Microstructure and mechanical properties of slowly cooled $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$

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$\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ was prepared by arc melting and solidified in situ by suction casting into 2–5-mm-diameter rods under various cooling rates (200–2000 K/s). The microstructure was investigated along the length of the rods by electron microscopy, differential scanning calorimetry and mechanical properties were investigated under compression. The microstructure of differently prepared specimens consists of macroscopic spherical shape chemically inhomogeneous regions together with a low volume fraction of randomly distributed CuZr B2 phase embedded in a 2–7 nm size clustered “glassy-martensite” matrix. The as-cast specimens show high yield strength (1721 MPa), pronounced work-hardening behavior up to 2116 MPa and large fracture strain up to 12.1–15.1%. The fracture strain decreases with increasing casting diameter. The presence of chemical inhomogeneities and nanoscale “glassy-martensite” features are beneficial for improving the inherent ductility of the metallic glass.

I. INTRODUCTION

Since Zr-based bulk metallic glasses (BMGs) with high glass-forming ability were fabricated,¹ many interesting mechanical and physical properties of BMGs have been investigated^{2–5} for commercial applications. The major advantages of BMGs are high strength, low elastic modulus, and good wear properties.^{2,6} However, the final fracture of BMGs occurs catastrophically and involves very little overall plastic deformation due to highly localized shear banding.⁶ To overcome the problem of limited plasticity in BMGs, several composite materials have been developed,^{7–17} which can be broadly classified

in two groups according to their processing: (i) ex situ and (ii) in situ formed composites. Several trials have previously been made to improve the ductility by introducing quasicrystalline^{18,19} or nanocrystalline^{20,21} precipitates in a glassy matrix upon partial crystallization during annealing treatment of the amorphous precursors. The ex situ composites are formed by directly introducing a crystalline solid phase as reinforcement into the glass-forming melt during processing and consist of either particle reinforcements^{7–9} or fiber reinforcements^{9,11} (continuous or discontinuous fibers). On the other hand, the in situ composites are formed from their melts during the process of solidification itself, containing either particle reinforcements^{12,13} or ductile dendritic phase reinforcements.^{14–17} The latter type of composites has been found to be more suitable for suppressing catastrophic shear banding compared to the other nanocrystalline/quasicrystalline composites whereby the room temperature ductility of BMGs is increased due to the reinforcement with a ductile phase. For the first time, Hays et al.¹⁴

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reported the formation of a composite microstructure consisting of body-centered cubic (bcc) β -Zr(Ti)-type dendrites in a glassy matrix for a Zr-Ti-Nb-Cu-Ni-Be alloy exhibiting 5–6% compressive plastic strain at room temperature. A similar microstructure has also been reported for Zr-Nb-Cu-Ni-Al alloys,^{15,16} and Mg-based alloys.¹⁷ It was suggested^{14,22} that in such composite microstructures, the β phase acts as a seed for the initiation of organized shear bands and confines the propagation of individual shear bands.

Along this line, bcc dendrite phase reinforced composites have been developed in a series of Ti-based^{23–26} and Zr-based^{27–29} multicomponent alloys. These composites exhibit promising mechanical properties, i.e., high strength of more than 2 GPa and large ductility of more than 15%, thus showing superior plastic deformability compared to monolithic bulk metallic glasses,^{3,6} previously reported other bulk metallic glass composites,^{14,15} and single-phase nanocrystalline³⁰ materials. It was observed that a bimodal grain size distribution is an effective way of improving the ductility of nanostructured materials without sacrificing strength.³¹ Moreover, it was reported that the appropriate choice of casting conditions has a strong impact on the supersaturation of the dendritic phase, dendrite arm spacing, and refinement of the nanocrystalline matrix, which can significantly alter the mechanical properties.²⁸

Very recently, a large number of metallic glasses have been reported to show ductility.^{32–35} In this paper, we present the effect of the casting diameter (and thus the achieved cooling rate upon solidification) on the microstructure evolution and the resulting mechanical properties of the $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ glassy alloy. Even though there is no significant microstructural change along the length of the rods, larger casting diameters (i.e., slower cooling) exhibit lower plastic deformability. A lower cooling rate promotes the formation of CuZr B2 phase and monoclinic martensite. However, the glassy phase of this alloy contains nanoscale structural inhomogeneities with a “glassy martensite” feature for all the differently cooled samples with different diameters.

