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Longchao Huang,1 Xinkai Tang,2 Guochen Jiang,2 Kaixuan Fang,2 Kefu Yao,2 Zhengjun Zhang,3 Na Chen,2,a) and Zhiwei Shan1,a)

AFFILIATIONS
1 Center for Advancing Materials Performance from the Nanoscale (CAMP-Nano) & Hysitron Applied Research Center in China (HARCC), State Key Laboratory for Mechanical Behavior of Materials, Xi’an Jiaotong University, Xi’an 710049, People’s Republic of China
2 Key Laboratory for Advanced Materials Processing Technology (MOE), School of Materials Science and Engineering, Tsinghua University, Beijing 100084, People’s Republic of China
3 Key Laboratory for Advanced Materials (MOE), School of Materials Science and Engineering, Tsinghua University, Beijing 100084, People’s Republic of China

a) Authors to whom correspondence should be addressed: chennadm@mail.tsinghua.edu.cn and zwshan@xjtu.edu.cn

ABSTRACT

Oxide glasses are intrinsically brittle at room temperature when loaded under tension. In this study, a high-strength CoFe-based metallic glass was used as a strengthening phase to make a Co–Fe–Ta–B–O oxide glass become stronger and ductile in tension. The developed metallic-glass-reinforced oxide glass nanocomposite possessed a supra-nanometer-sized dual-phase structure. Owing to the dispersion strengthening effects, the nanocomposite showed a tensile strength $\sigma_t$ of $\sim 2.7$ GPa, about 29% higher than that of the single-phase oxide glass. Meanwhile, its tensile plasticity $\epsilon_p$ was enhanced from zero to $\sim 2.7\%$. The continuous glass/glass interfaces of the dual-phase mixture are thought to enable the tensile plasticity in the nanocomposite. Our results provide an approach to effectively enhance both the strength and tensile ductility of intrinsically brittle oxide glasses.

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Oxide glasses (OGs) are usually brittle, i.e., showing zero plasticity preceding fracture especially under tension conditions. It is recognized that surface etching, chemical ion exchange, nanocrystallization, and second phase strengthening can increase the strength of OGs. For example, glass-ceramics usually have higher flexural strength and fracture toughness than the parent glasses. The crystal size, shape, orientation, and volume fraction of the crystalline phase in the glass-ceramics all affected their mechanical performance. Both experimental and simulation results suggested that the crystalline phase in the glass-ceramics caused the crack deflection and crack bridging, leading to the enhanced strength and fracture toughness. The strengthening methods utilized to date, however, are seldom effective in enhancing their tensile plasticity. The main reason is that the global plastic deformability is still dominated by the intrinsically brittle OGs themselves. Therefore, making OGs become ductile in tension at room temperature is a challenging task.

Similar to OGs, most of the metallic glasses (MGs) are brittle in tension with only a few exceptions. It was found that a brittle Sc$_{75}$Fe$_{25}$ metallic glass (MG) became ductile under uniaxial tension due to the introduction of continuous glass/glass interfaces at the nanoscale. Accompanied by the enhancement in tensile ductility, the strength of the nanostructured Sc$_{75}$Fe$_{25}$ MG decreased drastically from 1.8 to 1.3 GPa because of the softening effect of the nanoscale interfaces. Recent simulation results on MG nanocomposites showed that a secondary phase with a higher volume fraction and smaller crystallite size could have a higher propensity to affect the deformation mode of the glass matrix. These results shed light on a useful strategy to enhance the tensile plasticity of brittle OGs by introducing nanostructures into them. In addition, the OGs could sustain their strength or even become stronger if the introduced nanostructures give rise to hardening effects.
MGs are well known for their high fracture strength caused by the absence of crystall-slip mechanisms for deformation.20–24 A Co43Fe20Ta5.5B31.5 MG exhibited an ultrahigh fracture strength of more than 5 GPa, while a Co55Ta10B35 MG created the highest strength record for metallic materials by showing the maximum compressive strength of about 6 GPa.25,26 The strength of this order of magnitude is higher than most of the OGs. Nevertheless, there are few reports on the use of MGs as strengthening phases to enhance the strength and toughness of OGs.27,28 It is because MGs usually possess much lower glass-forming ability than OGs. MGs prefer to crystallize if a mixture of the raw materials for forming MGs and OGs is melted and rapidly solidified by using the conventional melt-quenching technique. This poses an extreme difficulty in preventing MGs from crystallization when introducing them into OGs. To break this hurdle, we utilized physical vapor deposition to in situ grow the suprananometer-sized MG phase into an OG matrix for developing OG–MG nanocomposites.29,30 These dual-phase nanocomposites showed continuous glass/glass interfaces between the MG phase and the OG matrix, which may enable the nanocomposite to optimize its strength and ductility. In this study, a high-strength CoFe-based MG was utilized as a strengthening phase to reinforce an intrinsically brittle strength and ductility. In this study, a high-strength CoFe-based MG showed enhanced tensile strength and plasticity.

