Impact of Microstructural Inhomogeneities on the Ductility of Bulk Metallic Glasses

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To circumvent the limited ductility of bulk metallic glasses (BMGs), heterogeneous materials with glassy matrix and different type and length-scale of heterogeneities (micrometer-sized second phase particles or fibers, nanocrystals in a glassy matrix, phase separated regions, variations in short-range order by clustering) have been developed in order to control the mechanical properties. As example, recent results obtained for Cu- and Ti-base structurally inhomogeneous bulk metallic glasses will be presented. This type of clustered glasses is able to achieve high strength together with pronounced work hardening and large ductility by controlling the instabilities otherwise responsible for early failure. We emphasize the possibilities to manipulate such spatially inhomogeneous glassy structures based on martensitic alloys in favor of either strength and ductility, or a combination of both and also discuss the acquired ability to synthesize such M-glasses in bulk form through inexpensive processing routes. [doi:10.2320/maiertrans.MJ200725]

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1. Introduction

Usually monolithic bulk metallic glasses (BMGs) undergo inhomogeneous plastic deformation at room temperature, which results in a very limited macroscopic plastic strain (<1%).1–3 In order to overcome this disadvantage of monolithic BMGs, several attempts have been made to improve the plastic deformability by introducing nanometer-scale precipitates4–6 and micrometer-scale ducile crystalline phases.7–9 This idea opens a door for processing a new class of Ti,10,11 and Zr-based12 alloys with glassy or nanostructured matrix and ductile primary dendrites, has been already reported.

Very recently, bulk metallic glasses with large plastic deformability and even work hardening-like behavior have been found in glass-forming Zr,13 Pt,14 (Cu-Zr),15–18 and Pd-Si,19 based alloys. Several different potential mechanisms have been proposed for enhancing the macroscopic ductility of BMGs, like to achieve a critical value of Poisson’s ratio,14,20 or to introduce atomic-scale inhomogeneities13,15,16 or a phase separated glassy structure.17,19 However, all these explanations deal with homogeneous nucleation of shear bands and their delocalization due to the elastic constants of the bulk materials17 or an effective interaction between nanometer-size crystalline21,22/non-crystalline (phase separated) particles,17,19,23 or with voids as observed in the case of porous metallic glasses.24

The underlying mechanism of plastic deformation of metallic glass is related to shear transformation zones (STZs) consisting of 200–300 atom clusters which undergo cooperative shear.25,26 The shear localization is a result of a rapid dilation accompanying high-rate shear deformation of short-range ordered clusters.1,27 This shear rate is significantly higher than the strain rate imposed during experiments.28 Spreading of such localized shearing events occurs around STZs26 and creates free volume.13 Localized shear transformations along certain preferred directions (i.e., direction of maximum shear stress) create microstructural shear bands.29 Accumulation of free volume inside the shear bands decreases the viscosity which finally appears as strain softening/thermal softening.30,31 However, failure occurs catastrophically along a single shear band without macroscopic plasticity.32

Besides the theoretical ideas on the plastic deformation of amorphous solids, the experimental results suggest that most of the ductile bulk metallic glasses are spatially structurally/chemically inhomogeneous,15–17,19,22 and are rather not monolithic material.14 It has been proven that relaxed monolithic Zr65Al17.5Ni10Cu12.5Pd8 alloys with 2–5 nm sized nanocrystals exhibit enhanced plastic deformability compared to the as-cast condition. On the other hand, monolithic Zr65Al17.5Ni10Pd17.5 glass34 shows large plastic deformability (6%) and nano-scale multi-step “bandlike” structure after deformation. The true stress–true strain curve clearly reveals “macroscopic hardening”.34 This rises several questions in order to interpret the structural backbone of metallic glass, which is responsible for facilitating the plastic flow in glassy material at room temperature.

In this work, we present bulk metallic glasses exhibiting large plastic deformability in Cu-Zr- and Ti-(Cu,Ni)-base martensitic alloys. Our experimental evidence together with supporting literature data indicates that a spatially inhomogeneous clustered glassy structure can be achieved in these rather poor glass-forming alloys, which does not depend on a specific pin-pointed alloys composition but seems to exist for a wide variety of ductile BMGs which one could term martesite-glasses or ‘M-Glasses’. Easy inelastic shearing events repeatedly occur around the STZs, which releases the
local stress concentration, and delocalizes the shear in order to originate multiple shear bands.

