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Plastic deformation by glassy structure control in Zr–Al–Ni–Cu-based BMGs

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ABSTRACT

$Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5-x}Pd_x$ (x = 0–17.5) bulk metallic glasses (BMGs) were produced in various chamber atmospheres in Cu mold casting. The glassy structure with a larger amount of relaxation enthalpy can be obtained casting under the ambient Ar and He atmospheres, which originates from enhanced cooling effect. These unrelaxed BMGs exhibit an improvement of ductility in the compressive deformation. Especially, Pd-containing BMGs have a significant plasticity of approximately 6%, in which deformation-induced inhomogeneous nanocrystallization also occurs. The synergistic effect of unrelaxed glassy structure and deformation-induced nanostructure change is regarded as a new technique for the improvement of ductility in the BMGs.

1. Introduction

BMGs are well known as unique structural materials owing to their attractive mechanical properties [1,2]. However, BMGs generally exhibit poor room temperature ductility. It originates from the deformation mechanism by shear band propagation, which is different from that in crystalline materials. Due to the homogeneous structure in the monolithic BMGs, shear band can move easily under the applied stress. A number of works about BMGs or BMG composites with improved ductility have been reported. The origin of good ductility were explained by a large Poisson's ratio [3], the presence of heterogeneity and/or short-/medium-range order [4], liquid–liquid phase separation [5], introduced porosity [6], *in situ* secondary phase [7] and *ex situ* foreign particles [8]. Recently, we have reported a significant plasticity owing to the deformation-induced nanocrystallization in the $Zr_{65}Al_{7.5}Ni_{10}Pd_{17.5}$ BMG [9], which is attributed to the unstable supercooled liquid state. In the present paper, we intend to report the production of Zr–Al–Ni–Cu(–Pd) BMGs by casting in the ambient Ar and He atmospheres. It is expected that this method brings a high cooling rate comparing to that cast in the vacuum atmosphere, which also results in the formation of unrelaxed glassy structure. In this work, we attempt to improve plasticity in monolithic BMGs by the synergistic effect of unrelaxed glassy structure and dynamic nanocrystallization during deformation in the Zr–Al–Ni–Cu–Pd BMGs.

2. Experimental procedures

The bulky samples of $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5-x}Pd_x$ (x = 0–17.5) metallic glasses were produced by the Cu mold casting technique in the various Ar and He pressures. The cooling process was monitored by measuring the temperature of the melts using a thin (0.3 mm in diameter) K-type thermocouple connected to an analog-to-digital converter [9]. The unrelaxed glassy structure was evaluated by an enthalpy of relaxation which was calculated from a specific heat measurement using DSC (Perkin-Elmer Pyris Diamond DSC). The compressive mechanical test was performed with a cylindrical shape in 2.5 mm diameter and 5 mm high at room temperature at strain rate of $5 \times 10^{-4}\ s^{-1}$. The structure of fractured sample was examined using the field-emission transmission electron microscopic (TEM) observation with an accelerating voltage of 300 kV (JEOL JEM 3000F). The detail of sample preparation for TEM has been reported in our previous paper [10].

3. Results and discussion

3.1. Cooling effect in various atmospheres

Recently, we have reported that the apparent glass-forming ability (GFA) strongly depends on the atmosphere pressure and the noble metal content in the Zr–Al–Ni–Cu–Pd alloys by the Cu mold casting method [11]. Fig. 1 shows results of experimental measurement of cooling curves in the glassy phase formation under the vacuum, Ar with 10^3 Pa, ambient (10^5 Pa) Ar and He atmospheres. No significant difference among all cooling curves is observed in the

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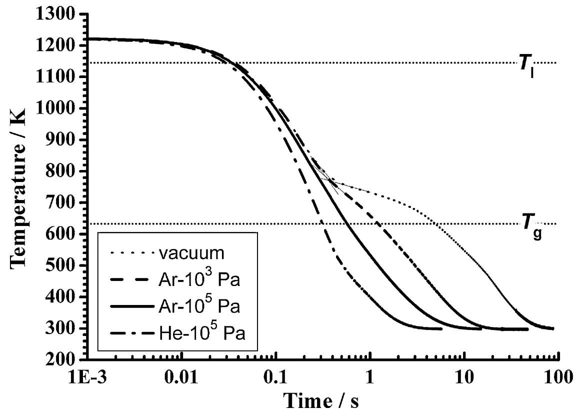

