Corrosion Behavior of Zr–(Nb–)Al–Ni–Cu Glassy Alloys

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The melt-spun glasses Zr$_{60-x}$Nb$_x$Al$_{10}$Ni$_{15}$Cu$_{20}$ ($x = 0, 5, 10, 15, 20$ at%) alloys were found to exhibit a large supercooled liquid region ($\Delta T_m$) exceeding 42 K before crystallization. The largest $\Delta T_m$ for the glassy alloys containing Nb reaches as large as 82 K for the Zr$_{65}$Nb$_{5}$Al$_{10}$Ni$_{15}$Cu$_{20}$ alloy. The glass transition temperature ($T_g$) increases and the $\Delta T_m$ value decreases with increasing Nb content. The corrosion behavior of the Zr–(Nb–)Al–Ni–Cu glassy alloys was examined by mass loss (=weight loss) and electrochemical measurements. In 1N HCl solution at 298 K, the addition of Nb for replacing some portion of Zr is effective in improving the corrosion resistance of the investigated Zr-based glassy alloys. The corrosion rate significantly decreases with increasing Nb content. The pitting potential and open circuit potential rise with Nb content. In 3% NaCl solution, the addition of Nb effectively increases the pitting potentials of the glassy alloys. In 1N H$_2$SO$_4$ solution, the corrosion rates of the glassy alloys are $10^{-4} \sim 10^{-5}$ mm·year$^{-1}$ (1 mm·year$^{-1}$ = 0.317 pm·s$^{-1}$). They are spontaneously passivated and have a wide passive region with significantly low passive current density. The open circuit potential increases with an increase in Nb content.

(Received June 5, 2000; Accepted July 3, 2000)

Keywords: metallic glass, zirconium-based alloy, glass transition, supercooled liquid region, corrosion resistance, passivity

1. Introduction

Since the glassy alloys with a large supercooled liquid region before crystallization were discovered in the Mg$^{1,2}$-Pd$^{3}$-La$^{4}$-Ti$^{5}$ and Zr-based$^{6}$ systems, many studies on the amorphous formation$^{1,6-8}$ amorphous structure$^{9}$ mechanical properties$^{10}$ glass transition and/or structural relaxation$^{11}$ and crystallization process$^{12,13}$ of the glassy alloys have been conducted extensively. Among these metallic glasses, the Zr–TM–Al alloys, where TM is a transition metal, are particularly interesting because they exhibit an extremely large temperature interval of supercooled liquid region exceeding 100 K. However, up to now, little is known about the corrosion resistance of the Zr–TM–Al metallic glasses in acid solutions and brine. It is of importance scientifically and technologically to investigate the corrosion behavior of these glassy alloys. Therefore, the main purpose of this work is to characterize the corrosion resistance of Zr–(Nb–)Al–Ni–Cu glassy alloys. The glass transition behavior and thermal stability of the supercooled liquid of the alloys prepared by melt-spinning were investigated. The corrosion behavior of the resulting glassy alloys in acid and chloride containing solutions was basically characterized by mass loss (=weight loss) and electrochemical measurements. This paper is also intended to clarify the effect of additional Nb element on the formation ability and corrosion behavior of the glassy alloys.

2. Experimental Procedure

The glassy alloys with nominal compositions of Zr$_{60-x}$Nb$_x$Al$_{10}$Ni$_{15}$Cu$_{20}$ ($x = 0, 5, 10, 15, 20$ at%) were used. Alloy ingots were prepared by arc melting the mixture of pure Zr (99.6 mass%), Al (99.9 mass%), Ni (99.9 mass%), Cu (99.99 mass%) and Nb (99.5 mass%) metals under an argon atmosphere. Glassy alloy ribbons of 0.02 mm in thickness and 1 mm in width were produced by melt-spinning from the ingots. The amorphous structure was examined by X-ray diffraction with Cu-K$\alpha$ radiation. The thermal stability was investigated by differential scanning calorimetry (DSC) at a heating rate of 0.67 K·s$^{-1}$.