II. EXPERIMENTAL DETAILS

The $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ alloy was designed by adding 5 at.% Al to the $\text{Cu}_{50}\text{Zr}_{50}$ bulk glass forming alloy composition. The alloy was fabricated after melting elemental pure Zr, Cu, and Al by arc melting under a Ti-gettered Ar atmosphere. Cylindrical rods of 2, 3, and 5 mm diameter ($\varnothing$) and 50–90 mm length were solidified by in situ suction casting in the arc melter. Structural investigations were carried out by using x-ray diffraction (XRD) in transmission geometry (Bragg–Brentano) on a STOE (Darmstadt, Germany) STADI P diffractometer equipped with a Mo source (monochromator, $\lambda = 0.7093 \text{ \AA}$), and

$2\theta/\omega$ scans were performed with a position sensitive detector (PSD) covering an angle range of 6° . In this case, the specimens were polished and thinned down to $70 \mu\text{m}$. A Zeiss axiophot optical microscope, a Zeiss DSM 962 scanning electron microscope (SEM) operated at 25 kV, and a Phillips XL 30 FEG (SEM) and equipped with an in situ energy-dispersive spectrometer (EDX) were used for microstructure observation and phase composition determination. Samples were taken from different positions (top part of the rods, the section where the liquid entered into the mold; middle and bottom, the sections where the liquid solidified first) of the as-cast cylinders to reveal possible variations in the microstructure and the mechanical properties along the rod axis. Selected-area electron diffraction (SAED) and microstructural studies were performed with a Phillips CM 20 transmission electron microscope (TEM) operated at 200 kV. The TEM samples were prepared by the conventional method of slicing and grinding, followed by dimpling and finally ion-milling under liquid nitrogen cooling (BAL-TEC RES 010). To reveal the artifact-free sample, the preparation condition was optimized as reported earlier.^{34,36,37} For evaluation of the mechanical properties, cylindrical specimens with a length/diameter ratio 2:1 were tested under compression in an Instron (Norwood, MA) 5569 electromechanical testing machine under quasistatic loading (initial strain rate of 8×10^{-5}) at room temperature.

III. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns ($2\theta/\omega$ coupled scan) from the different sections along the length of the

FIG. 1. XRD patterns from different sections of 2-mm-diameter specimens showing the reflections from the CuZr B2 phase superimposed on the amorphous diffraction maxima. The crystalline peaks completely disappear after stopping the sample rotation indicating the presence of big crystallite in the microstructure.

2-mm-diameter rod. The XRD patterns clearly show the existence of crystalline peaks superimposed on the amorphous diffraction maxima. The as-cast specimens obtained from the different sections along the length of the rod do not show any structural difference. The crystalline phase is identified as CuZr B2 ($Pm\bar{3}m$).³⁸ Rietveld refinement (considering the crystalline phase only) yields lattice parameter of B2 phase to be 0.3275 nm. The crystalline peaks disappear when ω is kept constant (ω is the angle between incident x-ray beam and specimen). A similar effect was observed when the sample rotation around the x-ray beam axis was stopped. A complete amorphous structure can be revealed in all these samples, as depicted in Fig. 1. This signifies that the volume fraction of the crystalline phase cannot be determined from such a diffraction pattern because of an inhomogeneous distribution of the phases in the sample. In addition, this also indicates that a low fraction of rather large and textured B2 phase crystallites exists in a few regions throughout the cross section of the cast rod.

The XRD pattern taken at different sections along the length of the 3-mm-diameter rods shows structural features similar to those observed for the 2-mm-diameter rods. A typical XRD pattern of the middle section of the 3-mm-diameter rod is presented in Fig. 2. In contrast, the different sections cut from the 5-mm-diameter rod show variations in their structures. The top part of the rod contains a mixture of the CuZr B2 phase and a CuZr martensitic phase with monoclinic structure ($P2_1/m$ and Cm space groups), as depicted in Fig. 2.³⁸ The formation of the CuZr martensite phase has already been reported for $\text{Cu}_{50}\text{Zr}_{50}$ and in a Cu–Zr–Al alloy.^{39,40} In contrast,

FIG. 2. XRD patterns from different sections of 3- and 5-mm-diameter specimens showing the presence of CuZr B2 peaks superimposed on the amorphous diffraction maxima. The top section of the 5-mmØ rod contains CuZr B2 and monoclinic (M) martensitic phases.

the middle and bottom sections of the 5-mm-diameter rod show very similar XRD pattern as the 2- and 3-mm-diameter rods.

