Microstructure and Corrosion Resistance of Ti–Zr–Cu–Pd–Sn Glassy and Nanocrystalline Alloys

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The microstructure and corrosion behavior of the $\text{Ti}_{47.5}\text{Zr}_{15}\text{Cu}_{30}\text{Pd}_{7.5}\text{Sn}_5$ as-spun ribbons and as-cast rod have been investigated using HREM and potentiodynamic polarization study in simulated body fluids. The results of HREM reveal that, with decreasing cooling rate, the size and volume of nano-particles dispersed in glassy matrix increase for the $\text{Ti}_{47.5}\text{Zr}_{15}\text{Cu}_{30}\text{Pd}_{7.5}\text{Sn}_5$ as-prepared samples. The as-spun ribbons with small size nano-particle show high corrosion resistance in PBS(–) and Hanks' solution, may be due to the formation of CuZr phase, resulting in the enrichment of Ti and Pd in the glassy matrix, which is helpful to form protective passive film. Comparatively, poor corrosion resistance is observed for the as-cast rod sample with larger nano-particles in both solutions. [doi:10.2320/matertrans.48.167]

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1. Introduction

It is well known that the glassy alloys have higher corrosion resistance than that crystalline counterpart due to chemically and structurally homogenous state which provides the formation of a uniform passive film without weak points.^{1–3)} However in some cases, the glassy state itself does not exhibit superior corrosion resistance in Zr–Ti–Ni–Cu–Be⁴⁾ and Zr–Cu–Ni–Al⁵⁾ alloy systems, even though they contain a large amount of passivating elements. Mehmood *et al.*⁶⁾ reported that the formation of nano-crystalline phases formed by heat treatment ennobled the pitting potential in Cr–Zr glassy alloys in aggressive Cl-containing solution. Alvarez⁷⁾ also found that the crystallized alloys were more anticorrosive than the pure amorphous alloy in NaCl solution in Ni–B–Sn alloys. Mondal *et al.*⁸⁾ reported that nano- and quasi-crystalline state in Zr–Pd and Zr–Pt alloys shows better corrosion resistance than glassy state in NaCl, NaOH and H_2SO_4 solutions. Zander and Köster⁹⁾ also discussed that the nano-crystalline phase is assumed to have higher corrosion resistance than that of crystalline alloy due to the large number of grain boundaries which help to form protective film and homogenous structure. But it is still unclear why and how the critical size, spacing and composition of nano-crystallite control corrosion behavior in different alloy systems. From the above mentioned behavior, it is obvious that both structure and composition affect the corrosion behavior of metallic materials.

Ti-based bulk glassy alloys have attracted high attention due to their high strength, low modulus, excellent corrosion resistance and good bio-compatibility, having high potential applying as biomaterials. Recently, new Ti-based bulk glassy alloys without toxic elements in Ti–Zr–Cu–Pd–Sn system have been prepared.¹⁰⁾ The authors have found that the Ti–Zr–Cu–Pd–Sn glassy alloys exhibit high corrosion resistance in simulated body fluid and the high corrosion resistance is attributed to the enrichment of Ti and Zr in the oxide film formed on the glassy alloy. But with increase Zr content to

over 10 at%, the glass-forming ability decreased. In this paper, the microstructure and corrosion resistance of $\text{Ti}_{47.5}\text{Zr}_{15}\text{Cu}_{30}\text{Pd}_{7.5}\text{Sn}_5$ glassy specimens prepared under different cooling conditions have been investigated in simulated body fluids.

