Relationship between the Precipitation of Face-centered Cubic Zr$_2$Ni Phase and the Stability of Supercooled Liquid State in Zr–Cu–Ni–Al Metallic Glasses

Chunfei Li$^1$, Junji Saida$^1$ and Akihisa Inoue$^{1,2}$

$^1$Inoue Superliquid Glass Project, ERATO, JST, Yagiyamamini 2-1-1, Sendai 982-0807, Japan
$^2$Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

The crystallization processes of (Zr$_{0.64}$Ni$_{0.36}$)$_{100-x}$Al$_x$ ($x = 5, 7.5$ and 10) and (Zr$_{0.64}$Ni$_{0.36}$)$_{100-x}$Cu$_{0.02}$Al$_x$ ($x = 0, 6, 10, 13$ and 16) metallic glasses were studied by using differential scanning calorimetry (DSC), X-ray diffraction (XRD) and transmission electron microscopy (TEM). For the (Zr$_{0.64}$Ni$_{0.36}$)$_{100-x}$Al$_x$ ($x = 5$ and 7.5) and (Zr$_{0.64}$Ni$_{0.36}$)$_{100-x}$Cu$_{0.02}$Al$_x$ ($x = 0, 6, 10, 13$ and 16) alloys, crystallization proceeds through double-stage exothermic reactions. The first exothermic reaction corresponds to the precipitation of a metastable face-centered cubic Zr$_2$Ni (F-Zr$_2$Ni). For the (Zr$_{0.64}$Ni$_{0.36}$)$_{100-x}$Al$_x$ ($x = 10$) and (Zr$_{0.64}$Ni$_{0.36}$)$_{100-x}$Cu$_{0.02}$Al$_x$ ($x = 16$) alloys, crystallization proceeds through a single-stage exothermic reaction, corresponding to the precipitation of stable crystalline phases. Accompanying the above changes in crystallization mode, the supercooled liquid region $\Delta T_c$, defined as the temperature interval between the glass transition temperature $T_g$ and the crystallization temperature $T_c$, increases from 39 K for (Zr$_{0.64}$Ni$_{0.36}$)$_{100}$Al to 64 K for the (Zr$_{0.64}$Ni$_{0.36}$)$_{100}$Al$_{10}$ in (Zr$_{0.64}$Ni$_{0.36}$)$_{90}$Al$_{10}$ ($x = 5, 7.5$ and 10) alloy series, and from 39 K for (Zr$_{0.64}$Ni$_{0.36}$)$_{100}$Al$_{10}$ to 70 K for (Zr$_{0.64}$Ni$_{0.02}$Cu$_{0.08}$)$_{95}$Al$_5$ in the (Zr$_{0.64}$Ni$_{0.36}$)$_{100-x}$Cu$_{0.02}$Al$_x$ ($x = 0, 6, 10, 13$ and 16) alloy series. The reason for the stabilization of the supercooled liquid state at higher Al concentrations in the (Zr$_{0.64}$Ni$_{0.36}$)$_{100-x}$Al$_x$ ($x = 5, 7.5$ and 10) alloy series and at higher Cu concentrations in the (Zr$_{0.64}$Ni$_{0.36}$)$_{100-x}$Cu$_{0.02}$Al$_x$ ($x = 0, 6, 10, 13$ and 16) alloy series is discussed.

(Received May 17, 2000; Accepted June 23, 2000)

Keywords: zirconium-nickel-aluminium metallic glass, zirconium-nickel-copper-aluminium metallic glass, supercooled liquid region, crystallization process, metastable phase

1. Introduction

The existence of a wide supercooled liquid region at temperatures below the onset crystallization temperature is expected to enable the warm-working to various bulk amorphous alloys. In addition, the production of a bulk amorphous alloy by casting the melt into a metallic mold seems to be possible due to the high resistance of the supercooled liquid against the nucleation and growth of a crystalline phase. Up to 1990’s, systems with a supercooled liquid region have been limited to noble metal-based alloy systems, e.g., Pd–Ni–P and Pt–Ni–Si. In 1993, Inoue et al. reported the Zr–Ni–Al system which contains no noble metals. Further, addition of Cu to Zr–Ni–Al leads to the well-known Zr–Ni–Cu–Al system. Zr–Ni–Cu–Al has the highest glass-forming ability (GFA), defined as the critical cooling rate required to avoid the formation of any detectable crystalline phases, among metal-metal alloy systems. Bhatnagar et al. and Bruton et al. studied the crystallization processes of (Zr$_{0.64}$Ni$_{0.36}$)$_{100-x}$Al$_x$ ($x = 0$ to 25) amorphous alloys. They reported that the crystallization mode of the amorphous alloy changes with Al concentration. For the alloys with Al concentrations less than 5 at%, the crystallization proceeds through double-stage exothermic reactions. For the alloys with Al concentrations more than 10 at%, the crystallization proceeds through a single-stage exothermic reaction. However, little has been investigated about the relationship between the crystallization mode and the stability of supercooled liquid state.

