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Effects of Cu and Sb on Corrosion Resistance of ZnAl27 Alloy

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Abstract. The corrosion behavior of ZnAl27 alloys in 35g/L NaCl solution has been studied by electrochemical and immersion corrosion tests. The effects of Cu and Sb on the Tafel curves, electrochemical parameters of free corrosion potential, linear polarisation resistance (LPR) and free corrosion current, of the ZnAl27 alloy have been investigated. The surface morphologies of the alloy after immersion corrosion tests have been observed through SEM. The results indicate that addition of proper Cu can improve its corrosion resistance of the alloy, or the free corrosion potential the corrosion current shift towards the positive and negative,respectively. However, excessive addition of Cu can deteriorate the corrosion resistance of the alloy. On the other hand, the corrosion resistance of the ZnAl27 alloy decreases with the increasing of Sb content.

Introduction

The ZnAl27 alloy is of excellent casting and mechanical properties as well as low manufacturing cost, therefore the alloy is widely used for materials of sliding bearings, bearing bush and mould in mine and metallurgical equipments [1-6]. In our previously research, The ZnAl27 alloy has been studied as a hot dipped alloy due to its good strength and wear resistance. It can be used for such structural components as machine tools, guardrails by the highway and communication towers, etc. Cu is the main reinforcing element in the alloy. It is generally believed that the addition of Cu can strongly increase strength of the alloy [7-9], moreover Sb is an impurity commenly present in the alloy. However, some researchers found a trace of Sb is beneficial to the appearance of galvanized steel plate [10-11]. As a new developed hot dipped alloy, the electrochemical tests experiments has been carried out in the present work to valuate the effect of Cu and Sb on the corrosion resistance of ZnAl27 alloy in 3.5wt% NaCl solution.

Experiments

The sample preparation. The test alloy composition is shown in Table 1, the raw material is aluminum with purity of 99.7%, zinc with purity of 99.99%, Al-Cu master alloy and pure Sb. High-frequency induction furnace is used for smelting the alloy, the melting alloy was cast into Cylindrical casting in dimension of Ø16mm×100mm, then cut into the sample in dimension of Ø16mm×15mm.

Table 1 The composition of test alloy

No.	Experimental alloy	ω_B/%			
		Al	Cu	Sb	Zn
1	ZnAl27	27	-	-	balance
2	ZnAl27-Cu1	27	1.0	-	balance
3	ZnAl27-Cu2	27	2.0	-	balance
4	ZnAl27-Cu3	27	3.0	-	balance
5	ZnAl27-Cu4	27	4.0	-	balance
6	ZnAl27-Sb1	27	-	0.2	balance
7	ZnAl27- Sb1	27	-	0.4	balance
8	ZnAl27- Sb1	27	-	0.6	balance
9	ZnAl27- Sb1	27	-	0.8	balance

Testing methods. Electrochemical tests including: grinding the sample from 200# to 1500# sandpaper, mechanical polishing it, smearing the sample's surface with the etched surface exposure, measuring the Tafel curves, as well as electrochemical parameters of free corrosion potential, linear polarisation resistance (LPR) and free corrosion current of the ZnAl27 alloy. Scanning speed is 1 mV/s, sampling rate is 500 ms, reference electrode is 232 calomel electrode, corrosion medium is 35 g/L NaCl solution. Every sample is measured 5 times and the obtained data is analyzed statistically.

Immersion corrosion tests including: cleaning the sample surface with ultrasonic in acetone and alcohol for degreasing and dust-removing to weigh the sample with electronic balance before the tests are conducted, immersing the prepared sample in 35g/L NaCl solution for 20 days, cleaning the corrosion product on the surface of the sample with soft brush, ultrasonic cleaning the surface of the alloy, weighing the sample with electronic balance, observing the surface morphology of the sample with S750 TEM.

