Corrosion Behavior of Cu–Zr–Ti–Nb Bulk Glassy Alloys

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Bulk glassy ($\text{Cu}_{0.6}\text{Zr}_{0.3}\text{Ti}_{0.1}$)_{100-x}Nb_x ($x = 0\text{--}5\text{ at\%}$) alloys with high thermal stability and good mechanical properties were synthesized and the effects of Nb on the glass formation and corrosion behavior were clarified. As the Nb content increases, the glass transition temperature (T_g) remains constant while the crystallization temperature (T_x) decreases slightly, resulting in a decrease in $\Delta T_x (= T_x - T_g)$ from 42 K at 0 at%Nb to 36 K at 5 at%Nb. The maximum diameter for glass formation was 4.0 and 2.0 mm for the 2 at% and 5 at%Nb alloys, respectively. The corrosion rates in various solutions significantly decrease with increasing Nb content. The addition of Nb to the glassy alloys shows higher corrosion potential and lower current density in 1 N HCl and 3% NaCl solutions. In 1 N H₂SO₄ and 1 N HNO₃ solutions, they are spontaneously passivated in wide passive region and low passive current density range of $10^{-2}\text{--}10^{-1}\text{ A}\cdot\text{m}^{-2}$. The XPS results revealed that the Zr was enriched in the surface film by addition of Nb to the Cu–Zr–Ti bulk glassy alloy. It was suggested that the role of Nb is to improve the protectiveness of Zr-rich surface film by decreasing Cu concentration in the surface film.

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1. Introduction

Since the syntheses of Ln⁻¹ (Ln = Lanthanide metals), Mg-,²⁾ Zr-^{3,4)} and Pd–Cu-⁵⁾ based bulk glassy alloys, a number of bulk glassy alloys have been developed in multi-component systems during the last decade.^{6–8)} Especially the Zr- and Pd–Cu-based bulk glassy alloys have been used as practical materials.^{6–8)} For further extension of application fields, it is important to find a new bulk glassy alloy with better mechanical properties in conjunction with less cost and higher corrosion resistance.

Very recently, new Cu-based bulk glassy alloys with high tensile strength and significant plastic elongation have been formed in Cu–Zr–Ti,⁹⁾ Cu–Hf–Ti,¹⁰⁾ Cu–Zr–Hf–Ti,¹¹⁾ Cu–Zr–Ti–Y,¹²⁾ Cu–Zr–Ti–Be¹³⁾ and Cu–Zr–Ti–(Nb, Ta)¹⁴⁾ systems. It has been reported that these Cu-based bulk glassy alloys have a large critical diameter of 5 mm in the case of copper mold casting and exhibit high tensile fracture strength exceeding 2500 MPa. However, the corrosion resistance of these Cu-based bulk glassy alloys is low in acidic solutions especially when the solution contains chloride ions.¹⁵⁾ The chemical unstability of the Cu-based bulk glassy alloys has limited future application fields. It is therefore important to investigate and improve the corrosion behavior of these glassy alloys and subsequently to evaluate the effects of additional elements on glass-forming ability and corrosion resistance of the Cu-based bulk glassy alloys. The main purpose of this work is to present the effects of Nb on the glass formation and corrosion behavior of Cu–Zr–Ti–Nb glassy alloys. The origin for the effects of Nb is also discussed.

2. Experimental

Multi-component Cu-based alloy ingots with nominal composition of ($\text{Cu}_{0.6}\text{Zr}_{0.3}\text{Ti}_{0.1}$)_{100-x}Nb_x ($x = 0\text{--}5\text{ at\%}$) were

prepared by arc melting the mixtures of pure Cu, Zr, Ti and Nb metals in an argon atmosphere. The alloy compositions represent nominal atomic percentages. Bulk samples in a cylindrical rod form of 5 mm in length and of 1.5 mm in diameter were prepared by copper mold casting. Glassy structure was identified by X-ray diffraction and optical microscopy (OM). Thermal stability associated with glass transition temperature (T_g) and onset temperature of crystallization (T_x) was examined by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s.