2. Experimental

The alloys used in this work were designed from Cu$_{50}$Zr$_{50}$ and Ti$_{50}$(Cu$_{3}$Ni)$_{50}$ alloys. The alloys have been prepared by mixing the pure elements in an arc melter. Different amounts of Al (5, 6 at%) have been added to Cu$_{50}$Zr$_{50}$ in order to prepare Cu$_{47.5}$Zr$_{47.5}$Al$_{5}$ and Cu$_{47}$Zr$_{47}$Al$_{6}$ alloys. Similarly, (Ti$_{43}$Zr$_{57}$)Cu$_{43}$Ni$_{7}$ and (Ti$_{48}$Zr$_{52}$)(Cu$_{50}$Ni$_{7.5}$Sn$_{2.5}$) alloys have been prepared by replacing Ti by different amounts of Zr (5, 7 at%) and Sn has been added in order to substitute Cu in the Ti$_{50}$(Cu$_{3}$Ni)$_{50}$ composition. The ingots have been remelted several times in order to obtain homogeneity of the alloy. Rods of φ2–4 mm have been produced by in-situ solidification in a suction casting facility attached to the arc melter. A optical microscope (OM), Zeiss DSM 962 scanning electron microscope (SEM) and a Philips XL 30 high resolution SEM operated at 25 kV with an attached energy dispersive spectroscopy analysis unit were used for the microstructure observation for differently solidified rods and ingots. A Philips CM20 transmission electron microscope (TEM) coupled with energy-dispersive X-ray analysis (EDX), differential scanning calorimetry (Perkin-Elmer DSC), and a Siemens D500 X-ray diffractometer (XRD) with Cu-K$_\alpha$ radiation were used for structural characterization and to investigate the formation of metastable phases during solidification at different cooling rates. The TEM specimens were prepared by the conventional method of slicing and grinding, followed by ion-milling with liquid nitrogen cooling. In order to evaluate the mechanical properties under compression, cylindrical specimens with a 2 : 1 aspect ratio were prepared and tested in a Schenck servo-hydraulic testing machine under quasistatic loading at an initial strain rate of 8 × 10$^{-4}$ s$^{-1}$ at room temperature. Both ends of the specimens were polished to make them parallel to each other prior to the compression tests.

3. Results and Discussion

3.1 Cu-Zr-base alloys

The stress-strain curves of differently prepared Cu-Zr-Al alloys subjected to room temperature compression test are shown in Fig. 1. All the stress-strain curves of the Cu$_{50}$Zr$_{50}$-base alloys show elastic-plastic deformation behavior. The Cu$_{47.5}$Zr$_{47.5}$Al$_{5}$ (φ2 mm) and Cu$_{47}$Zr$_{47}$Al$_{6}$ rods (φ2.5 mm) have a significantly higher yield strength ($\sigma_y$ = 1547 MPa and 1687 MPa) compared to the Cu$_{50}$Zr$_{50}$ ingot ($\sigma_y$ = 1193 MPa) and φ2.5 mm rods (1716 MPa) together with large plastic strain ($\varepsilon_p$ = 16%$^{15}$) and 5.5%). Interestingly, the investigated Cu$_{50}$Zr$_{50}$ φ2 mm glassy alloy (Fig. 1) displays high strength ($\sigma_y$ = 1272 MPa) and work hardening up to 1794 MPa and 6.2% plastic strain. In an extreme case, more than 50% plastic strain was observed for 1 mm diameter rods of Cu$_{50}$Zr$_{50}$.$^{21}$ Figure 1 reveals that the yield strength of Cu$_{50}$Zr$_{50}$ increases with decreasing casting thickness. Moreover, the yield strength of 2.5 mm diameter rods of Cu$_{47}$Zr$_{47}$Al$_{6}$ is higher than for Cu$_{50}$Zr$_{50}$. The true stress-strain curve for φ2.5 mm Cu$_{47}$Zr$_{47}$Al$_{6}$ displays work-hardening-like behavior, as presented the inset of Fig. 1.