Experimental results and analyses

Tafel curves and electrochemical parameters of the alloy. The effects of Cu and Sb on the Tafel curves, as well as electrochemical parameters of free corrosion potential, linear polarisation resistance (LPR) and corrosion current density of the samples are shown in Fig. 1-Fig. 4. As is shown in Fig. 1 and Fig. 3, the effect of Cu on the samples is complicated, with the addition of Cu, Tafel curve shifts left, free corrosion potential shifts to positive and the corrosion current density decreases; when the addition of Cu exceeds 1.0 wt.%, Tafel curve shifts right, free corrosion potential shifts to negative and the corrosion current density increases, while linear polarisation resistance Rp decrease.

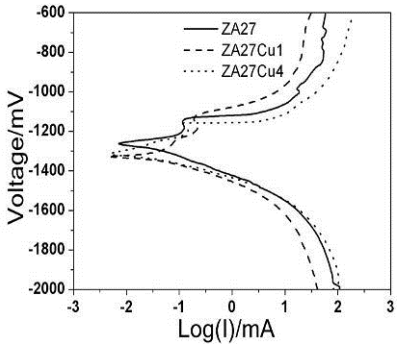

Fig. 1 Influence of Cu on Tafel curve

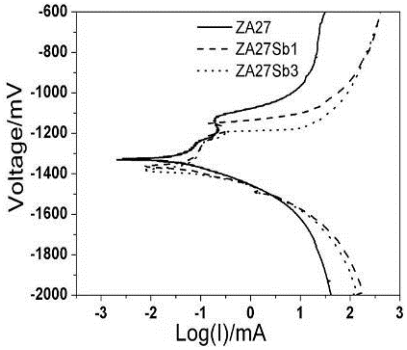

Fig. 2 Influence of Sb on Tafel curve

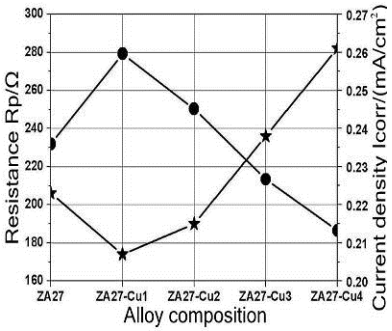

Fig. 3 Influence of Cu on corrosion resistance

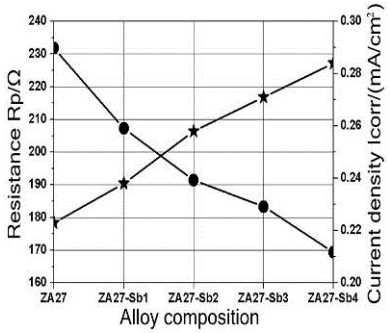

Fig. 4 Influence of Sb on corrosion resistance

As is shown in Fig. 2 and Fig. 4, with the addition of impurity elements Sb, Tafel curve shifts right, free corrosion potential shifts to negative and the corrosion current density increases, while linear polarisation resistance Rp decrease. Based on the four figures, J_{corr} of ZnAl27-Cu1 reach the minimum value, and R_p of the alloy reach the maximum value, the corrosion resistant of the alloy is best; while J_{corr} of ZnAl27-Sb4 reach the maximum value, and R_p of the alloy reach the minimum value, the corrosion resistant of the alloy is worst.

Free corrosion potential E_k. Free corrosion potential reflects the metal dissolving ability in solution. Under the condition that the reactions on electrodes are same, the lower the free corrosion potential is, the easilier the metal dissolves. The free corrosion potentials measured in the test are shown in Table 2, the measured value basically agrees well with Tafel curves, as well as electrochemical parameters of linear polarisation resistance (LPR) and corrosion current density. Trace addition of Cu make free corrosion potential of the alloy shifts to positive, which improves its corrosion resistant; excessive addition of Cu, or increasing addition of Sb, make free corrosion potential of the alloy shifts to negative, which deteriorates its corrosion resistance.

