Nanocrystallization of Zr-Cu-Ni-Al-Au glassy alloys during severe plastic deformation

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Abstract. A study has been carried out into the formation of nanocrystalline grains during high-pressure torsion (HPT) deformation of Zr₆₅Cu₁₇Ni₅Al₁₀Au₃ bulk alloys prepared using tilt casting. As a preliminary to this, X-ray diffraction (XRD) and differential scanning calorimetry (DSC) analyses were carried out on as-cast Zr₆₅₊ₓCu₁₇₋ₓNi₅Al₁₀Au₃ (x=0~5 at.%) and Zr₆₅Cu₂₀Ni₅Al₁₀ alloys, in order to determine the effect on the microstructure of the excess Zr content x and the presence of Au. From the XRD patterns, it was determined that all of the alloys had a metallic glassy nature. For Zr₆₅Cu₂₀Ni₅Al₁₀, the DSC results indicated the presence of a wide supercooled liquid region between the glass transition temperature (T_g) of 644 K and the crystallization temperature of 763 K, where the stable body-centered tetragonal Zr₂Cu phase was formed. In contrast, for the Zr₆₅₊ₓCu₁₇₋ₓNi₅Al₁₀Au₃ alloys, precipitation of an icosahedral quasicrystalline phase (I-phase) was observed in the supercooled liquid region at about 715 K. HPT deformation of the Zr₆₅Cu₂₀Ni₅Al₁₀Au₃ alloys was carried out under a high pressure of 5 GPa. Both as-cast specimens and those annealed at T_g-50 K for 90 min were used. Following a single HPT rotation (N=1), transmission electron microscopy identified the presence of face-centered cubic Zr₂Ni precipitates in the as-cast alloy, with a size of about 50 nm. For the annealed alloy, a high density of I-phase precipitates with sizes of less than 10 nm was observed following HPT with N=10, indicating that the combination of severe plastic deformation and annealing is effective at producing extremely small grains.

Keywords. Zr-Cu-Ni-Al-Au, glassy alloys, nanocrystallization, high-pressure torsion

1. Introduction
It is of fundamental importance to understand the grain size dependence of the mechanical properties of nanocrystalline materials, in which the grains have sizes of up to several tens of nanometers. However, the formation of such a nanocrystalline structure is very difficult using methods based on condensation of nanoscale powder [1, 2], and has only been successfully achieved for electrodeposited thin films of Ni and a limited number of Ni-based alloys [3-5]. In order to study the mechanical properties of nanocrystalline materials, it is necessary to obtain well-characterized, dense bulk specimens. Severe plastic deformation (SPD) is known to be a very useful technique for producing bulk nanocrystalline metallic alloys with different compositions. It has been reported that SPD of Zr-Cu-Al based bulk glassy alloys leads to structural changes such as reversible structural rejuvenation [6] and nanocrystallization [7].

In the present study, the effect of the presence of Au was examined by comparing to a Zr-Cu-Ni-Al alloy, and the mechanical properties of the nanocrystalline alloys were investigated using Vickers microhardness tests.

2. Experimental Procedures
Zr$_{65}$Cu$_{20}$Ni$_{5}$Al$_{10}$ and Zr$_{65+x}$Cu$_{17-x}$Ni$_{5}$Al$_{10}$Au$_{3}$ ($x = 0 \sim 5$ at. %) bulk alloys were prepared by the tilt-casting method [8]. The specimens were cast in a cylindrical copper mold with a length of 60 mm and inner diameters of 3.5~10 mm in an argon atmosphere. In order to remove residual crystalline inclusions in the arc-melted alloy liquids, the liquid flowing during casting was reheated using a second arc-torch.