Thin films at a thickness of ~10 μm were deposited on square shaped Si substrates with dimensions of ~2 × 2 cm² by using magnetron sputtering of an alloy target with a nominal composition of Co43Fe20Ta5.5B31.5 (in atomic percentage). The background gas pressure was lower than 5 × 10⁻⁵ Pa, and the working pressure was ~0.3 Pa. The single-phase MG sample was prepared with the alloy target under the high purity argon gas condition. To oxidize the MG phase for forming the OG matrix, we used a gas mixture of high purity argon and oxygen in the sample preparation chamber during the sputtering process. The degree for the in situ oxidation of the MG phase was controlled by varying the oxygen partial pressures. At a low oxygen partial pressure of ~0.009 Pa, the MG phase was partially oxidized. In addition, the affinity of Co, Fe, Ta, and B to oxygen follows the sequence of Ta > B > Fe > Co.31 Therefore, most Ta and B were first oxidized and diffused outward to form the surface oxide surrounding the residual MG phase. This selective oxidation of the constituents in the alloy system gave rise to the formation of the oxide matrix and the MG nanoparticles. Meanwhile, the oxidation occurred simultaneously during the deposition of the thin films, resulting in the homogeneous MG core-OG shell structure along the thickness of the thin films. Upon increasing the oxygen partial pressure to ~0.019 Pa, almost all the constituents were oxidized. As a result, a single-phase OG sample was prepared. High-resolution transmission electron microscopy (HRTEM) characterization was performed by using a JEM-2100F TEM (JEOL, 200 kV).

The dual-phase nanocomposite presents a supra-nanometer-sized core–shell structure comprising dark-contrast MG cores and light-contrast OG matrix [Fig. 1(a)]. The selected-area-electron-diffraction (SAED) pattern taken for the nanocomposite, exhibiting two sets of broad halos resulted from the MG and OGM phases, respectively. The inset at the top-right corner shows the illustration of the core-shell-matrix structure. (b) Bright-field high resolution transmission electron microscopy (HRTEM) image showing the continuous glass/glass interfaces of the dual-phase mixture. (c) High angle annular dark field (HAADF)-scanning transmission electron microscopy (STEM) image showing the bright-contrast MG phase. (d) Compositional distributions of the line scanning of Co, Fe, Ta, and O.

