[文章编号] 1004- 0609(2001)S1- 0079- 04

Influence of chemical composition on corrosion resistance of AZ91D magnesium alloy ingots ①

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[Abstract] The influence of chemical composition on corrosion resistance of AZ91D magnesium alloys ingots has been investigated. Mass-loss method was applied to evaluate the corrosion resistance of AZ91D alloys and the data were analyzed by multiple regression. The results show that the corrosion resistance of this alloy can be improved by increasing Al, Zn and Mn in a certain degree, and will drop with increasing Si and heavy metals (Fe, Cu, Ni). It is found that ingots received from company F should be listed into unusable materials in terms of the corrosion resistance, while among the five suppliers, the only local company E supplied excellent AZ91D magnesium alloy ingots with the best corrosion resistance.

[Key words] AZ91D magnesium alloy; chemical composition; property of corrosion resistance; corrosion rate
[CLC number] TG 146.22; TG 172.63 **[Document code]** A

1 INTRODUCTION

Magnesium alloys have found more and more uses in telecommunication and transportation industries due to their excellent properties such as high strength to weight radio, good conductivity, appropriate electro-magnetic shielding property. However their corrosion behavior requires special attention in view of the thermodynamic instability of Mg in wet and humid environments. Mg is the most active structural metal as indicated by its negative electrochemical potential. As a result of this potential, Mg reacts spontaneously with water forming H_2 and $Mg(OH)_2$. However this reaction may result in passivation of the Mg by the precipitated $Mg(OH)_2$ provided an alkaline pH[1].

The reaction can be expressed by the following equation:

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

This reaction may also be presented as the sum of the following partial electrochemical reactions:

$$Mg \longrightarrow Mg^{2+} + 2e^- \quad (2)$$

$$2H_2O + 2e^- \longrightarrow 2(OH)^- + H_2\uparrow \quad (3)$$

$$Mg^{2+} + 2(OH)^- \longrightarrow Mg(OH)_2\downarrow \quad (4)$$

To broaden the application of Mg, studies have to be conducted to enhance its corrosion resistance. A dramatic improvement in corrosion resistance can be obtained by the application of two type principles as reported by earlier studies[2]: alloying with Al and reduction of heavy metal impurities. The positive effects of Al stems from its strong passivation tendency in the presence of oxygen. The passive film is stable in a wide range of environments, thus the presence of Al in Mg alloy widens the range of environmental conditions in which the alloy is resistant to corrosion.

Commercial alloy AZ91D is an example of the application of the mentioned principles to obtain a relatively corrosion resistant alloy. Increasing attention is paid to this alloy and some studies have been reported recently[3~5]. The present investigation is concentrated on the corrosion behavior of AZ91D alloy in form of ingots produced by five companies (W, H, F, Y, E) both from local and abroad. The experiments were carried out to select the best AZ91D alloy ingot for a foreign capital corporation in which computer fittings were produced.

2 EXPERIMENTAL

Chemical composition analysis for the five different AZ91D samples was conducted with a Baird DV-5 spark emission spectrometer. All ingots were sectioned and nine slices of each ingot were machined to an acceptable finish. In order to evaluate the chemical integrity of the ingots, nine spectrographic burns were taken across the face of each slice and then averaged.

The immersion corrosion tests were carried out in 5% NaCl (pH = 6.25) solution at room temperature according to the ASTM Standard G31-72[6]. Mass-loss method was used to determine the average corrosion rate (C_R) over the test period in millimeter per year (mm/a) as

$$C_R = V_g \times 365/(\gamma \times 1000) \quad (5)$$

where γ —the density in grams per cubic centimeter; V_g —the mass loss rate after corrosion as

$$V_g(g/(cm^2 \cdot d)^{-1}) = (g_0 - g_1)/(S_0 \cdot t) \quad (6)$$

where g_0 —the initial mass of the specimen in

① [Received date] 2000- 10- 23; [Accepted date] 2001- 02- 12

grams; g_1 —the mass of the specimen after corrosion in grams; S_0 —the total surface area in square centimeters; t —the immersion period in salt solution in days.