Corrosion behavior of the glassy alloys was evaluated by weight loss and electrochemical measurements. Prior to immersion test and electrochemical measurements, the specimens were mechanically polished in cyclohexane with a silicon carbide paper up to No. 2500, degreased in acetone and dried in air. Electrolytes used were 1 N HCl, 1 N H₂SO₄, 1 N HNO₃, 1 N NaOH and 3% NaCl aqueous solutions, which were prepared from reagent grade chemicals and distilled water. Electrochemical measurements were conducted in a three-electrode cell using a platinum counter electrode and a Ag/AgCl reference electrode. Potentiodynamic polarization curves were measured with a potential sweep rate of $50\text{ mV}\cdot\text{min}^{-1}$ after immersing the specimens for 20 min when the open-circuit potentials became almost steady. The corrosion rates were estimated from the weight loss after immersion for one or two weeks in the solutions open to air at 298 K. After immersion test, the specimen was washed in distilled water, dried in air and subjected to weight loss measurement.

X-ray photoelectron spectroscopy (XPS) measurements for surface analysis of the bulk metallic glasses before and after immersion in solutions were performed by using a SSI SSX-100 photoelectron spectrometer with monochromatized Al-K α excitation ($h\nu = 1486.6\text{ eV}$). The composition and thickness of the surface film and the composition of the underlying alloy surface were determined quantitatively by a previously proposed method using the integrated intensities of photoelectrons under the assumption of a three-layer

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model.^{16,17)} The binding energies of electrons were calibrated by using the method described elsewhere.^{18,19)}

3. Results and Discussion

3.1 Effect of Nb on glass formation

Bulk alloys with a diameter of 1.5 mm consisting only of a broad peak were formed in the composition range of 0–5 at%Nb for $(\text{Cu}_{0.6}\text{Zr}_{0.3}\text{Ti}_{0.1})_{100-x}\text{Nb}_x$ alloys. Figure 1 shows DSC curves of the Cu-based bulk glassy alloys. All the alloys exhibit the sequential transition of distinct glass transition, supercooled liquid and crystallization. The glass transition temperature (T_g) is almost independent of Nb content, while the onset temperature of crystallization (T_x) decreases with increasing Nb content, resulting in a decrease in the supercooled liquid region ΔT_x . The changes in T_g , T_x and ΔT_x as a function of Nb content are shown in Fig. 2. It is seen that the Cu–Zr–Ti–Nb alloys keep high glass-forming ability in the investigated composition range, though the addition of Nb causes a decrease in the supercooled liquid region. The maximum diameter for glass formation was 4.0 mm at 2 at%Nb and 2.0 mm at 5 at%Nb. The outer surface appearance of the 2 at%Nb bulk glassy rods with diameters of 1.5, 2.0, 3.0 and 4.0 mm is shown in Fig. 3. These rod samples exhibit good metallic luster and no distinct concave due to a crystalline phase is recognized.

Since Nb element has nearly zero or positive heats of mixing against the base constituent elements of Cu, Zr and Ti,²⁰⁾ it is important to investigate the effect of Nb addition on the glass-forming ability and thermal stability of the $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ bulk glassy alloys. It has previously been

Fig. 1 DSC curves of bulk glassy $(\text{Cu}_{0.6}\text{Zr}_{0.3}\text{Ti}_{0.1})_{100-x}\text{Nb}_x$ ($x = 0$ –5 at%) alloys.

Fig. 2 Changes in T_g , T_x and ΔT_x with Nb content for the bulk glassy $(\text{Cu}_{0.6}\text{Zr}_{0.3}\text{Ti}_{0.1})_{100-x}\text{Nb}_x$ alloys.

Fig. 3 Outer shape and surface morphology of the cast glassy $(\text{Cu}_{0.6}\text{Zr}_{0.3}\text{Ti}_{0.1})_{98}\text{Nb}_2$ rods with diameters of 1.5, 2, 3 and 4.

reported that the high glass-forming ability leading to the formation of a bulk glassy alloy is obtained in the multi-component alloy systems with the following three empirical rules,^{21–23)} *i.e.*, (1) multicomponent consisting of more than three elements, (2) significant atomic size mismatches above 12%, and (3) suitable negative heats of mixing. The addition of Nb to Cu–Zr–Ti alloys is expected to cause a decrease in glass-forming ability because the addition of Nb generates the bonding pair of Cu–Nb, Zr–Nb or Ti–Nb with positive

and nearly zero heat of mixing, in good agreement with the present result.