Prior to corrosion tests and electrochemical measurements, the alloy ribbons, pure Zr and pure Ni were mechanically polished in cyclohexane with silicon carbide paper up to No. 1500, degreased in acetone, dried in air and then further exposed to the laboratory air for 24 h for good reproducibility. Electrolytes used were 1N HCl, 3 mass% NaCl, and 1N H$_2$SO$_4$ solutions, which were prepared from reagent grade chemical and deionized water. The corrosion rates were estimated from the mass loss after immersion for two weeks. The minimum digit of the balance for mass loss measurements was 1 × 10$^{-5}$ g. The initial mass of the specimens were about 20 mg and the surface area were 1 × 2 cm$^2$. 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 mV/min in 1N HCl, 3% NaCl and 1N H$_2$SO$_4$ solutions open to air at room temperature (298 K) after immersing the specimens for about 20 min, when the open-circuit potentials became almost steady. In addition, the change in open-circuit potential with immersion time was also investigated.

3. Results

Figure 1 shows X-ray diffraction patterns of the melt-spun Zr$_{60-x}$Nb$_x$Al$_{10}$Ni$_{15}$Cu$_{20}$ ($x = 0, 5, 10, 15, 20$ at%) alloys. The melt-spun alloys consist of a single amorphous phase as is evidenced from broad peaks without crystalline peaks. No harmful influence of the Nb addition on the formation of the amorphous phase in the concentration range up to 20 at%Nb is observed.

Figure 2 shows DSC curves of the melt-spun Zr-based amorphous alloys. All the alloys exhibit the sequential tran-
sition of the distinct glass transition, supercooled liquid and crystallization. The glass transition temperature ($T_g$) increases with increasing Nb content, while the onset temperature of crystallization ($T_x$) remains almost constant. The resulting temperature interval of the supercooled liquid region before crystallization defined by the difference between $T_x$ and $T_g$, $\Delta T_x (=T_x - T_g)$ together with $T_g$ and $T_x$ is shown in Fig. 3 as a function of Nb content. It is seen that the Zr-(Nb-)Al-Ni-Cu 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 large $\Delta T_x$ exceeding 40 K is maintained even at 20% Nb.

Figure 4 shows the corrosion rates of the glassy Zr-(Nb-)Al-Ni-Cu alloys in 1N HCl, 3% NaCl, and 1N H$_2$SO$_4$ solutions at 298 K. The corrosion rates of constituent metals, Zr and Ni, in the same solutions are also shown by solid symbols for comparison. The corrosion rate of pure Zr metal is about $6.6 \times 10^{-4}$ mm·yr$^{-1}$ (1 mm·yr$^{-1}$ = 0.317 pm·s$^{-1}$) in 1N HCl solution, 4.8 $\times$ 10$^{-4}$ mm·yr$^{-1}$ in 3% NaCl solution and 2.0 $\times$ 10$^{-4}$ mm·yr$^{-1}$ in 1N H$_2$SO$_4$ solution. The corrosion rate of Ni metal is about 1.2 $\times$ 10$^{-3}$ mm·yr$^{-1}$ in NaCl solution and in the order of 10$^{-3}$ mm·yr$^{-1}$ in HCl and H$_2$SO$_4$ solutions.

In 1N HCl solution, with increasing Nb content, the corrosion rates of the glassy Zr$_{60-x}$Nb$_x$Al$_{10}$Ni$_{10}$Cu$_{20}$ alloys show a significant decrease: from $10^{-1}$ mm·yr$^{-1}$ for the 0% Nb alloy, to $10^{-3}$ mm·yr$^{-1}$ for the 20% Nb alloy. The corrosion rate of the alloy without Nb is about half that of pure Ni, while that of the 20% Nb alloy is almost the same as that of pure Zr.

In 3% NaCl and 1N H$_2$SO$_4$ solutions, the corrosion rates of the glassy alloys and pure Zr are in the range of $10^{-4}$ $\sim$ $10^{-3}$ mm·yr$^{-1}$ which are very close to the reproducibility limit.
Fig. 4 Corrosion rates of the Zr_{x0-\%},Nb_{x0},Al_{x0},Ni_{x0},Cu_{x0} alloys at 298 K open to air.

Fig. 5 Anodic polarization curves of the Zr_{x0-\%},Nb_{x0},Al_{x0},Ni_{x0},Cu_{x0} alloys at 298 K open to air.

for the present measurement. Therefore the alloy composition dependence of the corrosion resistance in these environments should be evaluated by the electrochemical measurements.

