Synthesis of High Strength Bulk Amorphous Zr–Al–Ni–Cu–Ag Alloys with a Nanoscale Secondary Phase

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Bulk amorphous alloys in a cylindrical form were prepared in the diameter range up to about 5 mm for Zr_{x}Al_{y}Ni_{z}Cu_{s}Ag_{t} (x=0 to 1 at%) by copper mold casting. These bulk amorphous alloys exhibit a wide supercooled liquid region before crystallization and the temperature interval defined by the difference between glass transition temperature (Tg) and crystallization temperature (Tc). ΔTc = Tc − Tg = 111 K for the 0%Ag alloy and 63 K for the 5%Ag alloy. The replacement of Cu by 5 at%Ag causes the change in the crystallization process from a single stage of Am → Zr_{s}Cu (Ni) + Zr_{t}Al (Ni) to two stages of Am → Am′ + Zr_{s}Al (Ag) + Zr_{t}Al (Ag) + Zr_{s}Cu (Ni). The Zr_{t} (Al, Ag)_{s} phase has a spherical shape with a small size of about 20 nm and is dispersed homogeneously at an interparticle spacing of about 30 nm. The change in the crystallization process by the addition of Ag is presumably due to the generation of the distinction of bonding nature among the constituent elements because of the positive heats of mixing for Ag–Ni and Ag–Cu pairs. The dispersion of the nanoscale Zr_{s}Al (Ag)_{t} phase causes a significant increase in tensile fracture strength (σf) from 1150 MPa for the amorphous single phase to 1520 MPa for the amorphous phase containing about 14% volume fraction of Zr_{s}Al (Ag)_{t} phase. The shear-type fracture mode along the maximum shear plane remains unchanged. The effectiveness of the Zr_{s}Al (Ag)_{t} phase for the increase in σf is presumably because the size of the phase is too small to contain dislocations. The success of synthesizing the high-strength bulk amorphous alloy consisting of nanoscale Zr_{s}Al (Ag)_{t} phase embedded in an amorphous matrix is encouraging for future development of bulk amorphous alloys as a high-strength material.

(Received May 16, 1997)

Keywords: zirconium-based bulk amorphous alloy, bulk nanocrystalline alloy, nanocrystallization, compound-dispersed structure, glass transition, supercooled liquid region, high mechanical strength

I. Introduction

It has been reported that homogeneous dispersion of nanoscale fcc-Al particles in an amorphous matrix gives rise to a significant increase in tensile strength as compared with that for the corresponding amorphous single phase alloy. The increase in tensile strength is as large as about 1.4 times and the resulting highest tensile strength reaches 1560 MPa for Al_{10}Cu_{12}Ni_{15}Fe_{2} alloy. In addition to the Al-based alloys, the increase in tensile strength by partial nanocrystallization has been confirmed for Fe–Ni–Mg–Ni–Mg–Ni–Mg based amorphous alloys containing nanocrystalline particles of bcc-Fe(Ni)+fcc-Ni(Fe), hcp-Mg and fcc-Ni, respectively. Thus, the increase in tensile strength by the formation of nanocrystalline phase is independent of crystal structure, but the nanocrystalline precipitates have been limited to their base metal phases. There has been no datum on the increase in tensile strength by the precipitation of compound phase from the amorphous matrix. Recently, bulk amorphous alloys have been prepared by copper mold casting in Ln–Al–TM and Mg–Ln–TM. Zr–Al–TM, Zr–Ti–Al–TM, Zr–Ti–TM–Be, Pd–Cu–Ni–P and Fe–(Al, Ga)–(P, C, B, Si) systems. These bulk amorphous alloys have a wide supercooled liquid region before crystallization and crystallize by simultaneous precipitation of more than multiple crystalline phases from the supercooled liquid. The crystalline phases are mainly composed of intermetallic compounds and a key point of achieving a high tensile strength for the partially crystallized alloys is dependent on the good ductility of the residual amorphous alloys containing nanoscale intermetallic compounds. The increase in tensile strength by the partial crystallization has been limited to melt-spun amorphous ribbon alloys and little knowledge has been obtained about the strengthening phenomenon of bulk amorphous alloys by partial crystallization. More recently, we have examined systematically the influence of additional elements on the crystallization behavior of bulk amorphous Zr–Al–Cu–Ni alloys and found that the addition of Ag element which has positive heats of mixing and is insoluble against Cu and Ni causes the change from the single-stage crystallization mode to the double-stage mode consisting of Am→primary compound + residual amorphous→two compounds. Besides, the mixed phase alloy consisting of nanoscale Zr_{s}Al (Ag)_{t} + residual amorphous phases exhibits higher tensile strength than that for the amorphous single phase alloy in the bulk sample form. This paper is intended to present the two-stage crystallization behavior of the nanoscale Zr_{s}Al (Ag)_{t} bulk amorphous alloys and the increase in the tensile strength by the dispersion of nanoscale Zr_{s}Al (Ag)_{t} particle embedded in an amorphous matrix for the bulk amorphous alloys.
II. Experimental Procedure