3.2 Effect of Nb on corrosion behavior

Corrosion rates of the bulk glassy $(\text{Cu}_{0.6}\text{Zr}_{0.3}\text{Ti}_{0.1})_{100-x}\text{Nb}_x$ ($x = 0\text{--}5\text{ at\%}$) alloys in 1 N HCl, 3% NaCl, 1 N H_2SO_4 , 1 N HNO_3 and 1 N NaOH solutions at 298 K were measured. The results are shown in Figs. 4 and 5. It is seen that addition of Nb to the alloys results in a decrease of corrosion rate in all solutions. The glassy Cu–Zr–Ti–Nb alloys have extremely corrosion resistance to alkaline solution because the samples exhibit no weight losses, even after immersion for 336 h in 1 N NaOH solution. In 1 N HCl and 3% NaCl solutions, with increasing Nb content, the corrosion rates of the glassy $(\text{Cu}_{0.6}\text{Zr}_{0.3}\text{Ti}_{0.1})_{100-x}\text{Nb}_x$ alloys show a significant decrease. The decrease in corrosion rates of the alloys substituted with Nb from 1 at% to 5 at% is about half to one order of magnitude of the Nb-free alloy. Effects of

substitution are more clear in 1 N H_2SO_4 and 1 N HNO_3 solutions and the alloys by substituting 3 at% Nb show undetectable weight losses.

The corrosion behavior of the bulk glassy $(\text{Cu}_{0.6}\text{Zr}_{0.3}\text{Ti}_{0.1})_{100-x}\text{Nb}_x$ alloys was also examined by the potentiodynamic polarization measurement. Figure 6 shows their polarization curves in 1 N HCl and 3% NaCl solutions open to air at 298 K. It is seen that these glassy $(\text{Cu}_{0.6}\text{Zr}_{0.3}\text{Ti}_{0.1})_{100-x}\text{Nb}_x$ alloys have similar polarization behavior to each other. Their anodic current densities increase rapidly by slight anodic polarization because of general corrosion, but the increase of Nb content in the glassy alloys shows nobler corrosion potential and lower anodic current density, leading to an improvement of corrosion resistance. Their potentiodynamic polarization curves in 1 N H_2SO_4 and 1 N HNO_3 solutions are also shown in Fig. 7. These alloys are spontaneously passivated with significantly low passive current density of the order $10^{-2}\text{ A}\cdot\text{m}^{-2}$. More-

Fig. 4 Corrosion rates of the $(\text{Cu}_{0.6}\text{Zr}_{0.3}\text{Ti}_{0.1})_{100-x}\text{Nb}_x$ glassy alloys in 1 N HCl, 3% NaCl and 1 N NaOH solutions at 298 K open to air.

Fig. 5 Corrosion rates of the glassy $(\text{Cu}_{0.6}\text{Zr}_{0.3}\text{Ti}_{0.1})_{100-x}\text{Nb}_x$ alloys in 1 N H_2SO_4 , 1 N HNO_3 solutions at 298 K open to air.

Fig. 6 Potentiodynamic polarization curves of the $(\text{Cu}_{0.6}\text{Zr}_{0.3}\text{Ti}_{0.1})_{100-x}\text{Nb}_x$ bulk glassy alloys in 1 N HCl and 3% NaCl solutions at 298 K open to air.

Fig. 7 Potentiodynamic polarization curves of the $(\text{Cu}_{0.6}\text{Zr}_{0.3}\text{Ti}_{0.1})_{100-x}\text{Nb}_x$ bulk glassy alloys in 1 N H_2SO_4 and 1 N HNO_3 solutions at 298 K open to air.

over, the addition of Nb to the glassy alloy is clarified to be effective on decreasing the passive current density and hence enhancing the corrosion resistance.

For exploring the effect of Nb on the corrosion resistance for the glassy $(\text{Cu}_{0.6}\text{Zr}_{0.3}\text{Ti}_{0.1})_{100-x}\text{Nb}_x$ alloys, X-ray photoelectron spectroscopic analysis (XPS) was performed for the specimens exposed to air after mechanical polishing and those immersed for 168 h in 1 N HCl and 3% NaCl solutions and for 336 h in 1 N H_2SO_4 and 1 N HNO_3 solutions.

Figure 8 shows the fraction of the elements Cu, Zr and Ti in the surface films and underlying alloy surfaces for the glassy $(\text{Cu}_{0.6}\text{Zr}_{0.3}\text{Ti}_{0.1})_{100-x}\text{Nb}_x$ ($x = 0$ and 5 at%) alloys exposed to air, where ox and m represent oxidized and metallic states, respectively. The Cu concentration in the underlying alloy surfaces for the 0 and 5 at% alloys is almost the same and higher than their nominal level, while the Zr and Ti compositions are inversely decreased. In the surface film, the ratio of the fractions of Cu, Zr and Ti is 35 : 49 : 16

for the 0 at% Nb alloy and 21 : 67 : 12 for the 5 at% Nb alloy (the nominal ratio $\text{Cu} : \text{Zr} : \text{Ti} = 60 : 30 : 10$). This fact could be realized that Zr and Ti are preferentially oxidized in the surface film and depleted in the underlying alloy surface. On the other hand, the Zr concentration in surface film increases with addition of 5 at% Nb, suggesting that the existence of Nb promotes diffusion of Zr to the surface and depresses that of Cu.