In order to correlate the plastic deformability and the evolution of the microstructure in differently solidified Cu$_{50}$Zr$_{50}$ alloys, structural analysis has been performed by using XRD DSC, OM, SEM, and high resolution TEM. Figure 2 shows the XRD patterns of differently solidified Cu-Zr-Al alloys. The XRD pattern of the Cu$_{50}$Zr$_{50}$ rod with φ2.5 mm reveals the presence of a monoclinic CuZr (P2$_1$/m and Cm space group) martensite phase.$^{35}$ In contrast, 2 mm diameter rods were identified to be amorphous, as verified by XRD, TEM and DSC.$^{15}$ The slowly cooled Cu$_{50}$Zr$_{50}$ arc-melted ingot shows a mixture of parent CuZr austenite (B2 phase, Pm3m) and monoclinic martensite. Cu$_{47.5}$Zr$_{47.5}$Al$_{5}$ (φ2 mm)$^{15}$ and Cu$_{47}$Zr$_{47}$Al$_{6}$ (φ2.5 mm) alloys solidified at a higher cooling rate (500–200 K/s) exhibit a glassy structure, as depicted in Fig. 2. This agrees well with the finding that φ5 mm glassy rods can be prepared by adding 4–6 at% Al to Cu$_{50}$Zr$_{50}$.$^{37}$

Figure 3 shows the microstructures of Cu$_{50}$Zr$_{50}$-base alloys. The φ2.5 mm Cu$_{50}$Zr$_{50}$ rod exhibits a needle-shape microstructure, as shown in Fig. 3(a). Since the XRD pattern
reveals the presence of a monoclinic structure, the presence of martensite is also evident in the microstructure of this alloy. The DSC scan displays an endothermic event at low temperature within the range of 553–623 K (not shown here), which is related to the martensite-austenite transformation.38) The slowly cooled microstructure of the Cu$_{50}$Zr$_{50}$ ingot is similar to that of the 2.5 mm diameter rod indicating the presence of martensite also in the rods as shown in (Fig. 3(b)). Addition of 5–6 at% Al to Cu$_{50}$Zr$_{50}$ shifts the composition from the line compound (CuZr) and the Cu-Zr-Al ingots solidify with a dendritic microstructure and a eutectic-like matrix, as shown in Fig. 1(c) for a Cu$_{47}$Zr$_{47}$Al$_6$ arc-melted ingot. EDX analysis gives the average composition, the composition of the dendrites and that of the eutectic matrix as Cu$_{47}$:Zr$_{46}$:Al$_6$ respectively. Therefore, the dendrites are CuZr B2 phase together with the monoclinic martensitic phase, as proven by XRD (Fig. 2). Cu$_{47.5}$Zr$_{47.5}$Al$_5$ (φ2 mm) and Cu$_{47}$Zr$_{47}$Al$_6$ (φ2.5 mm) rods solidified at a higher cooling rate (500–200 K/s) exhibit a glassy structure, as proved by XRD (Fig. 2), DSC and TEM.15) This indicates that the glass formation in Cu$_{50}$Zr$_{50}$-base alloys competes with the formation of other metastable phases, i.e. austenite and martensite. Even though the selected area electron diffraction obtained for the Cu$_{47.5}$Zr$_{47.5}$Al$_5$ (φ2 mm) and Cu$_{47}$Zr$_{47}$Al$_6$ glassy rods (φ2.5 mm) shows a diffuse amorphous ring (shown in Fig 4(a); right inset) but a contrast in the bright field images has been observed pointing to the presence of structural inhomogeneities in these glasses. Nanobeam diffraction patterns (spot size 7 nm) from some of these nano-scale dark contrast regions show twin diffraction, as marked by arrows in the left inset of Fig. 4(a). High resolution images from these areas with spherical dark contrast do not show any long range periodicity. A Fourier filtered image from such a region reveals the glassy nature at high resolution. However, the appearance of two spots in Fast Fourier transformation (FFT) form such regions (marked by a dotted square; Fig. 4(b)) indicates the presence of atomic-scale order. From such images, the presence of 2–5 nm scale lattice periodicity can be deduced without any sharp crystall-amorphous boundaries (marked by dashed circles, Fig. 4(b)) indicating the presence of clusters in these glassy alloys.

3.2 Ti-(Cu,Ni) alloys

Similar aspects on the microstructural features and the mechanical response during compressive loading have also
been found for Ti-(Cu,Ni)-base glass-forming alloys. Figure 2 shows typical room-temperature engineering stress-strain curves under compression together with a true stress-true strain curve. The ultimate compression stress $\sigma_{\text{max}}$ and the Young’s modulus ($E$) for Ti$_{43}$Cu$_{40}$Zr$_7$Ni$_7$ rods with $\phi 2$ mm are 1975 MPa and 130 GPa, respectively, and the plastic strain is very limited ($\varepsilon_p = 0.2\%$). On the contrary, the values of Young’s modulus $E$, yield stress $\sigma_y$, yield strain $\varepsilon_y$, ultimate compression stress $\sigma_{\text{max}}$ and plastic strain $\varepsilon_p$ for the Ti$_{45}$Cu$_{40}$Ni$_7$Zr$_5$Sn$_{2.5}$ BMG are 109 GPa, 1865 MPa, 1.9%, 2277 MPa and 14.8%, respectively. In addition to the large plastic strain under compression, it is worth to note that also the Ti$_{45}$Cu$_{40}$Ni$_7$Zr$_5$Sn$_{2.5}$ BMG exhibits a work hardening-like behavior, as shown in the inset of Fig. 5.