Figure 3 displays the DSC scans for the differently solidified samples. All the specimens show a glass transition preceding two crystallization steps. The glass transition temperature (T_g) and the onset of the first crystallization event (T_x) are 699 and 763 K at a heating rate of 40 K/s. This yields a supercooled liquid region ($\Delta T_x = T_x - T_g$) of 64 K. The enthalpy of crystallization varies from 56 to 65 J/g, 35 to 60 J/g, and 48 to 54 J/g for the 2-, 3-, and 5-mm-diameter rods, respectively. This variation is attributed due to sampling and uneven distribution of the bigger crystallites in the specimen. However, the average enthalpy of crystallization decreases with increase of the diameter of the rods, indicating an increase of the crystal fraction with a decrease in cooling rate. Besides this, the top portion of the 5-mm-diameter rod shows a different behavior before the glass transition and crystallization events as shown in the inset of Fig. 3. An endothermic event has been detected between 392 and 494 K. These temperatures are indicated as the austenite start A_s temperature and the austenite finish A_f temperatures since XRD has proved that this specimen contains CuZr monoclinic martensite and austenitic B2 phase (Fig. 2). A martensitic transformation between B2 (parent phase) and monoclinic structure (martensite) and shape-memory behavior of the CuZr phase have previously been reported.^{38,39} The onset of the low-temperature endothermic phase transformation for the $\text{Cu}_{50}\text{Zr}_{50}$ alloy is $A_s = 553$ K and $A_f = 623$ K.³⁹ Even though there is no indication for a glassy structure in the XRD pattern (Fig. 2), it is interesting to note a glass transition and crystallization event in the DSC trace (inset of Fig. 3), which points to a small-volume fraction of

FIG. 3. DSC traces of the differently solidified samples at a heating rate of 40 K/min. (inset) DSC trace from the top section of a 5-mmØ rod showing martensitic transformation.

glassy material, which cannot be detected by XRD, even in this sample.

The cross-sectional microstructures from different sections of the 2-mm $\varnothing$ rod are shown in Fig. 4. The overall microstructure of the top section is displayed in Fig. 1(a). The back scattered electron (BSE) image shows spherical darker regions (marked by arrows) in a brighter matrix. Such spherical particles 100–200 μm in size and agglomerates of these particles are mostly observed near the specimen surface. The presence of such dark regions near the parting line of the Cu-mold/“cast-fin” is presented in the inset of Fig. 1. Higher magnification of this region reveals dendrites [Fig. 4(b)]. However, no difference in the overall microstructure has been found along the length of the rod. Figure 4(c) depicts the presence of such darker regions together with a few dendrites near the surface of the specimen. Apart from the surface edge, no substructure can be found in those darker regions, as shown in Figs. 4(c) and 4(d). This corroborates that these dendrites correspond to the CuZr B2 phase detected by XRD investigation.

A similar microstructure has been observed in the case of the 3- and 5-mm-diameter rods. A typical microstructure near the specimen surface of a 3-mm-diameter rod is presented in Fig. 5(a). A spherical morphology of 20–200- μm -sized darker regions can be observed near the specimen surface. The macroscopic brighter regions are