Surface film compositions of the bulk glassy $(\text{Cu}_{0.6}\text{Zr}_{0.3}\text{Ti}_{0.1})_{100-x}\text{Nb}_x$ ($x = 0$ and 5 at%) alloys immersed for 168 h in 1 N HCl and 3% NaCl solutions and for 336 h in 1 N H_2SO_4 and 1 N HNO_3 solutions were analyzed as shown in Fig. 9. The surface films of all immersed specimens are too thick to be determined its underlying alloy surface by XPS. Comparing the changes in the cationic fractions of the surface film during immersion in different solutions, it is seen that the Cu concentration in the Nb-free alloy is the highest after immersion in 1 N HCl, while the reverse tendency is seen for Zr and Ti concentrations, indicating that the Cu-enriched surface film is responsible for the low corrosion resistance. Because Cu is a unstable element in electrolytes open to air, the corrosion rate will be high when its concentration in the surface is high. In addition, the Cu concentration in the 5 at% Nb alloy is the lowest after immersion in 1 N HNO_3 , and the Zr and Ti concentrations were enriched twice of the nominal compositions, implying that Nb depresses the diffusion of Cu to surface and gives effect on improvement of corrosion resistance.

Figure 10 shows the cationic fractions in the surface film as a function of Nb content for the bulk glassy $(\text{Cu}_{0.6}\text{Zr}_{0.3}\text{Ti}_{0.1})_{100-x}\text{Nb}_x$ alloys immersed in 1 N H_2SO_4 solution at 298 K for 336 h. The Cu concentration in the surface films greatly decreases with increasing Nb content, while the Zr concentration in the surface films significantly increases with an increase of Nb content in the alloys. The Nb also helps itself and the Ti is enriched in surface film. It is well known that Nb, Ti and Zr elements are corrosion-resistant elements in aggressive acids with low oxidizing

Fig. 8 Fractions of the elements M ($M = \text{Cu}, \text{Zr}$ and Ti) in the surface films and the underlying alloy surfaces for the bulk glassy $(\text{Cu}_{0.6}\text{Zr}_{0.3}\text{Ti}_{0.1})_{100-x}\text{Nb}_x$ ($x = 0$ and 5 at%) alloys exposed to air after mechanical polishing.

Fig. 9 The changes in the cationic fractions in the surface film for the bulk glassy (Cu_{0.6}Zr_{0.3}Ti_{0.1})_{100-x}Nb_x alloys ($x = 0$ and 5 at%) immersed in various solutions at 298 K.

ability. The addition of Nb to the bulk glassy Cu₆₀Zr₃₀Ti₁₀ alloy is beneficial to form corrosion-resistant Zr (Ti, Nb)-rich surface film.

4. Conclusions

We have examined the effects of additional Nb element on glass-forming ability and corrosion behavior of the (Cu_{0.6}Zr_{0.3}Ti_{0.1})_{100-x}Nb_x bulk glassy alloys. The results obtained are summarized as follows.

- (1) Although the glass-forming ability of the Cu–Zr–Ti–Nb alloys decreases by addition of Nb, the 2 at%Nb alloy was able to form glassy rods with diameters up to 4 mm. The corrosion rate of the 2 at%Nb alloy decreases to 1/3 of the Nb-free alloy in 1 N HCl solution and one order of magnitude of the Nb-free alloy in 1 N H₂SO₄ solution.
- (2) The substitution of Nb up to 5 at% is effective on improving the corrosion resistance in all the solutions.

Fig. 10 The changes in the cationic fractions in the surface film as a function of Nb content for the bulk glassy (Cu_{0.6}Zr_{0.3}Ti_{0.1})_{100-x}Nb_x alloys immersed in 1 N H₂SO₄ solution at 298 K for 336 h.

No weight loss has been detected for the 3 at%Nb alloy in 1 N H₂SO₄ and 1 N HNO₃ solutions.

- (3) The addition of Nb to the Cu–Zr–Ti bulk glassy alloy depresses the diffusion of Cu to surface and promotes that of Zr, Ti and Nb, leading to the formation of Zr-rich protective surface film.

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