Fig. 1. Experimental measurement of cooling curves in the glassy phase formation under the vacuum, 10^3 Pa Ar, ambient (10^5 Pa) Ar and He atmospheres.

high temperature range of supercooled liquid. In contrast, cooling effect is significantly enhanced with increasing the pressure in the low temperature range. The onset temperature exhibiting such an enhancement of cooling effect is approximately $T_g + 200$ K. We have already suggested that it is due to the change of cooling mechanism governing by heat transfer via a cavity between cast alloy and Cu mold [12]. The cavity is formed by the shrinkage of cast molten alloy during cooling, in which it might occur around the temperature of approximately $T_g + 200$ K. In such case, the difference of thermal conductivity of atmosphere brings the different cooling effects, that is, it should be enhanced in the Ar and He atmospheres rather than vacuum.

The enhancement of cooling effect casting in the ambient Ar or He atmosphere also brings the production of unrelaxed BMGs. Fig. 2 shows thermograms of the $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ BMG in the as-prepared state ($C_{p,q}$) cast in vacuum and ambient Ar atmospheres. Data for the relaxed state ($C_{p,s}$) is also shown for comparison. The enthalpy of relaxation can be obtained by the integral of ΔC_p ($=C_{p,s} - C_{p,q}$) [13], and it is calculated to be 5.4 J/g in vacuum and 10.2 J/g in ambient Ar, indicating the formation of unrelaxed glassy structure cast in the ambient Ar atmosphere. The enthalpy of relaxation generally correlates to an amount of free volume in the glassy state [14]. In the recent studies on mechanical behavior of BMGs, free volume is regarded as one of the factors for deformability. It is, therefore important to produce the unrelaxed BMG for the improvement of plasticity as well as the development of new BMGs.

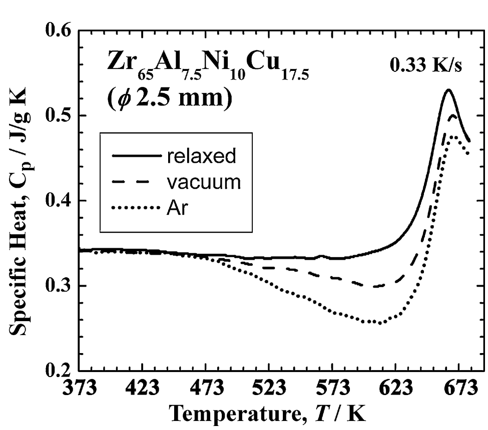

Fig. 2. Thermograms of the $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ BMG in the as-prepared state ($C_{p,q}$) cast in the vacuum and ambient Ar atmospheres. Data for the relaxed state ($C_{p,s}$) is also shown for comparison.

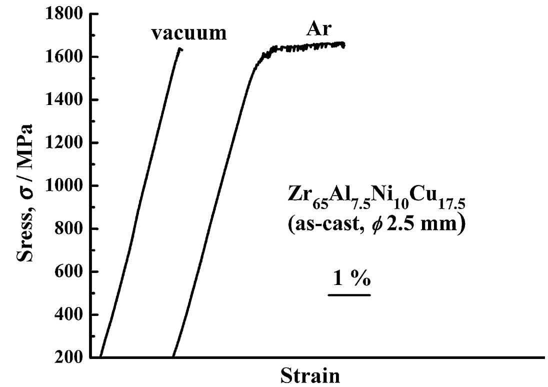

Fig. 3. Stress–strain curves of the $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ BMG cast in the vacuum and ambient Ar atmospheres.