Figure 5 shows the anodic polarization curves of the glassy Zr_{x0-\%},Nb_{x0},Al_{x0},Ni_{x0},Cu_{x0} alloys measured in 1N HCl solution at 298 K. The anodic polarization curves of the Zr and Ni metals are also presented for comparison. The Zr metal has a corrosion potential which is nobler than those of the alloys and Ni metal, and is spontaneously passivated. The anodic current density of pure Zr shows an abrupt increase at about +0.15 V (vs Ag/AgCl), which corresponds to the initiation of pitting. The corrosion potential of the pure Ni is about -0.27 V (vs Ag/AgCl) and the anodic current density of Ni increases by a slight anodic polarization because of general corrosion. The corrosion potentials of the glassy alloys are higher than that of Ni metal and increase with increasing Nb content. The anodic current density of the 0%Nb alloy increases very rapidly even by a very slight anodic polarization. The steep increase of the current density corresponds to pitting corrosion. Actually, several clear corrosion pits were observed after immersion for 336 h. However, the alloys containing 5% or more Nb are spontaneously passivated and show a clear passive region before pitting. The pitting potential of the alloys increases almost linearly with increasing Nb content, though their pitting potentials are still lower than that of Zr metal. The changes in the open circuit potentials with immersion time for the glassy alloys in 1N HCl solution at 298 K are shown in Fig. 6. It is clearly seen that the open circuit potential after long immersion time increases with Nb content of the alloys. Moreover, the open circuit potentials increase with immersion time for the Nb-containing alloys except 10%Nb alloy. The potentials initially rise quickly and slow down to reach stationary values. The open circuit potentials of the alloys containing Nb after 3 h immersion are not necessarily lower than their pitting potentials obtained by potentiodynamic polarization curves, indicating the improvement of stability of the surface films during immersion. The specimen with 10%Nb may have acquired stable surface film before immersion because its open circuit potential is high from the initial stage. The alloy without Nb also shows no increase in the open-circuit potential because its surface film is unable to be stabilized in 1N HCl solution. These facts indicate that the addition of Nb for replacing some portion of Zr is effective in improving the corrosion resistance of the Zr-based glassy alloys in 1N HCl solution.

The anodic polarization curves of the glassy alloys in 3%NaCl solution are shown in Fig. 7. It is seen that the specimens are spontaneously passivated, though they suffer pitting by anodic polarization. The passive current densities increase slowly and keep lower values less than $10^{-2}$ A m$^{-2}$ before pitting. Moreover, the addition of Nb effectively increases the pitting potential of the glassy alloys.

Figure 8 shows the anodic and cathodic polarization curves of the 0%Nb, 15%Nb and 20%Nb glassy alloys measured in 1N H$_2$SO$_4$ solution open to air at 298 K. The polarization behavior of the 5% and 10%Nb glassy alloys, which is not shown in this figure, was nearly the same as that of the 0% and 15%Nb alloys. The polarization curves of pure Zr and pure Ni are also shown for comparison. It is seen that pure Ni shows an active-passive transition by anodic polarization in 1N H$_2$SO$_4$ solution. Pure Zr also shows an active state,
passivated with a wide passive region. Their passive current densities are about $1/3 \sim 1/5$ of those of Ni and Zr metals. Especially, the current density of the glassy alloy containing 20\%Nb is lower than that of the other alloys, indicating its relatively high corrosion resistance. The changes in the open circuit potentials with immersion time and Nb content under the same condition are shown in Fig. 9. The corrosion potentials increase with immersion time and reach stationary values. These values are in the passive regions of respective glassy alloys, implying their high corrosion resistance. In addition, the open circuit potential has an increasing tendency with an increase in Nb content.

