Enhanced mechanical properties in a Zr-based metallic glass caused by deformation-induced nanocrystallization

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Bulk metallic glass with composition Zr62Cu18Ni10Al10 exhibits high yield stress, large elasticity and large plasticity when compressed. During nanoindentation, strain hardening is observed until the maximum applied load reaches 100 mN; for higher maximum loads the typical softening found in metallic glasses is evidenced. Transmission electron microscopy observation of the nanoindented and compressed samples reveals the occurrence of deformation-induced nanocrystallization, which is likely to be related to the mechanical properties observed in this alloy.

Keywords: Metallic glasses; Crystallization; Nanoindentation

Bulk metallic glasses (BMGs) have been widely investigated due to their good mechanical properties such as high strength, large elasticity and good corrosion resistance. In recent years the study of BMGs has focused on improving the low plasticity typically found in these alloys, to make them suitable materials for structural and engineering applications [1].

Unlike crystalline materials, the deformation behavior of metallic glasses is inhomogeneous; plasticity is accommodated in narrow shear bands facilitated by the creation and coalescence of free volume. As a result of this inhomogeneous flow behavior, BMGs usually fracture in a brittle manner with plastic strains <2%. However, in some cases values of more than 80% of plastic deformation have been achieved. A high plastic strain has been reported, for example, in Pd-based BMG [2] where the authors attribute this result to a nanoscale phase separation which hinders the propagation of shear bands facilitating their uniform initiation and branching. An improvement of plasticity has also been reported in a Zr-based BMG annealed below Tg [3]. This improvement is caused by its tendency towards chemical decomposition, i.e. phase separation that leads to the development of nanoscale compositional inhomogeneities (Cu clusters). Similar results have been found in other Zr-based BMG without evidence for the presence of nanocrystals or phase separation [4]. In this case, the large degree of plasticity was ascribed to intrinsic material properties. Indeed, it is claimed that plasticity in BMG can be enhanced with an appropriate choice of composition using Poisson’s ratio strategies, i.e. a larger Poisson’s ratio (v) promotes a larger toughness [5,6]. In some cases the ductility of BMG (Zr- and Cu-based) has been increased by nanocrystallization caused by deformation [7–10]. An exceedingly high degree of crystallization leads to embrittlement of the alloy but in the case when the crystallites are only of nanometer size, the resulting amorphous–nanocrystalline composite exhibits more plasticity than the original material [11]. All these BMG systems exhibiting large plasticity deform via formation of numerous shear bands throughout the compressed specimen. The local structural inhomogeneities favor multiple branching of these bands, which interact with each other. As a result, catastrophic failure caused by rapid propagation of a single shear band is avoided. Hence, a high density of shear bands, often with a wavy trajectory (due to the local inhomogeneities that hinder their immediate and straight propagation), is expected in these systems.
Generally, deformation in metallic glasses is also accompanied by production of free volume [12–16], which leads to strain softening [13,14,17–19]. However, in some cases, the presence of atomic-scale inhomogeneities and the irregular, chemically heterogeneous, domains leads to work hardening behavior. This has been observed under compression in Ti- [20], Pd- [2] and Cu-[8,20] based metallic glasses.

This paper is focused on the unusual mechanical behavior of a Zr-based BMG. This alloy exhibits larger plasticity than most metallic glasses during compression tests (deformation strains up to 120% before fracture). In addition, strain hardening is observed during nanoindentation at low applied forces, whereas mechanical softening occurs when the applied maximum load is larger than 100 mN. The large plasticity and strain hardening are likely to be related to deformation-induced nanocrystallization, which is investigated in detail by transmission electron microscopy.

A metallic alloy with composition Zr$_{62}$Cu$_{18}$Ni$_{10}$Al$_{10}$ was prepared by arc melting mixtures of pure elements in an Ar atmosphere. Rods of 2 mm in diameter were obtained from the arc-melt by copper mold casting. The amorphous character of the sample was checked by X-ray diffraction (XRD) using Cu-K$_\alpha$ radiation. The thermal stability of the system was investigated by differential scanning calorimetry (DSC) using a temperature heating rate of 40 K min$^{-1}$. The elastic properties were evaluated by means of ultrasonic measurements (pulse-echo overlap technique) along with density assessment (Archimedes' method).

To evaluate the mechanical properties (plasticity and yield strength), cylindrical specimens were cut to a perfect orthogonal geometry with an aspect ratio of 2:1 according to the American Society for Testing Materials (ASTM) standards, and measured at room temperature at an approximately constant loading rate of $1.8 \times 10^{-4}$ s$^{-1}$. Nanoindentation experiments were also carried out at room temperature using a Berkovich pyramidal-shaped indenter tip applying maximum loads ranging from 2 to 500 mN (with corresponding loading rate varying from 0.05 to 3.20 mN s$^{-1}$). A load holding period of 20 s was applied in all cases before unloading and the thermal drift was always kept below ±0.05 nm s$^{-1}$. At least 30 indentations for each loading condition were performed to verify the accuracy of the indentation data. Prior to nanoindentation, the specimens were carefully polished to mirror-like appearance using diamond paste. The hardness values were evaluated at the beginning of the unloading segment after proper corrections for the contact area, instrument compliance and initial penetration depth; the corrections for the contact area were calculated from a calibration on a fused quartz specimen.

