Article ID: 1003-6326(2004)05-0961-05

Corrosion resistance of Zr-Al-Ni-Cu(Nb) bulk amorphous alloys①

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Abstract: The corrosion resistance of Zr-Al-Ni-Cu(Nb) bulk amorphous alloys was systematically investigated. The experimental results show that the corrosion resistance of Zr-based bulk amorphous alloys can not be considered to be excellent at any situation, whereas it is affected by many factors such as the kind of corrosive medium, solution concentration and the alloy composition. It is found that Zr-Al-Ni-Cu bulk amorphous alloys are seriously corroded in HCl solution in comparison with their excellent corrosion resistance at other acid, alkali and salt circumstances for passivating. Its resistance ability against the chlorine ion induced pitting corrosion can be greatly improved by the addition of Nb element.

Key words: amorphous materials; corrosion resistance; corrosive medium
CLC number: TG 174.2 **Document code:** A

1 INTRODUCTION

New bulk metallic glasses (BMGs)[1-7] with large glass-forming ability(GFA) have been discovered since 1980s. In comparison with traditional amorphous alloys, they could be prepared at lower critical cooling rate with larger sample thickness and possess superior mechanical properties, high workability at slightly high temperatures, special magnetic properties and good corrosion resistance. All these characteristics make bulk amorphous alloys have good foreground in application fields. It is very helpful for high corrosion resistance property (especially for pitting corrosion resistance) that metallic glass does not have segregation and lattice defects, e. g. crystal boundary, dislocation, which cannot be avoided in crystalline alloy. The previous researches[8-15] indicated that the metallic glass has much better corrosion resistance than crystalline alloys with the same composition or representative stainless steels. Because the related studies have mainly been made on traditional amorphous alloys and the research about the BMGs is just at the beginning, it should be systematically and deeply investigated how the corrosive mediums and alloy composition affect the corrosion resistance of the BMGs.

Zr-Al-Ni-Cu(Nb) BMGs with large GFA and excellent mechanical properties[16, 17] are known to be one of the best metallic glass formers. In this paper, the corrosion resistance of Zr-based BMG in different corrosive mediums was systematically studied by the immersion experiment method, and the results showed that the corrosion resistance ability of bulk amorphous alloys could not be considered to be excellent at any situation, which was affected by many conditions such as the kind of corrosive medium, solution concentration and alloy's composition.

2 EXPERIMENTAL

Two kinds of representative Zr-based bulk amorphous alloys, $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ and $Zr_{57}Al_{10}Ni_{12.6}Cu_{15.4}Nb_5$, presented nominally by mole fraction, were selected in the experiments. The cylindrical amorphous alloy samples with the dimensions of d10 mm × 135 mm were obtained by sucking the remelted mother alloys, prepared with pure elements (99.9%), into the copper mould. The amorphous nature of the cast sample was confirmed by X-ray diffraction with CuK_α radiation(Fig. 1).

$Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ and $Zr_{57}Al_{10}Ni_{12.6}Cu_{15.4}Nb_5$ samples were incised to fine strips, and then the surface was polished to remove the oxidation layer. The surface areas and the initial mass of each sample were measured, and the incised samples were finally immersed into the corrosive mediums listed as follows:

1) 5 mol/L HCl solution (strong reductive

① **Foundation item:** Project(50371024) supported by the National Natural Science Foundation of China; project(RC2002-01) supported by the Expert Indraught and Selection Foundation of Hefei University of Technology
Received date: 2004-02-06; **Accepted date:** 2004-05-17
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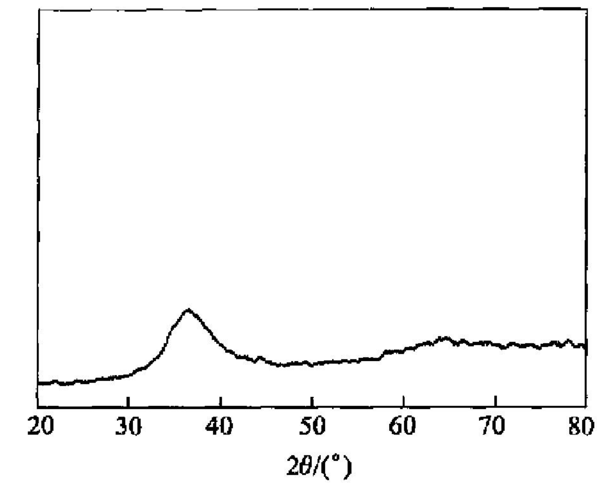

Fig. 1 XRD pattern of $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ BMG

acid);

2) HNO_3 solution of 30% and 66% (mass fraction) respectively (strong oxidative acid);

3) NaCl solution of 9.1% (3%, mole fraction) and 17.2% (6%, mole fraction) respectively;

4) NaOH solution of 20% and 40%.

