Editor’s Announcement


Mechanical Properties of Bulk Amorphous Zr-Al-Cu-Ni-Ag Alloys Containing Nanoscale Quasicrystalline Particles

Akihisa Inoue, Tao Zhang, Min Wei Chen and Toshio Sakurai

The Editorial Committee of Materials Transactions has affirmed that this article contains the following errors that are improper for scientific paper, and retracts this article with the primary author’s agreement.

A) The photograph of Zr-Al-Cu-Ni-Ag samples shown in Fig. 1 is the photograph of Nd-Fe-Al samples as given in Fig. 2 in the paper, and is a patched one of Fig. 2 in the paper.

B) The sample diameters described in the caption of Fig. 1, and in the text (Results, line 2, p. 1383) do not agree with the picture (Fig. 1).

C) The X-ray diffraction patterns of samples shown in Figs. 2 and 6 were previously published as Figs. 3 and 6 in the paper respectively, with different heat-treatment conditions and with different indices.

D) This article contains no proper descriptions of the relationship between this article and the paper, including the different experimental conditions and the different conclusions.

The notice has been issued to the authors to pay more careful attention to contributing papers.

REFERENCES

Mechanical Properties of Bulk Amorphous Zr–Al–Cu–Ni–Ag Alloys Containing Nanoscale Quasicrystalline Particles

Akihisa Inoue, Tao Zhang, Min Wei Chen and Toshio Sakurai

Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

Nanoscale icosahedral quasicrystalline particles were found to precipitate at high volume fractions of nearly 100%, as a metastable phase in the crystallization process of bulk amorphous Zr_{60}Al_{15}Cu_{21.6−x}Ni_{x}Ag, (x=5 and 10 at%) alloys. The icosahedral particles precipitate from the supercooled liquid and have a spherical morphology. The average particle size is in the range of 30 to 40 nm and tends to decrease with increasing Ag content. The maximum volume fraction \( V_f \) of the icosahedral phase is about 85% for the 5%Ag alloy and nearly 100% for the 10%Ag alloy. The mixed amorphous plus icosahedral phases change into an equilibrium structure of Zr\(_2\)Cu\(_2\)Ni\(_2\)+Zr\(_2\)Al\(_2\) phases with a further increase in temperature. Tensile fracture strength (\( \sigma_f \)) of the bulk amorphous rod is 1650 MPa at \( V_f = 0\% \), increases to 1900 MPa at \( V_f = 45\% \) and then decreases with further increasing \( V_f \). The increase in \( \sigma_f \) is due to the suppression effect of the nanoscale icosahedral particles on the shear deformation of the amorphous matrix. The finding that the tensile strength of the bulk amorphous alloys is improved by the precipitation of high volume fraction of nanoscale icosahedral particles points to the future development of bulk nanoquasicrystalline amorphous alloys for application.

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I. Introduction

Since the finding of a series of amorphous alloys with a wide supercooled liquid region before the crystallization as well as a high glass-forming ability in the Ni\(_50\)-La\(_{32}\)-C\(_{18}\) lanthanide metal (Ln)\(_{-2}\) and Zr\(_{3}\) based systems for several years between 1988 and 1990, much attention has been paid to the bulk amorphous alloys. After the general recognition of good mechanical properties, i.e., the high tensile strength, high bending strength, high fatigue strength, high Charpy impact fracture energy, high fracture toughness and high corrosion resistance for the Zr-based bulk amorphous alloys\(^ {15}\), the bulk amorphous alloys have attracted steadily increasing interest. The Zr-based bulk amorphous alloys in the Zr–Al–Cu–Ni, Zr–Ti–Al–Cu–Ni and Zr–Ti–Be–Cu–Ni systems have already been used as face materials of golf clubs\(^ {18}\) owing to the advantage points of the higher tensile strength, higher bending strength, lower elastic modulus, higher elastic elongation and higher fatigue strength as compared with conventional Ti-based crystalline alloys. It has subsequently been reported that the high tensile strength of the Zr-based amorphous alloys increases further in a coexistent structure of amorphous and nanoscale compound particles and no degradation of ductility is recognized\(^ {17} (\text{to}) \). The bending strength of the Zr-based bulk amorphous alloys containing nanocrystalline particles attains as high as \( 4400 \text{ MPa} \) which is about 2.2 times higher than that for the corresponding amorphous single phase alloys. The effectiveness of the dispersion particles for the Zr-based amorphous alloys has also been recognized in the compressive stress condition\(^ {11}\).

