Acta Materialia 129 (2017) 343–351

Contents lists available at ScienceDirect

Acta Materialia

journal homepage: www.elsevier.com/locate/actamat

Full length article

On room-temperature quasi-elastic mechanical behaviour of bulk metallic glasses

D.V. Louzguine-Luzgin [a,*], V. Yu. Zadorozhnyy [b], S.V. Ketov [a], Z. Wang [a,1], A.A. Tsarkov [b], A.L. Greer [c,a]

[a] WPI Advanced Institute for Materials Research, Tohoku University, Sendai, 980-8577, Japan
[b] National University of Science and Technology "MISiS", Moscow, 119049, Russia
[c] Department of Materials Science & Metallurgy, University of Cambridge, Cambridge CB3 0FS, UK

ARTICLE INFO

Article history:
Received 9 December 2016
Received in revised form
17 February 2017
Accepted 18 February 2017
Available online 20 February 2017

Keywords:
Bulk metallic glass
Elastic cycling
Anelastic strain
Enthalpy

ABSTRACT

Uniaxial compression is used to apply cyclic loading within the elastic range to samples of $Zr_{61}Cu_{27}Fe_2Al_{10}$ bulk metallic glass (BMG). The results are twofold. On one hand the microhardness measured on the end-faces of the samples shows an increase of ~8% together with a slight gradual increase in the Young's modulus after the 2nd cycle. This appears similar to hardening induced by elastic cycling in nanoindentation. The microhardness measured in the centre of the sample or on the side faces of the BMG samples show little or no change as a result of cyclic loading. These results suggest that the apparent hardening of the end-faces is a surface effect attributed, not to relaxation, but to a build-up of anelastic strain, associated with local anisotropy and stresses arising from uneven loading of the samples. This is confirmed by the decay of the apparent hardening after a several days of natural ageing at room temperature. On the other hand an effect similar to structure rejuvenation takes place in the central part of the samples leading to higher specific heat capacity of the cycled samples, larger crystallization and relaxation enthalpies.

1. Introduction

Metallic glasses (MGs) [1,2] and bulk metallic glasses (BMGs) [3,4] are fascinating materials which attract attention of materials scientists all over the world owing to their attractive physical, mechanical and chemical properties [5]. It is well understood that a glass of a given composition can exist in a range of structural states, depending on the cooling rate at which it was formed from the liquid [6]. Slower cooling produces glasses of lower enthalpy and specific volume, and such states can also be reached by thermal annealing of a faster quenched glass. For metallic glasses, as for polymers [7], there has been interest in reaching different glassy states through mechanical processing. There have been many studies of the effects of plastic deformation on MGs e.g. [8–13]. The present work focuses on the effects of cyclic elastic deformation, a subject opened up by Packard et al. [14], when they showed that the mechanical properties of a MG could be altered by prior cyclic loading in the nominally elastic range. Their tests, as for all those reported in the present work, were conducted at room temperature. In a nanoindentation (instrumented-indentation) study using a spherical-tip indenter, they characterized the state of the MG by cumulative-distribution curves of the initial yield load P_y, i.e. the load at which the loading curve shows its first plasticity in the form of a *pop-in* event. For a given sample, the values of P_y show significant variation, interpreted as due to inhomogeneity in the MG itself [15].

Packard et al. found that cycles of loading and unloading in the apparently fully elastic range (i.e. well below the lowest value of P_y) lead, on subsequent indentation, to a shift of the distribution curve of P_y to higher values, i.e. a hardening effect [14]. The effect is specific to cycling, as prior static loading to similar values gives no detectable hardening. Later work showed that there is a threshold load below which there is no effect and the hardening saturates as the number of cycles increases, that the hardening due to cycling can greatly exceed that due to thermal annealing, and that there is a

* Corresponding author.
E-mail address: dml@wpi-aimr.tohoku.ac.jp (D.V. Louzguine-Luzgin).
[1] Current address: National Engineering Research Center of Near-net-shape Forming for Metallic Materials, School of Mechanical and Automotive Engineering, South China University of Technology, 381 Wushan Road, Guangzhou, 510640, China.

http://dx.doi.org/10.1016/j.actamat.2017.02.049
1359-6454/

partial loss of the hardening if there is a delay between the cycling and the indentation [15–17]. Molecular-dynamics (MD) simulations were used to study the mechanisms of the hardening [18], and successfully showed the threshold and saturation effects. It was concluded that during the cycling there are microplastic events. Events on loading and unloading lead to behaviour that is apparently elastic, though the atomic rearrangements are not individually reversed; there is an accumulation of permanent structural change. Many types of change are possible, including the introduction of anisotropy, but as the effect is hardening, which the MD simulations show is accompanied by an increase in indentation modulus, it is generally assumed that the cycling takes the MG to a denser, more relaxed state [18]. Indeed, Packard et al. noted that the saturation of hardening could be attributed to "gradually shaking down to an 'ideal glass' configuration of higher structural order than the as-cast material" [16]. Hardening of this kind, induced by cyclic elastic loading, is of great interest. It could enable states, in particular relaxed states, to be reached that are not accessible through thermal annealing, and one might speculate that relaxed states could be reached with less danger of crystallization than in conventional annealing.

Anelastic and viscoplastic strains can have distinct, even opposite, effects on properties. For example, relaxation enthalpy was found to decrease after indentation [19] and in an as-cast Pd-based BMG subjected to shot peening [20]. On the other hand, shot peening-induced rejuvenation of the annealed glass. In a Zr-based BMG cold-rolled to thickness reductions of up to 50%, relaxation enthalpy first increased and then decreased [21]. A similar effect was observed in the case of a Zr-based BMG deformed in compression [22,23].