Each sample was weighed at intervals and the total corrosion time for each sample is 400 − 500 h at room temperature. The experimental data were processed by two kinds of functions:

1) Sample corrosion percentage:

$$\alpha=\left(\frac{M_0-M_1}{M_0}\right)\times 100\% \qquad (1)$$

where M_0 is the sample initial mass, M_1 is the mass measured currently.

2) Sample corrosion speed(mg/(cm^2·h)):

$$v=\frac{M_1-M_2}{St}$$

where M_1 is the mass measured last time, M_2 is the mass measured currently, S is the surface area, t is the corrosion time during the measure interval.

3 RESULTS AND DISCUSSION

Some corrosion data of $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ BMG in various kinds of corrosive solutions are listed in Table 1, indicating its excellent corrosion resistance ability at acid, alkali and salt corrosive circumstances except for strong corrosion behavior occurred in 5 mol/L HCl solution.

In the most of corrosive mediums other than the 5 mol/L HCl solution, the BMG sample was rapidly passivated in a definite time after a little corrosion phenomenon occurred, and the developed passivation layer at the sample surface prevented further corrosion effectively. For example, in 9.1% NaCl solution during the passivating period the corrosion speed decreased from 0.031 mg/(cm^2·h) to 0.005 mg/(cm^2·h) for the development of passivation layer. In 20%, 40% NaOH solution and 17.2% NaCl solution, the sample's passivation speed was so fast that almost no corrosion was observed. It reveals Zr-based BMGs excellent corrosion resistance ability under acid, alkali and salt corrosive circumstances.

Table 1 Corrosion results of $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ BMG in various kinds of corrosive solutions

Corrosive solution	Corrosion time/h	Corrosion quantity/%	Corrosion speed/(mg·cm^{-2}·h^{-1})
30% HNO_3 solution	22.5	0.144 9	0.009
	103.5	0.289 8	0.002
	150	0.289 8	≈0
	200	0.289 8	≈0
	300	0.289 8	≈0
60% HNO_3 solution	22.5	≈0	
	103.5	≈0	
	150	≈0	
	200	≈0	
	300	≈0	
9.1% NaCl solution	20.5	0.386 6	0.031
	59	0.515 5	0.005
	100	0.5155	≈0
	200	0.515 5	≈0
	300	0.515 5	≈0
17.2% NaCl solution	20.5	≈0	
	59	≈0	
	100	≈0	
	200	≈0	
	300	≈0	
20%, 40% NaOH solution	20.5	≈0	
	59	≈0	
	100	≈0	
	200	≈0	
	300	≈0	
5 mol/L HCl solution	20.5	0.175	0.024
	59	0.526	0.025
	200	7.504	0.2475
	250	11.75	0.723
	400	25.25	0.060

Fig. 2 shows the corrosion curves of $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ in 9.1% NaCl solution and 30% HNO_3 solution respectively . The passivating process of