The cast rods were sliced into disc shapes with thicknesses of 0.85 mm and diameters of 10 mm. Some specimens were annealed at $T_g$-50 K for 90 min in order to accelerate precipitation of the $I$-phase during HPT deformation. The HPT process was carried out using quasi-constrained-geometry anvils under a compressive pressure of 5 GPa at room temperature. The rotation speed was 1 rpm, and rotation numbers of $N=1, 10, 20$ and 50 were used. The structure of the as-cast and annealed specimens was investigated using X-ray diffraction (XRD) with Cu-K$_\alpha$ radiation (40 kV, 20 mA). Differential scanning calorimetry (DSC; Perkin Elmer, Diamond DSC) was used to determine the glass transition temperature $T_g$ and the crystallization temperature $T_x$ at a heating rate of 40 K/min. The difference between these values ($T_x - T_g$) is denoted $\Delta T_x$ in the present study. The specimens weighed about 10 mg, and were obtained from a position about 4 mm from the center of the disc. The enthalpy associated with structural relaxation induced by HPT was evaluated from the difference between the first and second DSC heating curves in the temperature range 400-650 K. The Vickers microhardness of the HPT deformed alloys was measured under a 20 N load and a loading time of 15 s. Laser microscopy was used to examine the specimen surface following the indentation tests.

3. Results

Figure 1 shows XRD patterns and DSC profiles for as-cast Zr$_{65}$Cu$_{20}$Ni$_{5}$Al$_{10}$ and Zr$_{65+x}$Cu$_{17-x}$Ni$_{5}$Al$_{10}$Au$_{3}$ ($x = 0 \sim 5$ at. %) alloys. In the XRD patterns, only a single broad diffraction peak is observed at 2$\theta$ values between 30 and 45°, which confirms that the alloys contain only a metallic glass phase. The DSC results show that for the Zr$_{65}$Cu$_{20}$Ni$_{5}$Al$_{10}$ specimen,
crystallization of the stable body-centered tetragonal (bct) Zr$_2$Cu phase occurs at $T_c=763$ K, and a wide supercooled liquid region with $\Delta T_s=119$ K is present. In contrast, for the Zr$_{65}$Cu$_{17}$Ni$_5$Al$_{10}$Au$_3$ alloy, precipitation of the I-phase occurs in the supercooled liquid region at $T_x=715$ K, before precipitation of the stable bct-Zr$_2$Cu phase takes place at $T_x=760$ K, resulting in a drastic reduction in $\Delta T_x$ to 50 K. With increasing Zr content, $T_x$, $T_c$ and $\Delta T_s$ decrease slightly, but no other major changes occur. Since 40 mm $\times$ 10 mm cylindrical specimens could only be obtained for $x=0$ at. %, the Zr$_{65}$Cu$_{17}$Ni$_5$Al$_{10}$Au$_3$ alloy was used for the HPT tests.

Figure 2 shows XRD patterns for as-cast and annealed Zr$_{65}$Cu$_{17}$Ni$_5$Al$_{10}$Au$_3$ specimens before and after HPT deformation. For both specimens, weak diffraction peaks associated with face-centered cubic (fcc) Zr$_2$Ni appear at diffraction angles $2\theta$ of about 27 and 47°, and their intensity increases with number of rotations. Apart from this, no significant changes are induced in the XRD patterns by HPT. In optical micrographs of the HPT deformed specimens, small crystalline regions with dimensions of a few micrometers were found near macroscopic cracks at the specimen edges, but no major change in the microstructure was observed.

![XRD patterns for as-cast and annealed Zr$_{65}$Cu$_{17}$Ni$_5$Al$_{10}$Au$_3$ specimens before and after HPT deformation.](image)

**Fig. 2** XRD patterns for (a) as-cast and (b) annealed Zr$_{65}$Cu$_{17}$Ni$_5$Al$_{10}$Au$_3$ specimens before and after HPT deformation. The diameter of $\phi$ and the sampling site of the length of L from bottom of the each rod were indicated in (a) and (b).

Figure 3 shows DSC profiles for the as-cast and annealed specimens before and after HPT deformation. Apart from a slight decrease in $T_g$, no major changes appear to be induced by the HPT process. However, there does appear to be a change in the amount of exothermic heat flow due to structural relaxation at temperatures below $T_g$, as determined from the difference between the first and second DSC heating runs in the range 400-650 K (shaded area in the figure).