Table 2 The free corrosion potential E_k of test alloy

No.	1	2	3	4	5	6	7	8	9
E_k [mV]	-1081	-1069	-1089	-1096	-1111	-1090	-1118	-1103	-1108

Results of immersion corrosion tests. Results of immersion corrosion tests are shown in Table 3, while results of analysis of typical parts of the samples with SEM after immersion corrosion treatment are shown in Fig. 5.

As is shown in Fig. 5a, preferential corrosion originates from phase α and intergranular gaps of ZnAl27 alloy, corrosion pits are formed after corrosion products exfoliate. With the addition of Cu, local accumulation of new compounds ε ($CuZn_4$) occur in grain boundary [5, 6]. With the corrosion tests proceeding, corrosion first originates from phase ε in grain boundary, then develops around and in the depths of the region, as shown in 5b. The surface of the samples after corrosion tests consist of Cl, C and a large number of O, which are resulted from corrosion products on the surface of the samples which should have cleaned thoroughly. Zn and Al are dissolved partly; what's more, as is shown in Table 3, when Cu content of ZnAl27 alloy is more than 2 wt.%, its corrosion rate increases with the addition of Cu, and corrosion type shifts from pitting corrosion to intergranular corrosion.

With the addition of Sb, rich-Al phase of the alloy and the end of dendrite becomes dendrite fragmentation and tact, respectively. Sb combined with Zn and Al to form Sb-Al-Zn acicular compound. With the corrosion tests proceeding, corrosion originates and develops from grain boundary due to the presence of compound Sb-Al-Zn in grain boundary, as shown in 5C. The surface of the samples after corrosion tests consist of Cl, C and a large number of O, which are resulted from corrosion products on the surface of the samples which should have cleaned thoroughly. Zn, Al and especially Sb are dissolved partly; what's more, corrosion rate increases with the addition of Sb.

Table 3 Results of immersion corrosion tests

No.	before test [g]	after test [g]	Mass loss [g]	Corrosion rate/%
1	5.14520	5.00755	0.13765	2.68
2	5.23650	5.11250	0.12400	2.37
3	5.21565	5.09920	0.11645	2.23
4	5.08350	4.89950	0.18400	3.62
5	5.35410	5.14820	0.20590	3.85
6	5.53620	5.39255	0.14365	2.59
7	5.28650	5.13030	0.15620	2.95
8	5.33150	5.15250	0.17900	3.36
9	5.26505	5.04545	0.21960	4.17

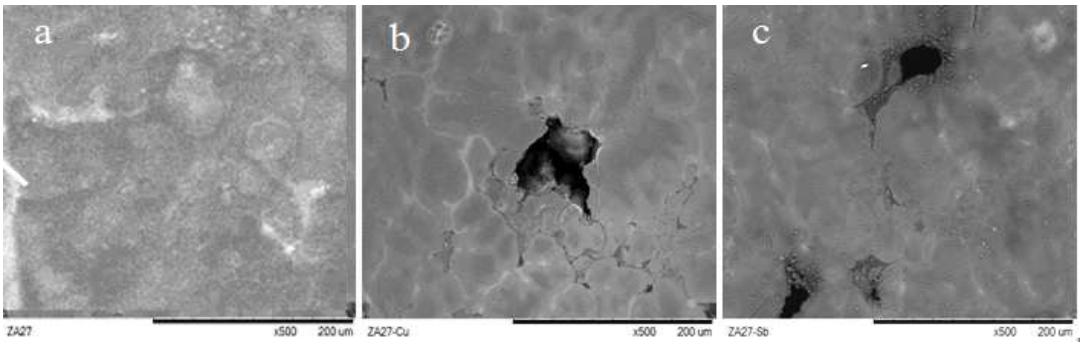

Fig.5 The typical SEM morphology of ZnAl27 alloys after corrosion

By comparison of morphology pictures before and after corrosion tests, intergranular corrosion is the main corrosion type of zinc-based alloy. Intergranular corrosion of the alloy is featured that corrosion crack growth and depth increase are resulted from the dissolution of rich-Al and rich-Zn phase in grain boundary. The surface of the samples after corrosion tests consist of Cl, C and O, which conforms well to the study of Mccafferty E [12].

