Thermodynamic Structural Stability and Polarization Behavior of Cast Amorphous Alloy

Sachiko Hiromoto, Takao Hanawa and Kazuyuki Ogawa

National Institute for Materials Science, Tsukuba 305-0047, Japan

The thermodynamic structural stability and anodic polarization behavior in Hanks' solution of cast amorphous $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ alloy rods with a diameter of 2.0 mm and 2.5 mm and a length of 35 mm were evaluated. The change of the magnitude of the super-cooled liquid region owing to structural relaxation was obtained from the differential scanning calorimetry (DSC) curve. Since the super-cooled liquid region of the distant region from the sprue of mold was larger than that of the proximate region to the sprue, the structural stability was lower in the distant region than in the proximate region. It was revealed that the structural stability varies along the distance from the sprue. In electrochemical analysis in a simulated body fluid, the specimens sampled from the distant region showed higher open-circuit potential, lower passive current density, and lower pitting potential than those from the proximate region. In other words, the amorphous structure with low stability shows higher passivity but lower pitting corrosion resistance than that with high stability. Consequently, the corrosion behavior of zirconium-based amorphous alloy sensitively depends on the structural stability in a biological environment.

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1. Introduction

Various kinds of amorphous alloys with high glass forming ability, such as zirconium-based, iron-based, and copperbased alloys, are developed as structural materials.^{1–3)} The zirconium-based amorphous alloy shows a large supercooled liquid region. Then, bulk-size amorphous alloy specimens with a thickness of 1–100 mm are produced with the casting method. Furthermore, the alloy has high potential for biomedical use because of its high corrosion resistance and good fatigue strength in simulated bio-environments.^{4,5)}

The chemical and physical properties of amorphous alloys, such as corrosion behavior and electric resistance, depend on the structural relaxation (i.e., the thermodynamic structural stability).⁶⁻¹²⁾ The structural relaxation proceeds during annealing of an amorphous alloy and increases with the increase in the annealing temperature.^{13,14} On the other hand, the structural relaxation is a distinct process of ordering atoms within the amorphous phase, indicating that the structural change during annealing is very small. The effect of the structural relaxation on the corrosion behavior depends on the alloy's composition and manufacturing process. The structural relaxation of sputter-deposited amorphous Al-Cr alloys leads to the increase in the corrosion resistance.⁶⁾ In addition, the passivity of amorphous (Ni-Pd)₈₂Si₁₈ alloys increases with the structural relaxation by annealing, possibly because quenched-in stresses are released.¹⁰⁾ On the other hand, the corrosion resistance of melt-spun amorphous Fe-Cr–W–P–C alloys decreases with the structural relaxation.⁹⁾ However, the corrosion resistance sometimes does not change with the structural relaxation, depending on which manufacturing process is used for the amorphous alloy. The corrosion resistance of electrodeposited amorphous Ni-P alloys does not change with the structural relaxation, whereas that of melt-spun amorphous Ni-P alloys decreases with it.^{7,8)}

The manufacturing process, especially the cooling rate of the melt at quenching, changes the thermodynamic structural stability of amorphous alloys. When the $Zr_{65}Al_{7.5}Cu_{27.5}$ alloy

is cast in a wedge-shaped copper mold, the amorphous phase is obtained with the decrease in the vertical-wedge angle because the cooling rate increases.¹⁴⁾ This result simultaneously indicates that the structural stability of cast amorphous alloys varies according to the mold shape. However, the inhomogenation of structural stability within one solid cast amorphous alloy has not been investigated yet.

In this study, the thermodynamic structural stability and polarization behavior of cast amorphous alloy rods were evaluated along the distance from the sprue. Rod-shaped amorphous Zr–Al–Ni–Cu alloys with different diameters were prepared using the copper-mold casting method. Then, specimens sampled from the regions proximate to and distant from the sprue of the copper mold were anodically polarized in a simulated body fluid. Also, their thermodynamic structural stability was characterized with a differential scanning calorimeter (DSC). For the application of amorphous alloys to biomaterials, a simulated body fluid was employed for the polarization test in this study.