3.2. Mechanical properties of unrelaxed BMGs

It is well-known that the unrelaxed glassy structure contains a large amount of free volume [15]. During compression, it plays a role as shear transformation zone, in which the shear bands nucleate [16]. That is, a large amount of free volume leads to the multiple shear band formation with an improvement of plasticity [17]. Stress–strain curves of the $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ BMG cast in the vacuum and ambient Ar atmospheres are shown in Fig. 3. No significant differences in the fracture strength and Young's modulus are observed between two casting atmospheres. The fracture strength and Young's modulus are 1639 MPa and 92 GPa in the BMG cast in vacuum and 1675 MPa and 85 GPa in the BMG cast in ambient Ar pressure, respectively. Almost no plastic strain is detected in the vacuum cast sample, however, it is slightly improved (~1.4%) in the BMG cast in ambient Ar pressure. We suggest that the increase in free volume in the unrelaxed glassy structure contributes to the enhancement of nucleation of shear band, which results in the slight improvement of plasticity. Similar effect is also observed in the BMG cast in the He atmosphere.

Obvious effect by changing casting atmosphere on the improvement of plasticity is observed in the Pd-containing BMGs. We have already clarified that plasticity is significantly improved in the $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Pd_5$ BMG cast in ambient Ar or He (~6%), comparing to that cast in vacuum (~2%) [18]. Here, the multiple shear bands are observed in the BMGs cast in Ar and He [19]. The measured enthalpy of relaxation is 4.4 J/g (vacuum), 8.2 J/g (ambient Ar) and 9.8 J/g (ambient He), indicating a correlation with plastic strain. It is, therefore suggested that the unrelaxed glassy structure has a good effect on the improvement of plasticity in the Pd-containing BMG. Recently, similar phenomenon of the enhancement of plasticity by increasing cooling rate has been also reported in the Cu–Zr–Al ternary BMGs [20].

3.3. Plasticity by deformation-induced nanocrystallization in Pd-containing BMGs

As described in Section 3.2, the unrelaxed glassy structure is effective on the slight increase in the plastic strain. However, it should be noted that the $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Pd_5$ BMG cast in the ambient Ar and He atmospheres exhibits a significant plasticity as compared to that in the $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ BMG. Therefore, we should consider other mechanism for the marked plasticity (~6%) in the $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Pd_5$ BMG cast in the ambient Ar or He pressure, in addition to the increase of free volume. In order to investigate the mechanism of plasticity, we performed the structural observation by TEM for the as-cast and fractured $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Pd_5$ BMG. Fig. 4 shows high-resolution TEM

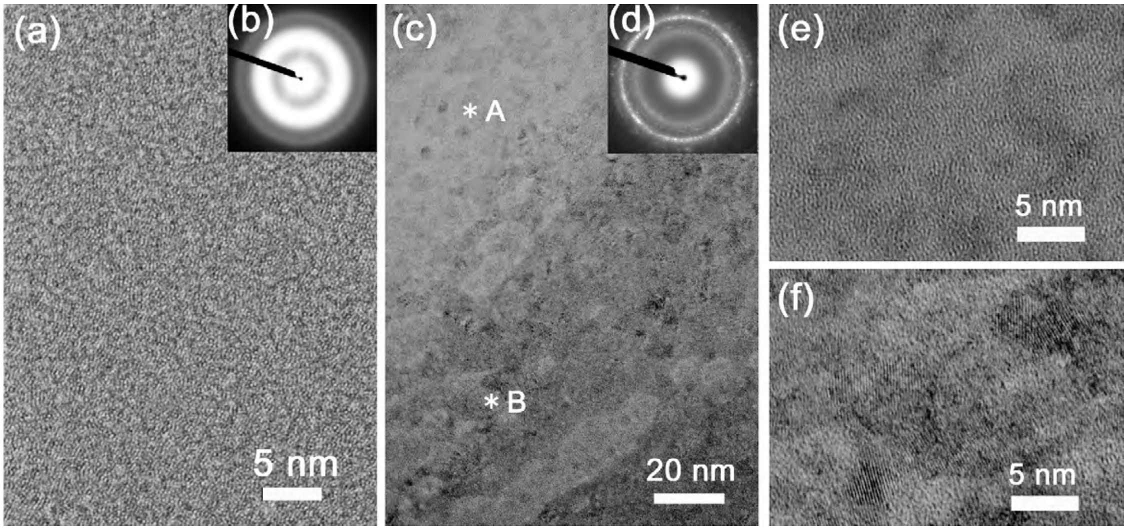

Fig. 4. HREM images and SADPs of the as-cast state (a and b) and the fractured tip (c and d) of the $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Pd_5$ BMG, respectively. Magnified HREM images taken from brighter region (region A) and darker region (region B) in (d) are shown in (e) and (f), respectively.