4. Discussions

As shown in Fig. 3, the increase in the additional Nb content causes a significant increase in $T_F$ and almost no change in $T_G$, resulting in a significant decrease in $\Delta T_F$ for the melt spun $\text{Zr}_{50-x}\text{Nb}_{x}\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{20}$ glassy alloys. Therefore, the decrease in the thermal stability of the supercooled liquid for the Nb-containing alloys is mainly due to the significant increase in $T_F$. It is presumed that the addition of Nb causes the change in the bonding nature among the constituent elements of the Zr–Al–Ni–Cu alloys. The bonding nature of the additional Nb against the base constituent elements is thought to be in a strongly repulsive state for Cu–Nb atomic pairs, according to the data on the heats of mixing and the equilibrium phase diagrams for the Cu–Nb and Zr–Nb binary systems. Although Nb also has a strongly attractive bonding nature with Zr and Al, the partial existence of the atomic pair with the repulsive nature causes the disturbance of the formation of a highly dense random packed structure through the unsatisfaction of the three empirical rules on the optimum negative heats of mixing for the appearance of a large supercooled liquid region for glassy alloys. Base on this concept, it can be found that the simultaneous satisfaction of the three empirical rules is essential for the appearance of the much larger supercooled liquid region before crystallization.

On the other hand, as shown in Figs. 4 to 9, the addition of Nb effectively improves the corrosion resistance of the Zr-based glassy alloys. It is well known that amorphous alloys consist of structurally and chemically homogeneous single phase solid solutions, which do not contain crystalline defects, such as grain boundaries or dislocations, acting as nucleation sites for corrosion, and thus the amorphous state provides the formation of a uniform passive film without weak points with respect to corrosion. However, the corrosion resistance of a metallic material depends on its composition and solution chemistry, no matter the material is amorphous or crystalline. It can be suggested that the alloy composition is of great importance for corrosion properties of amorphous alloys. All the alloying elements, Al, Ni and Cu are not corrosion resistant in acid and chloride containing solutions. Zr is corrosion resistant in the solutions examined in this work. However, the $\text{Zr}_{50}\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{20}$ alloy can not achieve high corrosion resistance comparable to that of pure Zr in 1N HCl solution even when it is amorphized. On the other hand in 1N H$_2$SO$_4$ solution, the amorphous $\text{Zr}_{50}\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{20}$ alloy seems to have higher corrosion resistance in compari-
son with pure Zr and pure Ni, judging from the polarization curves shown in Fig. 8, though the mass loss measurement failed to prove it. In order to improve the corrosion resistance of the Zr-based alloys, the addition of other elements, such as Nb, which can impart high corrosion resistance is promising. Here, it is noticed that the composition of glassy alloys is not restricted by solubility limits, allowing selective alloying of elements. Therefore, the strongly passivating Nb can be added even up to 20 at% in the Zr-based glassy alloys which effectively decreases the corrosion rate and increases the corrosion potential and pitting potential of the glassy alloys in 1N HCl and 3%NaCl solutions, as shown in Figs. 4 to 7.

5. Conclusions

A series of Zr-(Nb–)Al–Ni–Cu glassy alloys with 0 ~ 20 at% Nb were prepared by the melt-spinning technique. The glass transition behavior and corrosion behavior of the glassy alloys were investigated. The effect of the additional Nb for the glassy alloys was also clarified. The following conclusions are drawn.

1. The Zr_{50-x}Nb_xAl_{10}Ni_{10}Cu_{20} (x = 0, 5, 10, 15, 20 at%) alloys have high glass-forming ability. The melt-spun glassy alloys exhibit a large supercooled liquid region (∆T_s) exceeding 42 K before crystallization. The largest ∆T_s for the glassy alloys containing Nb reaches as large as 82 K for the Zr_{55}Nb_{3}Al_{10}Ni_{10}Cu_{20} alloy. The glass transition temperature (T_g) increases and the ∆T_s value decreases with increasing Nb content.

2. In 1N HCl solution at 298 K, the addition of Nb for replacing some portion of Zr is effective in improving the corrosion resistance of the Zr-based glassy alloys. The corrosion rate considerably decreases with increasing Nb content. The pitting potential and open circuit potential rise with Nb content.

3. In 3%NaCl solution, the addition of Nb effectively increases the pitting potential of the glassy alloys. The corrosion rate evaluated by mass loss in 3%NaCl solution is less or of the order of 10^{-4} ~ 10^{-3} mm·y^{-1}.

4. The investigated glassy alloys show high corrosion resistance in 1N H₂SO₄ solution. Their corrosion rates are 10^{-4} ~ 10^{-3} mm·y^{-1}. They are spontaneously passivated and have a wide passive region with passive current densities lower than those of Zr and Ni metals. The open circuit potential increases with Nb content.

REFERENCES