2. Experimental

2.1 Specimens

Amorphous $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ (at%) alloy rods were prepared using the copper mold casting method. First, a 10 g button-shaped ingot of $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ was prepared with arc-melting in an argon atmosphere with alloying elements of Zr, Al, Ni, and Cu with 99.9 at% purity. The ingot was crashed into small pieces, packed into a quartz nozzle, and re-melted using a high-frequency induction furnace in a vacuum. The electric power applied to the furnace was controlled to have the constant temperature of the melt. Subsequently, the melt in the nozzle was ejected with argon gas pressure into a copper mold with a diameter of 2.0 mm or 2.5 mm and a length of 40 mm, as shown in Fig. 1(a). Three rods of the alloy with each diameter were prepared. The tip of a rod with 5 mm of sprue side was cut away. The proximate region to the sprue and the distant



Fig. 1 (a) Schematic illustrations of copper mold and cast alloy rod. (b) Specimen coated with resin for the polarization test.

region from the sprue were named the A-region and the Bregion, respectively, as shown in Fig. 1(b). The surface of the prepared rod was polished with #600 grid SiC paper and ultrasonically rinsed with deionized water and acetone. Structure of the outermost surface of the A-region was measured by X-ray diffraction (XRD).

Rod specimens with a length of 3 mm were sampled from the A- and B-regions. The microstructure at the outermost surface of the rod specimen was investigated using a transition electron microscope (TEM) with selected-area electron diffraction.

2.2 Polarization test

The amorphous alloy rod was coated with epoxy resin excepting periphery with a length of 10 mm at A-region or B-region of the rod as shown in Fig. 1(b) to conduct the polarization test. Hanks' solution (Hanks) was employed as the electrolyte and was deaerated with bubbling nitrogen gas throughout the experiment. The composition of Hanks is listed in Table 1. The amorphous alloy rod was immersed in Hanks, and the open-circuit potential (E_{open}) was measured over 1.8 ks till the potential was stabilized; the stabilized potential was employed as E_{open} in the polarization test. The potential of the alloy was anodically swept from the E_{open} with a rate of 0.33 mV s⁻¹. The potential at which the current density rises above 10⁰ A m⁻² was defined as the pitting potential (E_{pit}).

2.3 Differential scanning calorimetry

One-mm thick disk was sampled from the center of the Aand B-regions, and thermodynamic property of each region

Table 1 Composition of Hanks.

Composition	Concentration, $C/\text{kmol}\text{m}^{-3}$
NaCl	1.37×10^{-1}
KCl	5.37×10^{-3}
CaCl ₂	1.26×10^{-3}
Na ₂ HPO ₄	4.23×10^{-4}
KH_2PO_4	4.41×10^{-4}
Mg_2SO_4	7.39×10^{-4}
NaHCO ₃	4.17×10^{-3}

was characterized by differential scanning calorimetry (DSC). The temperature was swept from 328 K to 873 K with a heating rate of 0.33 K s^{-1} .

3. Results

3.1 XRD and EDS

XRD patterns of the A-region of $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ alloy rods with diameters of 2.0 mm and 2.5 mm are shown in Fig. 2. Characteristic broad peaks at around 36° and 65° of the amorphous structure were obtained from both rods. There were several very small peaks at around 25°, 40°, and 50°, but the diffraction angle was not identified due to the low S/N ratio. Moreover, the measurement area was a convex surface of the thin rod, causing the scattering of the diffracted X-ray.

TEM images and selected-area electron diffraction patterns of the A- and B-regions of a rod with a diameter of 2.0 mm are shown in Figs. 3(a)–(h). There were two kinds of areas with and without diffraction spots in both the A- and Bregions. TEM images and diffraction patterns at the area without diffraction spots are shown in Figs. 3(a), (b), (e), and (f), and those at the area with diffraction spots are shown in Figs. 3(c), (d), (g), and (h). The diffraction pattern without spots (Figs. 3(b) and (f)) showed a halo pattern corresponding to the amorphous phase. The other pattern (Figs. 3(d) and (h)) showed many diffraction spots corresponding to the existence of fine crystalline phases. On the other hand, TEM images and selected-area electron diffraction patterns of the A- and B-regions of a rod with a diameter of 2.5 mm are shown in Figs. 3(i)–(1). The diffraction patterns of the A- and B-regions showed many diffraction spots corresponding to the existence of fine crystalline phases. The clusters of crystalline phases were dispersed in the amorphous phase in both the A- and B-regions.

The density of the crystalline phase in the 2.5-mm rod was larger than that in the 2.0-mm rod. In alloy rods with both diameters, no significant difference in the diffraction pattern and density of the crystalline phase was observed between the A- and B-regions.