Figure 4 shows the integrated structural relaxation enthalpy ($\Delta H$) for the HPT deformed specimens in the temperature range 400-650 K, together with the Vickers microhardness ($HV$) before and after deformation. For the as-cast specimens, $\Delta H$ increases and reaches a maximum of about 23 J·g$^{-1}$ at N=0.5, and then decreases to a local minimum of 18 J·g$^{-1}$ at N=1.
Fig. 3  DSC profiles of HPT deformed specimens of (a) as-cast and (b) annealed Zr65Cu17Ni5Al10Au3 bulk glassy alloys. The shaded areas in the temperature range 400-650 K indicate the structural relaxation enthalpy induced by HPT, evaluated from the difference between the first and second DSC heating runs.

Fig. 4  (a) Sample appearances before and after the HPT deformation, (b) Integral values of structural relaxation enthalpy, $\Delta H$, and (c) Vickers microhardness of the HPT-deformed specimens of as-cast and annealed Zr65Cu17Ni5Al10Au3 bulk glassy alloys.

which coincides with the maximum value of $HV$. Subsequently, as $N$ is increased, $\Delta H$ increases and $HV$ decreases. For the annealed specimens, $\Delta H$ is somewhat lower than for the
as-cast specimens, but exhibits a similar dependence on \( N \), reaching a maximum of \( 18 \text{ J}\cdot\text{g}^{-1} \) for \( N=0.5 \) and a minimum of \( 12 \text{ J}\cdot\text{g}^{-1} \) for \( N=10 \). This minimum again coincides with a local maximum in \( HV \).

![HR-TEM micrographs and selected area diffraction patterns for annealed Zr\(_{65}\)Cu\(_{17}\)Ni\(_5\)Al\(_{10}\)Au\(_3\) bulk glassy alloys before and after HPT deformation.](image)

**Fig. 5** HR-TEM micrographs and selected area diffraction patterns for annealed Zr\(_{65}\)Cu\(_{17}\)Ni\(_5\)Al\(_{10}\)Au\(_3\) bulk glassy alloys before and after HPT deformation. 
(a) As cast, (b) After HPT with \( N=10 \), (c) After HPT with \( N=50 \).

**Figure 5** shows HR-TEM micrographs and selected area diffraction patterns (SADPs) for annealed specimens before and after HPT deformation. For the as-cast specimen shown in Fig. 5(a), the microstructure appears amorphous, which is confirmed by the halo-like SADP. After HPT deformation with \( N=10 \), a high density of \( I \)-phase precipitates with sizes of less than 10 nm are observed. For \( N=50 \), these precipitates disappear and the structure returns to an amorphous state, which is consistent with the increase in \( \Delta H \) and the decrease in \( HV \) seen in Fig. 4. For the as-cast specimens, \( fcc \)-Zr\(_2\)Ni precipitates with sizes of about 50 nm were observed by TEM for the case of \( N=1 \), but the structure was again amorphous for \( N=10 \) and 50. Thus, the combination of SPD and annealing appears to be effective at forming nanocrystalline \( I \)-phase precipitates with sizes of less than 10 nm.

![Laser microscope images of indents in annealed specimens after HPT deformation for](image)

**Fig. 6** Laser microscope images of indents in annealed specimens after HPT deformation for
Figure 6 shows SEM images of indents in HPT deformed annealed specimens for \( N = 0 \) and 10. For \( N = 0 \), where the specimen was subjected only to high compression, many arcate shear bands appear around the indent. No such bands are found for the \( N = 10 \) case, indicating that HPT deformation eliminates or significantly reduces the extent of strain localization.