Penternary Zr_{65}Al_{19.5}Ni_{10}Cu_{17.5-x}Ag_x alloys were examined in the present study because the Zr_{65}Al_{19.5}Ni_{10}Cu_{20} alloy had the large glass-forming ability in the quaternary system. Their master ingots were prepared by induction melting mixtures of pure metals in an argon atmosphere. The cast cylindrical alloys were prepared by casting the molten alloy into a copper mold with an inner cavity of 5 mm in diameter and 100 mm in length. The ejection pressure and temperature of the molten alloy were fixed to be 0.02 MPa and 1520 K, respectively. The amorphous structure of the cast cylindrical samples was confirmed by X-ray diffractometry and optical microscopy. Thermal stability associated with glass transition, supercooled liquid, partial nanocrystallization and full crystallization was examined at a heating rate of 0.67 K/s by differential scanning calorimetry (DSC). The nanocrystallized structure was examined by high-resolution transmission electron microscopy (TEM). The hardness and tensile fracture strength were measured under a load of 0.98 N with a Vickers hardness indenter and at a strain rate of 5.0 × 10^{-4} s^{-1} with an Instron testing machine, respectively. The gauge dimension of the tensile testing specimen was 2 mm × 10 mm. The fracture surface appearance was examined by scanning electron microscopy (SEM).

III. Results

Figure 1 shows the DSC curves of melt-spun Zr_{65}Al_{19.5}Ni_{10}Cu_{17.5-x}Ag_x (x = 0, 5 and 10 at%) amorphous alloys. The three amorphous alloys crystallize from the supercooled liquid, but the crystallization takes place with a single exothermic peak for the Zr–Al–Ni–Cu alloy and with two exothermic peaks for the 5%Ag- and 10%Ag-containing alloys. Besides, the onset temperature of crystallization decreases with increasing Ag content, though the second exothermic peak shifts to the higher temperature side as compared with the single exothermic peak for the Zr–Al–Ni–Cu alloy without Ag. It is important to point out that the wide supercooled liquid region with ΔT_s of 63 K is retained for the 5%Ag-containing alloy.

Subsequently, we examined the possibility of forming a bulk amorphous alloy for the 5%Ag-containing alloy by the copper mold casting method. Figure 2 shows the outer shape and surface morphology of the cast Zr_{65}Al_{19.5}Ni_{10}Cu_{12.5}Ag_5 cylinders with diameters of 1, 3 and 5 mm. These samples have a smooth surface and good metallic luster and no appreciable ruggedness corresponding to the precipitation of a crystalline phase is seen over the whole outer surface. Figure 3 shows the X-ray diffraction patterns of the cast Zr_{65}Al_{19.5}Ni_{10}Cu_{12.5}Ag_5 cylinders with diameters of 3, 4 and 5 mm. All the samples show only a broad peak at a wave vector (K_p = 4π sin θ/λ) of 25.4 nm^{-1} and no diffraction peaks of any crystalline phase are seen. Consequently, the 5%Ag-containing alloy still keeps a large glass-forming ability which enables the formation of the bulk amorphous alloys with diameters up to 5 mm, though the ΔT_s value decreases from 111 K for the 0%Ag alloy to 63 K for the 5%Ag-containing alloy. In order to investigate the reason for the maintenance of the good glass-forming ability for the 5%Ag-containing alloy, the DTA curves of the 0%Ag, 5%Ag and 10%Ag alloys are shown in Fig. 4. As marked with T_{sm}, the melting temperature (T_{us}) is measured to be 1150 K for the 0%Ag alloy and 1084 K for the
5%Ag and 10%Ag alloys. Considering that the \( T_g \) remains almost unchanged, the reduced glass transition temperature \( (T_g/T_m) \) increases from 0.57 for the 0%Ag alloy to 0.60 for the 5%Ag and 10%Ag alloys. Consequently, the maintenance of the large glass-forming ability in spite of the significant decrease in \( \Delta T_x \) is thought to result from the increase in \( T_g/T_m \). Figure 5 shows the DSC curves of the cast bulk amorphous \( Zr_{65}Al_{13.5}Ni_{10}Cu_{12.5}Ag_5 \) alloy with a diameter of 3 mm subjected to annealing for 120 s at 730 K and for 60 s at 750 K. The DSC curve of the as-cast bulk alloy is similar to that for the melt-spun amorphous ribbon shown in Fig.
1. The annealing at 730 and 750 K causes the progress of partial crystallization leading to the precipitation of a crystalline phase of 14% and 23% volume fractions, respectively. The volume fractions were estimated from the decrease in the exothermic heat of crystallization on the DSC curve. Figure 6 shows the X-ray diffraction patterns of the 5%Ag-containing samples in different annealed states. It is seen that the progress of crystallization occurs by the precipitation of ZrAl₂ phase. The morphology, particle size and interparticle spacing of the ZrAl₂ phase were examined by TEM. As shown in Fig. 7, the precipitates have the spherical morphology and the particle size and interparticle spacing are measured to be about 20 and 30 nm, respectively, for the 14% V₁ alloy and about 15 and 25 nm, respectively, for the 23% V₁ alloy.

