Ti-Containing Zr Based Bulk Amorphous/Nanocrystalline Composite Alloys

Cang Fan and Akihisa Inoue*

Inoue Superliquid Glass Project, Japan Science and Technology Corporation, Sendai 982-0807, Japan

DSC curves show that the crystallization reactions change from a single exothermic peak to two exothermic stages by adding Ti up to 5 at% to Zr-Ni-Cu-Al amorphous alloys and bulk amorphous composites containing nanocrystalline particles were produced by annealing cast $Zr_{70-x-y}Ti_xNi_{10}Cu_{20}Al_y$ ($x = 5-7.5$ and $y = 10-15$ at%) amorphous alloys. The microstructure after the precipitation of a primary crystalline phase consists of the crystals less than 10 nm in size embedded in the amorphous matrix. Both the compressive strength and plastic strain increased significantly with increasing volume fraction of nanocrystals, and the maximum plastic strain was obtained in the early stage of nanocrystallization. High-resolution electron microscopy showed that the bulk nanocrystalline $Zr_{53}Ti_5Ni_{10}Cu_{20}Al_{12}$ alloy with the maximum plastic strain includes nanocrystals with a much smaller grain size of about 2.5 nm.

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1. Introduction

Nanocrystalline composite materials with nanoparticles dispersed in an amorphous matrix prepared by melt spinning and annealing have been reported to have particular properties,¹⁻⁴⁾ e.g., high hardness, high tensile strength, improvement of soft magnetic and hard magnetic properties, etc. However, alloys reported up to 1995 do not have high glass-forming ability and their formation requires high cooling rates of above 10^4 K/s. Recently, amorphous/nanocrystalline composite alloys with high tensile strength (σ_f) in a bulk form have been produced successfully in Zr-based alloy systems.⁵⁻⁸⁾

However with Ti-containing bulk amorphous/nanocrystalline composite alloys a decrease in ductility but with a concurrent increase in strength with increasing volume fraction of nanocrystals is observed.⁸⁾ This behavior was interpreted to be due to the supposed brittleness of the precipitated nanocrystals.

Recently, we investigated the mechanical properties and microstructures of a bulk $Zr_{53}Ti_5Ni_{10}Cu_{20}Al_{12}$ amorphous/nanocrystalline composite alloy and found that compressive plastic strain increased with increasing volume fraction of nanocrystals, contrast to previously reported results. This letter presents the crystallization process of the $Zr_{70-x-y}Ti_xNi_{10}Cu_{20}Al_y$ ($x = 2.5-7.5$ and $y = 10-15$ at%) amorphous alloys and the change in the mechanical properties by crystallization.

2. Experimental Procedure

$Zr_{70-x-y}Ti_xNi_{10}Cu_{20}Al_y$ ($x = 2.5-7.5$ and $y = 10-15$ at%) amorphous cylinders of 2–8 mm in diameter were prepared by copper mold casting in vacuum of 667×10^{-5} Pa. The amorphous alloys were partially crystallized by isothermal annealing in the supercooled liquid region. The structure was examined by X-ray diffraction with Cu K_α radiation,

high-resolution electron microscopy (HREM) and energy dispersive X-ray (EDX) spectrometry. The thermal stability was evaluated by differential scanning calorimetry (DSC). The volume fraction (V_f) of nanocrystals was estimated by DSC since V_f is proportional to the heat release upon partial crystallization. The mechanical properties were measured by compression tests using rod specimens of 2.0 mm in diameter and 4.5 mm in length at a strain rate of $4.4 \times 10^{-4} s^{-1}$ and room temperature. Young's modulus was measured with a strain gage. The shear band of the rods strained up to 0.6% compressive plastic strain was examined by optical microscopy. For comparison, a $Zr_{55}Ni_5Cu_{30}Al_{10}$ amorphous alloy with typical high glass-forming ability,⁹⁾ was also examined.

3. Results and Discussion

Figure 1 shows DSC curves of the $Zr_{70-x-y}Ti_xNi_{10}Cu_{20}Al_y$ ($x = 2.5-7.5$ and $y = 10-15$ at%) amorphous rods of 2.2 mm in diameter with different Ti and Al contents. The 2.5%Ti alloy shows a single exothermic peak, but the crystallization reaction changes to two exothermic stages with increasing Ti or Al contents. With increasing Ti content and with decreasing Al content, the first peak shifted to the lower temperature side. The magnitude of enthalpy for the second exothermic peak decreases with increasing Ti or Al content. With the aim of checking the phases of the first exothermic reaction, the amorphous alloys were isothermally annealed at the temperature T_a in the supercooled region (Fig. 1) until the primary transformation stage finished. It is noted that the overlapped peaks in Fig. 1 are separated for the isothermally annealed sample. Transmission electron microscopy images showed that the size of particles embedded in the amorphous matrix of the $Zr_{70-x-y}Ti_xNi_{10}Cu_{20}Al_y$ ($x = 5-7.5$ and $y = 10-15$ at%) alloy is less than 10 nm at the completion of the first exothermic reaction. Here, we mainly deal with the results of $Zr_{53}Ti_5Ni_{10}Cu_{20}Al_{12}$ alloy, which exhibits a large supercooled liquid region ΔT_x of 57 K ($\Delta T_x = T_x - T_g$) (T_g the glass transition temperature, T_x crystallization temperature) and high reduced glass transition temperature (T_g/T_m) of 0.64.