Five slices of each ingot were machined, washed with acetone and dried in air before immersion. After weighing the samples with PRECISA-180A gravity balance they were marinated into the corrosion solution, which was being stirred slightly all the time, and after immersion in the salt solution for twelve days, the samples were again washed, dried and weighed to measure the mass loss during the immersion period. The morphology of the corrosion attacks of immersion samples of AZ91D alloy ingots was observed at BX60M metallurgical microscope.

3 RESULTS AND DISCUSSION

The chemical compositions of the five AZ91D ingots are listed in Table 1. It demonstrates that the chemical compositions of all the ingots are basically in agreement with the requirements of ASTM Standard B93/B93M-94b for AZ91D alloys, except that the Al contents of ingots received from company E and company W are slightly higher than that of the standard, and sample E contains much lower Si than others, while sample F has an obvious higher content of Fe and Si.

The results of standard salt water corrosion tests are shown in Table 2, which illustrates the discrepancy of corrosion rate of the five AZ91D alloy ingots. It should be pointed out that sample F exhibited a corrosion rate considerably higher than any of the other alloys and thus should be listed into unusable materials according to ASTM Standard[7]. While ingot received from company E shows an excellent property of corrosion resistance. The morphology of the corrosion attacks of the samples after immersion in the salt water for 12 days is presented in Fig. 1. The results of the corroded areas and pits distributing in agreement with the results are listed in Table 2.

General service conditions are only at temperatures where direct oxidation doesn't play a significant role for magnesium alloys. Hence, the corrosion behavior is more important in salt containing environment for evaluation of magnesium alloys. Table 2 and Fig. 1 show the results of standard salt water corrosion tests. Correlating with the chemical compositions shown in Table 1, it is indicated that the major alloying elements and heavy metal impurities have intricate influence on the corrosion behavior of AZ91D alloy ingots.

Computer multiple regression analysis was performed in this paper to assess the influence of alloying elements and heavy metal impurities on the corrosion rate. The following equation represents the correlation that was obtained based on the experimental results of the present study and referenced some data of correlative investigation[8]:

$$C_R(\mathrm{mm/a}) = 4w(\mathrm{Mg}) - 41w(\mathrm{Al}) - 23w(\mathrm{Zn}) - 197w(\mathrm{Mn}) + 26.8w(\mathrm{Si}) + 26\times10^3 w(\mathrm{Fe}) + 9.85\times10^4 w(\mathrm{Ni}) + 9.4\times10^3 w(\mathrm{Cu}) \quad (7)$$

Eqn. (7) shows that the alloying elements Al, Zn and especially Mn improve the corrosion resistance of AZ91D alloy ingots. On the other hand, heavy metal impurities and silicon have a detrimental effect. Of course, there are many other factors influence the corrosion rate of AZ91D alloy ingots, but with no change or little change in the other factors, Eqn. (7) may give a useful evaluation of the corrosion behavior of AZ91D alloy ingots.

For example, the data of the present study may also be illustrated in other way as shown in Fig. 2 which indicates the favorable influence of Al content on the corrosion resistance of this alloy due to the passivation effects mentioned above. Zn and Mn have the similar effect trend on the corrosion rate according to Table 2. Fig. 3 demonstrates the influence of Si content on the corrosion rate as an example of detrimental effects. But the affecting mechanism of these elements has not yet made quite clear. Apparently both Fig. 2 and Fig. 3 fit well in with Eqn. (7), and the results of the present work are in good agreement with those of earlier studies[6, 8, 9].