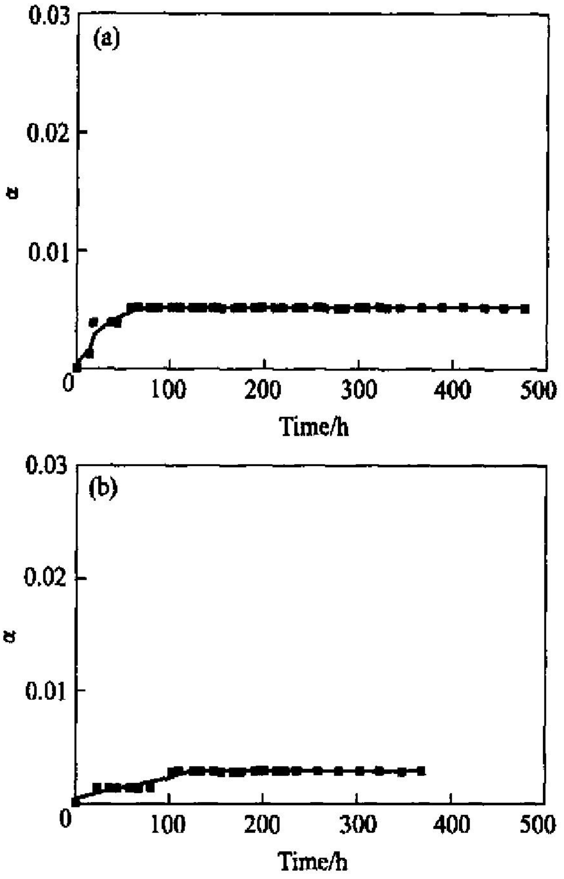

Fig. 2 Corrosion curves of $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ at different kinds of corrosive mediums
(a) —9.1% NaCl solution; (b) —30 % HNO_3 solution

$Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ was completed after 59 h in 9.1% NaCl solution and 103 h in 30% HNO_3 solution. Though the passivation speed in NaCl solution is faster than in HNO_3 solution, its corrosion quantity in NaCl solution is still much higher than that in HNO_3 solution. It is indicated that $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ alloys have lower corrosion resistance against NaCl solution than against HNO_3 solution.

It should be noted that the passivation speed of BMG sample is quickened with the increase of solution concentration in a certain range, and its corrosion resistance becomes stronger as well. For instance, with the solute concentration increasing from 30% to 66% for HNO_3 solution and from 9.1% to 17.2% for NaCl solution, both the passivation time and corrosion quantity decrease to the level that almost can be ignored.

In the solution of 5 mol/L HCl, the corrosion patterns of $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ and $Zr_{57}Al_{10}Ni_{12.6}Cu_{15.4}Nb_5$ BMG samples are shown in Fig. 3 and Fig. 4. It is found that the sample $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ BMG is seriously corroded in the solution, with the average corrosion speed about 0.17 mg/(cm^2•h) and the total corrosion quantity near to 30% at the end of the experiment. It can be seen from Fig. 4 that the corrosion process can be divided into three periods for $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ in the

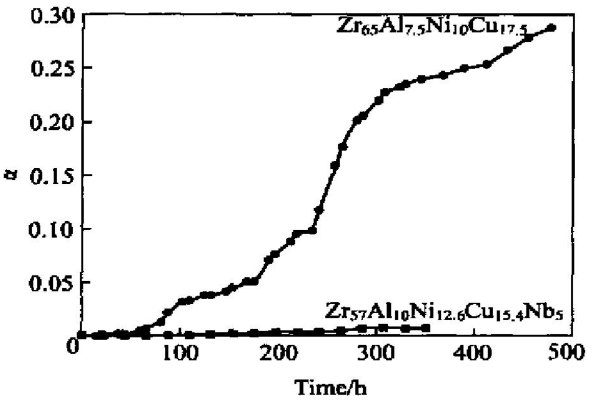

Fig. 3 Corrosion quantity curves of $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ and $Zr_{57}Al_{10}Ni_{12.6}Cu_{15.4}Nb_5$ BMGs in 5 mol/L HCl solution

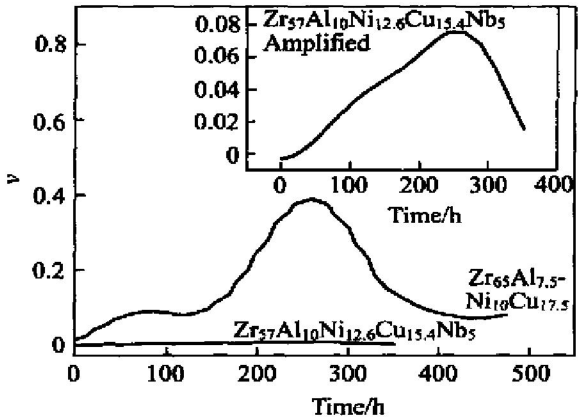

Fig. 4 Corrosion speed curves of $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ and $Zr_{57}Al_{10}Ni_{12.6}Cu_{15.4}Nb_5$ BMGs in 5 mol/L HCl solution