Recently, it has been reported that an icosahedral phase precipitates as the primary precipitation phase in Zr–Al–Cu–Ni\(^ {10}\) and Zr–Al–Cu–Ni–Ti\(^ {14}\) amorphous alloys containing a small amount of oxygen. These previous results have pointed out that the existence of oxygen is important for the precipitation of the icosahedral phase\(^ {15}\). However, for the Zr-based alloys, the precipitation of the icosahedral phase lacks in reproducibility, and there has been no subsequent data on the precipitation of icosahedral phase by other researchers. If we can find a new amorphous alloy in which the nanoscale icosahedral phase steadily precipitates and the high glass-forming ability is maintained, it is expected that the nanoquasicrystalline alloys develop as a new type of high-strength quasicrystalline alloys. Very recently, we have found that nanoscale icosahedral quasicrystalline particles precipitate homogeneously in an amorphous phase of the Zr–Al–Cu–Ni–Ag system and the addition of Ag increases the precipitation tendency of the quasicrystalline phase\(^ {17} (\text{to}) \). The precipitation of the nanoscale icosahedral particles was also found to be effective for the increase in the tensile fracture strength without detriment to good ductility in a wide volume fraction range of the icosahedral phase. This paper is intended to present the formation, microstructure and mechanical properties of the coexistent amorphous and nanoscale icosahedral phases in Zr\(_{60}\)Al\(_{15}\)Cu\(_{17.5−x}\)Ni\(_x\)Ag\(_{5}\) alloys subjected to optimum annealing treatments and to investigate the effectiveness of the nanoscale icosahedral phase on the mechanical properties of the Zr-based bulk
amorphous alloys.

II. Experimental Procedure

Multicomponent Zr-based alloys with the composition of Zr$_{60}$Al$_{23}$Cu$_{17.5}$Ni$_{10}$Ag$_{6}$ ($x$ = 0, 5 and 10 at%) were examined in the present study. Their alloy ingots were prepared by arc melting the mixtures of pure metals in an argon atmosphere. Cylindrical bulk samples, 50 mm long with various diameters of 1 to 7 mm, were produced from the alloy ingots by a copper mold casting method. Ribbon samples with a cross section of 0.03 × 1.2 mm$^2$ were also produced by a melt spinning method. Annealing was performed for different periods of 60 to 120 s in the temperature range of 703 to 750 K in an evacuated atmosphere. The amorphous structure in the as-cast and melt-spun states as well as the decomposition structure in the annealed state was examined by X-ray diffractometry, optical microscopy and transmission electron microscopy. The nanobeam electron diffraction technique was also used for the structural analysis of the nanoscale precipitation particles. Mechanical properties were measured using the cast bulk specimens with gauge dimensions of 1 to 3 mm in diameter and 7 mm in length at a strain rate of 4.4 × 10$^{-5}$ s$^{-1}$ with an Instron testing machine. The fracture morphology was examined by scanning electron microscopy.

III. Results

Figure 1 shows the outer shape and surface morphology of the cast bulk rods with diameters of 3, 4 and 5 mm for the Zr$_{60}$Al$_{23}$Cu$_{17.5}$Ni$_{10}$Ag$_6$ alloy and a diameter of 1.5 mm for the Zr$_{60}$Al$_{23}$Cu$_{17.5}$Ni$_{10}$Ag$_{10}$ alloy. All the bulk rods have the smooth outer surface and metallic luster and neither cavity due to the inclusion of gas nor ruggedness due to the precipitation of a crystalline phase is seen on the outer surface. Figures 2 and 3 show the X-ray diffraction patterns of the cast Zr$_{60}$Al$_{13.7}$Cu$_{12.5}$Ni$_{10}$Ag$_6$ rods with diameters of 3, 4 and 5 mm and Zr$_{60}$Al$_{13.7}$Cu$_{12.5}$Ni$_{10}$Ag$_{10}$ cylinders with diameters of 1.5 and 2 mm, respectively. All the diffraction patterns con-

**Fig. 1** Optical micrograph of cast bulk amorphous Zr$_{60}$Al$_{23}$Cu$_{17.5}$Ni$_{10}$Ag$_6$ rods with diameters of 3, 4 and 5 mm (a to c) and Zr$_{60}$Al$_{23}$Cu$_{17.5}$Ni$_{10}$Ag$_{10}$ cylinders with a diameter of 1.5 mm (d).