In the present work, the initial crystallization processes of (Zr$_{0.64}$Ni$_{0.36}$)$_{100-x}$Al$_x$ ($x = 5, 7.5$ and 10) and (Zr$_{0.64}$Ni$_{0.36}$)$_{100-x}$Cu$_{0.02}$Al$_x$ ($x = 0, 6, 10, 13$ and 16) metallic glasses were studied. The (Zr$_{0.64}$Ni$_{0.36}$)$_{100-x}$Al$_x$ alloy series were designed to observe the relationship between the changes of supercooled liquid state and the initial crystallization processes with the increase of Al concentration. The (Zr$_{0.64}$Ni$_{0.36}$)$_{100-x}$Cu$_{0.02}$Al$_x$ ($x = 0, 6, 10, 13$ and 16) alloy series were designed to observe the effect of substitution of Ni by Cu.

2. Experimental Procedure

The alloy ingots were prepared by arc melting a mixture of pure Zr, Ni, Cu and Al metals. From these alloy ingots, ribbons with a cross-section of about 0.03 × 1 mm$^2$ were prepared by a single roller melt-spinning method in an argon atmosphere. The melt-spun ribbon was annealed at different temperatures by inserting to an evacuated quartz tube. The thermal property of the melt-spun ribbon was examined by DSC. The amorphicity and crystalline phases of the specimen were examined by XRD. Some of the specimens were supplied for TEM observation to check the microstructure with a high-resolution transmission electron microscope JEM-3000F, operated at 300 kV.

3. Results

All the as-quenched (as-q) ribbons were verified to be single amorphous phase by XRD. Figures 1(a) and (b) show the DSC curves of the as-q ribbons. In the (Zr$_{0.64}$Ni$_{0.36}$)$_{100-x}$Al$_x$ ($x = 5, 7.5$ and 10) series, the amorphous phase changes to a supercooled liquid state accompanying an endothermic reaction marked with the glass transition temperature $T_g$ followed by two exothermic peaks, for alloys with $x = 5$ and 7.5. For the $x = 10$ alloy, a single exothermic peak is observed. In the (Zr$_{0.64}$Ni$_{0.36}$)$_{100-x}$Cu$_{0.02}$Al$_x$ ($x = 0, 6, 10, 13$ and 16)
Fig. 1 DSC curves of as-quenched \((\text{Zr}_{0.64}\text{Ni}_{0.36})_{100-x}\text{Al}_x\) \((x = 5, 7.5 \text{ and } 10)\) (a) and \((\text{Zr}_{0.64}\text{Ni}_{0.36-0.001}\text{Cu}_{0.01}\text{Al}_{0.95})\) \((x = 0, 6, 10, 13 \text{ and } 16)\) (b) metallic glasses.

Fig. 2 DSC curves (a) and XRD patterns (b) of a \((\text{Zr}_{0.64}\text{Ni}_{0.36})_{95}\text{Al}_5\) metallic glass annealed under different conditions.
series, two exothermic peaks are observed in the DSC curves of $x = 0, 6, 10$ and 13 alloys. For the $x = 16$ alloy, a single exothermic peak is observed. The supercooled liquid region $\Delta T_x$ increases with the change in crystallization mode from double exothermic reactions to single exothermic reaction. In $(Zr_{0.64}Ni_{0.36})_{100-x}Al_x$ ($x = 5, 7.5$ and 10) alloy series, $\Delta T_x$ increases from 39 K for $x = 5$ alloy to 64 K for $x = 10$ alloy. In the $(Zr_{0.64}Ni_{0.36-0.05}Cu_{0.05})_{95}Al_5$ ($x = 0, 6, 10, 13$ and 16) alloy series, $\Delta T_x$ increases from 39 K for $x = 0$ alloy to 70 K for the $x = 16$ alloy.

