Corrosion Behavior of Ti-Based Metallic Glasses

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The corrosion behavior of the $\text{Ti}_{47.5}\text{Cu}_{42.5}\text{Ni}_{7.5}\text{Zr}_{2.5}$ metallic glass as well as its modified glasses by the addition of 5 at% Co, Nb or Ta was investigated by electrochemical measurements. Potentiodynamic polarization was carried out in 0.14 kmol/m³ NaCl solution and 0.2 kmol/m³ phosphate buffer solution with 0.14 kmol/m³ Cl⁻ ion. All the metallic glasses examined were spontaneously passivated with significantly low passive current density in sodium chloride solution and phosphate buffer solution. The additional elements improve the corrosion resistance and the effect of Nb or Ta is particular. The results of XPS revealed that the passive films were rich in titanium and deficient in copper and nickel. The higher corrosion resistance for the modified glasses is attributed to stable and protective passive films enriched with titanium cation contained certain amount of additional elements. In phosphate buffer solution, the pitting potentials for all glasses are higher than those in NaCl solution possibly due to inhibiting ability of phosphate ion absorbing on the glassy surface. [doi:10.2320/matertrans.47.1934]

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1. Introduction

The metallic glasses are expected to have high corrosion resistance due to their chemical and structural homogeneity. They do not contain crystalline defects, such as grain boundaries or dislocations acting as nucleation sites for corrosion. Thus, the glassy state provides the formation of a uniform passive film without weak points with respect to corrosion. Ti-based metallic glasses have high strength, low Young's modulus and excellent biocompatibility with a high potential to be applied as aerospace materials and biomaterials in the future. So far Ti-based metallic glasses are mainly developed on Ti-Cu-Ni¹⁾ system. Based on the Inoue's three empirical rules,^{2,3)} i.e., 1) multicomponent consisting of more than three elements, 2) significant atomic size mismatches above 12% among the main three elements, and 3) negative heats of mixing among the main elements, a series of Ti-based metallic glasses have been developed by adding some elements, for example, Ti-Cu-Ni-Co,⁴⁾ Ti-Cu-Ni-Zr,⁵⁾ Ti-Cu-Ni-Zr-Sn,⁶⁾ Ti-Cu-Ni-Sn-B-Si,⁷⁾ Ti-Cu-Ni-Sn-Be,⁸⁾ Ti-Cu-Ni-Zr-Be⁹⁾ and Ti-Cu-Ni-Zr-Hf-Si¹⁰⁾ and so on, for which the critical diameters for glass formation range from 1 to 8 mm by copper mold casting. The maximum size of 8 mm for Ti-based bulk metallic glass has been fabricated in Ti-Cu-Ni-Zr-Be system. So far many researchers have studied glass-forming ability, thermal stability and mechanical properties of all those Ti-based metallic glasses. But the data on the corrosion behavior of Ti-based metallic glasses have been comparatively rare. The application of Ti-based metallic glasses needs an acceptable life time in different environments. So it is of scientific and technological importance to research on corrosion behavior of Ti-based metallic glasses. In this paper, the corrosion resistance of $\text{Ti}_{47.5}\text{Cu}_{42.5}\text{Ni}_{7.5}\text{Zr}_{2.5}$ metallic glass and its modified alloys with 5 at% Co, Nb or Ta substituted for a part of Cu was investigated in 0.14 kmol/m³ NaCl solution and 0.2 kmol/m³ phosphate buffer solution.

2. Experimental Procedure

The alloys with nominal compositions of $\text{Ti}_{47.5}\text{Cu}_{37.5}\text{Ni}_{7.5}\text{Zr}_{2.5}\text{M}_5$ (M = Cu, Co, Nb or Ta) were prepared by arc melting the mixture of pure metals (> 99.9 mass%) in an argon atmosphere. The metallic glassy ribbons of 1 mm in width and 35 μm in thickness were produced by melt spinning. The structure of as-spun samples was examined by X-ray diffraction (XRD) with Cu K α radiation. Thermal stability was characterized by differential scanning calorimetry (DSC) under argon atmosphere with a heating rate of 0.67 K/s.