The as-cast microstructures and XRD pattern of differently solidified Ti-(Cu,Ni)-base alloys are presented in Figs. 6 and 7. The DSC traces of both alloys cast into $\phi 2$ mm rods reveal a glass transition at 677 K (for Ti$_{43}$Zr$_5$Cu$_{40}$Ni$_7$) and 690 K (for Ti$_{43}$Zr$_5$Cu$_{40}$Ni$_7$Sn$_{2.5}$) in cases of and at a heating rate of 40 K/min with a supercooled liquid regions of 23 K and 30 K, respectively. From these results, it appears that the addition of Sn enhances the thermal stability of the amorphous phase/supercooled liquid. Figures 6(a) and (b) show TEM bright-field images with insets of selected-area diffraction patterns and HRTEM images (Figs. 6(c) and (d)) for the as-cast Ti$_{43}$Cu$_{40}$Zr$_5$Sn$_{2.5}$ glasses; inset: true stress-true strain curve of Ti$_{43}$Zr$_5$Cu$_{40}$Ni$_7$Sn$_{2.5}$ revealing work hardening-like behavior.

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The as-cast microstructures of differently solidified Ti$_{43}$Cu$_{40}$Zr$_5$Sn$_{2.5}$ BMGs. (a) and (c): Uniform contrast for the TiZrCu$_5$Ni$_7$Sn$_{2.5}$ BMG. (b) and (d): Nano-scale inhomogeneity of the TiZrCu$_5$Ni$_7$Sn$_{2.5}$ BMG.

The TEM bright-field images with inset of selected-area diffraction pattern [(a) and (b)] and HRTEM images [(c) and (d)] of Ti$_{43}$Zr$_5$Cu$_{40}$Ni$_7$ and Ti$_{43}$Zr$_5$Cu$_{40}$Ni$_7$Sn$_{2.5}$ BMGs. (a) and (c): Uniform contrast for the Ti$_{43}$Zr$_5$Cu$_{40}$Ni$_7$Sn$_{2.5}$ BMG. (b) and (d): Nano-scale inhomogeneity of the Ti$_{43}$Zr$_5$Cu$_{40}$Ni$_7$Sn$_{2.5}$ BMG.

Fig. 5 Engineering stress-strain curves for Ti$_{43}$Zr$_5$Cu$_{40}$Ni$_7$ and Ti$_{43}$Zr$_5$Cu$_{40}$Ni$_7$Sn$_{2.5}$ glasses; inset: true stress-true strain curve of Ti$_{43}$Zr$_5$Cu$_{40}$Ni$_7$Sn$_{2.5}$ revealing work hardening-like behavior.

Fig. 6 TEM bright-field images with inset of selected-area diffraction pattern [(a) and (b)] and HRTEM images [(c) and (d)] of Ti$_{43}$Zr$_5$Cu$_{40}$Ni$_7$ and Ti$_{43}$Zr$_5$Cu$_{40}$Ni$_7$Sn$_{2.5}$ BMGs. (a) and (c): Uniform contrast for the Ti$_{43}$Zr$_5$Cu$_{40}$Ni$_7$Sn$_{2.5}$ BMG. (b) and (d): Nano-scale inhomogeneity of the Ti$_{43}$Zr$_5$Cu$_{40}$Ni$_7$Sn$_{2.5}$ BMG.

reported for the Ti$_{45}$Zr$_5$Cu$_{40}$Ni$_7$Sn$_{2.5}$ BMG,$^{30}$ the presence of a spatially structural inhomogeneity in the glassy phase can be easily revealed from the high resolution images.

