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Ion irradiation enhances the mechanical performance of metallic glasses

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We demonstrate that irradiation may enhance the plasticity in metallic glasses by increasing the free-volume content via micropillar compression experiments on an ion-irradiated bulk metallic glass (BMG). Results show that irradiation decreases the flow stress and enhances the shear band formation by lowering the magnitude of stress serrations in plastic flow regime. These results highlight that amorphous alloys can mitigate the deleterious affects of severe ion irradiation as compared to their crystalline counterparts.
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Plastic flow and fracture in amorphous alloys is controlled by the amount of free volume that is available in them [1,2]. Systematic experiments to establish this connection on a squantitative basis are hampered by the limitations associated with varying the free volume in a predetermined manner while keeping all other parameters constant. Structural relaxation, annealing of the alloy below its glass transition temperature, T_g, leads to annihilation of the free volume and hence allows for gradual reduction of it from that of the as-cast condition. Extensive plastic deformation can potentially increase the free-volume content, as deformation through the formation of shear transformation zones (STZs) requires large dilatation of the surrounding matrix [3]. However, the excess free volume can be unstable and coalesces readily into nanovoids [4,5]. Also, the enhancement in free volume that can be induced is not significant, as illustrated by recent experiments of Dubach et al. [6], wherein it has been shown that the compressive yield strength of a shot peened BMG is similar to that of the as-cast alloy. It is also noteworthy that other BMG-forming alloys also exhibit size-independent strength and deformation mechanism [7,8].

Thus, a number of alternative methods for enhancing the free-volume content in an amorphous alloy are being attempted. One possible way of doing this is through ion irradiation of the amorphous alloy. In crystalline metals and alloys, it is well known that ion irradiation leads to severe modifications of the structure through the formation of self-interstitials, vacancy loops and suchlike. These, in turn, harden the material considerably with a concomitant loss of ductility which leads to a precipitous loss in toughness. Whether metallic glasses are susceptible to similar modification of their mechanical behavior upon irradiation has not been considered yet. It is not only important from a scientific point of view, but also technologically relevant, as bulk metallic glasses (BMGs) can be fully exploited as structural elements in the nuclear industry depending on how they respond to irradiation. With this in mind, we examine the influence of ion irradiation on the mechanical properties of $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ (at.%) BMG, which is an excellent glass-forming alloy with high thermal stability [9]. Since the penetration depth of the ions tends to be in the order of a few micrometers, micropillar compression experiments were conducted so as to ascertain the irradiated BMG's mechanical response.

Three millimeter thick plates of the Zr-based BMG Vitreloy 1 were obtained from Liquidmetal Technologies,

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USA. Prior to irradiation, a 10×10 mm^2 block was cut from the plate and polished using a 0.25 μm diamond suspension. The irradiation was carried out on 3×3 mm^2 areas at two separate locations on the polished surface. The specimen was irradiated with Ni atoms using the tandem accelerator of the Swiss Federal Institute of Technology at Hönggerberg [10]. The aim was to ensure uniform irradiation of the material to a certain depth below the surface. Hence, the sample was irradiated using four different energies, starting from 15 MeV and subsequently irradiating with 10, 5 and 2.5 MeV. The resulting damage profile (which is a superposition of the four irradiation profiles for the different energies) is shown for the 100 dpa case (Fig. 1a). The profile was calculated using TRIM, which is part of the SRIM software package [11]. This procedure ensures uniform irradiation to a depth of 4 μm within the alloy.

It is possible that amorphous alloys, being metastable, may crystallize on irradiation. Indeed, nanocrystallization was reported on irradiation of a Cu-based glass despite the critical glass formation rate being lower than the quenching rate post-irradiation-induced localized melting [12,13]. It was argued that rapid quenching leads indirectly to amorphous to crystalline phase transformation through an increase in the diffusivity in the surrounding regions. However, the possibility of crystallization on irradiation in the present context can be ruled out owing to two reasons. First, the BMG used in this work exhibits high glass-forming ability and thermal stability [14]. Note that ion irradiation did not induce crystallization in a Zr-based BMG with less thermal stability than the BMG used in the present study [15]. Secondly, the relative rise in temperature during irradiation was estimated to be ~473 K, which is much lower than the T_g of this alloy (625 K).