The corrosion behavior of the metallic glasses was evaluated by electrochemical measurements. Electrolytes used was 0.14 kmol/m³ NaCl solution (pH5.7) and 0.2 kmol/m³ phosphate buffer solution (0.2 kmol/m³ Na₂HPO₄+0.2 kmol/m³ NaH₂PO₄) with 0.14 kmol/m³ Cl⁻ ion (pH5.5) at room temperature open to air, which was prepared from reagent grade chemical and deionized water. Electrochemical measurements were conducted in a three-electrode cell using a platinum counter electrode and a saturated calomel reference electrode (SCE). Potentiodynamic polarization curves were measured with a potential sweep rate of 0.83×10^{-3} V/s in the solutions after immersing the specimens for about 600 s, when the open-circuit potentials became almost steady. XPS spectra for the surface of the metallic glasses after potentiostatic polarization were measured by means of a SSI SSX-100 photoelectron spectrometer with monochromatized Al K α excitation ($h\nu = 1486.6$ eV).

3. Results and Discussion

3.1 Thermal stability

The structure of the as-spun Ti-based metallic glasses was confirmed to be glassy by XRD. The corresponding DSC curves of the samples under a constant heating rate of 0.67 K/s are shown in Fig. 1. The glass transition temperature (T_g) and onset temperature of crystallization (T_x) appear in all alloys demonstrating their glassy nature. Moreover, a

Fig. 1 DSC curves of the melt-spun $\text{Ti}_{47.5}\text{Cu}_{37.5}\text{Ni}_{7.5}\text{Zr}_{2.5}\text{M}_5$ ($\text{M} = \text{Cu}, \text{Co}, \text{Nb}$ or Ta) metallic glasses.

Fig. 2 Anodic and cathodic polarization curves of the melt-spun $\text{Ti}_{47.5}\text{Cu}_{37.5}\text{Ni}_{7.5}\text{Zr}_{2.5}\text{M}_5$ ($\text{M} = \text{Cu}, \text{Co}, \text{Nb}$ or Ta) metallic glasses in 0.14 kmol/m^3 NaCl solution.

Fig. 3 Anodic and cathodic polarization curves of the melt-spun $\text{Ti}_{47.5}\text{Cu}_{37.5}\text{Ni}_{7.5}\text{Zr}_{2.5}\text{M}_5$ ($\text{M} = \text{Cu}, \text{Co}, \text{Nb}$ or Ta) metallic glasses in 0.2 kmol/m^3 phosphate buffer solution.

large supercooled liquid region ΔT_x before crystallization can be observed, meaning that these alloys exhibit a high thermal stability against crystallization. It can be seen that T_g slightly increases from 662 K for the $\text{Ti}_{47.5}\text{Cu}_{42.5}\text{Ni}_{7.5}\text{Zr}_{2.5}$ (denoted as base glass) to 664, 665 and 673 K for the Ta-, Nb- and Co-containing metallic glasses, respectively. T_x increase from 714 K for the base glass to 731 K for the Co-containing glass, while it decreases to 708 and 692 K for the Ta- and Nb-containing glasses. So it can be deduced that ΔT_x is 52, 44, 30 and 58 K for the base alloy, Ta-, Nb- and Co-containing glasses, respectively. And the crystalline peaks combine to a single peak with the addition of Co.

