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3D nano-architected metallic glass: Size effect suppresses catastrophic failure

Rachel Liontas [a], Julia R. Greer [b, *]

[a] Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, USA
[b] Division of Engineering and Applied Science, California Institute of Technology, Pasadena, CA 91125, USA

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ABSTRACT

We investigate the mechanical behavior of 3D periodically architected metallic glass nanolattices, constructed from hollow beams of sputtered Zr-Ni-Al metallic glass. Nanolattices composed of beams with different wall thicknesses are fabricated by varying the sputter deposition time, resulting in nanolattices with median wall thicknesses of ~88 nm, ~57 nm, ~38 nm, ~30 nm, ~20 nm, and ~10 nm. Uniaxial compression experiments conducted inside a scanning electron microscope reveal a transition from brittle, catastrophic failure in thicker-walled nanolattices (median wall thicknesses of ~88 and ~57 nm) to deformable, gradual, layer-by-layer collapse in thinner-walled nanolattices (median wall thicknesses of ~38 nm and less). As the nanolattice wall thickness is varied, large differences in deformability are manifested through the severity of strain bursts, nanolattice recovery after compression, and in-situ images obtained during compression experiments. We explain the brittle-to-deformable transition that occurs as the nanolattice wall thickness decreases in terms of the "smaller is more deformable" material size effect that arises in nano-sized metallic glasses. This work demonstrates that the nano-induced failure-suppression size effect that emerges in small-scale metallic glasses can be proliferated to larger-scale materials by the virtue of architecting.

1. Introduction

Metallic glasses are a class of materials that offer beneficial mechanical properties such as high strength and a large elastic strain limit [1,2]. The lack of grain boundaries in metallic glasses leads to excellent corrosion and wear resistance as well as great soft magnetic properties [1–3]. Despite these desirable properties, metallic glasses have seen limited use in applications owing to their low ductility and characteristic catastrophic failure. Room temperature deformation of metallic glasses typically involves localization of plastic strain into narrow shear bands [4]. Studies have found that this catastrophic failure can be alleviated by reducing the sample size of metallic glass to the nanoscale, where a size-induced brittle-to-ductile transition occurs, observed under both compression [5–7] and tension [8–10]. Tensile ductility at room temperature in metallic glasses is particularly elusive, and has only been shown to emerge in monolithic metallic glasses when the sample size is reduced to these nanoscale dimensions. Previous studies have found that ~100 nm diameter metallic glass pillars can reach true tensile strains of ~25% prior to failure [8,9], and our previous work demonstrated that sputtered Zr-Ni-Al metallic glass nanopillars can reach true strains of ~150% for sample widths up to ~150 nm [11]. These studies show that reducing the characteristic dimension of metallic glass to the nano-scale can alleviate metallic glasses' Achilles' heel of brittle failure, thereby enabling the use of metallic glasses without catastrophic failure.

Advances in small-scale technological devices such as MEMS (microelectromechanical systems), biomedical devices and implants, microelectronics, micromanipulators, and microrobotics have increased the demand for miniature parts fabricated from materials with suitable properties [12,13]. The combination of metallic glasses' enhanced plasticity at small scales [5–11] with their other desirable properties (including high elasticity, an isotropic/homogeneous nature, and excellent corrosion/wear resistance) [1,2] points towards metallic glasses as promising candidates for use in such small-scale technological devices. Fabricating metallic glasses as thin films, for example by sputtering, presents a unique opportunity to create very thin coatings that may more readily benefit from the size-induced brittle-to-ductile

* Corresponding author.
E-mail address: jrgreer@caltech.edu (J.R. Greer).

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transition in metallic glasses. The use of thin film deposition also interfaces well with existing micro- and nano-fabrication techniques utilized in creating small-scale technological devices. Thin films can be extended to 3-dimensions by "wrapping" the thin film around some 3-dimensional architecture.

Large deformable metallic glasses may be envisioned through nano-architecting, that is maintaining a key dimension of the metallic glass (such as the thin film thickness) at the nanoscale without limiting the overall macroscopic dimensions of the architecture. We utilize this nano-architecting approach by fabricating hollow metallic glass nanolattices with the beam wall thickness in the "smaller is more deformable" nanoscale size range, while the entire nanolattice structure spans tens of microns. These nanolattices can be made arbitrarily large when experimental practicalities are neglected. We chose to work with sputter-deposited Zr-Ni-Al as the thin film metallic glass "coating" for the nanolattices based on this material's substantial tensile ductility at dimensions up to ~150 nm [11].

Nanolattices, or architected structural metamaterials, exhibit hierarchical ordering ranging from nanometer length scales in wall thickness to micron length scales in defining unit cells and beyond millimeter scales in the overall macroscale architecture, with many nano-architectures produced by using direct-laser-writing two-photon lithography [14–17]. Existing work on nanolattices has primarily focused on hollow ceramic nanolattices [18–22], due to the ease of depositing conformal coatings of ceramic materials by atomic layer deposition (ALD) and the inertness of these ceramic materials to oxygen plasma, which has thus far been the plasma of choice for etching away the internal polymer scaffold to produce nanolattices. One of the key findings from these studies is that by optimizing the wall thickness-to-radius ratio of the nanolattice beams, hollow alumina nanolattices can recover to their original shape after compression in excess of 50% strain [20]. There have also been a few studies on hollow Au nanolattices [23,24], which demonstrated that strength and stiffness can be increased by an order of magnitude by tuning nanolattice geometry while maintaining a constant relative density [24]. Metallic glass nanolattices have been studied less frequently than metal or ceramic nanolattices due to experimental difficulties in extending the fabrication process to metallic glass.