(HREM) images and selected-area electron diffraction patterns (SADPs) of as-cast state (a), (b) and the fractured tip (c), (d) of the $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Pd_5$ BMG, respectively. A homogeneous maze contrast is observed and no obvious fringe contrast or medium-range ordered region can be seen in the HREM image in the as-cast state. Considering the SADP revealing only a halo ring as well as the homogeneous HREM image, the as-cast BMG has a monolithic glassy structure. In contrast, a band-like contrast can be observed in the fracture tip of the $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Pd_5$ BMG as shown in Fig. 4(c). Significant diffraction spots appeared in the SADP in Fig. 4(d) may indicate the structure change. Magnified HREM images taken from brighter region (region A) and darker region (region B) in (d) are shown in Fig. 4(e) and (f), respectively. In the brighter area, the HREM image (e) clearly denotes the homogeneous maze contrast similar to that in the as-cast state. Meanwhile, several regions in diameters of 5–10 nm with fringe contrast are confirmed in the darker region in Fig. 4(f), indicating a precipitation of nanocrystalline particle. We have already reported that the precipitated particles are identified as the metastable fcc Zr_2Ni structure, of which formation has been also clarified in the highly distorted ball-milled $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Pd_5$ glassy alloy powder [9,21]. The unique inhomogeneous nanoscale structure change might be regarded as deformation-induced nanocrystallization correlated with shear band propagation. With the propagation of the shear band associated with localized viscous flow, structural segregation and transformation are induced owing to the localized temperature arising [22] or the change in chemical short-range order (CSRO) in the metallic glass with the less stable supercooled liquid state such as the $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Pd_5$ alloy. Actually, the $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Pd_5$ metallic glass has a narrower supercooled liquid region than that in the $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ alloy [23]. Repeating the process of such deformation-induced nanocrystallization, a significant plasticity is exhibited by shear band branching compared to that in deformation without any structural change. We have already reported that similar nanocrystallization induced by deformation is also observed in the BMGs with the Pd concentration over 10 at.% [10,19].

Table 1
Mechanical properties of $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5-x}Pd_x$ (x = 0–17.5) BMGs cast in ambient Ar pressure.

Pd content, x (at.%)	σ_y (MPa)	σ_{max} (MPa)	E (GPa)	$\varepsilon_{pl.}$ (%)
0	1582	1675	85	1.4
5	1530	1643	84	6.0
10	1501	1623	85	5.7
12.5	1587	1668	86	5.0
15	1641	1688	86	6.0
17.5	1582	1689	86	6.9

Table 1 summarizes mechanical properties of several Pd-containing BMGs cast in ambient Ar pressure. The enhancement of cooling effect brings a success of production of new BMGs containing a large amount of Pd over 10 at.% as well as the formation of unrelaxed glassy structure. Moreover, we found that the significant plasticity (5–7%) is obtained in the Pd-containing BMGs by the deformation-induced nanocrystallization. It is, therefore concluded that the plasticity can be improved significantly by the synergistic effect of unrelaxed glassy structure and deformation-induced nanostructure change in the present Pd-containing BMGs cast in ambient Ar or He pressure.

4. Conclusions

We investigate the cooling effect of casting atmosphere on glassy structure and the deformation behavior in $Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5-x}Pd_x$ (x = 0–17.5) BMGs. The unrelaxed glassy structure can be obtained casting under the ambient Ar or He atmosphere, which originates from enhanced cooling effect in the low temperature range ($\sim T_g + 200$ K) in the supercooled liquid state. The unrelaxed BMGs exhibit an improvement of ductility in the compressive deformation. Moreover, we found that the Pd-containing BMGs have a significant plasticity of approximately 6%, in which the deformation-induced inhomogeneous nanocrystallization by shear band propagation also occurs. We conclude that the synergistic effect of unrelaxed glassy structure and deformation-induced nanostructure change is regarded as a new technique for the improvement of ductility in the BMGs.

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