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Effect of ion irradiation on tensile ductility, strength and fictive temperature in metallic glass nanowires

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Abstract

Ion irradiation of thermoplastically molded $Pt_{57.5}Cu_{14.3}Ni_{5.7}P_{22.5}$ metallic glass nanowires is used to study the relationship between glass structure and tensile behavior across a wide range of structural states. Starting with the as-molded state of the glass, ion fluence and irradiated volume fraction are systematically varied to rejuvenate the glass, and the resulting plastic behavior of the metallic glass nanowires probed by *in situ* mechanical testing in a scanning electron microscope. Whereas the as-molded nanowires exhibit high strength, brittle-like fracture and negligible inelastic deformation, ion-irradiated nanowires show tensile ductility and quasi-homogeneous plastic deformation. Signatures of changes to the glass structure owing to ion irradiation as obtained from electron diffraction are subtle, despite relatively large yield strength reductions of hundreds of megapascals relative to the as-molded condition. To reconcile changes in mechanical behavior with glass properties, we adapt previous models equating the released strain energy during shear banding to a transit through the glass transition temperature by incorporating the excess enthalpy associated with distinct structural states. Our model suggests that ion irradiation increases the fictive temperature of our glass by tens of degrees – the equivalent of many orders of magnitude change in cooling rate. We further show our analytical description of yield strength to quantitatively describe literature results showing a correlation between severe plastic deformation and hardness in a single glass system. Our results highlight not only the capacity for room temperature ductile plastic flow in nanoscaled metallic glasses, but also processing strategies capable of glass rejuvenation outside of the realm of traditional thermal treatments.

Keywords: Metallic glass; Nanowire; Tensile ductility; Ion irradiation; Fictive temperature

1. Introduction

Since their discovery in 1960, metallic glasses (MGs) have garnered significant interest due to a suite of attractive properties [1]. In particular, the combination of metallic bonding and the absence of long-range order has produced materials with superior mechanical properties compared to their crystalline counterparts. MG alloys have demonstrated high elastic strain limits, high strengths, potential for high fracture toughness, good wear resistance and low mechanical dissipation [2,3]. Coupled with versatile processing through thermoplastic molding, the mechanical properties make MGs appealing for many structural applications, particularly at miniature length scales, such as those in microelectromechanical system (MEMS) devices [4–6].

Despite this promise, widespread applications of MG alloys as structural materials have been hampered by poor plastic performance and a tendency towards catastrophic failure at room temperature. Specifically, deformation in

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metallic glasses at room temperature is characterized by a deleterious propensity for localized plastic shearing into thin bands, known as shear bands, that progress in a self-catalytic fashion and are incipient to final fracture [7]. Prior to such macroscopic level shearing, plastic deformation is understood to be accommodated by the activation of shear transformation zones (STZs) [8]. An STZ is a local collection of atoms that undergoes a cooperative shear rearrangement, the operation of which is biased under an applied shear stress [9]. While STZs have been shown to carry plasticity over all temperature ranges, the ensuing plastic response of MGs strongly depends on temperature and strain rate [10]. At temperatures close to the glass transition temperature (T_g), plastic deformation is homogeneous and can be adequately described by Newtonian flow [11]. At low temperatures relative to T_g and high strain rates, STZ operation leads to strain localization and the formation of shear bands [7].

However, such propensity for shear localization and its ubiquity in plastic deformation at room temperature have not been definitively linked to specific structural or compositional features. Many theories rely on order parameters, such as free volume [8,11] or effective temperature [12], to predict deformation modes. For instance, Argon's seminal work on STZs related deformation to the generation and annihilation of free volume during STZ operation [8]. During low-temperature deformation, the MG structure is unable to relax sufficiently rapidly and the free volume persists (or its rate of generation increases). As deformation proceeds, the strain rate localizes in the softer, dilated regions. However, free volume and effective temperature are often experimentally intractable or strongly sensitive to the measurement approach [13–17], thereby limiting their predictive capability for macroscopic experiments. Instead, a large portion of glass development has focused on improving intrinsic glass performance based on empirical evidence guided by semi-physical analytical modeling [18–21]. One example of a common strategy is the synthesis of MGs with high Poisson's ratio (or low μ/B), which has been linked to a large capacity for plastic deformation via facile shear band nucleation and propagation coupled with large resistance to cavitation and fracture [22,23].

However, within a given alloy, the properties and deformation mode depend strongly on processing conditions [24–26]. The loading modality also influences the mechanical response. Both yield stress and capacity for plasticity increase in confined loading geometries (i.e. compression or bending) as compared to uniaxial tension [27–29]. The increased plasticity is a result of the arrest of shear bands due to confinement. Various heat treatments influence the plastic response as well. Sub-T_g annealing has been shown to relax the glass structure. Structural relaxation leads to embrittlement in normally ductile glasses due to a reduction in shear band activity [25,30]. Subsequent annealing above T_g rejuvenates the structure and the glass regains its capacity for plastic deformation.

Recently this transition in mechanical behavior was rationalized by considering the fictive temperature (T_f) of the glass following distinct thermal treatments [31]. Fictive temperature is defined as the temperature at which the frozen-in liquid structure is at equilibrium [32]. By performing bending tests on MG samples prepared at different T_fs, an alloy-dependent critical fictive temperature (T_{fc}) was observed. A specimen prepared above T_{fc} exhibited plastic deformation in bending while a specimen prepared below T_{fc} responded in a brittle manner [31].

Similar to the thermal treatments mentioned before, mechanical deformation was shown to induce structural relaxation or rejuvenation of MGs. For instance, cyclic loading within the elastic regime was observed by Packard et al. [33,34] to lead to hardening of metallic glasses. Molecular dynamics simulations have provided insight into the observed hardening, with the hardening being attributed to relaxation of the glass structure and annihilation of free volume [35–37]. Interestingly, this indicated that plastic deformation occurred at the atomic scale, while the macroscopic behavior remains seemingly elastic. Conversely, severe plastic deformation was shown to rejuvenate MGs, leading to softening [28,38–42] as a result of large cumulative plastic shearing. The large strains required for such reported changes were achieved in MGs through confined loading techniques that accumulate large shear deformations, such as high-pressure torsion (HPT) [43]. Rejuvenation of MGs manifested as increased free volume, increased stored enthalpy, and reduced elastic modulus and hardness [39,41,42]. Furthermore, examining the indents of these severely deformed MGs showed a suppression of shear bands relative to the undeformed glass [42]. Similar changes have been reported following shot peening of MGs, producing a severely deformed surface layer on the order of 100 μm thick [44–46]. When measured parallel to the surface, the hardness was observed to decrease closer to the shot-peened surface, where the damage was expected to be most pronounced [44]. The softening due to shot peening was also associated with structural rejuvenation, as measured by increased stored enthalpy during calorimetric studies [46]. Thus, provided a given MG alloy, mechanical properties may be altered by various treatments (both thermal and mechanical); in some cases, a transition in plastic deformation mode was possible.

The structural changes created by thermal processing and severe mechanical treatments were remarkably similar to the bombardment of MGs with energetic particles [47]. Recent molecular dynamics studies of simulated ion irradiation in metallic glass have demonstrated a persistent, yet subtly different, amorphous structure as well as significant changes in mechanical response [48–50]. Mayr observed an increase in free volume and reduction of yield stress in irradiated MGs as compared to a more relaxed sample [48]. Xiao et al. observed a reduction in the fraction of icosahedral clusters coupled with a softening and delocalization of deformation in MG samples prepared by simulated casting [49]. A similar study by Avchaciov et al. also reported