2. Experimental Procedure

The alloy with nominal composition of $\text{Ti}_{47.5}\text{Zr}_{15}\text{Cu}_{30}\text{Pd}_{7.5}\text{Sn}_5$ was prepared by arc melting the mixture of pure metals (> 99.9 mass %) in an argon atmosphere. The bulk sample with a diameter of 3 mm was prepared by injection casting into copper mold. The ribbon samples of 1 mm in width and 20 μm in thickness, and 3 mm in width and 60 μm in thickness were prepared by melt-spinning at the rotating wheel speeds of 40 m/s and 20 m/s, respectively. The structure of as-prepared alloys was examined by X-ray diffraction (XRD) with Cu $K\alpha$ radiation. The microstructures of the samples were investigated by high resolution transmission electron microscopy (HREM, JEOL 2010). The samples for transmission electron microscopy (TEM) observation were prepared by the ion milling method. Thermal stability was characterized by differential scanning calorimetry (DSC) under an argon atmosphere with a heating rate of 0.67 K/s.

The corrosion behavior of the samples was evaluated by electrochemical measurements. Prior to corrosion testing, the samples were mechanically polished in cyclohexane with a silicon carbide papers up to 1500 grit, degreased in acetone, washed in distilled water, dried in air and further exposed in air for 24 h. Each condition testing was performed at least three times for good reproducibility. Electrolytes used were phosphate-buffer saline solution [PBS(–)] and Hanks' solution with pH 7.4 at 310 K open to air, which were prepared from reagent grade chemicals and deionized water. The compositions of PBS(–) and Hanks' solutions are shown in Table 1. 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

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Table 1 Composition of simulated body fluids with pH 7.4.

Constituent(g/L)	NaCl	NaHCO ₃	KCl	CaCl ₂ ·2H ₂ O	Na ₂ HPO ₄ ·7H ₂ O	MgSO ₄ ·7H ₂ O	KH ₂ PO ₄	Glucose
PBS(—)	8.00	—	0.20	—	2.07	—	0.2	—
Hanks	8.00	0.35	0.40	0.19	0.09	0.2	0.06	1.00

Fig. 1 XRD patterns of the $\text{Ti}_{47.5}\text{Zr}_{15}\text{Cu}_{30}\text{Pd}_{7.4}\text{Sn}_5$ as-spun ribbons and as-cast rod. Fig. 2 DSC curves of the $\text{Ti}_{47.5}\text{Zr}_{15}\text{Cu}_{30}\text{Pd}_{7.4}\text{Sn}_5$ as-spun ribbons and as-cast rod.

sweep rate of 0.83×10^{-3} V/s after immersing the specimens for 600 s.

3. Results and Discussion

3.1 Thermal stability

Figure 1 shows the XRD patterns of as-prepared $\text{Ti}_{47.5}\text{Zr}_{15}\text{Cu}_{30}\text{Pd}_{7.4}\text{Sn}_5$ rod and ribbons at different wheel surface velocities. It is clear that only a halo peak appear in the XRD pattern of the as-spun ribbon sample at 40 m/s. As for the ribbon of 20 m/s, weak diffraction peaks appear and identified as cubic CuZr. While many crystalline peaks appear in the XRD pattern of the as-cast rod, which are identified as tetragonal Ti_3Cu_4 , cubic CuZr and hexagonal Ti_3Sn . The average grain size L of a crystalline phase can be estimated from the Scherrer formula:¹¹⁾

$$L = \frac{0.9\lambda}{\beta \cos \theta}$$

where λ is the radiation wavelength, β is the maximum half-width and θ is the diffraction angle. The average grain size of the as-cast $\text{Ti}_{47.5}\text{Zr}_{15}\text{Cu}_{30}\text{Pd}_{7.4}\text{Sn}_5$ rod calculated is about 50 nm.

The DSC curves of these as-prepared $\text{Ti}_{47.5}\text{Zr}_{15}\text{Cu}_{30}\text{Pd}_{7.4}\text{Sn}_5$ rod and ribbons at a heating rate of 0.67 K/s are shown in Fig. 2. The glass transition temperature (T_g) and onset temperature of crystallization (T_x) appear in the as-spun ribbon at 40 m/s, implying the formation of a mostly glassy state. The glass-transition temperature for the ribbon at the speed of 20 m/s is not as significant as that of the ribbon at the speed of 40 m/s. The first crystallization completely disappears for the as-cast bulk sample due to precipitation of crystalline phases in the glassy matrix, as distinguished in the XRD pattern in Fig. 1.