It is obvious that the addition of Nb or Ta for Ti-Cu-Ni-Zr metallic glass results in the decrease of thermal stability, while the addition of Co increases the thermal stability. It has been reported that the addition of Nb, Ta or Mo decreases ΔT_x in Cu-Zr-Ti glassy system,¹¹⁾ and the same effect is recognized with the addition of Nb in Cu-Hf-Ti glassy system¹²⁾ due to the departure from the three empirical rules. In the case of Co addition, T_g , T_x and ΔT_x have all been increased. The predicted heat of mixing¹³⁾ for glassy alloy is -28 kJ/mol for Ti-Co, 1 kJ/mol for Ti-Ta and 2 kJ/mol for Ti-Nb pairs. Furthermore, the addition of Co causes a more large change in atomic size. The atomic radius is 2.00, 2.08, 2.07 and 1.67 nm for Ti, Nb, Ta and Co, respectively. These changes by the addition of Co increase the degree to satisfy the three empirical rules for the thermal stability of the supercooled liquid. The atomic size effect and the large negative heat of mixing are believed to be helpful for stabilizing a glassy structure.¹⁴⁾ It may be the reason why the thermal stability of the $\text{Ti}_{47.5}\text{Cu}_{42.5}\text{Ni}_{7.5}\text{Zr}_{2.5}$ metallic glass has been improved by adding 5 at% Co element.

3.2 Potentiodynamic polarization curves

The polarization curves of the $\text{Ti}_{47.5}\text{Cu}_{42.5}\text{Ni}_{7.5}\text{Zr}_{2.5}$ metallic glass and its modified glasses comparing with commercial pure Ti in 0.14 kmol/m^3 NaCl solution are shown in Fig. 2. All Ti-based metallic glasses are spontaneously passivated in anodic polarization process. As compared with the base glass, the modified glasses containing Co, Nb or Ta exhibit much lower passive current density and wider passive regions, indicating that the addition of Co, Nb or Ta can promote the formation of more protective film on the surface of the Ti-based metallic glasses. The passive current densities

of the Co-, Nb- or Ta-containing glass are located between 10^{-2} and 10^{-3} A/m^2 , much lower than that of pure Ti and more than one order of magnitude lower than that of the base glass. And substitution of Cu by the additional elements also results in the decrease of corrosion current density. The corrosion current densities were obtained from the polarization curves by extrapolation of the cathodic branch of the polarization curves to the corrosion potential. The corrosion current densities are 5.1×10^{-3} , 1.5×10^{-3} , 1.8×10^{-4} and $1.7 \times 10^{-4} \text{ A/m}^2$ for the base glass, Co-, Nb- and Ta-containing glasses, respectively. However, at potentials above 0 V the sharp increase in current density suggests that the passive film is seriously destroyed, that is pitting corrosion occurs. Furthermore the pitting potential for Ta-, Nb- or Co-containing glass is about 400, 200 and 150 mV, respectively, higher than that of the base glass. Recently, it has been reported that,^{11,12)} in Cu-Zr-Ti and Cu-Hf-Ti bulk metallic glasses, addition of Nb or Ta is effective for corrosion resistance in different solutions because Nb or Ta can improve the stability of passive film.

Figure 3 presents the anodic and cathodic polarization curves for Ti-based metallic glasses and pure Ti in 0.2 kmol/m^3 phosphate buffer solution with $0.14 \text{ kmol/m}^3 \text{ Cl}^-$. The current density of all Ti-based metallic glasses increases with the potential till 500 mV by anodic polarization. Then the current density maintains constant value between 10^{-2} and 10^{-1} A/m^2 till the pitting potential. Different from the results in NaCl, higher pitting potential can be observed in phosphate buffer solution. The pitting potentials for all metallic glasses in phosphate buffer solution are much higher than those in sodium chloride solution. Hiromoto¹⁵⁾ also reported that the adsorbed phosphate ion inhibited pitting corrosion in Zr-Al-Ni-Cu glassy ribbon in the phosphate buffer solution.

3.3 Composition of surface film

For a better understanding of the corrosion behavior, XPS was performed for the glassy samples after potentiodynamic polarization at -50 mV in NaCl and at 100 mV in the phosphate buffer solution.