The first demonstration that elastic-cycling effects extend to macroscopic loading, and are not confined to nanoindentation, was by Caron et al. [24]. They loaded a Zr-based bulk metallic glass (BMG) in uniaxial compression at (37 ± 15)% of the yield stress σ_y. As a result of this cycling, the MG had a lower relaxation enthalpy as measured in DSC, indicating a more relaxed state, consistent with observed decreases in internal friction. Load-free samples showed a residual contraction along the loading axis, taken to indicate a densification, though there was no measurable change in Young's modulus (measured by ultrasonic pulse-echo technique). The structural changes underlying these effects were attributed to an accumulation of anelastic strains associated with the cycle periods being much shorter than the anelastic recovery time. The cyclic loading was found to induce partial nanocrystallization of the metallic glass forming an equilibrium Zr_2Fe phase. Further work on the same BMG at significantly higher stress values of (63 ± 13)% confirmed that cyclic loading can induce crystallization, but of a metastable phase [25]. There was a detectable shift of the first halo in X-ray diffraction patterns of the MG, and it was noted that this could be associated with anisotropic structural change. Cyclic loading was found to lead to a 0.5% decrease in density of the MG and increase in the crystallization enthalpy, opposite to the change expected for relaxation. This could be the result of initial nanoscale heterogeneity in the MG [26].

As noted above, elastic static loading in nanoindentation has no detectable effect on MGs, but of course the loading times are short. In contrast, in macroscopic tests, static loading can easily be maintained for several hours. BMG samples elastically loaded for such times in uniaxial compression show significant changes in properties [27,28], even though there is typically only a very small residual contraction along the loading axis. The relaxation enthalpy, measured in DSC, is increased, indicating that the loading has induced *rejuvenation* (i.e. the opposite of relaxation and ageing). This should be associated with a decrease in density, and such a decrease was later confirmed by direct measurement [29]. The rejuvenated samples show increases in plasticity and decreases in bulk and shear moduli [27–29].

It is clear from the work reviewed above that cyclic elastic loading has many interesting, even surprising, effects on MGs [30]. Although the stress states in nanoindentation and in macroscopic uniaxial compression are very different, there are some analogous effects of cycling in the two cases. MD simulations which, as noted above, can reproduce the observed effects of cycling in nanoindentation, have failed to detect any clear changes in MG structure [18] though such changes are clearly observed within the shear bands on plastic deformation [31]. The property changes even leave it in doubt whether the cycling induces relaxation (consistent with observed hardening) or rejuvenation (consistent with lowered density and the increased mobility that must underlie crystallization). It is possible, even probable, that mechanical treatments such as elastic cycling induce structural changes that are qualitatively different from those normally associated with relaxation and rejuvenation (such as would be achieved by annealing or by forming the glass from the liquid by quenching at different rates). For example, the relative changes in topological and in chemical short-range order [32] may be different in the mechanical and thermal treatments. The present work explores further the parallels between elastic cycling in macroscopic uniaxial compression and in nanoindentation, and exploits the longer times accessible in the former to explore the underlying mechanisms of the effects on MG structure and properties.

2. Experimental methods

Cylinders of $Zr_{61}Cu_{27}Fe_2Al_{10}$ (at.%) BMG, 2 mm in diameter (in some cases 3 mm), and samples of rectangular 2 × 3 mm cross-section of the same composition, both several centimetres long, were prepared by arc-melting high-purity (99.9%) elements in a Ti-gettered Ar atmosphere and then injection-casting into a copper mould, pre-prepared by polishing with diamond paste and cleaning with ethanol. The nature of the samples was checked by conventional X-ray diffractometry (XRD) with monochromatic CuKα radiation (Bruker D8) and by differential scanning calorimetry (Perkin Elmer 8500). The as-cast samples were found to be fully glassy.

Cylinders 4 mm long and 2 mm in diameter (in some cases 6 mm long and 3 mm diameter to allow improved mapping of the distribution of hardness) and 4 × 3 × 2 mm cuboids (polished from every direction), cut from the as-cast ingots, were cyclically loaded at room temperature in uniaxial compression. The top and bottom faces of the cylindrical samples were polished to be accurately parallel using a high-grade polishing paper while fixing the sample with a steel frame. The variation in height across the end-faces of the samples was ±4 μm for a 6-mm-long sample and ±2 μm for a 4-mm-long sample. The cuboid samples were polished to a depth of at least 30 μm from each side to have a nearly ideal morphology independent of surface casting defects.

Mechanical testing was conducted using Instron 5581 and Shimadzu AG-50kN-Xplus universal testing machines. Strain values were obtained from a KYOWA KGF-1N-120 polyimide strain gauge attached to the samples. From several tests, the minimum yield strength of the BMG was ~1600 MPa. The samples were subjected to cyclic compression (10 cycles at loading and unloading rates of $5\cdot10^{-4}$ s^{-1}) in the range 200–1400 MPa (i.e. 50 ± 37.5% of σ_y); no yield was observed in this nominally elastic range. A BN lubricant was used on the top and bottom faces of the samples to reduce barrelling under compression. Unless stated specifically, the as-cast samples were used.

The Young's modulus was determined from the cyclic loading tests by fitting the nearly perfectly linear loading curves (goodness-