relatively enriched in Zr, whereas the darker regions are relatively enriched in Cu. Away from the specimen surface, the darker regions in the sample do not show any grain boundaries [Fig. 5(b)], but near the edge of the specimen, grain boundaries and a dendritic microstructure can be observed [Fig. 5(a)]. EDX analysis revealed that the composition of the bright regions is $\text{Cu } 44.24 \pm 0.49 \text{ at.}\%$, $\text{Zr } 51.88 \pm 0.52 \text{ at.}\%$, $\text{Al } 3.88 \pm 0.3 \text{ at.}\%$, and the dark regions contain $44.87 \pm 0.59 \text{ at.}\%$ Cu, $51.1 \pm 0.41 \text{ at.}\%$ Zr, $4.3 \pm 0.2 \text{ at.}\%$ Al. These differences in chemical composition are not significant. However, the observed contrast in the BSE images clearly reveals that there exists a difference in the chemical composition between the brighter matrix and the darker regions, indicating a possible liquid phase separation.⁴¹ The observation of phase separation in this alloy has already been reported by Kim et al., employing TEM investigations.³⁶ It is well known that the cooling rate decreases from the surface towards the center of the cast rods.⁴² The observed microstructural features found for the 2 and 3-mm $\varnothing$ rods suggest that these featureless darker regions are more pronounced near the specimen surface of the cylinders, which is completely the opposite of what one should expect. Rather, a mostly glassy structure is expected to form near the Cu-mold surface due to the higher cooling rate realized close to the mold, and crystalline phases should appear at the center of the

FIG. 4. SEM backscattered images of different sections from the 2-mm $\varnothing$ rod showing (a) the overall microstructure consisting of a bright glassy phase and spherical dark regions (marked arrows), (inset) the dark region near cast-fin, and (b) magnified view showing the dendritic CuZr phase. Featureless darker regions (c) near the surface of the middle section with a few dendrites (marked by an arrow) and (d) from the center of the bottom section.

FIG. 5. (a) Optical micrograph near the specimen surface and (b) SEM backscattered electron image of the featureless darker spheres in a bright matrix in the middle section of the 3-mm $\varnothing$ rods. (c) The 5-mm $\varnothing$ top section is fully crystalline and contains a dendritic CuZr B2 phase embedded in an interdendritic matrix, and (d) the middle section of the rod shows crystalline darker regions in a bright glassy matrix.

specimen. Possibly, the extra surface free energy of the liquid enhances the decomposition of the liquid around the specimen surface, and heterogeneous nucleation of crystals occurs in this region.⁴³

Besides the top portion, which is about 10 mm length, the cross section of the remaining 80 mm length of the 5-mm $\varnothing$ rod shows a microstructure similar to that of the 2- and 3-mm $\varnothing$ rods. The whole cross section of the top portion is fully crystalline [Fig. 5(c)]. Dendrites form in a eutectic-like matrix, as shown in the inset of Fig. 5(c). The composition of the dendrites is enriched in Cu and Zr ($\text{Cu}_{43}\text{Zr}_{52.6}\text{Al}_{4.4}$), compared to the nominal composition of the alloy, and the matrix is enriched in Al ($\text{Cu}_{46.2}\text{Zr}_{45.5}\text{Al}_{8.3}$). This indicates that the dendritic phase is in fact B2 CuZr phase. The residual section of the rod is identified to be predominantly glassy with featureless dark spherical particles and a layer of crystalline surface regions, as shown in Fig. 5(d). It has been reported that the cooling rate across the length of a rod decreases from the bottom to the top of the rod.⁴² Even though the bulk glass formation of 5-mm-diameter rods for this alloy composition has been reported,⁴⁴ we found that the solidified microstructure can vary from glassy to fully crystalline (Figs. 2 and 5) and strongly depends on the actual cooling rate adopted along the length of the rod. This cooling rate can be locally higher or lower than the critical cooling rate (10^2 K/s) required for the glass formation of this alloy.

Figure 6 shows a typical TEM bright-field image from the middle section of the 2-mm-diameter rod. The microstructure is identified to be glassy from the selected

area electron diffraction (SAED) pattern. Besides, nano-scale regions of dark contrast can be observed in the amorphous phase. The SAED patterns of these regions also reveal diffuse amorphous halos, as depicted in the inset of Fig. 6(a). The high-resolution images from this spherical dark contrast phase do not show any long-range periodicity. However, a few regions exhibit highly faulted crystallites, as marked by the square in Fig. 6(a). A Fourier filtered image from such a region is shown in Fig. 6(b). The fast Fourier transformation in Fig. 6(c) reveals that the very small faulted crystallites are highly twinned. It can be clearly seen that the glassy structure has very fine 2–5-nm scale of medium range order, as marked by dotted circles. The nanobeam (7 nm) diffraction pattern from such a spherical dark contrast region also shows twinned diffraction [Fig. 6(d)]. Such a microstructure can be interlinked with twinned martensites, which is observed to form in the slowly cooled sample (5 mm diameter). The observation of such a glassy nature of martensite has already been reported in shape-memory CuZr and NiTi alloys.^{39,45}