**Fig. 2** X-ray diffraction patterns of the cast bulk amorphous Zr$_{60}$Al$_{13.7}$Cu$_{12.5}$Ni$_{10}$Ag$_6$ rods with diameters of 3, 4 and 5 mm.

**Fig. 3** X-ray diffraction pattern of the cast bulk amorphous Zr$_{60}$Al$_{13.7}$Cu$_{12.5}$Ni$_{10}$Ag$_{10}$ rod with diameters of 1.5 and 2 mm.
retained broad peaks without any crystalline diffraction peaks, indicating that the Ag-containing alloys have the high glass-forming ability. The attainable maximum diameter was evaluated to be about 7 mm for the 5 at%Ag-containing alloy and about 2 mm for the 10 at%Ag-containing alloy. Thus, the glass-forming ability for the Zr–Al–Cu–Ni–Ag alloys tends to decrease with increasing Ag content. However, the rather high glass-forming ability is maintained even for the Zr-based alloys containing 10 at%Ag, though the Ag element deviates from the three empirical rules for the stabilization of supercooled liquid, i.e., multicomponents of more than three elements, significant atomic size ratios of more than 12% and negative heats of mixing, because of the positive heats of mixing between Ag and Cu or Ni elements. The maintenance of the high glass-forming ability is presumably due to the attractive bonding force between Ag and Zr or Al as well as the systematic change in atomic sizes in the order of Zr > Al > Ag > Ni > Cu.

**Figure 4** shows the DSC curves of the Zr<sub>55</sub>Al<sub>13</sub>Cu<sub>17</sub>Ni<sub>10</sub>Ag<sub>8</sub> (x=0, 5 and 10 at%) bulk amorphous rods with diameters of 1.5 and 3 mm. The Zr–Al–Cu–Ni quaternary alloy has a wide supercooled liquid region of 108 K which is defined by the difference between T<sub>g</sub> and T<sub>α</sub> and crystallizes through a single exothermic peak from the supercooled liquid region. However, the Ag-containing alloys have an extra exothermic peak on the lower temperature side and the crystallization mode changes to a two-stage process by the addition of Ag. The separation into the two stages becomes significant with increasing Ag content, accompanying the decrease in ΔT<sub>c</sub> to 82 K at 5%Ag and 51 K at 10%Ag.

We examined the precipitation phases corresponding to each exothermic reaction by the X-ray diffraction and TEM. Figures 5 to 7 show the X-ray diffraction patterns of the Zr<sub>55</sub>Al<sub>13</sub>Cu<sub>17</sub>Ni<sub>10</sub>Ag<sub>8</sub> (x=0, 5 and 10 at%) alloys, respectively, heated for 60 to 120 s at the temperatures in the vicinity of the first exothermic reaction. The X-ray diffraction patterns are identified as Zr<sub>2</sub>Ni + Zr<sub>2</sub>Cu + Zr<sub>2</sub>Al + ZrNi phases at 0%Ag, amorphous + icosahedral phases at 5 at%Ag and a mostly single icosahedral phase at 10%Ag. The peak intensity of the icosahedral phase increases significantly with in-
creasing Ag content. Considering that no icosahedral phase is recognized for the 0%Ag alloy, the addition of Ag is essential for the formation of the icosahedral phase. Figure 8 shows the X-ray diffraction patterns of the 5%Ag and 10%Ag alloys heated for 60 s at 873 K above the second exothermic peak. The diffraction peaks are composed of Zr,Cu + Zr,Ni + Zr,Al phases and no appreciable diffraction peak of the icosahedral phase is seen. The absence of the icosahedral phase after the complete crystallization indicates that the icosahedral phase is a metastable phase which appears as an intermediate phase in the crystallization process of the Ag-containing alloys.