The XRD pattern from the Ti$_{43}$Zr$_5$Cu$_{40}$Ni$_7$Sn$_{2.5}$ ingot reveals a tetragonal CuTi phase (P4-nmm) together with weak unidentified peaks as shown in Fig. 7(a). The microstructure of Ti$_{43}$Cu$_{40}$Zr$_5$Sn$_{2.5}$ investigated under SEM displays elongated dark and gray grains together with a small fraction of a brighter phase, as shown in Fig. 7(b). EDX analysis reveals that the average composition of the alloy is Ti$_{45}$Zr$_5$Cu$_{40}$Ni$_7$Zr$_5$Sn$_{2.5}$. The composition of the white phase is Ti$_{34.5}$Cu$_{21.1}$Ni$_{15.1}$Zr$_{20.1}$Sn$_{18.1}$, and that of the dark and gray grains is Ti$_{47.3}$Cu$_{45.5}$Ni$_{14.8}$Zr$_{15.1}$Sn$_{10.7}$ and Ti$_{45.9}$Cu$_{37.3}$Ni$_{13.5}$Zr$_{15.1}$Sn$_{10.9}$, respectively. This indicates that the dark grains corresponds to the CuTi phase (Ti$_{12.5}$Cu$_{45.5}$Ni$_{13.5}$Zr$_{15.1}$Sn$_{10.7}$) having a low solubility of Sn. On the other hand, $\phi 4$ mm rods of this alloy exhibit a NiTi (B2) phase (inset in Fig. 2(a)). This indicates that a higher cooling rate promotes the formation of the B2 NiTi austenite phase upon solidification, as observed earlier.$^{40}$ However, the as-solidified microstructure of the $\phi 2$ mm rod is that of a clustered inhomogeneous glassy alloy, as proved by TEM (see above paragraph).

The common microstructural features in the differently solidified Cu-Zr-(Al) and Ti-(Cu,Ni) ductile alloys clearly suggest the evolution of a parent B2 phase (austenite) at a lower cooling rate (100–10 K/s) in the case of arc-melted ingots and of a glassy phase with 2–5 nm medium-range ordered clusters at higher cooling rate ($10^3$–$10^2$ K/s) in the case of 2–2.5 mm diameter rods. Martensitic transformation and shape memory behavior in CuZr,$^{35,36}$ and Ti-(Ni,Cu)$^{41}$
B2 phases has already been reported, previously. All these alloys either with micrometer-size, 10 nm size B2 phase, or medium-range ordered structure exhibit strain hardening and ductility. Since very fine scale (5–10 nm) nanocrystals are not capable of dislocation multiplication and this cannot explain the observed strain hardening, this strongly suggests that the large ductility and the observed work hardening is associated with some structural ordering/twin-like inelastic shearing event in the spatially inhomogeneous clustered glassy microstructure based on martensitic alloys, which is not considered in the STZ theory. The investigated Cu-Zr-(Al) and Ti-(Cu,Ni) glasses based on martensitic alloys are rather fragile-type than strong glasses according to Angell’s classification. Fragile glasses can be viewed as a mixture of ‘solid-like’ and ‘liquid-like’ structural entities. Upon deformation, the more ‘liquid-like’ regions carry plasticity similar like the dislocation motion in crystals. It has also been found that the liquid-like and solid-like exhibits give rise to the possibility of finding repeatable inelastic atomic level structural changes associated with the transformation of liquid-like atomic environments to solid-like ones and vice versa. In addition, irreversible production of free-volume due to external stress has been observed to be the reason for work hardening in amorphous materials. Therefore, plastically deformable inhomogeneous glasses with martensitic structural features, termed M-Glasses, can probably be viewed as a rather unique class of materials which opens new perspectives for the future design of high strength and ductile materials.

4. Conclusions

A wide range of superior mechanical properties of both chemically and structurally inhomogeneous bulk metallic glasses renders a unique opportunity for developing new advanced materials, which can be exploited for a variety of engineering applications. Monolithic bulk metallic glasses do not show macroscopic plastic deformability but recent advances in the area of structurally inhomogeneous glasses with high Poisson’s ratio open a new door for ‘processing for unique properties’ of bulk metallic glasses. Even though the deformation mechanisms of BMGs are rather poorly understood, high elastic strain and high strength, good corrosion resistance and high fracture toughness of BMGs and their composites bring an intriguing perspective for replacing conventional crystalline metals and alloys. Clustered glasses based on martensitic alloys exhibit high compressive strength and large plastic deformability providing an unique opportunity to develop a large number of ductile BMGs or ‘M-Glasses’ in Ni-Zr, Ni-Ti, Fe-Ni, Fe-Pt, Ti-Pt and several other near-martensitic alloys.

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