*Present address: Institute for Materials Research, Tohoku University.

Fig. 1 DSC curves of $Zr_{70-x-y}Ti_5Ni_{10}Cu_{20}Al_{12}$ ($x = 2.5-7.5$ and $y = 10-15$ at%) amorphous rods of 2.2 mm in diameter.

Fig. 2 X-ray diffraction patterns of (a) $Zr_{53}Ti_5Ni_{10}Cu_{20}Al_{12}$ and (b) $Zr_{50}Ti_5Ni_{10}Cu_{20}Al_{15}$ amorphous alloys subjected to different annealing treatments.

Figure 2(a) shows the X-ray diffraction patterns of the $Zr_{53}Ti_5Ni_{10}Cu_{20}Al_{12}$ alloy in the states of as-solidified, annealed for 1.2 ks at 700 K to complete the first exothermic reaction, and for 0.9 ks at 823 K to complete the full crystallization reaction. After the completion of the first exothermic reaction, some weak crystalline peaks were seen. These

Fig. 3 HREM images of the specimen of $Zr_{53}Ti_5Ni_{10}Cu_{20}Al_{12}$ alloy annealed at 700 K for 1.2 Ks.

peak positions are close to that of the tetragonal Zr_2Al phase. The reaction type of the first peak (Fig. 1) is supposed to be the same in all the $Zr_{70-x-y}Ti_5Ni_{10}Cu_{20}Al_{12}$ ($x = 5-7.5$ and $y = 10-15$ at%) amorphous alloys. The second exothermic reaction causes the precipitation Zr_2Ni and Zr_2Cu phases in addition to the Zr_2Al phase.

Figure 3 shows the HREM image of the $Zr_{53}Ti_5Ni_{10}Cu_{20}Al_{12}$ alloy annealed at 700 K for 1.2 ks. The image shows fine crystalline particles with a diameter of about 5 nm surrounded by the residual amorphous phase. Nanocrystals are indicated by black arrows and the residual amorphous phase are marking by white arrow. The existence of a quasicrystalline phase in the Zr-based alloys containing Ti has been reported.⁸⁾ However, nano-beam diffraction in the present study showed the absence of quasicrystalline diffraction pattern.

We measured mechanical properties of the nanocrystalline alloys by a compressive deformation mode using the $Zr_{55}Ni_5Cu_{30}Al_{10}$ and $Zr_{53}Ti_5Ni_{10}Cu_{20}Al_{12}$ rod samples of 2.0 mm in diameter and 4.5 mm in length. Figure 4 shows the compressive stress-strain curves of these bulk amorphous alloys in the as-quenched and annealed states (in the supercooled liquid region). The stress-strain relation is linear in the strains up to about 1.8–2%. Followed by slight plastic deformation is evident from the unloading curves. No significant plastic deformation is recognized for the $Zr_{55}Ni_5Cu_{30}Al_{10}$ amorphous alloy. The Ti-containing as-quenched alloy exhibits a plastic strain which is several times larger than that of $Zr_{55}Ni_5Cu_{30}Al_{10}$ the amorphous alloy, indicating the improved ductility of the nanocrystal-forming alloy. Furthermore, in the partially crystallized $Zr_{53}Ti_5Ni_{10}Cu_{20}Al_{12}$ alloy with V_f of 16%, the curve shows a further improved plastic strain being about two times as large as that of corresponding as-quenched alloy. In addition, the stress decreases significantly after reaching the maximum value. Plastic strain in the $V_f = 43\%$ sample is smaller than that of the as-quenched

Fig. 4 Compressive stress-strain curves at room temperature: (a) as-quenched bulk $Zr_{55}Ni_5Cu_{30}Al_{10}$ amorphous alloy; (b) as-quenched and (c), (d) annealed nanocrystalline bulk $Zr_{53}Ti_5Ni_{10}Cu_{20}Al_{12}$ alloys.

Table 1 Mechanical properties of bulk $Zr_{53}Ti_5Ni_{10}Cu_{20}Al_{12}$ amorphous/nanocrystalline composite alloy with different volume fractions of nanocrystals.

Fraction of nanocrystals (vol%)	Yield strength (MPa)	Maximum strength (MPa)	Young's modulus (MPa)	Plastic strain (%)
0	1490	1760	81	1.4
10	1530	1770	82	2.2
16	1540	1810	92	2.5
28	1730	1890	95	1.5
43	1820	1950	106	1.0

one, though it is much larger than that of the $Zr_{55}Ni_5Cu_{30}Al_{10}$ amorphous alloy.