In order to study the eventual deformation-induced structural changes, transmission electron microscopy (TEM) observations using a JEOL-2011, operating at an accelerating voltage of 200 kV, were carried out in the as-cast, compressed and indented specimens. In the latter case, thin foils of 2 mm in diameter were cut into 200 μm thick slices with a diamond bladed saw. These slices were mechanically polished using SiC paper and diamond paste to achieve a mirror-like appearance. After indentation, the center of the specimen was thinned down to 20 μm using a mechanical dimple from the side opposite to the indented surface. Ion milling was then performed only on the side opposite to the indented surface. Exactly the same cutting and polishing procedures were applied to prepare the as-cast and compressed TEM specimens.

The XRD pattern of the as-cast Zr$_{62}$Cu$_{18}$Ni$_{10}$Al$_{10}$ sample (not shown) consisted of a broad diffraction halo without any detectable trace of crystalline peaks, indicating the amorphous nature of the sample. The glass transition temperature ($T_g$), the crystallization temperature ($T_x$) and the supercooled liquid region ($\Delta T$) were determined from the DSC curve (not shown) and the obtained values were $T_g = 670$ K, $T_x = 768$ K and $\Delta T = 98$ K, in agreement with the literature [4,21]. There is a tendency for the glass-forming ability (GFA) to augment with increasing $\Delta T$ [22,23] therefore, it is important to search for glassy alloys with high $\Delta T$ values, like the Zr-based one investigated here.

From uniaxial compression tests, it is remarkable that the Zr$_{62}$Cu$_{18}$Ni$_{10}$Al$_{10}$ rods could be compressed without fracture up to 120% strain deformation, similar to the results reported by Liu et al. in an alloy with analogous composition [4]. Serrated flow was observed after yielding, as typically found in many metallic glasses, implying that abundant shear bands are activated during plastic flow [24,25]. From the compression tests, the yield stress, $\sigma_y$, and Young's modulus, $E$, were determined: $\sigma_y = 1.55$ GPa and $E = 86$ GPa (note that a similar Young's modulus was also obtained from acoustic measurements). The great plasticity observed in this material may be ascribed to deformation-induced nanocrystallization or be due to intrinsic material properties such as a large Poisson's ratio ($\nu = 0.3786$).

Actually, in Cu–Zr-based BMG, chemical heterogeneities and Cu-rich nanocrystals are considered to be the cause of the large plasticity [8,26]. However, Liu et al. [4] claimed that the large plasticity of this Zr-based BMG is not a result of the stress-induced nanocrystallization but, instead, is an intrinsic property of the material. To shed light onto this issue, TEM imaging was performed on the as-cast and compressed specimens. Figure 1(a) shows that, as expected, the as-cast BMG does not contain nanocrystals. The fully amorphous structure of this specimen is confirmed by the lack of lattice fringes in the high-resolution TEM image and by the selected area electron diffraction (SAED) pattern (inset Fig. 1a), where only the amorphous halos were detected. However, the TEM image of the compressed specimen (Fig. 1b) shows the presence of some nanocrystals with less than 10 nm in size embedded in the amorphous structure. Ion milling was then performed only on the side opposite to the indented surface. Exactly the same cutting and polishing procedures were applied to prepare the as-cast and compressed TEM specimens.

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matrix. The second ring in the SAED pattern, marked with an arrow (inset Fig. 1b), indicates the formation of a crystalline phase that may be the tetragonal Zr$_2$Ni (space group $I4/mcm$, $a = 0.649$ nm and $c = 0.527$ nm). Therefore, our results indicate that deformation promotes nanocrystallization. It should be noted that Deng et al. [27] also presented a direct high-resolution TEM observation of nanocrystallization in a Zr–Al–Ni–Cu BMG fractured by compression test. They suggested that, due to the concentration of plastic flow, the local atomic neighbor distance increases producing nanocrystallization in the amorphous structure. Other authors have obtained evidence for nanocrystallization in shear bands [28,29]. The temperature increase associated with deformation is claimed to play a role in the formation of nanocrystals.

In order to better understand the deformation behavior in this metallic glass, nanoindentation tests were performed at different maximum loads ($P_{\text{max}}$), both in the as-cast and the compressed specimen. Generally, in bulk metallic glasses, hardness is expected to decrease when the indentation depth increases. This effect is usually referred to as the indentation size effect [30–35] and is attributed to the softening caused by deformation-induced creation of free volume. In the present study (Fig. 2), hardness of the as-cast alloy is found to decrease for $P_{\text{max}}$ larger than 100 mN. However, it is interesting to remark that an increase of hardness is observed when indentations were performed at lower loads (see Fig. 2a).