Fig. 2 XRD patterns of $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ alloys with diameters of 2.0 mm and 2.5 mm.

(d)



Fig. 3 (a), (c), (e), (g), (i), (k) Bright-field TEM images and (b), (d), (f), (h), (j), (l) selected-area electron diffraction patterns of the surfaces of A- and B-regions of amorphous $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ alloy rods.



Fig. 4 Anodic polarization curves of A- and B-regions of amorphous $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ alloy rods.

3.2 Polarization behavior

Anodic polarization curves of the A- and B-regions of $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ alloy rods are shown in Fig. 4. Both regions of the alloy rods spontaneously passivated and showed constant passive current density (I_p). Subsequently, both regions showed an abrupt increase in the current density, corresponding to the occurrence of pitting corrosion.

3.3 DSC

DSC curves obtained from both the A- and B-regions of amorphous alloy rods are shown in Fig. 5(a). All specimens showed the same glass-transition temperature (T_g) and crystallization temperature (T_x). Structural relaxation proceeds in the temperature range below to above T_g ,¹³⁾ and the intensity of exothermic peak immediately below T_g indicates the degree of structural relaxation. However, it was difficult to obtain the exothermic peak of the structural relaxation because the peak was very broad and the baseline of the DSC curve gradually increased. On the other hand, the intensity of the super-cooled liquid region also reflects the degree of structural relaxation, which is shown in the change of the intensity of the super-cooled liquid region with preannealing of the amorphous Zr–Al–Ni–Cu alloy at several temperatures.¹³⁾ Therefore, in this study, the intensity of the super-

Table 2 Index for the degree of structural relaxation (dI_{peak}) of A- and Bregions on amorphous $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ alloy rods.

S	Sample	
Diameter	Region	UI _{peak}
2.5 mm	А	1.10 ± 0.19
	В	1.12 ± 0.18
2.0 mm	А	1.09
	В	1.12 ± 0.12

Mean \pm Standard deviation

cooled liquid region was adopted to indicate the degree of structural relaxation. Since the spectrum of the super-cooled liquid region is very broad, the endothermic value was differentiated by the temperature to define the peak and the intensity of the peak, as shown in Fig. 5(b). Then, the differentiated peak intensity at T_g (dI_{peak}) was used to indicate the degree of structural relaxation. With the progress of structural relaxation, the dI_{peak} decreases. The dI_{peak} values are listed in Table 2. The dI_{peak} values were smaller in the A-regions of the rods than in the B-regions.

The E_{open} , I_{p} , and E_{pit} are summarized versus the dI_{peak} , as shown in Figs. 6(a)–(c). With the increase in dI_{peak} , E_{open} increased, I_{p} decreased, and E_{pit} decreased.

4. Discussion

4.1 Thermodynamic structural stability in cast amorphous alloy rod

Several small XRD peaks and many diffraction spots on the electron diffraction pattern showed that fine crystalline phases were dispersed in the amorphous phase. The density of the crystalline phase increased with the increase in the diameter of the alloy rod, indicating that the cooling rate at the outermost surface of the thick alloy rod was smaller than that of the thin alloy rod. On the other hand, no significant difference in the density of the crystalline phase was observed between the A- and B-regions. Therefore, the nucleation of the crystalline phase in the thick alloy rod occurs more frequently than that in the thin alloy rod,



Fig. 5 (a) DSC curves of A- and B-regions of amorphous Zr₆₅Al_{7.5}Ni₁₀Cu_{17.5} alloy rods. (b) Differentiated DSC curve (partially magnified).



Fig. 6 (a) E_{open} , (b) I_{p} , and (c) E_{pit} in Hanks versus dI_{peak} of amorphous $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ alloy rod.

although the nucleation of the crystalline phase is not distributed along the direction of the rod axis.

On the other hand, the dI_{peak} was smaller in the A-region than in the B-region (Table 2). That is, when a certain region in mold is nearer the sprue, the alloy quenched at the region has more stable amorphous structure. In other words, the thermodynamic structural stability of a cast amorphous alloy rod varies along the direction of the rod axis. Amorphous phase rather than crystalline phase is obtained with the increase in the cooling rate, according to the decrease in the vertical wedge angle of the copper mold.¹⁴⁾ Therefore, the cooling rate at the region proximate to the sprue is smaller than that at the region distant from the sprue. This may be because the melt ejected from the quartz nozzle directly hit the bottom of the copper mold and chilled with the large cooling rate. The subsequent melt is cooled with a rather small cooling rate because the copper wall is already heated with the first impact of the melt. However, the density of the crystalline phase was not distributed along the direction of the rod axis. Therefore, the stability of the amorphous phase is more sensitive to the cooling rate than the nucleation of the crystalline phase.