4. Discussion

Quasicrystal (QC)-forming Zr-Cu-NM (NM: noble metal) and Zr-(Pd or Pt) glassy alloys have been reported [9, 10]. Saida et al. investigated the effects of noble metals on the local structure of Zr_{70}Pd_{30} and Zr_{80}Pt_{20} glassy alloys using a Voronoi analysis [10]. They reported that in Zr_{70}Pd_{30}, quasicrystallization originates from medium-range order associated with perfect Zr-centered icosahedra and Pd-centered prism-like polyhedra that remain during formation of the QC phase. In contrast, in Zr_{80}Pt_{20} glassy alloys, distorted icosahedral-like polyhedra are favored around both Zr and Pt, and may contribute to nucleation of the QC phase.

As shown in Fig. 1, the addition of a small amount of Au to Zr-Cu-Ni-Al based glassy alloys is very effective at accelerating the precipitation of the icosahedral quasicrystalline phase in the supercooled liquid region, and may contribute to the nucleation of the QC phase. The HR-TEM image in Fig. 5 clearly shows that HPT deformation with \( N = 10 \) leads to the occurrence of nanocrystallization in Zr_{50}Cu_{40}Ni_{10}Al_{10}Au_{3}. In addition, the results shown in Fig. 4 indicate that \( N = 10 \) yields a local minimum in the relaxation enthalpy, and a local maximum in the hardness. These results support the idea that partial crystallization begins to occur during HPT deformation. This bulk glassy alloy exhibits a very high yield stress of about 1.5 GPa, with a strain hardening exponent (\( n \)) of almost zero. As a result, plastic deformation can proceed by the formation of localized shear bands. Within these shear bands, the supercooled liquid phase may be generated, so that plastic deformation can occur under very low applied stress along the bands. The large amount of plastic strain associated with HPT deformation can introduce an extremely high number of shear bands, resulting in uniform deformation of the alloy. Nanocrystallization may then take place by precipitation of the QC phase from the supercooled liquid phase within the shear bands.

Deformation induced nanocrystallization in Zr-based [11, 12] and Cu-based [13] bulk metallic glasses has been reported. Saida et al. found direct evidence that precipitation of nanocrystalline particles was induced by micro-shear-band propagation in Zr_{50}Al_{17,5}Ni_{10}Pd_{17,5} metallic glass during compressive deformation. Such dynamic nanocrystallization may suppress the propagation of the shear bands and so provide a new method for improving the mechanical properties of bulk metallic glasses [12]. The laser microscope images of the indents in Fig. 6 clearly show the evolution of HPT induced nanocrystallization. Many arc-shaped shear bands are found around the indent in the pre-HPT sample (\( N = 0 \)), whereas after HPT deformation with \( N = 10 \), no shear bands can be seen. Thus, HPT deformation eliminates or significantly reduces the extent of strain localization. It can therefore be speculated that deformation induced nanocrystallization may be effective at causing stress-induced hardening in bulk metallic glasses.

As seen in Fig. 4, HPT deformation with \( N = 50 \) causes the relaxation enthalpy to sharply increase and the hardness to decrease, and the TEM results in Fig. 5 show that this specimen is amorphous. In this case also, no shear bands were formed around the indent. Meng et al. [6] reported that HPT deformation caused large-scale homogeneous rejuvenation of Zr_{50}Cu_{40}Al_{10} bulk metallic glass. Such rejuvenated regions are preferential sites for the formation of homogeneous shear transformation zones under applied stress, which leads to a
lower elastic modulus and hardness, in addition to homogeneous plastic deformation without strong strain localization or shear band formation.

5. Conclusions
The use of HPT to induce nanocrystallization in as-cast and annealed Zr_{65}Cu_{17}Ni_{5}Al_{10}Au_{3} bulk glassy alloys was investigated. In these alloys, the Au atoms may contribute to the nucleation of the QC phase. After HPT deformation of an annealed specimen using 10 rotations, a high density of nanocrystalline $I$-phase precipitates was observed, with sizes of less than 10 nm. The large plastic strain associated with HPT deformation can introduce an extremely high number of shear bands, resulting in highly uniform deformation of the alloy. Nanocrystallization may then proceed by precipitation of the QC phase from the supercooled liquid phase that is generated within uniformly distributed shear bands.

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