solution of 5 mol/L HCl. At the first period, the sample corrosion speed is very slow for the function of passivating, and correspondingly the corrosion quantity is close to 0 as shown in Fig. 3. This period ends after 50 − 60 h. At the second period, the corrosion speed begins to increase with the experiment proceeding. After achieving a climax point, the corrosion speed begins to decrease gradually. A great number of fine holes appear on the sample surface, which can be accounted for strong pitting corrosion occurred in 5 mol/L HCl solution. At the third period, the corrosion speed remains changeless at a certain level, without completed passivation due to the effect of active chlorine ion. The above-mentioned facts indicate that Zr-Al-Ni-Cu BMG is quite poor at resisting the pitting corrosion caused by chlorine ion at strong deoxidization acid circumstance, manifesting it is not universally correct that the corrosion resistance of metallic glasses is excellent at any situation as has been generally believed.

$Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ BMG exhibits excellent corrosion resistance ability in NaCl solution in comparison with in HCl solution. It's believed that Zr-based

BMGs have better resistance to pitting corrosion caused by chlorine ion at neutral pH value environment, because its special structure features can effectively destroy the self-catalysis-acidification growth mechanism of pitting corrosion. The pH value of corrosion medium plays an important role in the resistance to pitting corrosion of Zr-Al-Ni-Cu BMG.

In comparison with $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$, the components and compositions of $Zr_{57}Al_{10}Ni_{12.6}Cu_{15.4}$-$Nb_5$ have been appropriately adjusted by the addition of Nb element. The corrosion quantity and corrosion speed of $Zr_{57}Al_{10}Ni_{12.6}Cu_{15.4}Nb_5$ in 5 mol/L HCl solution are much smaller than those of $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ as revealed in Figs. 3, 4 and Table 1 and 2, indicating that the addition of Nb element can greatly improve Zr-based BMGs' resistance ability to pitting corrosion.

Table 2 Corrosion results of $Zr_{57}Al_{10}Ni_{12.6}Cu_{15.4}$-$Nb_5$ BMG in various kinds of corrosive solutions

Corrosive solution	Corrosion time/h	Corrosion quantity/%	Corrosion speed/(mg·cm^{-2}·h^{-1})
64%−68% HNO_3 solution	22.5	≈0	
	103.5	≈0	
	150	≈0	
	200	≈0	
	300	≈0	
17.2% NaCl solution	20.5	≈0	
	59	≈0	
	100	≈0	
	200	≈0	
	300	≈0	
40% NaOH solution	20.5	≈0	
	59	≈0	
	100	≈0	
	200	≈0	
	300	≈0	
5mol/L HCl solution	15	≈0	≈0
	60	≈0	≈0
	110	0.07	0.007
	280	0.747 4	0.020
	350	0.747 4	≈0

Furthermore, $Zr_{57}Al_{10}Ni_{12.6}Cu_{15.4}Nb_5$ BMG exhibits excellent corrosion resistance under the other corrosive circumstances such as acid, alkali and salt. Corrosion phenomenon almost could not be observed in 66% HNO_3 solution, 17.2% NaCl solution and 40% NaOH solution for rapid passivating, which could be seen from Table 2.

4 CONCLUSIONS

1) Both the two kinds of Zr-based BMGs exhibit excellent corrosion resistance in 30%, 66% HNO_3 solution; 9.1%, 17.2% NaCl solution and 20%, 40% NaOH solution for the function of passivating, which indicates its high corrosion resistance ability at acid, alkali and salt circumstances.

2) During the passivating period the corrosion speed varies with the process of time. At the initial passivating period the corrosion speed is very fast and the corrosion quantity increases quickly, then they gradually decrease to a very low value finally. In addition the passivation speed of BMG sample also changes with the increase of solution concentration in a certain range.

3) From the different corrosion behaviors of $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ BMG in NaCl, HCl solution, it can be seen that the pH value of corrosion environment plays an important role in the resistance ability against pitting corrosion.

4) $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ BMG sample is seriously corroded in 5 mol/L HCl solution. However, by adding appropriate Nb element, its resistance to pitting corrosion can be greatly improved. The addition of Nb element is important for the improvement of the corrosion resistance ability (especial to pitting corrosion) by comparing the two amorphous alloys' corrosion behaviors. The results indicates that the corrosion resistance ability of bulk amorphous alloys is affected by many conditions such as the kind of corrosive medium, solution concentration and the compositions of amorphous alloys.

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(Edited by YUAN Sai-qian)