Some studies have attempted to impart plasticity to metallic glasses by utilizing stochastic architectures, or metallic glass foams with a random distribution of heterogeneities and pores. Stochastic metallic glass foams have been fabricated by incorporating gas into metallic glass during processing [25,26] or by creating a two-phase mixture of metallic glass and another material, which is subsequently removed [27–29]. One study found ~80% compressive ductility for open-cell Zr-based amorphous metal foams with relative densities of 14–28% and pores sizes of 150–355 μm [30] Another study found that the commercial glass-forming alloy Vit106, which exhibits no significant plasticity in the monolithic alloy, can become ductile under compression, reaching ~50% strain, when it is made into an open-cell foam with porosity ~78% and pore size 212–250 μm [31]. In another study, open-cell $Zr_{41.25}Ti_{13.75}Cu_{12.5}Ni_{10}Be_{22.5}$ metallic glass foams, fabricated by using NaCl as a space-holder material, were shown to exhibit high energy absorption capacity with ductile cracking resulting from the complex stress state that arises from the presence of pores in the foam [32]. These and other stochastic cellular structures almost always contain imperfections, which render them difficult to manipulate and study systematically. The randomness in their mesoscale architecture also naturally leads to a reduction in mechanical performance, i.e. stiffness and strength, compared with periodically ordered metallic glass foams [33–35].

Periodically architected foams may be precisely engineered to attain optimal mechanical performance. Studies on such periodically architected metallic glass foams have been limited due to the difficulty in fabricating such materials, particularly in 3D. One study utilized thermoplastic replication of metallic glass to fabricate 2D metallic glass cellular structures that ranged from perfectly periodic to highly stochastic [35]. These authors observed that while the periodic structures generally had a higher elastic modulus and yield strength compared to stochastic structures, the stochastic onees exhibited higher flaw tolerance [35]. To create 3D periodically architected metallic glass structures, one study utilized thermoplastic forming-based patterning of metallic glass sheets combined with parallel joining, which resulted in honeycomb-like architectures exhibiting high elastic energy storability and absorption [36]. 3D periodically architected metallic glass cellular structures were also fabricated using electroless deposition of Ni-P metallic glass onto a sacrificial polymer microlattice [37]. These Ni-P microlattices consisted of ~1 mm unit cells with metallic glass wall thicknesses of 60–600 nm and reported structures with wall thicknesses above 150 nm failed catastrophically while those with wall thicknesses below 150 nm failed with plasticity [37]. The dimensions of metallic glass lattices in nearly all of these existing studies were far from the nanoscale, including ~1 mm unit cells and 20–70 μm wall thicknesses [35], cm-sized unit cells and ~0.4 mm wall thickness [36] and mm-sized unit cells and ~60–600 nm wall thicknesses [37]. In designing periodically nano-architected metallic glasses, both the periodic and nanoscale aspects are key to take advantage of both structural and material size effects. Experimental difficulty in fabricating hollow metallic glass nanolattices has resulted in a dearth of studies on that length scale. The only study to date on metallic glass nanolattices [38] did not consider several factors in nanolattice fabrication and characterization, which will be discussed in section 4.3. That study did report a promising suppression of brittle failure as the $Cu_{60}Zr_{40}$ metallic glass tube-wall thickness was decreased [38].

We report the fabrication of hollow Zr-Ni-Al metallic glass nanolattices with median beam wall thicknesses of 10, 20, 30, 38, 57, and 88 nm fabricated by sputter deposition for the durations of 15, 30, 45, 60, 120, and 240 min, respectively. In-situ nanomechanical experiments demonstrate that reducing the wall thickness leads to a transition in the deformation behavior of the metallic glass nanolattices from catastrophic failure with large strain bursts in thick-walled nanolattices (wall thicknesses greater than ~50 nm) to smooth continuous deformation with gradual layer-by-layer collapse in thinner-walled nanolattices.

2. Experimental section

2.1. Fabrication of hollow metallic glass nanolattices

Hollow metallic glass nanolattices were fabricated through the multi-step process shown schematically in Fig. A1 of the Appendix A. The basic steps in this nanolattice fabrication process were originally established for other material systems [18–20,23]. First, polymer scaffolds were fabricated utilizing the direct-laser-writing two-photon lithography process developed by Nanoscribe GmbH. The 3D geometry of the polymer scaffold was chosen as repeating ~7 μm octahedron unit cells connected at their vertices, as shown in Fig. 1 (a). Octahedron unit cells were selected as they represent a fundamental, commonly studied geometry [19,21,23,24] and thus serve as a good base unit cell for one of the first studies on metallic glass nanolattices. Further, the lack of additional beams in an octahedron, as opposed to octet [39] geometry, allows the unit cells to be more open, which facilitates better conformality in the sputter-deposited metallic glass coating. The ~7 μm size was chosen to maximize unit cell size to further facilitate openness of the unit