For clarifying the morphology, particle size and inter-particle spacing of the metastable icosahedral phase in coexistence with the amorphous phase, the bright-field TEM image and selected-area electron diffraction patterns of the 10%Ag alloy annealed for 120 s at 680 K are shown in Fig. 9. It is seen that spherical particles with a size of 20 to 40 nm disperse homogeneously with an

![Fig. 7 X-ray diffraction patterns of the cast bulk Zr,Al,Cu,Ni,Ag rods annealed for 60 and 120 s at 703 K, respectively.](image)

![Fig. 8 X-ray diffraction patterns of the cast bulk Zr,Al,Cu,Ni,Ag (x = 5 and 10%) rods annealed for 60 s at 873 K.](image)

![Fig. 9 Bright-field TEM image and selected-area electron diffraction patterns of the cast bulk amorphous Zr,Al,Cu,Ni,Ag rod annealed for 120 s at 680 K.](image)

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average interparticle spacing of about 10 nm in the amorphous matrix. The selected-area electron diffraction pattern (b) taken from the region with a diameter of 1 μm consists of halo rings due to an amorphous phase and reflection rings due to an icosahedral phase. In order to confirm the precipitation of the icosahedral phase, nanobeam electron diffraction patterns of the precipitation particles were examined from the region with a diameter of 2.4 nm. The nanobeam electron diffraction patterns of the 10%Ag-containing alloy in Fig. 10 (a), (b) and (c) reveal the five-, three- and two-fold symmetries, respectively, indicating clearly that the spherical particles are composed of the icosahedral phase. The similar precipitation of spherical icosahedral particles with a size of about 40 nm has also been observed for the 5%Ag-containing alloy. Although there was no distinct difference in the morphology of the icosahedral particles between the 5%Ag- and 10%Ag-containing alloys, the 10%Ag alloy had a higher volume fraction, smaller icosahedral particle size and smaller interparticle spacing.

Figure 11 shows the Vickers hardness ($H_v$), Young's modulus ($E$), tensile fracture strength ($\sigma_t$) and tensile fracture elongation ($\varepsilon_t$) as a function of volume fraction ($V_t$) of the icosahedral phase for the 5%Ag-containing amorphous rods annealed for different periods at various temperatures. The $V_t$ of the icosahedral phase was determined from the change in the heat of exothermic reaction due to the precipitation of the icosahedral phase. The $\sigma_t$ of the 5%Ag-containing alloy increases from 1650 MPa at $V_t=0\%$ to 1900 MPa at $V_t=45\%$ and decreases with further increasing $V_t$. The similar change with $V_t$ is seen for $\varepsilon_t$. The $\sigma_t$ of 1.95% at $V_t=0\%$ increases slightly to 2.20% at $V_t=45\%$ and then decreases significantly in the higher $V_t$ range. On the other hand, the $H_v$ and $E$ increase almost linearly from 450 to 480 and 84.5 to 90.1 GPa, respectively, with increasing $V_t$ from 0 to 85%. The similar changes in $H_v$, $E$, $\sigma_t$ and $\varepsilon_t$ with $V_t$ are also recognized for the 10%Ag-containing alloy and the best mechanical properties of the highest $\sigma_t$ and $\varepsilon_t$ values of 1870 MPa and 2.0%, respectively, are obtained at $V_t=55\%$. It is thus noticed that the precipitation of the nanoscale icosahedral phase in the $V_t$ range up to about 50% causes the distinct increase in $\sigma_t$, $\varepsilon_t$ and $E$ values of the Zr-based bulk amorphous alloys. Figure 12 shows the fracture surface appearance of the 5%Ag-containing alloys with 0% $V_t$ and 45% $V_t$. The fracture of the bulk samples takes place along the maximum shear plane which is declined by about 45 degrees to the direction of tensile load. The fracture surface consists of a well-developed vein pattern which is typical for ductile amorphous alloys. Figure 13 also shows the tensile fracture surface of the 5%Ag-containing alloy rod with 70% $V_t$ obtained by annealing for 60 s at 750 K. The shear-type fracture mode changes to a mixed type of
Fig. 12  Tensile fracture surface of the bulk amorphous Zr$_{56}$Al$_{15}$Cu$_{15}$Ni$_{10}$Ag$_5$ rod in as cast state of $V_f=0\%$ (a and b) and annealed (730 K, 120 s) state of $V_f=45\%$ (c and d).