Surface profiles of the irradiated regions were obtained by force microscopy carried out using a Hysitron® nanoindenter. A significant increase in surface roughness in the 100 dpa region (Fig. 1c–e) is seen. A possible reason for this could be the volumetric dilatation due to irradiation, which implies that there was a significant enhancement in the free-volume content. Backscattered scanning electron microscopy (SEM) of the cross-section obtained by focused ion-beam (FIB) cutting did not reveal any void formation or the formation of nanocrystallites (Fig. 1b) [16]. Nevertheless, it is possible that the voids are smaller than the resolution limit of the scanning electron microscope (10 nm) used for the imaging.

Micropillars with a diameter of ~1 μm and an aspect ratio (i.e. height/diameter) of 2.5–3.5 were fabricated by FIB using a Tescan Lyra instrument in a two-step process: initially, coarse pillars were cut to 2.3 nA at 30 kV, which was followed by milling at 0.79 nA to obtain finished pillars of the desired dimensions. The compression tests were carried out using an in situ SEM set-up, which allows precise pillar-punch positioning and in situ characterization of deformation events [17]. All the pillars were compressed in displacement control at a strain rate of $\sim 3 \times 10^{-3}$ s^{-1}. A Hitachi S4800 high-resolution scanning electron microscope was used for imaging the pillars before and after compression.

Figure 2 shows representative stress–strain curves obtained by compression of micropillars in the irradiated regions. As compared to the as-cast material [6], the yield strength of the severely irradiated (100 dpa region)

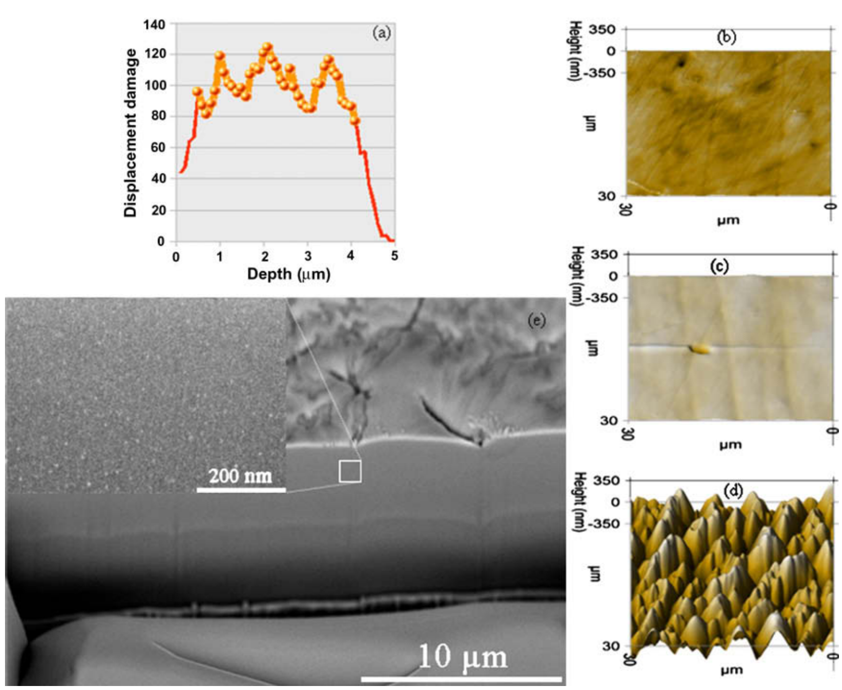

Figure 1. (a) Profile of displacement damage (dpa) as a function of the implantation depth (100 dpa). The three-dimensional representation of the surface topography reveals the large increase in surface roughness of the as-cast BMG beyond 10 dpa irradiation (right): (b) as-cast; (c) 10 dpa; (d) 100 dpa. (e) Backscattered SEM images of a FIB trench cut in the 100 dpa region; the inset is a high-resolution image.

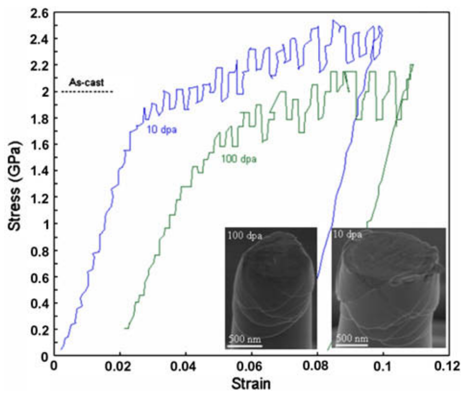

Figure 2. Stress–strain curves reveal apparent strain-hardening in addition to reduced yield strength. Shear bands intersections (inset) and smaller stress drops are observed during compression of 10 and 100 dpa pillars.