FIG. 1. (a) Supra-nanometer-sized dual-phase structure of the OG–MG nanocomposite comprising an ultraline nanometer-sized MG phase embedded in the OG matrix. The inset at the top-right corner shows the selected-area-electron-diffraction (SAED) pattern taken for the nanocomposite, exhibiting two sets of broad halos resulted from the MG and OGM phases, respectively. The inset at the bottom-left corner shows the illustration of the core-shell-matrix structure. (b) Bright-field high resolution transmission electron microscopy (HRTEM) image showing the continuous glass/glass interfaces of the dual-phase mixture. (c) High angle annular dark field (HAADF)-scanning transmission electron microscopy (STEM) image showing the bright-contrast MG phase. (d) Compositional distributions of the line scanning of Co, Fe, Ta, and O. In order to explore the ductility of the as-prepared nanocomposites, we choose to use the challenging but more convincing tensile tests. All "dog-bone" shaped samples for tensile tests were fabricated by dual-beam focused ion-beam (FIB) micromachining (FEI, Helios NanoLab 600i, 30 keV). Tensile tests were performed inside the JEM-2100F TEM (JEOL, 200 kV) at room temperature using a Hysitron picoindenter (P195 J1B) with strain rates ranging from ~8 × 10⁻⁴ to ~3.8 × 10⁻⁵ s⁻¹ in displacement control mode. The picoindenter was equipped with a diamond tip as well as a nano-mechanical loading/sensing system, which enabled us to acquire the force-displacement data with a high resolution. Scanning electron microscopy (SEM) was used to observe the samples before and after mechanical tests.

To identify the effects of the nano-sized MG phase on the mechanical properties of the OG phase, tensile tests of the single-phase MG, single-phase OG, and dual-phase OG–MG samples were performed at a strain rate of ~5 × 10⁻⁵ s⁻¹. The dimensions of the tensile samples have the relationships of w ≈ t ≈ l/3, where w is the width (for all samples, w ranges from 400 to 450 nm), t is the thickness, and l is the effective length [see Fig. 2(a)]. The outer appearance
of one tensile sample is shown in Fig. 2(b). The tensile strains were determined by measuring the length variation between the markers on the samples [Figs. 2(a) and 2(b)]. Engineering stress–strain curves of the OG samples and the dual-phase nanocomposites are shown in Fig. 2(c) [Multimedia view]. The inset of Fig. 2(c) shows the stress–strain curve of the MG sample [see Fig. 2(c)]. Both the OG and MG samples were brittle without showing apparent tensile plasticity [see Fig. 2(c)]. The OG sample showed a fracture strength of $\sigma_f = 2.1 \pm 0.1$ GPa, while the MG sample showed $\sigma_f = 4.4 \pm 0.3$ GPa [see Fig. 2(d)]. As expected, owing to the dispersion strengthening effects of the MG phase, the dual-phase nanocomposite showed an enhanced tensile strength of $\sigma_f = 2.7 \pm 0.1$ GPa. However, it is interesting to see that the tensile plasticity $\epsilon_p$ was enhanced from near zero to $2.7\% \pm 0.5\%$ simultaneously [see Figs. 2(c) and 2(d)]. This is against our traditional understanding of the relationship between strength and ductility, i.e., they are mutually exclusive of each other.