The XPS spectra from the $\text{Ti}_{47.5}\text{Cu}_{37.5}\text{Ni}_{7.5}\text{Zr}_{2.5}\text{M}_5$ ($\text{M} = \text{Cu}, \text{Co}, \text{Nb}$ or Ta) after polarization treatment in NaCl over a wide binding energy region exhibited peaks of carbon, oxygen, titanium, zirconium, copper and the additional elements. The C 1s peaks were those from carbon in alloys

Fig. 4 XPS peaks of the $\text{Ti}_{47.5}\text{Cu}_{37.5}\text{Ni}_{7.5}\text{Zr}_{2.5}\text{M}_5$ ($\text{M} = \text{Cu}(\text{i}), \text{Co}(\text{ii}), \text{Nb}(\text{iii})$ or $\text{Ta}(\text{iv})$) metallic glasses after polarization at potential of -50 mV in 0.14 kmol/ m^3 NaCl for 3600 s. (a) Ti 2p; (b) Zr 3d; (c) Cu 2p.

and so-called contaminant carbon on the top of surface of specimens. All the oxygen came from surface oxide. The O 1s spectra measured were composed of two peaks at 530.1–530.8 and 529.9–533.2 eV, which were assigned to OM oxygen and OH oxygen, respectively. The OM oxygen denotes oxygen with a metal-oxygen bond, such as O^{2-} ions. The XPS of Ti 2p, Zr 3d and Cu 2p electrons obtained from the alloy surface after polarized at -50 mV in NaCl are presented in Fig. 4. The Ti 2p spectra are composed of two main peaks, which are identified as Ti $2p_{1/2}$ and Ti $2p_{3/2}$, originating from TiO_2 (Fig. 4(a)). The Zr 3d spectrum consists of two peaks by multiplet splitting, $3d_{5/2}$ and $3d_{3/2}$. The peaks at 182.7–182.9 eV and 185.0–185.3 eV were assigned as Zr $3d_{5/2}$ and Zr $3d_{3/2}$ electrons originating from the Zr^{4+} , as shown in Fig. 4(b). Peaks at 932.8–933.3 eV and 952.2–953.0 eV are observed on the Cu 2p spectrum region for all metallic alloys (Fig. 4(c)), with a specific peak between the $2p_{3/2}$ and $2p_{1/2}$ spectra, characteristic of the peak for CuO. In the spectra of Nb 3d (not shown), a doublet of oxidized state was observed at about 208.0 and 210.6 eV. Ta $4f_{7/2}$ and Ta $4f_{5/2}$ electron peaks (not shown) corresponding to the oxidized state of Ta^{5+} were located at about 27.0 and 28.5 eV, respectively. In addition, no metallic peaks corresponding to Ti, Cu, Zr, Nb and Ta were detected as metallic peaks after polarization, which indicates that all the elements have mostly been oxidized in the sample surfaces. It should be pointed out that no peak corresponding to Ni for all the metallic glasses and Co for the Co-containing glass is detected not only for polarization samples but also for native samples. These results suggest that films grown anodically on the Ti-based metallic glasses consist of mixed oxides containing TiO_2 , CuO and ZrO_2 as well as Nb_2O_5 or Ta_2O_5 . Kawashima *et al.* have found that¹⁶⁾ Ni is largely deficient in air-formed film, while it is slightly enrichment in the underlying alloy surface because Ni is not oxidized by air exposure in Ni-Nb-Ta-P amorphous alloy system. In our study, the main constitute Ti is easily oxidized in air, at the same time Ni is not oxidized by air exposure.¹⁷⁾ So Ni can not be detected after the diffusion of a large amount of Ti to the outer surface. Considering that Co has similar chemical properties as Ni, it is deduced that Co may play the same role in this alloy system.

Similar results were obtained from the surface of the Ti-based metallic glasses polarized at 100 mV in phosphate buffer solution. In addition to the alloy composition elements, P 2p spectra were also detected in the wide spectra

Fig. 5 Fractions of element M (Ti, Zr, Cu, Nb or Ta) in the surface film of the $\text{Ti}_{47.5}\text{Cu}_{37.5}\text{Ni}_{7.5}\text{Zr}_{2.5}\text{M}_5$ ($\text{M} = \text{Cu}, \text{Co}, \text{Nb}$ or Ta) metallic glasses after polarization for 3600 s in (a) 0.14 kmol/ m^3 NaCl solution and (b) 0.2 kmol/ m^3 phosphate buffer solution.

for the surface of the metallic glasses after polarization treatment in phosphate buffer solution. P 2p electron peak was obtained at 134.2–134.6 eV, which was assigned to the P 2p electron from HPO_4^- ,¹⁸⁾ which originated from the solution.