The mechanical properties of the $Zr_{53}Ti_5Ni_{10}Cu_{20}Al_{12}$ rods with different volume fractions of nanocrystals are summarized in Table 1. The plastic strain is 1.4% for the as-quenched one, increases with increasing V_f and reaches a maximum value of 2.5% at $V_f = 16\%$. The further increase in V_f decreases the plastic strain, but the strain still keeps the level of about 1.0% at $V_f = 43\%$. Although the magnitude of plastic strains is different from the previous results,⁸⁾ one can notice a definite increase phenomenon of Young's modulus, compressive yield strength and the maximum strength in the nanocrystalline alloys.

We have also studied the microstructure of the specimen, which showed the maximum value of plastic strain. Figure 5 shows the HREM image of the bulk $Zr_{53}Ti_5Ni_{10}Cu_{20}Al_{12}$ alloy with V_f of 16%. The nanocrystals of the metastable compound phase have an average particle size of about 2–3 nm. The particles appear to be spherical and their crystal orientations are supposed to be in a random state.

We examined macroscopic deformation behavior of the amorphous/nanocrystalline composite alloys by optical microscopy. Figure 6 shows the surface appearance of the specimen with $V_f = 16\%$ which was deformed to about 0.6% plastic strain. At an early stage of plastic deformation, a number of localized slip bands marked by arrows are seen and the angle of the slip bands to the direction of compressive load is approximately 50 degrees. This is different from the speci-

Fig. 5 HREM images of the bulk $Zr_{53}Ti_5Ni_{10}Cu_{20}Al_{12}$ alloy with $V_f = 16\%$. Nanocrystals are indicated by arrows.

Fig. 6 Deformation structure of the bulk $Zr_{53}Ti_5Ni_{10}Cu_{20}Al_{12}$ amorphous/nanocrystalline composite alloy ($V_f = 16\%$) subjected to about 0.6% plastic strain observed by optical microscope ($\times 10$). Localized shear bands are marked by arrows.

men with much larger V_f , as well as $Zr_{55}Ni_5Cu_{30}Al_{10}$ specimens, where only few slip bands are seen even after fracture occurred. This suggests that the plastic flow takes place more homogeneously in the $Zr_{53}Ti_5Ni_{10}Cu_{20}Al_{12}$ specimens with $V_f = 16\%$.

It is important to understand the mechanism for the strengthening recognized in the partially crystallized alloys. The increase in strength and the decrease in ductility in the partially crystallized bulk amorphous/nanocrystalline composite alloys are considered to be attributed to the higher hardness and more brittleness of the nanocrystals comparing

with amorphous reference.⁸⁾ Upon loading the nanoparticles do not deform and act as obstacles against the movement of shear bands. The yield stress increases while at the same time ductility decreases, because the shear bands can not easily move through the material. Although the present argument may qualitatively explain the observed increase in strength, it fails to explain the increased ductility.

However, our results may be explained if one assumes an additional factor. One can imagine that shear bands are easily nucleated at the stress concentration sites near nanocrystals. In this case the deformation behavior strongly depends on the size, morphology and spatial distribution of these nanocrystals. In the $\text{Zr}_{53}\text{Ti}_5\text{Ni}_{10}\text{Cu}_{20}\text{Al}_{12}$ alloy the nanocrystals have the spherical morphology and their sizes are about 2–3 nm. As seen in the HREM image, they are homogeneously distributed. From the nanostructures, it is expected that thin shear bands develop at many points in the material. The deformation might be restricted within one shear band. However there are a number of shear bands and the deformation becomes more homogeneous over the material leading to better ductility. The model can also explain the loss of ductility of other partially crystallized bulk amorphous alloys.¹⁰⁾

4. Summary

We conclude that the nanocrystallization occurs by annealing in supercooled liquid region of bulk $\text{Zr}_{70-x-y}\text{Ti}_x\text{Ni}_{10}\text{Cu}_{20}\text{Al}_y$ ($x = 5\text{--}7.5$ and $y = 10\text{--}15$ at%)

amorphous alloys, and the microstructure consists of crystals with a size less than 10 nm embedded in the amorphous matrix. The existence of nanocrystals with a few nanometers in diameter dispersed in an amorphous matrix was found to lead to an increase of both the strength and ductility with increasing V_f in the early stage of nanocrystallization for the $\text{Zr}_{53}\text{Ti}_5\text{Ni}_{10}\text{Cu}_{20}\text{Al}_{12}$ alloy. The increase in ductility was explained by multiplication of shear bands due to the stress concentration around the nanocrystals. This multiplication is suggested to lead to a macroscopically more homogeneous deformation and, thus, to an increase of ductility.

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