The change in mechanical properties by the precipitation of ZrAl₂ was examined for the cast bulk
Zr56Al12.5Ni10Cu12.5Ag5 cylinder. Figure 8 shows Vickers hardness ($H_v$) as a function of $V_t$. The $H_v$ is about 450 in the as-cast state and increases significantly in the partially crystallized state, i.e., 465 at $V_t=14\%$, 476 at $V_t=23\%$ and 480 at $V_t=35\%$. Similarly, the tensile fracture strength ($\sigma_t$) also increases from 1150 MPa at $V_t=0\%$ to 1520 MPa at $V_t=14\%$, as shown in Fig. 9. The further increase in $V_t$ causes a significant decrease in $\sigma_t$ presumably because of the increase in the degree of embrittlement. Figures 10 and 11 show the tensile fracture outer and surface appearance, respectively, of the 5%Ag-containing alloys with different $V_t$ of 0%, 14% and 23%. As seen in Fig. 10, the fracture of the 0% $V_t$ and 14% $V_t$ alloys takes place along the maximum shear plane which is declined by about 45 degrees to the direction of tensile load. Figure 11 also shows that the fracture surface of the 0% $V_t$ alloy is rather smooth on a macroscopic scale and consists mainly of a well-developed vein pattern. However, the fracture surface of the 14% $V_t$ alloy changes into a rugged state, though the fracture mode along the maximum shear plane remains unchanged. Besides, one can see that the development of the vein pattern becomes significant for the 14% $V_t$ sample. These changes in the fracture surface appearance are interpreted in the presumption that the nanoscale Zr$_7$Al$_1$ particles act as an effective resistant medium against shear deformation, leading to the increase in the degree of the adiabatic viscous flow at the final fracture stage. The further increase in $V_t$ to 23% causes a change in fracture mode from the shear type to a mixed shear and perpendicular type, accompanying a significant decrease in $\sigma_t$. The perpendicular-type fracture mode is thought to occur by the generation of embrittled regions. It is therefore said that the 23% $V_t$ sample is in a coexistent state of ductile and embrittled regions and the ductile-brittle transition for the Zr–Al–Ni–Cu–Ag alloy occurs in the $V_t$ range between 14 and 23%.

IV. Discussion

1. The reason for the change into the two-stage crystallization mode by the addition of Ag

It has previously been reported\(^{21}\) that the single-stage crystallization of the Zr–Al–Ni–Cu amorphous alloy occurs by the simultaneous precipitation of Zr$_7$(Al, Ni) and Zr$_2$(Cu, Ni) phases. However, the addition of Ag causes the change in the crystallization reaction to $\text{Am} \rightarrow \text{Am' + Zr}_7(\text{Al, Ag}) \rightarrow \text{Zr}_2(\text{Al, Ag})_2 + \text{Zr}_2(\text{Cu, Ni})$. It is generally known\(^{21,22}\) that Ag has negative heats of mixing against Cu and Ni and is insoluble to Cu and Ni. On the other hand, the predicted heats of mixing between Ag and Al or Zr are negative values of 4.4 and 20 kJ/mol\(^{21}\), respectively. The significant difference in the bonding nature of Ag against the constituent elements is expected to cause the distinction of bonding nature to Zr–(Al, Ag) and Zr–(Cu, Ni), leading to the precipitation of Zr$_7$(Al, Ag)$_2$ and Zr$_2$(Cu, Ni) phases. The primary precipitation of the Zr$_7$(Al, Ag)$_2$ phase is presumably due to the easy
movement of Ag which has the repulsive interaction to Cu and Ni as well as to the increase in the total amount of Al+Ag from the optimum amount of 10 at%. The present result indicates that the addition of the insoluble and immiscible elements against the other constituent elements causes the change in crystallization mode to multistage reactions presumably because of the distinction of the bonding nature among the constituent elements. That is, the distinction of the bonding nature leading to the multistage crystallization reactions is thought to enable the homogeneous dispersion of the nanoscale Zr$_3$(Al, Ag)$_2$ particle in the amorphous matrix.

