dy	2.06±0.15	19.51±0.68	-
Mg-10Dy	4.92±0.09	21.67±0.86	-
Mg-15Dy	7.81±0.36	25.345±0.54	-
Mg-20Dy	11.2±0.62	28.9±0.92	51.8±1.2

Fig. 2 shows the corrosion rates of Mg-Dy alloys in 0.9 wt. % NaCl solution at room temperature. After immersion for one day, Mg-5Dy alloy exhibits the highest corrosion rate, while Mg-10Dy alloy exhibits the lowest corrosion rate. When the Dy content exceeds 10wt. %, the corrosion rate increases gradually. After immersion for 3 days, the trend of corrosion rate for all alloys is similar to that observed after 1 day immersion, however, the corrosion rate increases obviously.

The typical corrosion morphologies after 72 h immersion and removing corrosion products are shown in Fig. 3. Serious filiform corrosion occurred on Mg-5Dy alloy, which has developed into ditches for some areas. With the increase of Dy content, filiform corrosion diminished significantly. When Dy content exceeds 15 wt. %, little filiform corrosion is observed. But at the same time, pitting corrosion increases with the increase of Dy. From table 1 we can see that Mg-15Dy alloy has less impurity amount than Mg-10Dy alloy, but the pitting corrosion on Mg-15Dy alloy is more severe than it on Mg-10Dy alloy. Thus, it can be confirmed that the increase of pitting is due to the increment in Dy content instead of impurities. Both the filiform and pitting corrosion can lead to high corrosion rate. As a result, the lowest corrosion rate is obtained in Mg-10Dy alloy.

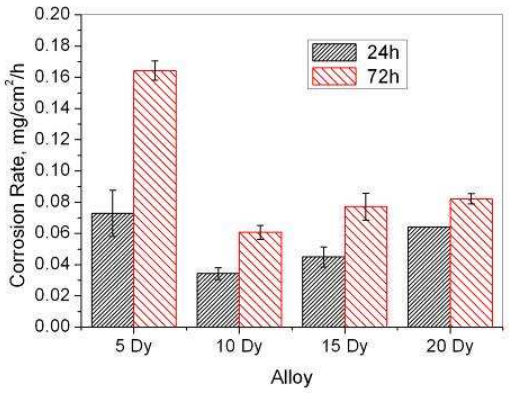

Fig. 2 Corrosion rate (calculated from H_2 volume) of Mg-Dy alloys in 0.9wt.%NaCl solution for different time at room temperature.

Fig. 3 Typical corrosion morphologies of samples after 72h immersion and removal of corrosion products

To further understand the corrosion process, samples were immersed into 0.9 wt. % NaCl for different time and the corrosion morphologies after different time points were studied. It can be seen that the initial pitting corrosion after 30 min transforms to filiform corrosion over time (Fig. 4a and b). After 24 h of immersion, filiform corrosion spreads all over the surface and reaches a depth of less than 20 μm (Fig. 4c and d). For Mg alloys, filiform corrosion has already been observed in NaCl solutions in several studies [12-15]. However, the mechanism is still not well understood. For Mg-Dy alloys, the reason for the reduction of filiform corrosion with the increment in Dy could be: i) the increase of Dy amount in the Mg matrix could improve the corrosion resistance of Mg matrix, thus filiform corrosion is inhibited; ii) the segregation area of Dy could block the propagation of filiform corrosion; iii) passive film with higher corrosion resistance can be formed with the increase in Dy content.

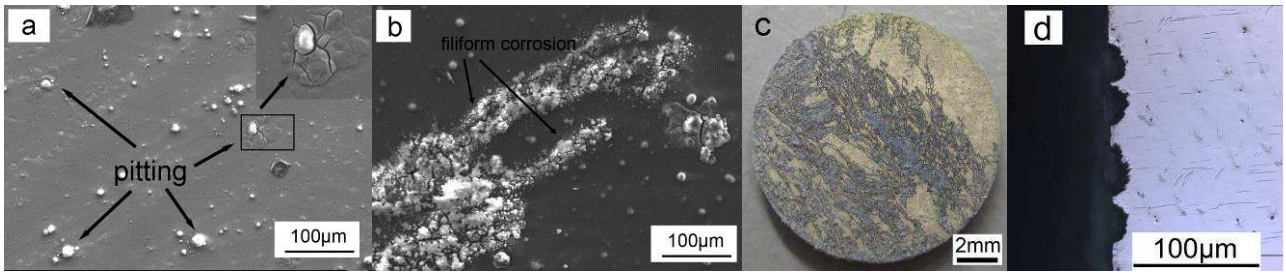

Fig. 4 Corrosion morphologies of Mg-5Dy alloy in 0.9wt.% NaCl solution at room temperature. (a) SEM morphology after 30min immersion; (b) SEM morphology after 3h immersion; (c) photo image after 24h immersion; (d) longitudinal cross-section morphology after 24h immersion

The corrosion morphology of Mg-20Dy alloy is shown in Fig. 5. Initial pitting corrosion was observable after 3 h immersion (Fig. 5a). After 24 h immersion, apparent pitting corrosion (covered by corrosion products) can be seen clearly even by eye, but little filiform corrosion can be found (Fig. 5b). The longitudinal cross-section corrosion morphology of the corrosion pitting (Fig. 5c) reveal that severe corrosion up to a depth of 100 μm has already occurred. Pitting corrosion is very common in Mg alloys, which is generally caused by galvanic corrosion between Mg matrix and second phase [16]. Research on Mg-RE (RE=Ce, La, Nd) and Mg-Y alloy [8, 9] indicates the galvanic corrosion is increased with the increment in alloying element content due to the increasing of second phase amount. For Mg-Dy alloys, it is found that the pitting corrosion increases with the increase of Dy, which could be due to the increase of the amount of Dy containing phase.

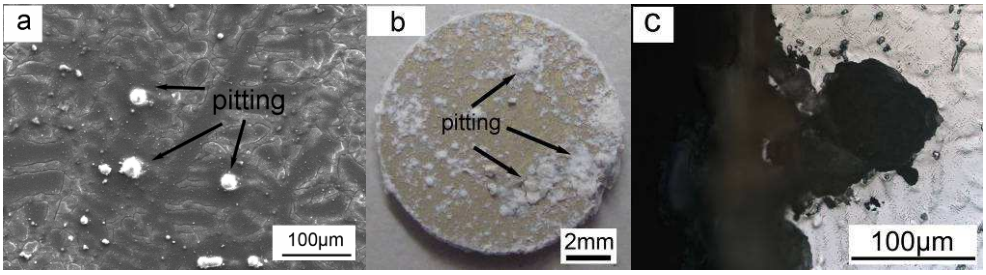

Fig. 5 Corrosion morphologies of Mg-20Dy alloy in 0.9 wt. % NaCl solution at room temperature. (a) SEM morphology after 3h immersion; (b) photo image after 24h immersion; (c) longitudinal cross-section morphology after 24h immersion

Conclusions

Dy plays different roles in influencing corrosion behavior of Mg-Dy alloys, which depends on its content and distribution. The increasing content of Dy results in increment of Dy amount in Mg matrix and segregation area. At the same time, the amount of second phase is also increased. As a result, filiform corrosion is reduced while pitting corrosion is increased.

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