To understand the deformation mechanisms, the fracture surfaces of the deformed OG, OG–MG, and MG samples were examined (Fig. 3). The fracture plane of the OG sample was nearly normal to the loading direction. The tear ridges observed on the fracture surface further confirmed its brittle nature [Fig. 3(a)]. It is known that covalent and/ or ionic bonds are dominant in OGs. Either covalent or ionic bonding is difficult to migrate between the neighboring atoms. In addition, OGs are highly sensitive to surface or internal flaws. These could lead to the high stiffness and brittleness of OGs. Different from OGs, MGs are characterized mainly by non-directional and non-saturated metallic bonds. Nevertheless, most monolithic MGs are brittle in tension because no effective strain carriers exist to cause work-hardening effects as those observed in crystalline metals. As a consequence, the catastrophic failure occurs once the cracks are triggered by the dominant shear bands. In our experiments, the fracture plane of the MG sample had an angle of $51^\circ$ with respect to the tension direction [Fig. 3(b)], indicative of a shear fracture mode typically observed for most MGs under tension. Vein patterns existed on the fracture surface, which were caused by the viscous flow with the dominant shear planes sliding. In contrast to the brittle fracture modes of both the OG and MG samples, visible tensile plasticity was achieved in the MG-reinforced OG matrix nanocomposite. In addition, a cup-cone shaped fracture surface was observed, on which dimple-like patterns were formed in the dual-phase nanocomposite [Fig. 3(c)]. This indicated that the nanocomposite fractured in a relatively ductile mode. The tensile testing results of these samples demonstrated that the introduction of the high-strength MG phase enabled a transition from strong-yet-brittle behavior of the single-phase OG sample to stronger-and-ductile deformation of the MG matrix nanocomposites. Shown in Fig. 3(d) is one typical side view of the fractured dual-phase nanocomposites under TEM observation. On the fracture surface, there existed many undulating nanostructures with sizes ranging from several nanometers to several tens of nanometers as indicated by arrows and dotted lines in Fig. 3(d). This result indicated that the crack propagated in a wavy manner during the fracture process. Namely, the cracking was hindered by high-strength obstacles from rapid propagation causing brittle fracture, which was consistent with the observation of a ductile cup-cone shaped fracture surface with dimple-like patterns [Fig. 3(c)]. We should keep in mind that the fracture strength of the single-phase MG sample was $4.4$ GPa, much higher than $2.1$ GPa of the single-phase OG sample [see Fig. 2(c)]. These high-strength MG cores in the dual-phase nanocomposite could play the role of a dispersion-strengthening phase to cause the work hardening-like effects and deflect the cracks. As a result, the tensile strength of the nanocomposite was enhanced to be $2.7$ GPa. In addition, the regions close to the undulating nanostructures exhibited interconnected interfaces surrounding the MG cores, which were extended throughout the sample as indicated by a yellow dotted circle in Fig. 3(d). It was therefore suggested that the tensile ductility should be mainly attributed to the homogeneous deformation of the glass/glass interfaces between the MG cores and the OG matrix. These interfaces, as transition regions linking the MG cores and OG matrix, were characterized by a mixture of metallic and covalent/ionic bonds. They could be more loosely packed than both the MG cores and the OG matrix. This was supported by the experimental results that the dual-phase nanocomposite showed the lowest elastic modulus of $88 \pm 4$ GPa, compared to the elastic moduli of $141 \pm 6$ GPa and $95 \pm 2$ GPa obtained for the single-phase MG and OG samples, respectively, [Fig 2(c)]. As a consequence, the plastic flow, developed from the percolation of shear transformation zones or flow units, can be activated favorably in the continuous glass/glass interface regions.
In response to the external stress, shear transformation zones or flow units were initiated at different sites of these interfaces. The size of the interfaces was only ~0.5 nm, which was much smaller than the normal size of about 20 nm of shear bands. In this case, homogeneous plastic flow would be generated instead of formation of matured shear bands. Owing to the strengthening effects from the high-strength MG cores, the plastic flow would be extended to the neighboring regions. More and more deformation regions via plastic flow were activated to accommodate the increased strain, leading to the overall tensile ductility. However, the OG matrix was intrinsically sensitive to the surface flaws in the dual-phase sample. Once the crack was initiated at the surface, a competition between the stable crack propagation and the further plastic deformation of the sample determined the eventual fracture strength and the overall tensile ductility prior to the fracture. The fracture strength of a material can be expressed by \( \sqrt{EG/\pi a} \) transformed from the Griffith strength relation, where \( E \) is the Young’s modulus, \( G \) is the strain energy release rate with the crack growth, and \( a \) is the half-length of a pre-existing crack. For brittle OGS, \( G \) is mainly determined by the released elastic energy dissipated for creating new surfaces of the crack. If no strengthening phase can hinder the crack’s rapid propagation, the OGS fracture without any plasticity as observed in the single-phase OG sample [Fig. 2(c)]. For the dual-phase nanocomposite with considerable tensile ductility, a plastic zone is developed at the crack tip. In addition, the cracking would deflect when it ran onto the high-strength MG cores, resulting in the hackly fracture surface as observed in Fig. 3(d). The crack deflection means the creation of additional new surfaces for the propagating crack. Therefore, higher strain energy is required to be dissipated for the increased new surfaces of the crack and the plastic deformation of the plastic zone. This leads to higher fracture strength of the nanocomposite than that of the single-phase OG [Fig. 2(c)], given that the nanocomposite and the single-phase OG sample have similar Young’s moduli.