Corrosion mechanism of high aluminum Zn-based alloys. According to Zn-Al binary alloy phase figure [13], the microstruction of the alloy under room temperature is α+η, while α is Al-based solid solution in which Zn is dissolved, η is Zn-based solid solution in which Al is dissolved. The tests indicated that the intergranular corrosion of ZnAl27 alloy is related with electrode potential between Zn and Al in grain boundary. The microbattery, whose reaction process makes ZnAl27 alloy intergranular corrosion, consists of α positive electrode, and η negative electrode which around the grain boundary of α.

Analysis of the elements effects on corrosion resistant of ZnAl27 alloy. Trace addition of Cu could improve corrosion resistant of ZnAl27 alloy. However, when Cu content of ZnAl27 alloy is more than 2 wt.%, its corrosion rate increases with the addition of Cu, and corrosion type shifts from pitting corrosion to intergranular corrosion; when Cu content of ZnAl27 alloy is more than 4 wt.%, corrosion cracks which is around grain boundary is observed obviously, mainly because trace addition of Cu inhibit eutectoid decomposition, which improves Al solid solubility in η to slow down the tendency of Al diffusion to grain boundary; what's more, relatively high Cu electrode potential decreases the electrochemical differences between α and impurity elements when Cu dissolves in α; however, Cu precipitate and distribute around α grain boundary in the form of ε when Cu content of ZnAl27 alloy exceeds Cu solubility in α [14], moreover, ε phase amount increases with addition of Cu. When Cu content of ZnAl27 alloy is more than 4 wt.%, ε phase forms reticula; corrosion comes into being when microbattery consists of α positive electrode and precipitated ε negative electrode works. What's more, excess Cu precipitate in the form of ε can result in atomic size swelling to generate internal stress, which accelerates the corrosion.

The addition of Sb mades free corrosion potential shifts to negative, while with the increasing addition of Sb, the trend becomes more obvious. After the addition of Sb, Rich-Al phase of the alloy becomes dendrite fragmentation, while Sb combined with Zn and Al to form and precipitate

Sb-Al-Zn acicular compound in grain boundary of phase α. With the increasing addition of Sb, the amount and size of acicular precipitated phase increase to increase grain boundary and Zn-Al as well as Sb-Matrix electrode potential difference, which changes the electrochemical properties of the alloy. Sb-Al-Zn acicular compound as well as phase α become positive electrode due to their high potential, η becomes new negative electrode, the electrodes above form microbattery to dissolve the alloy. With increasing addition of Sb, the corrosion resistance of the alloy becomes more deteriorated. Therefore, the content of Sb should be controlled below 0.2 wt.%, otherwise, the corrosion resistance of the alloy will be deteriorated strongly.

Conclusions

Based on the analyses above, conclusions could be drawn as followings,

(1) Preferential corrosion originates from phase α and intergranular gaps of ZnAl27 alloy in 35g/L NaCl solution, corrosion pits are formed after corrosion products exfoliate; the intergranular corrosion of ZnAl27 alloy is related with electrode potential between Zn and Al in grain boundary;

(2) With the addition of Cu, corrosion current density of ZnAl27 alloy decreases first, and then increases. Adding proper Cu into ZnAl27 alloy can improve its corrosion resistance, however, excessive Cu content of ZnAl27 alloy can deteriorate its corrosion resistance;

(3) Impurity element Sb changes the electrochemical properties of the alloy, Sb-Al-Zn acicular compound as well as phase α become positive electrode due to their high potential, η becomes new negative electrode, the electrodes above form microbattery to dissolve the alloy. With increasing addition of Sb, the corrosion resistance of the alloy becomes more deteriorated;

(4) The contents of Cu and Sb should be controlled below 2 wt.% and 0.2 wt.% respectively to ensure its excellent corrosion resistance.

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