Figure 7(a) shows the room-temperature deformation curves under compression. All specimens prepared from different sections of the differently solidified samples show plastic deformability. It is estimated that the fracture strain (ϵ_f) is higher (12.1–15.1%) for the 2-mm $\varnothing$ rod and decreases to 4.8–7.2% for the 3-mm $\varnothing$ rod and to 3.2–6.7% for the 5-mm $\varnothing$ rod. The yield strength varies between 1537 and 1682 MPa for the 2-mm $\varnothing$ rod, between 1482 and 1782 MPa for the 3-mm diameter rod, and between 1495 and 1680 MPa for the 5-mm $\varnothing$ rod.

FIG. 6. TEM bright-field image of the middle section of the 2-mm $\varnothing$ rod showing (a) a structurally inhomogeneous glass with faulted crystallites (marked by a square); (inset) SAED pattern from the overall glassy structure; (b) Fourier filtered image showing medium-range-ordered domains (marked by circles); (c) FFT from a faulted crystallite showing the twin diffraction; and (d) nanobeam diffraction pattern from some of the darker regions revealing twin diffraction (marked by arrows) indicating the presence of glassy martensite.

The true stress–strain curves of these samples show an increment of stress with further increasing strain indicating “work-hardening” like behavior, as shown in the inset of Fig. 7 for the 2-mm-diameter rod. This specimen also exhibits plastic deformability under room-temperature bending [Fig. 7(b)]. A change in the slope in the plateau region of the stress–strain curve can be observed near the yielding [marked by the arrow in Fig. 7(a)], which may be correlated to pseudo-elastic deformation of the martensite. The maximum stress for the 2-, 3-, and 5-mm-diameter rods varies between 1933 and 2116 MPa, 1892 and 1972 MPa, and 1737 and 1926 MPa, respectively. It should be noted that a fully crystalline (dendritic) microstructure [Fig. 5(c)] containing a mixture of B2 phase and martensite (inset, Fig. 3) shows lower plastic deformability (fracture strain of 3.2%) than the glassy samples. Hence, the chemically and structurally inhomogeneous glassy microstructure with 2–7-nm martensitic features is believed to be beneficial for enhancing the plastic deformability of the metallic glass.

(b)

FIG. 7. Engineering stress–strain curves for $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ from (a) 2-mm $\varnothing$ top part, 3-mm $\varnothing$ middle part, and 5-mm $\varnothing$ middle section of the rods; (inset) true stress–true strain curve for the 2-mm $\varnothing$ top part and (b) bending ductility of $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$.

IV. SUMMARY

The microstructure of slowly cooled $\text{Cu}_{47.5}\text{Zr}_{47.5}\text{Al}_5$ glass contains both macroscopic and nanoscale inhomogeneities. The inhomogeneous glassy structure can be obtained in a wide range of cooling rates (200–2000 K/s). The glassy rods contain a few larger sized (100–200 μm) CuZr B2 crystals inhomogeneously distributed in the specimen. Besides the top section of the 5-mm $\varnothing$ rod, macroscopic phase separated/chemically inhomogeneous regions exist. For the 5-mm-diameter rod, a gradual microstructural transition occurs from a fully crystalline (monoclinic martensitic and B2 phase) structure to an inhomogeneous glassy phase due to the differences in the adopted cooling rates along the length of the specimen, indicating that the critical casting diameter for obtaining the glassy phase is 5 mm. The inhomogeneous glassy phase contains 2–7-nm size medium range ordered clusters. Nanobeam diffraction patterns reveal that these clusters have similarities with a “twinned martensite-like” structure. A large fracture strain (15.1–3.2%) together with work hardening-like behavior can be achieved from such a spatially inhomogeneous glass. The presence of “glassy-martensite” features is beneficial for improving the inherent ductility of the metallic glass.

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