Due to the low ability of both the OG matrix and the MG cores themselves to induce strain hardening, the crack propagation in the deformation regions could not be well impeded. As a result, the eventual tensile plasticity of the nanocomposite was limited to be ~2.7%, still much lower than those of most crystalline metals. Even so, obtaining tensile ductility of this order has been an important step for intrinsic brittle OGS toward the load-bearing engineering applications. Given the high tensile stress of ~2.7 GPa and the tensile ductility of ~2.7%, the OG nanocomposite could gain a much more reliable and longer service life when used for functional components in Micro-Electromechanical Systems (MEMS) or electronic devices. In fact, significant tensile ductility of OGS has been hitherto reported only for <100 nm-sized samples as well as for high strain rates. In the present study, the tensile tests were performed at a much lower strain rate of \( \sim 5 \times 10^{-3} \) s\(^{-1} \) for the OG matrix nanocomposites with a much larger size of about 400 nm. It was suggested that high strain rates above \( 10^{6} \) s\(^{-1} \) drastically decreased the viscosity of the amorphous \( \text{Al}_{2}\text{O}_{3} \) thin film at a thickness of ~40 nm, enabling it to be in a supercooled liquid state. In this case, the \( \text{Al}_{2}\text{O}_{3} \) thin film deformed via the viscous creep mechanism. Note that the strain rates of the order of \( \sim 10^{6} \) s\(^{-1} \) were realized in molecular dynamics simulations rather than in the experimental tests. Furthermore, the deformation behavior of the OGS is highly strain rate sensitive. Increasing the strain rate at a determined temperature increased their strength. To investigate the strain rate effect on the mechanical properties of the present OG nanocomposites, we performed the \textit{in situ} tensile tests at additional strain rates of orders of \( 10^{-2} \) and \( 10^{-4} \) s\(^{-1} \) (see Fig. 4). It was found that increasing the strain rate increased the tensile strength of the OG nanocomposite [Fig. 4(a)]. Meanwhile, the tensile ductility increased with the decrease of strain rate [Fig. 4(a)]. The OG nanocomposite showed a tensile plastic strain of ~5.8% at a strain rate of \( 8 \times 10^{-4} \) s\(^{-1} \) [Fig. 4(b)]. This indicated that more shear transformation zones or flow units were involved to accommodate more deformation when a sufficient time was given to activate them. On the other hand, the tensile ductility of OGS could be further enhanced if the samples can be prepared to be free of geometrical flaws as crack sources. In addition, small-sized MGs (e.g., diameter <100 nm) usually exhibit large tensile plasticity. This indicated that the MG-cores in the present study contributed little to the macroscopic ductility of the dual-phase nanocomposite. The fundamental physics behind this could result from the huge strength difference.
between the MG and OG phases. It may be possible to match the strengths of the OG and MG phases through appropriately tuning their compositions or selecting another MG-forming system such as Cu–Zr, Pd–Si, or Zr–Cu–Ni–Al with much higher compressive ductility than the present Co–Fe–Ta–B system. This would promote the MG cores to contribute more plastic deformation as well, leading to a much higher tensile ductility.

In summary, a MG-reinforced OG matrix nanocomposite possessing a supra-nanometer-sized dual-phase structure was developed. The dual-phase OG–MG nanocomposite exhibited a tensile strength of ~2.7 GPa, which is about 29% higher than that of the single-phase OG. Meanwhile, the tensile plasticity of the nanocomposite was also enhanced from zero to ~2.7% through introducing nanoscale glass/glasmatrix interfaces into the intrinsically brittle OG phase. We anticipate that the approach for developing the dual-phase Co–Fe–Ta–B–O nanocomposite in this work is also applicable to many other OG systems, especially those silicate/borate-containing glasses, making them become stronger and ductile under tension.

AUTHOR’S CONTRIBUTION

L.H., X.T., and G.J. contributed equally to this work.

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REFERENCES

43. Y. B. Zhao, X. H. Peng, C. Huang, B. Yang, N. Hu, and M. C. Wang, Nanomaterials 9, 1535 (2019).