To clarify the precipitation phases due to the first exothermic reaction, the DSC curve and XRD pattern of the $(Zr_{0.64}Ni_{0.36})_{95}Al_5$ alloy heated at 719 K for different times are shown in Figs. 2(a) and (b), respectively. Changes in the DSC curves indicate that the annealing condition of 719 K-3ks corresponds to the first exothermic reaction. The XRD pattern of the sample annealed in this condition is different from that of the as-q amorphous state. However, lack of sharp diffraction peaks makes the phase determination difficult. Figures 3(a) and (b) show the selected-area electron diffraction pattern and high-resolution TEM image of the sample. The reflection rings observed in Fig. 3(a) was identified as the reflections from F-Zr$_2$Ni$^{(9)}$ by measuring the d-spacings. From Fig. 3(b), the size of the crystalline particles is approximately 2 nm.

The XRD patterns of the $(Zr_{0.64}Ni_{0.36})_{92.5}Al_{7.5}$ alloy annealed under different conditions are shown in Fig. 4. It has been verified by subsequent DSC scan that the annealing condition of 787 K-0.18ks corresponds to the first exothermic reaction. Diffraction peaks in the XRD pattern of specimen annealed in this condition are identified as the reflection of F-Zr$_2$Ni.$^{(9)}$ Figure 5(a) shows the nano-beam electron diffraction pattern with the incident electron beam parallel to the [110] orientation of F-Zr$_2$Ni. It should be pointed out that the intensities of some reflections, e.g., (220), are very weak. These reflections are not observed in the diffraction pattern of Fig. 5(a). The bright-field TEM image is shown in Fig. 5(b). The particle sizes range from 5 to 50 nm.

Figure 6 shows the change in the XRD pattern of the $(Zr_{0.64}Ni_{0.36})_{90}Al_{10}$ alloy annealed at 748 K and 1000 K for different times. The peak positions of the samples annealed at 748 K for different times agree with each other and agree also with that from sample annealed at 1000 K. These results together with the observation of single exothermic peak in the DSC curve of the as-q amorphous alloy imply that the crystal-

![Fig. 3](image.png)  
**Fig. 3** Selected-area electron diffraction pattern (a) and high-resolution TEM image (b) of a $(Zr_{0.64}Ni_{0.36})_{95}Al_5$ metallic glass annealed at 719 K for 3 ks. The sharp diffraction rings are identified as the reflections of a F-Zr$_2$Ni (Cubic, Fd3m (227), $a = 1.227$ nm) crystalline phase.

![Fig. 4](image.png)  
**Fig. 4** XRD patterns of a $(Zr_{0.64}Ni_{0.36})_{92.5}Al_{7.5}$ metallic glass annealed under different conditions. Annealing condition of 787 K-0.18ks corresponds to the first exothermic reaction.
lization proceeds through the precipitation of the stable crystalline phases. The stable crystalline phases are determined as tetrahedral Zr$_7$Ni$_2$ (T-Zr$_7$Ni$_2$), Zr$_7$Ni$_4$Al and Zr$_7$NiAl$_2$.

In the (Zr$_{0.64}$Ni$_{0.36-0.00}$Cu$_{0.00}$)$_{95}$Al$_5$ ($x = 0, 6, 10, 13$ and $16$) alloy series, similar results were obtained. For (Zr$_{0.64}$Ni$_{0.36-0.00}$Cu$_{0.00}$)$_{95}$Al$_5$ ($x = 0, 6, 10$ and $13$) alloys, the low temperature exothermic peaks were determined to correspond to the precipitation of metastable F-Zr$_7$Ni. The particle sizes of the F-Zr$_7$Ni phase are approximately $2$ nm for $x = 0$ alloy and $5$ nm for $x = 13$ alloy, respectively. For the (Zr$_{0.64}$Ni$_{0.36-0.00}$Cu$_{0.00}$)$_{95}$Al$_5$ alloy, the crystallization proceeds through the simultaneous precipitation of stable crystalline phases.