3.2 Microstructure

Figure 3 shows HREM, bright field TEM images and selected area electron diffraction (SAED) patterns of the $\text{Ti}_{47.5}\text{Zr}_{15}\text{Cu}_{30}\text{Pd}_{7.4}\text{Sn}_5$ alloys. In Fig. 3(a), the SAED pattern of the as-spun ribbon prepared at the speed of 40 m/s shows a diffuse halo, indicating that the main structure is a glassy state. However, some fine nano-particles dispersed in the glassy matrix can be observed in HREM image, although no obvious crystalline peaks appear in XRD pattern in Fig. 1. Recently it was also reported that, in Cu–Zr–Ti bulk glassy alloy,¹²⁾ even if only one broad peak was found in XRD, there were significant volume fraction of nano-crystals with several nanometers size embedded in the glassy matrix in HRTEM images. The SAED pattern of the as-spun ribbon prepared at the speed of 20 m/s consists of several ring patterns superimposed on a diffuse halo pattern (Fig. 3(b)), indicating a mixture of nano-crystalline and glassy phase. It is obvious that the size of nano-particles in the as-spun ribbon is smaller than 5 nm although both the size and volume fraction of nano-particles in glassy matrix increase with a decrease of melt-spinning speed. The fraction of the residual glassy phase is very low. Fig. 3(c)–(f) show bright field image and SAED patterns of the as-cast $\text{Ti}_{47.5}\text{Zr}_{15}\text{Cu}_{30}\text{Pd}_{7.4}\text{Sn}_5$ rod. It is seen that a number of nano-particles with a diameter of about 50 nm are randomly dispersed in the glassy matrix. The SAED patterns in Fig. 3(d) and (e) are obtained from the sits 1 and 2, confirmed as Ti_3Cu_4 and CuZr phases. Fig. 3(f) shows the micro-diffraction pattern of small particle, which can be identified as Ti_3Sn in the high resolution TEM. The results are consistent with those of XRD in Fig. 1. From the results of microstructure, it is clear that the volume fraction of nano-particles increases with a decreased of the cooling rate.

Fig. 3 HREM and bright field TEM images and selected area diffraction patterns of the $\text{Ti}_{47.5}\text{Zr}_{15}\text{Cu}_{30}\text{Pd}_{7.4}\text{Sn}_5$ as-spun ribbons and as-cast rod; (a) ribbon at 40 m/s, (b) ribbon at 20 m/s, (c)–(f) rod.

Fig. 4 Anodic polarization curves of the $\text{Ti}_{47.5}\text{Zr}_{15}\text{Cu}_{30}\text{Pd}_{7.4}\text{Sn}_5$ as-spun ribbons and as-cast rod at 310 K in PBS(–) and Hanks' solutions.

3.3 Potentiodynamic polarization curves

The potentiodynamic polarization curves of the $\text{Ti}_{47.5}\text{Zr}_{15}\text{Cu}_{30}\text{Pd}_{7.5}\text{Sn}_5$ at 310 K in PBS(–) and Hanks' solutions are shown in Fig. 4. For the sake of comparison the data of the commercial pure Ti and Ti–6Al–4V alloy were also included in the figure. In PBS(–) solution (Fig. 4(a)), the examined ribbons are spontaneously passivated with passive

current density located between 10^{-3} and 10^{-2} A/m^2 in anodic polarization curves. With further increasing anodic potential, the passivity breakdown occurred. On the other hand, the as-cast rod is directly dissolved at open-circuit potential in PBS(–) solution. The results in Hanks' solution (Fig. 4(b)) are similar as those in PBS(–) solution. Both the ribbons are passivated in anodic polarization, while the