Ingots received from company F exhibit the highest corrosion rate due to the higher contents of

Table 1 Chemical compositions of AZ91D alloy ingots (%)

Sample	Al	Mn	Zn	Si	Cu	Ni	Fe	Mg
ASTM Standard	8.3~ 9.7	0.15~ 0.50	0.35~ 1.0	< 0.10	< 0.03	< 0.002	< 0.005	Balance
W	9.77	0.269	0.840	0.0143	0.0013	0.0009	0.0036	89.1
F	9.05	0.252	0.548	0.0552	0.0015	0.0008	0.0069	89.9
H	9.48	0.314	0.575	0.0284	0.0013	0.0006	0.0041	89.6
Y	9.31	0.322	0.559	0.0234	0.0010	0.0007	0.0025	89.8
E	9.88	0.339	0.876	0.0067	0.0010	0.0006	0.0033	89.0

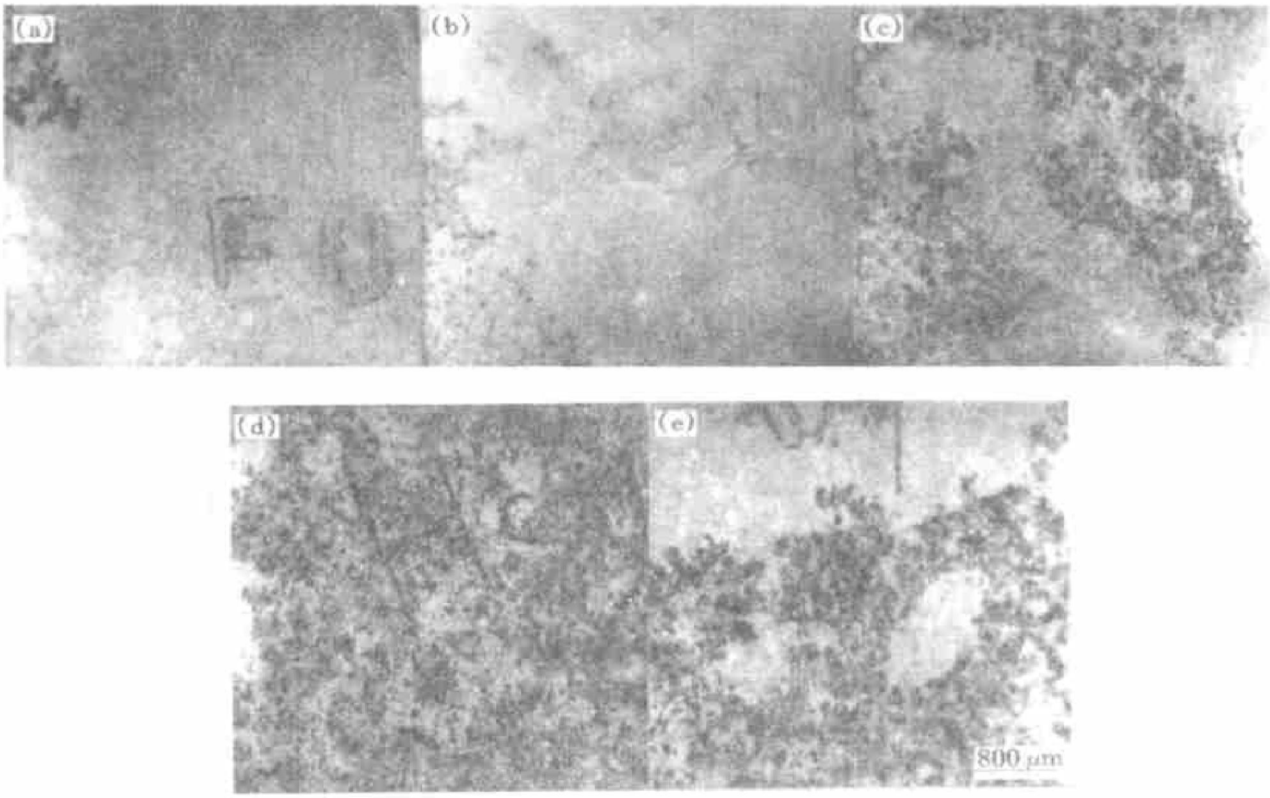

Fig. 1 Morphologies of corrosion attacks of AZ91D alloy ingots after immersion in 5% NaCl solution for 12 d