To elucidate the physical origin of this mechanical hardening, TEM specimens from the as-cast alloy, containing an array of nanoindent, were prepared. Figure 3a is an SEM image showing a hole (created during ion milling of the TEM sample preparation) surrounded by an array of $P_{\text{max}} = 100$ mN indentations separated by 20 μm from each other. The inset of Figure 3a is a small hole corresponding to one of the indent. Figure 3b, which is an enlargement of the square indicated in the inset, reveals the existence of nanocrystals with an average size below 7 nm near the indent. The corresponding SAED pattern confirms the presence of the crystalline phase. (c) TEM image performed in a region located at 1 μm from the edge of the hole indicated in panel (a) and enlarged in panel (b); (d) corresponds to a region located at 10 μm from the same indent. (e) An enlargement of a 10 mN indentation (displayed in the bottom right corner) revealing the presence of a high amount of nanocrystals inside the indent. (f) TEM dark-field image obtained on the diffraction ring marked on the inset SAED pattern confirming the existence of nanocrystallites in the amorphous matrix.

Figure 3. Microstructural features in the samples indented at a maximum force of 100 mN (a–d) and at 10 mN (e and f). (a) SEM image displaying an array of indentations (indicated by circles) separated by 20 μm from each other and prepared for subsequent TEM observation. The inset is a TEM bright-field image of an indentation which was perforated during ion milling. (b) An enlargement corresponding to the square drawn in the inset in (a), indicating the presence of nanosized crystals embedded in an amorphous matrix. The corresponding SAED pattern confirms the presence of the crystalline phase. (c) TEM image performed in a region located at 1 μm from the edge of the hole indicated in panel (a) and enlarged in panel (b); (d) corresponds to a region located at 10 μm from the same indent. (e) An enlargement of a 10 mN indentation (displayed in the bottom right corner) revealing the presence of a high amount of nanocrystals inside the indent. (f) TEM dark-field image obtained on the diffraction ring marked on the inset SAED pattern confirming the existence of nanocrystallites in the amorphous matrix.

The same preparation procedure was used to observe nanoindents performed at a maximum load of 10 mN. In this case, the observed nanoindent (inset Fig. 3e), which was not perforated during the thinning process, again contained several nanocrystals. Nanocrystallization is also evidenced in Figure 3f, which is a dark-field TEM image from the diffraction spot highlighted in the inset, corresponding to an interplanar distance of $d = 0.204 ±$
0.01 nm. The deformation-induced nanocrystals seem to be Zr$_2$Ni, the same phase as in the sample subjected to compression test. Our results are in agreement with some other recent reports from the literature where nanocrystalization was related to work-hardening phenomena in metallic glasses during nanoindentation [28,29]. Jiang et al. [29] observed that the obtained phases coincide with those of samples (with the same composition) subjected to ball milling [36] and bending [11]. Remarkably, as evidenced by TEM imaging, the nanocrystallization of the alloy investigated in this work already occurs during the first stages of deformation (Fig. 3e and f). At low indentation depths, the induced hardening counterbalances the softening effect typically found in metallic glasses. However, when the maximum applied load is larger than 100 mN the softening predominates over hardening, probably due to deformation-induced increase of free volume, which is more pronounced for higher loading rates [35]. Also note that shear band activity is observed inside and around the indented regions by SEM (see inset in Fig. 2a).

Finally, indentations using the same conditions were also carried out in the compressed specimen and the resulting hardness was evaluated as a function of the applied load. The compressed specimen was indented in its central part. As shown Figure 2b, no hardening is observed in this case; only the expected softening behavior is found. However, note that when the maximum applied load is 2 mN the hardness in the compressed specimen is already 62% larger than in the as-cast. In agreement with the literature [11,37,38], this hardness enhancement is attributed to the existence of some nanocrystals embedded in the amorphous matrix formed during the compression test, as shown in Figure 1b.

To conclude, rods of Zr$_{62}$Cu$_{18}$Ni$_{10}$Al$_{10}$ metallic glass were compressed without fracture up to 120% true strain deformation. Images of the compressed specimen, obtained by TEM, confirmed the formation of some nanocrystals during compression tests which could be responsible for the observed large plasticity.

Nanoindentation measurements were also performed at different maximum loads with the aim of understanding the deformation behavior of this metallic glass. In the as-cast alloy, hardness was found to increase until $P_{\text{max}} = 100$ mN and decreased for higher loads. By means of TEM the formation of nanocrystals inside the indents was observed, which presumably explains the hardening phenomenon. In the compressed specimens, nanoindentation at low applied loads also reveals a strengthening behavior, which is likely to be related to deformation-induced nanocrystallization that occurred during compression tests.

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