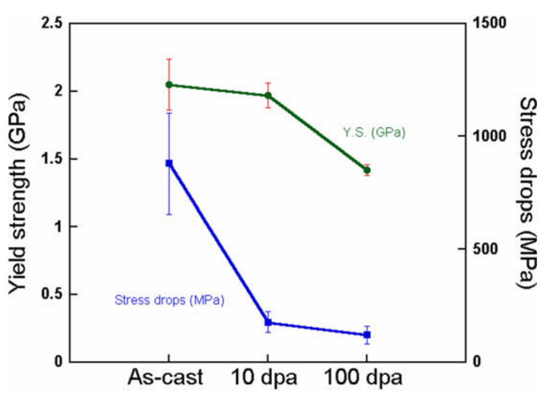

Figure 3. Reductions in yield strength and stress drops imply a brittle to ductile transition of the as-cast BMG on irradiation beyond 10 dpa.

is reduced by ~30% (Fig. 3). The "apparent" strain-hardening seen in the stress–strain curves is not intrinsic to the material but is an experimental artifact that arises due to the increase in cross-sectional area of the pillars during compression. These observations are in contrast to radiation effects in crystalline metals, where irradiation induces hardening. The hardening exhibits a power-law dependence on the radiation fluence at low doses (0–0.05 dpa), with a tendency to saturate at higher doses (>0.05 dpa) [18].

The stress–strain curves shown in Figure 2 exhibit periodic stress serrations which are typically seen during compressive deformation of amorphous alloys and are associated with the stick-slip shear band propagation [6,19]. The magnitude of the stress drops, ΔS, measured on the irradiated pillars was much smaller than that obtained on the as-cast pillars of the same size (Table 1). These data can be used to compute the energy released per unit area of shear plane, ΔE_A, as per the procedure outlined by Volkert et al. [20]. This parameter is an indicator of the intrinsic stability of the material against localization. A higher ΔE_A implies significant elastic strain energy release, when shear bands nucleate and propagate, which could lead to structural instability and fracture during tensile loading [21]. On the other hand, lower values of ΔE_A imply that significant plasticity takes place through homogeneous plastic deformation via STZs. The data for irradiated pillars presented in Table 1 shows that ΔE_A is smaller by ~80%, implying that ion-irradiated amorphous alloy accommodates significant amounts of strain energy through homogeneous deformation and hence can exhibit significant plasticity vis-à-vis the as-cast alloy.

Table 1. Analysis of irradiation damage and deformation behavior in the BMG. Calculation of the ΔE_A values is discussed in an earlier study [18].

dpa [9]	RMS roughness (nm)	σ_y (GPa)	$\Delta E/A$ (J/m^2)	ΔS (MPa)
100	120	1.42 ± 0.04	2.4 ± 0.36	121 ± 40
10	10	1.97 ± 0.09	1.58 ± 0.41	177 ± 46
As-cast	5	2.05 ± 0.19	9 ± 2	880 ± 224

Recent micropillar compression studies on the same BMG have shown that the deformation occurs by the formation of a few non-intersecting shear bands and negligible lateral flow [6]. While misalignment between pillar and punch is possible, it is interesting to note that extensive intersections exist among shear bands in the irradiated pillars (inset of Fig. 2). Amorphous alloys possess poor ductility because the lack of a microstructure allows the unhindered propagation of shear bands, with a dominant shear band becoming a shear crack rather readily. Hence, increasing the intersections among shear bands is an alternative way to enhance ductility. These observations thus indicate that an irradiation-induced increase in free volume leads not only to a reduction in strength, but also to an increase in plasticity of the BMG.

In summary, this study shows that irradiation damage can lead to a significant reduction in strength of BMGs due to enhancement in the free-volume content. Ion irradiation may thus be an alternative technique to enhance ductility in BMGs by promoting shear band intersection. These results suggest that irradiation of the BMGs, which are otherwise quasi-brittle, can enhance their overall mechanical performance instead of deteriorating it. Therefore, amorphous alloy components or coatings can become attractive candidates for structural applications in the nuclear energy industry, particularly in locations experiencing large levels of irradiation. A limiting factor could be the glass transition temperature (T_g) because some of the key components of the reactor may experience temperatures higher than T_g.

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