4. Discussion

In the (Zr$_{0.64}$Ni$_{0.36}$)$_{100-x}$Al$_x$ ($x = 5$ and $7.5$) alloy series, the metastable phase corresponding to the low-temperature exothermic peak is F-Zr$_7$Ni. The F-Zr$_7$Ni precipitates at the temperatures lower than that required for the precipitation of stable crystalline phases, leading to a lower stability of the supercooled liquid state. The crystalline particle size of the metastable F-Zr$_7$Ni varies with Al concentration. For $x = 5$ alloy, it is approximately $2$ nm and for $x = 7.5$ alloy, it ranges from $5$ to $50$ nm. These results indicate that the increase in the stability of the supercooled liquid state from (Zr$_{0.64}$Ni$_{0.36}$)$_{95}$Al$_5$ to (Zr$_{0.64}$Ni$_{0.36}$)$_{90}$Al$_{10}$ is due to the suppression of F-Zr$_7$Ni nucleation. Similar discussions should be applied to the effect of substitution of Ni by Cu in the (Zr$_{0.64}$Ni$_{0.36-0.00}$Cu$_{0.00}$)$_{95}$Al$_5$ ($x = 0, 6, 10, 13$ and $16$) alloy series.

Difference in atomic radius between Al and those of Zr and Ni is considered to be the reason for the effectiveness of Al addition to retard the precipitation of metastable F-Zr$_7$Ni. In the crystal structure of F-Zr$_7$Ni,$^8$,$^9$ Zr atoms form octahedron and Ni atoms form tetrahedron. The atomic radius of Al ($0.143$ nm) lies between those of Ni ($0.125$ nm) and Zr ($0.162$ nm).$^{10}$ Excessive introduction of Al will cause stress in the Zr-octahedron or Ni-tetrahedron, making the crystal structure of F-Zr$_7$Ni unstable.

The reason for the effectiveness of Cu retarding the precipitation of F-Zr$_7$Ni is explained as follows. Since the atomic radius of Cu ($0.128$ nm) is similar to that of Ni ($0.125$ nm), it is reasonable to consider that the added Cu will occupy the Ni site in the F-Zr$_7$Ni crystal structure. The Zr–Ni interatomic distance in F-Zr$_7$Ni is estimated as $0.241$ nm while this value is expected as $0.285$ nm from the atomic radii of Zr.
(0.160 nm) and Ni (0.125 nm). This implies that the atomic binding between Zr and Ni is important for the crystal stability of F-Zr$_2$Ni. The heats of mixing are $-49$ and $-23$ kJ/mol for Zr–Ni and Zr–Cu atomic pairs, respectively, implying that the atomic binding of Zr–Cu is weaker than that of Zr–Ni. For this reason, excessive introduction of Cu retards the precipitation of F-Zr$_2$Ni.

5. Summary

The main results in the present study are summarized as follows.

1) The crystallization of the (Zr$_{0.64}$Ni$_{0.36}$)$_{100-x}$Al$_x$ (x = 5 and 7.5) and (Zr$_{0.64}$Ni$_{0.36-0.05}$Cu$_{0.05}$)$_{50}$Al$_5$ (x = 0, 6, 10 and 13) metallic glasses proceeds through double exothermic reactions. The metastable phase corresponding to the low-temperature exothermic reaction is F-Zr$_2$Ni. The crystallization of (Zr$_{0.64}$Ni$_{0.36}$)$_{90}$Al$_{10}$ and (Zr$_{0.64}$Ni$_{0.36}$Cu$_{0.16}$)$_{50}$Al$_5$ proceeds through a single exothermic reaction, corresponding to the precipitation of stable crystalline phases from the amorphous matrix.

2) With the change of the crystallization mode from double stages to a single stage, the $\Delta T_x$ value increases from 39 K for x = 5 alloy to 64 K for x = 10 alloy in the (Zr$_{0.64}$Ni$_{0.36}$)$_{100-x}$Al$_x$ alloy series. In the (Zr$_{0.64}$Ni$_{0.36-0.05}$Cu$_{0.05}$)$_{50}$Al$_5$ alloy series, the $\Delta T_x$ value increases from 39 K for x = 0 alloy to 70 K for x = 16 alloy.

3) Higher Al concentrations in the (Zr$_{0.64}$Ni$_{0.36}$)$_{100-x}$Al$_x$ alloys or higher Cu concentrations in the (Zr$_{0.64}$Ni$_{0.36-0.05}$Cu$_{0.05}$)$_{50}$Al$_5$ alloys retards the precipitation of the metastable F-Zr$_2$Ni phase, leading to the increase in $\Delta T_x$ value. For the effect of Al, the difference in atomic radius of Al from those of Zr and Ni is addressed as the reason. For the effect of Cu, the weaker atomic binding between Zr–Cu atomic pair compared to that of Zr–Ni is addressed as the reason.

REFERENCES