current density for the as-cast rod rapidly increases with an increase in the anodic potential. This fact reveals that more protective and homogenous passive film was formed on the surface of the two ribbons in the anodic process. Furthermore, the breakdown potentials are about 500 mV higher than the open-circuit potentials, meaning that spontaneous pitting corrosion can not occur in human body environment.¹³⁾ It should be mentioned that, the $\text{Ti}_{47.5}\text{Zr}_{15}\text{Cu}_{30}\text{Pd}_{7.4}\text{Sn}_5$ as-spun ribbons exhibit much lower passive current densities than those of the commercial pure Ti and Ti–Al–V alloy in both the solutions, attributed to more protective passive film.

It is well known that the tendency of a metal to passivate depends on all of composition, structure and solution chemistry. In general, the basic chemical composition of metals and alloys is often a dominative factor in controlling the relative corrosion resistance in metallic materials. In this research, the composition of the examined samples was same. Therefore, it is the microstructure that brings different corrosion behavior among different samples in Fig. 4 except for Ti metal and Ti–6Al–4V alloy. The comparisons of micro-structure and corrosion property of the as-prepared samples indicated that the $\text{Ti}_{47.5}\text{Zr}_{15}\text{Cu}_{30}\text{Pd}_{7.4}\text{Sn}_5$ glassy ribbons even mixed with small size nano-particles showed high corrosion resistance in PBS(–) and Hanks' solutions. Mehmood *et al.*⁶⁾ reported that the Cr-rich nano-crystalline phase formed after heat treatment in Cr–Zr alloys ennobled the pitting potential in aggressive HCl solution, because the formation of the hcp zirconium phase leading to an increase in the Cr content of the matrix was able to form thin protective Cr-rich passive films covering the entire alloy surface. But the pitting potential of the Cr–Zr alloys after heat treatment was also dependent on heating temperature, i.e., the size of nano-crystalline phases played an important role in controlling the corrosion behavior. When the size of nano-crystalline phases exceeded a critical size of 20 nm, the protective passive films could not completely cover the precipitates, resulting in the pitting potential shifts less noble. Therefore, the high corrosion resistance obtained for the $\text{Ti}_{47.5}\text{Zr}_{15}\text{Cu}_{30}\text{Pd}_{7.4}\text{Sn}_5$ ribbons in Fig. 4 may be due to the formation of nano-scale CuZr phase,⁶⁾ resulting in the enrichment of Ti and Pd in the glassy matrix, which is helpful to form protective passive film. At the same time, it is seen that the phases are in several nanometers scale as seen in Fig. 3. Thus high density of interface defects is expected to lie in the nano-crystalline alloys. More uniform distribution of the new signal defects over the preferred corrosion attack sites allows the nano-crystalline alloys to maintain passivity over large potential range and resist localized Cl ion attack.^{8,14)} While the higher passive current density was

observed for the $\text{Ti}_{47.5}\text{Zr}_{15}\text{Cu}_{30}\text{Pd}_{7.4}\text{Sn}_5$ as-cast rod consisting of grains of about 50 nm, indicating that an oxide film formed on the surface of alloy was unable to protect the alloy matrix.

4. Conclusions

With decreasing cooling rate for the $\text{Ti}_{47.5}\text{Zr}_{15}\text{Cu}_{30}\text{Pd}_{7.4}\text{Sn}_5$ as-prepared samples, the size and volume of nano-particles in glassy matrix increase. The corrosion resistance of the as-spun ribbons in PBS(–) and Hanks' solutions is higher than that of the as-cast rod. This is presumably due to the formation of CuZr phase leading to the enrichment of Ti and Pd in the glassy matrix, which is helpful to form protective passive film. In addition, high density of interface defects is effective for uniform corrosion, resulting in the high corrosion resistance of the as-spun ribbons.

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