Fig. 13  Tensile fracture surface of the bulk amorphous Zr$_{43}$Al$_{13.5}$Cu$_{13.5}$Ni$_{10}$Ag$_5$ rod subjected to annealing for 60 s at 750 K, $V_f=70\%$. 
shear- and perpendicular-fracture modes in the higher $V_f$ range above 50%, accompanying the decreases in $\sigma_f$ and $\varepsilon_f$. No typical vein pattern is seen over the whole fracture surface of the samples with $V_f$ of over 50%, but the distinct ruggedness is recognized in the enlarged fracture surface as exemplified in Fig. 13(b). The fracture mode suggests that the icosahedral base alloy with a high $V_f$ of 70% can maintain a rather high degree of ductility.

IV. Discussion

1. The precipitation of the nanoscale icosahedral phase for the Ag-containing alloys

It was shown that the addition of Ag causes the change of the crystallization mode from the single stage to the two stages, accompanying the appearance of the extra exothermic peak at the lower temperature side. The extra exothermic peak corresponds to the precipitation of the icosahedral phase. This result indicates that the existence of Ag enables the precipitation of the icosahedral phase from the supercooled liquid. Considering that the Ni–Ag and Cu–Ag atomic pairs have positive heats of mixing, the separation tendency to Zr–Ni–Cu and Zr–Ni–Ag components seems to play an important role in the precipitation of the icosahedral phase. The icosahedral phase is presumed to contain Zr, Ag, and Al elements as main constituent elements. This presumption is supported by the experimental evidence that the icosahedral phase is formed as a primary precipitation phase in Zr–Al–Ag amorphous alloys containing a small amount of Ni.

2. The improvement of mechanical properties by the precipitation of the nanoscale icosahedral phase

It is well known that icosahedral alloys with stoichiometric compositions have high hardness and are extremely brittle at room temperature. It is therefore thought that the icosahedral phase itself embedded in the amorphous matrix does not have plastic deformability. The good mechanical properties of the mixed amorphous plus icosahedral phase alloy are attributed to the good ductility of the amorphous matrix. The deformation of amorphous alloys takes place along the maximum shear plane through a massive movement of constituent atoms within a width of 20 to 30 nm. The homogeneous dispersion of the icosahedral particles with a size of about 20 to 40 nm and an interparticle spacing of about 10 nm can act as an effective resistant medium against the shear deformation of the amorphous matrix. However, the increase in $V_f$ to over 50% causes the increase in the particle size of the icosahedral phase as well as the direct contact of the icosahedral particles, leading to easy initiation of crack at the icosahedral particles. As a result, the $\sigma_f$ and $\varepsilon_f$ decrease significantly and the fracture mode changes from the shear type to the perpendicular type. It is therefore expected that the $\sigma_f$ increases further, if much finer icosahedral particles can disperse more homogeneously at higher volume fractions.

V. Summary

The addition of 5 to 10 at% Ag was found to cause the homogeneous precipitation of nanoscale icosahedral quasicrystalline particles into the amorphous matrix of the Zr$_{65}$Al$_{17.5}$Cu$_{17.5}$Ni$_{10}$Ag$_{0.5}$ alloys. The precipitation occurs from the supercooled liquid in a homogeneous nucleation mode. The icosahedral particles have a spherical morphology and the particle size is about 20 to 40 nm. The volume fraction increases with increasing temperature and the highest $V_f$ is about 85% for the 5%Ag alloy and nearly 100% for the 10%Ag alloy. The icosahedral phase is a metastable phase and changes into a crystalline mixed structure of Zr$_3$Cu + Zr$_2$Ni + Zr$_2$Al$_3$ phases with further increasing temperature. For 5%Ag-containing bulk amorphous alloys, $\sigma_f$ increases from 1650 MPa at $V_f$=0% to 1900 MPa at $V_f$=45%, $E$ from 84.5 GPa to 86.0 GPa and $\varepsilon_f$ from 1.95% to 2.20%, respectively, maintaining the shear-type fracture mode. The further increase in $V_f$ causes the decreases in $\sigma_f$ and $\varepsilon_f$, accompanying the change to the perpendicular-type fracture mode. The achievement of high strength combined with good ductility in the coexisting structure of amorphous plus icosahedral phases indicates the possibility of the future development of the new material which can be named as bulk nanoquasicrystalline amorphous alloys.

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