4.2 Thermodynamic structural stability and polarization behavior

In the case of the amorphous structure, the increase in thermodynamic stability corresponds to the increase in the order of atomic configuration. On the other hand, the high protectiveness against corrosion of the surface oxide film on amorphous structure is generally due to its thinness, homogeneity, and lack of defects, which are the result of its homogeneous and random atomic structure. In addition, since a thermodynamically meta-stable random atomic structure requires very small activation energy for chemical reactions, chemical reactions such as dissolution and oxidation of the bare surface of an amorphous structure rapidly occur and form a defect-free surface oxide film.^{15–17)} There-

fore, the amorphous structure at a low stable level is expected to rapidly form thin, homogeneous, and defect-free surface oxide films and shows high protectiveness to corrosion.

The amorphous structure at a low stable level (B-region) showed higher E_{open} and lower I_p than that at a high stable level (A-region), as shown in Fig. 6. As expected, the surface oxide film of the amorphous structure at a low stable level shows higher protectiveness than that at a high stable level. This is because the amorphous structure at a low stable level (B-region) requires lower activation energy for the formation of the surface oxide film than that at a high stable level (Aregion). Here, the fine crystalline phases were dispersed in the amorphous phase, and the density of the crystalline phase at the A- and B-regions was the same, indicating that the defect in the surface oxide film probably derived from the fine crystalline phase is not as responsible for the polarization behavior of the alloy as is the stability of the amorphous structure. This may be because the size of the crystalline phase is too small to be covered by a homogeneous surface oxide film.

On the other hand, the amorphous structure at a low stable level (B-region) showed lower E_{pit} than that at a high stable level (A-region). Consequently, a surface oxide film with high protectiveness shows low durability against local corrosion on the amorphous structure at a low stable level (B-region). High protectiveness and low local corrosion resistance are contradictory properties because a homogeneous and defect-free surface oxide film generally shows both high protectiveness and high local corrosion resistance.

This contradictory phenomenon is also shown on the melt spun amorphous $Zr_{60}M_5Al_{7.5}Cu_{27.5}$ (M: various elements) alloy. The surface oxide film with a low relative concentration ratio of Al to Zr ([Al]/[Al+Zr]) shows higher protectiveness but lower resistance to pitting corrosion in phosphate buffered saline than the film with high [Al]/[Al+Zr] ratio.¹⁸⁾ In addition, the composition of surface oxide film varies according to the dissolution activity of each

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alloying element. In the immersion test of the amorphous $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ alloy in Hanks, Al preferentially dissolves.¹⁹⁾ Therefore, it is indicated that the preferential dissolution of Al is enhanced on the amorphous structure at a low stable level owing to the high dissolution activity. As a result, the amorphous structure at a low stable level (Bregion) in this study probably results in the formation of a surface oxide film with a small [Al]/[Al+Zr] ratio that shows high protectiveness and low local corrosion resistance.

5. Conclusions

The thermodynamic structural stability of the amorphous phase in cast amorphous $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ alloy rod varies along the direction of the rod axis. When the alloy is quenched nearer the sprue, the quenched alloy has more stable amorphous structure (in other words, the degree of structural relaxation of the quenched alloy is higher). The structural stability varies even on a solid short rod with a length of 35 mm. The anodic polarization behavior of the rod axis. Therefore, the corrosion behavior of the zirconium-based amorphous alloy sensitively depends on the thermodynamic structural stability in a biological environment.

The amorphous structure at a low stable level showed higher protectiveness and lower local corrosion resistance in Hanks than that at a high stable level. Because the structural stability governs the dissolution activity of each alloying element in an amorphous structure, the surface composition changes according to the structural stability. Then, the surface oxide film with high protectiveness probably contains alloying elements that are sensitive to local corrosion. The variation of the surface composition, in addition to the variation of the structural stability, causes the variation of the corrosion behavior along the direction of the rod axis.

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