Materials Science & Engineering A 692 (2017) 67–74

Contents lists available at ScienceDirect

Materials Science & Engineering A

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

The effects of thin coatings on the mechanical properties and resistance to annealing-induced embrittlement of bulk metallic glass

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ARTICLE INFO

Keywords:
Bulk metallic glass
Coating
Plasticity
Strength
Embrittlement

ABSTRACT

The effect of thin coating on the strength, plasticity and resistance to annealing-induced embrittlement was investigated for $Zr_{50.7}Cu_{28}Ni_9Al_{12.3}$ bulk metallic glass (BMG). To maintain the BMG structure in the most extent, very thin amorphous CuZr and crystalline W coatings were used. The crystalline coating performed much better in improving BMG plastic deformation than the amorphous one, for its superior retarding effect on shear band (SB) dynamics. Besides the coatings, softer layers near the sputtered surfaces also contributed to the enhanced plasticity of the coated BMG. The presence of these softer layers also led to the slightly lower strength of both amorphous CuZr and crystalline W coated BMGs relative to the uncoated ones. The BMG with crystalline W coating exhibited much better resistance to annealing-induced embrittlement than the amorphous CuZr-coated and uncoated ones, due to its much enhanced decomposition processes upon annealing. These experimental results provide useful guidance on choosing suitable coating materials to elevate BMG plasticity and avoid annealing-induced embrittlement.

1. Introduction

The inherent brittleness of bulk metallic glasses (BMGs), manifested as catastrophic fracture with deformation localized into a main narrow shear band (SB), severely limits their practical application as a structural material [1,2]. Even worse, annealing-induced embrittlement in BMGs due to running off of free volume (FV) [3,4] may further restrict their application in the environment of elevated temperature.

To improve the plasticity of BMGs, many kinds of soft crystalline coatings, such as Cu and Ni films, have been used to confine the unstable development of SBs so as to produce more homogeneously distributed SBs [5–10]. However, the soft coatings were about dozens to hundreds of micrometer thick, which distinctly altered the BMGs into BMG/crystal composites. Meanwhile, these soft coatings led to obvious reduction in yield strength of the coated BMGs, as they also participated in deformation besides the BMGs. To avoid this, a hard amorphous NiP coating was used to elevate the plasticity of BMG without obvious sacrifice of its strength [11]. The results indicated that amorphous coatings might be more suitable than crystalline coatings for improving the mechanical properties of BMG.

Concerning the amorphous structure, however, a crystalline coating might be more thermodynamically incompatible with structural defects, for during the exothermic process of grain boundary (GB) relaxation in nanocrystalline alloys, defects like dislocations or voids in the crystalline matrix would annihilate in the GBs with amorphous structure [12–15]. In addition, the FV tends to annihilate at the free surface of MGs [16–18]. Accordingly, the crystalline coating might be more suitable than the amorphous one to prevent the running off of FV in BMGs upon annealing and hence elevate the resistance of BMGs to annealing-induced embrittlement.

This study attempted to evaluate experimentally the effects of thin coatings on the overall performance (e.g., strength, plasticity and resistance to annealing-induced embrittlement) of BMGs. To maintain the BMG structure in the most extent and avoid obvious reduction in yield strength of the coated BMGs, very thin amorphous CuZr and crystalline W coatings were used. The experimental results demonstrated that crystalline coatings could greatly improve both the plasticity and the resistance to annealing-induced embrittlement of BMGs, while amorphous coatings could only mildly improve the plasticity but not the resistance to annealing-induced embrittlement. Both the amorphous CuZr and crystalline W coated BMGs exhibited slightly lower strength than the uncoated ones.

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http://dx.doi.org/10.1016/j.msea.2017.03.049
Received 25 October 2016; Received in revised form 10 March 2017; Accepted 12 March 2017

2. Experimental methods

Zr-based BMG ($Zr_{50.7}Cu_{28}Ni_9Al_{12.3}$) ingots were prepared by arc melting the mixture of high-purity (above 99.9%) metal compositions in a Ti-gettered argon atmosphere. Rectangular plates with dimensions of 35 mm×10 mm×2.0 mm were cut from 40 mm×35 mm×2.0 mm dimensional ingots. The two surfaces with a maximum in-plane area of 35 mm×10 mm of selected plates were mechanically grinded, polished to a mirror finish (The final dimensions of the plates were 35 mm×10 mm×1.5 mm), and then coated with amorphous $Cu_{50}Zr_{50}$ (or crystalline W) thin films (~100 nm in thickness) via magnetron sputtering to form sandwich samples. Subsequently, both the as-cast and the coated BMGs were annealed at 573 K for 3 h in a vacuum furnace (~10^{-5} Pa) and eventually cooled down to room temperature in vacuum for more than 24 h. Thence, the six different kinds of samples, i.e., as-cast BMG, annealed BMG, as-deposited CuZr-coated BMG, annealed CuZr-coated BMG, as-deposited W-coated BMG and annealed W-coated BMG samples were termed hereafter as BMG$_{\text{as-cast}}$, BMG$_{\text{annealed}}$, CuZr/BMG/CuZr$_{\text{as-deposited}}$, CuZr/BMG/CuZr$_{\text{annealed}}$, W/BMG/W$_{\text{as-deposited}}$ and W/BMG/W$_{\text{annealed}}$, respectively.