2. The reason for the increase in tensile strength by the dispersion of Zr$_3$Al$_2$

It was shown that the homogeneous dispersion of Zr$_3$(Al, Ag)$_2$ caused the significant increase in $\sigma_f$ at $V_f=14\%$, accompanying the decrease in $\varepsilon_p$ and the
change in the shear-type fracture surface from the smooth mode to the rugged mode. The change in the fracture surface suggests that the nanoscale Zr\(_5\)(Al, Ag)\(_2\) particles act as a resistant medium against the shear deformation of the amorphous matrix. It is therefore said that the increase in \(\sigma_t\) is due to the dispersion strengthening of the nanoscale Zr\(_5\)(Al, Ag)\(_2\) particle. Here, it is important to estimate the strength level of the nanoscale Zr\(_5\)(Al, Ag)\(_2\) particles themselves. As shown in Fig. 7, the particle size of the Zr\(_5\)(Al, Ag)\(_2\) phase is as small as about 20 nm. The Zr\(_5\)(Al, Ag)\(_2\) phase is too small to contain dislocations. That is, the nanoscale particle is thought to have a perfect crystal structure with high mechanical strength. The absence of any internal defects in the nanoscale particles has previously been confirmed from high-resolution TEM images of Al-based amorphous alloys containing nanoscale fcc-Al particles\(^{(1)}\)-\(^{(3)}\). Furthermore, the particle size and interparticle spacing of the Zr\(_5\)(Al, Ag)\(_2\) phase have been measured to be as small as 20 and 30 nm, respectively, at 14% \(V_t\). These values are comparable to the thickness of about 20 nm\(^{(2)}\)-\(^{(26)}\) in which the massive movement of atoms for shear sliding takes place along the maximum shear plane. The nearly same nanoscale implies that the Zr\(_5\)(Al, Ag)\(_2\) phase can act as an effective resistant medium against the shear deformation, leading to the increase in \(\sigma_t\) by the dispersion of Zr\(_5\)(Al, Ag)\(_2\) phase.

**V. Summary**

We examined the possibility of synthesizing a bulk amorphous alloy with high tensile strength and good ductility in a mixed structure of amorphous and nanocrystalline phases for the Zr\(_{65}\)Al\(_{15}\)Ni\(_{10}\)Cu\(_{7.5}\)Ag\(_{5}\) alloy with copper mold casting. The \(T_g\) and \(T_s\) are, respectively, 635 and 746 K for the 0%Ag alloy and 660 and 723 K for the 5%Ag alloy.

The crystallization changes from the single stage reaction of Am\(\rightarrow\)Zr\(_5\)(Al, Ni)\(\rightarrow\)Zr\(_5\)(Cu, Ni) for the 0% Ag alloy to Am\(\rightarrow\)Am\(\leftarrow\)Zr\(_5\)(Al, Ag)\(_2\)\(\rightarrow\)Zr\(_5\)(Al, Ag)\(_2\)\(\rightarrow\)Zr\(_5\)(Cu, Ni) for the 5%Ag alloy. The change is presumably due to the distinction of bonding nature which results from the positive heats of mixing for Ag-Cu and Ag-Ni pairs. The Zr\(_5\)(Al, Ag)\(_2\) phase in coexistence with the remaining amorphous phase has a nanoscale size of about 20 nm and an interparticle spacing of about 30 nm.

The \(\sigma_t\) of the 5%Ag alloy increases from 1150 MPa for the amorphous single phase to 1520 MPa for the mixed amorphous phase containing 14% \(V_t\) of Zr\(_5\)(Al, Ag)\(_2\) phase. The fracture mode due to shear sliding along the maximum shear plane remains unchanged for the mixed phase alloy, though the shear-type fracture surface changes from a smooth to a rugged state.

(4) The dispersion strengthening due to the nanoscale Zr\(_5\)(Al, Ag)\(_2\) phase is presumably because the Zr\(_5\)(Al, Ag)\(_2\) phase has an optimum nanoscale which leads to the formation of a perfect crystalline structure without dislocations and can act as an effective resistant medium against shear sliding with a thickness of about 20 nm along the maximum shear plane. The synthesis of the bulk amorphous alloy containing nanoscale Zr\(_5\)(Al, Ag)\(_2\) particles which exceeds largely the \(\sigma_t\) of the amorphous single phase is important for future development of a high-strength bulk amorphous alloy.

**Acknowledgment**

The authors are grateful to the Grant-in-Aid for Specialty Promoted Research of The Ministry of Education, Science, Sports and Culture, Japan for support of this research.

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