The atomic concentrations of elements in the surface film were calculated from the integrated intensity of the spectra. Figure 5 shows the concentration of the elements of Ti, Cu and Zr as well as Nb or Ta in the surface films formed on the alloys. Comparing the changes in the cationic fractions of the surface film for the samples after polarization in NaCl solution, it is seen that the Ti concentration of the Nb- or Ta-containing glass is increased, and Zr also increases slightly, while the Cu concentration in surface films decreases seriously with the addition of Nb or Ta. But the change for the Co-containing glass is not remarkable. Asami *et al.*¹¹⁾ also reported that Zr was enriched with addition of Nb in Cu-Zr-Ti bulk metallic glass, and the high corrosion resistance is attributed to the formation of Zr-rich surface film in Cl^- ion containing solutions. It is well known that titanium oxide is very stable in many solutions and Ta or Nb is generally effective in improving corrosion resistance. As indicated by the results of polarization curves in Fig. 2, much lower passive current densities have been obtained with the addition of Nb or Ta. The enrichment of Ti, and the mixing of certain amount of Nb or Ta oxides in the passive film are responsible to the higher corrosion resistance. But the role of Co is not so clear in this study. Further study should be carried out. The concentrations of Ti in the oxide film formed in the phosphate buffer solution are also considerably higher than that of the normal alloy due to the preferential oxidation. The atomic fraction of Cu is much lower than that of the normal alloy, suggesting that the Cu elements are

preferentially dissolved from the glass surface during the process of polarization in the solution containing Cl^- ion. Although the basic chemical composition is often a dominant factor in controlling the relative corrosion resistance in all materials, the tendency of a metal to passivate depends on all of composition, structure and solution chemistry. In different cases, different factors or combinations of several factors may control corrosion resistance of metal materials. In this study, both the solutions contain $0.14 \text{ kmol/m}^3 \text{ Cl}^-$ ion. In $0.14 \text{ kmol/m}^3 \text{ NaCl}$ solution, the addition of Co, Nb or Ta enhances the formation of more protective film in the surface. But pitting corrosion still occurs at the potential higher than 0 V due to the existence of aggressive Cl^- ion. On the other hand, in phosphate buffer solution, although the same amount of Cl^- ion exists as that in NaCl solution, the phosphate ion seems to inhibit the pitting corrosion, *i.e.*, the phosphate ion plays an important role in inhibiting corrosion. Consequently the Ti-based metallic glasses exhibited high pitting resistance in this solution.

4. Conclusions

The corrosion behaviour of the melt-spun $\text{Ti}_{47.5}\text{Cu}_{37.5}\text{-Ni}_{7.5}\text{Zr}_{2.5}\text{M}_5$ ($\text{M} = \text{Cu, Co, Nb or Ta}$) glasses in $0.14 \text{ kmol/m}^3 \text{ NaCl}$ solution and 0.2 kmol/m^3 phosphate buffer solution has been investigated by electrochemical method and XPS. By addition of 5 at% Co, Nb or Ta, corrosion resistance is improved in NaCl. The passive current density of the modified glasses is located between 10^{-2} and 10^{-3} A/m^2 , one order of magnitude lower than that of the $\text{Ti}_{47.5}\text{Cu}_{42.5}\text{-Ni}_{7.5}\text{Zr}_{2.5}$ alloy, meaning that stable and more protective film formed during anodic polarization. The higher corrosion resistance is attributed to the enrichment of Ti and certain amounts of additional elements existing in the surface film for the modified glasses. The pitting potentials in phosphate buffer solution are higher than those in NaCl possibly due to inhibition of phosphate ion absorbing on the glasses surface.

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