(a) —Sample E; (b) —Sample W; (c) —Sample Y; (d) —Sample H; (e) —Sample F

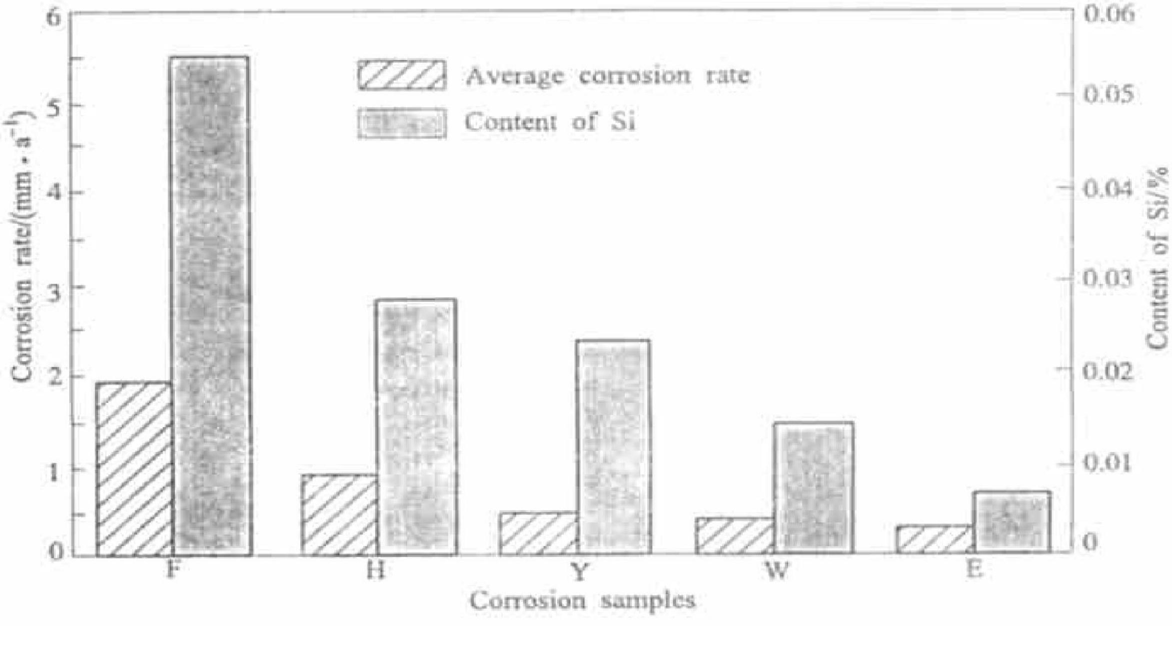

Fig. 2 Influence of Al contents on corrosion rate of AZ91D alloy ingots

Table 2 Corrosion rate of AZ91D alloy ingots after immersion in 5% NaCl solution for 12 d (mm/a)

Corrosion site	1	2	3	4	5	Average
Sample E	0.33	0.31	0.29	0.25	0.28	0.29
Sample W	0.43	0.38	0.35	0.42	0.32	0.38
Sample Y	0.54	0.47	0.46	0.43	0.45	0.47
Sample H	0.87	1.12	0.92	0.76	0.98	0.91
Sample F	2.13	1.77	1.89	2.08	1.94	1.96

silicon and heavy metals. The corrosion behavior of magnesium alloys is based on the pitting mechanism. The pitting corrosion in these alloys starts with an incubation period in which the pit is formed. Heavy metals, especially Fe may shorten the incubation period and accelerate pitting corrosion[10] as seen in Fig. 1 (d) and (e). While ingots produced by company E demonstrate the most excellent property of corrosion resistance due to higher contents of Al, Zn and Mn and more amount of discontinuous precipitation of βthe only local supplier.

4 CONCLUSIONS

1) The results of multiple regression analysis show that the corrosion resistance of AZ91D alloy in the form of ingots can be improved by increasing Al, Zn and Mn in certain degree, and will drop with increasing Si and heavy metals (Fe, Cu, Ni).

2) It was found that ingots received from company F should be listed into unusable materials, while among the five suppliers, the only local company E supplied excellent AZ91D alloy ingots with the best corrosion resistance.

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(Edited by HE Xue-feng)