The microstructure of each sample was characterized with X-ray diffraction (XRD-7000Shimadzu Corporation) and transmission electron microscopy (TEM, JEOL JEM-2100F). The energy disperse spectroscopy (EDS) equipped in the TEM was used to verify the composition of the samples. For each sample, the rectangular plate was cut into small compression specimens with identical dimensions of 1.5 mm×1.5 mm×3.0 mm. For each compression specimen, the lateral surfaces (except for the coated ones) were grinded and then polished using waterproof abrasive paper. Quasi-static uniaxial compression tests were conducted on a computer-controlled testing machine (SUNS CMT 5105) at room temperature, with a constant strain rate of 5.6×10^{-4} s^{-1}. At least three specimens were tested for each sample to ensure the reliability of experimental results. After each test, scanning electron microscopy (SEM, SU6600) was used to examine the fracture surface.

3. Results and discussion

The amorphous nature of BMG$_{\text{as-cast}}$, BMG$_{\text{annealed}}$, CuZr/BMG/CuZr$_{\text{as-deposited}}$ and CuZr/BMG/CuZr$_{\text{annealed}}$, as well as BMGs in W/BMG/W$_{\text{as-deposited}}$ and W/BMG/W$_{\text{annealed}}$ were verified by the XRD results shown in Fig. 1. Due to surface coating, the peak position of amorphous hump in the XRD pattern for these BMG samples had shifted, and the induced shifts were somewhat different between samples having amorphous CuZr and crystalline W coatings. No obvious difference could be observed in the XRD patterns between BMG$_{\text{as-cast}}$ and BMG$_{\text{annealed}}$, CuZr/BMG/CuZr$_{\text{as-deposited}}$ and CuZr/BMG/CuZr$_{\text{annealed}}$, as well as W/BMG/W$_{\text{as-deposited}}$ and W/BMG/W$_{\text{annealed}}$, which indicated that amorphous structures were maintained in all the coated and uncoated BMG samples after annealing treatment.

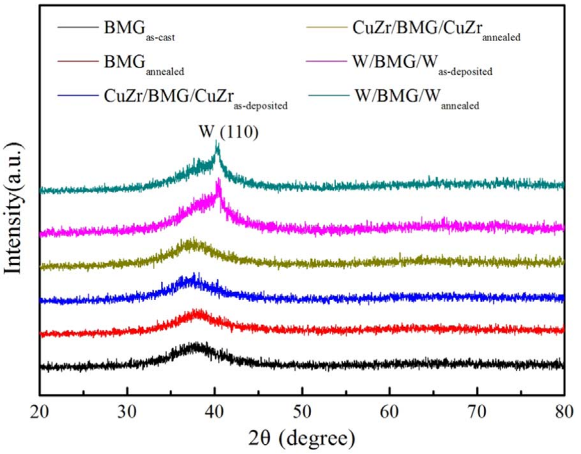

Fig. 1. XRD patterns of coated and uncoated BMG samples before and after annealing treatment.

Fig. 2 displayed the cross-sectional TEM images of amorphous CuZr coatings for CuZr/BMG/CuZr$_{\text{as-deposited}}$ and CuZr/BMG/CuZr$_{\text{annealed}}$, as well as crystalline W coatings for W/BMG/W$_{\text{as-deposited}}$ and W/BMG/W$_{\text{annealed}}$. No obvious difference could be observed between CuZr/BMG/CuZr$_{\text{annealed}}$ [Fig. 2(b)] and CuZr/BMG/CuZr$_{\text{as-deposited}}$ [Fig. 2(a)]. In contrast, compared to W/BMG/W$_{\text{as-deposited}}$ shown in Fig. 2(c), though no other obvious difference could be detected, detachment between crystalline W coating and BMG was observed in W/BMG/W$_{\text{annealed}}$ as indicated by the yellow arrow in Fig. 2(d). This should be induced by the mismatch of thermal expansion between the coating and the BMG [19].

Cross-sectional TEM images shown in Fig. 3 revealed the internal structure of each sample. In the presence of both amorphous CuZr and crystalline W coatings, the internal structure of the BMG sample remained almost unchanged, as similarly homogeneous structures were observed in BMG$_{\text{as-cast}}$ [Fig. 3(a)], CuZr/BMG/CuZr$_{\text{as-deposited}}$ [Fig. 3(b)] and W/BMG/W$_{\text{as-deposited}}$ [Fig. 3(c)]. Nonetheless, different extents of inhomogeneous structures were observed in these samples after annealing treatment. Particularly, BMG$_{\text{annealed}}$ [Fig. 3(d)] possessed the least inhomogeneous structure, in which tiny dark clusters (about several nanometers in diameter) were sparsely distributed, while CuZr/BMG/CuZr$_{\text{annealed}}$ [Fig. 3(e)] possessed slightly more inhomogeneous structure with sparsely distributed dark clusters (slightly larger, about a dozen nanometers in diameter). In sharp contrast, the most inhomogeneous structure was observed in W/BMG/W$_{\text{annealed}}$ [Fig. 3(f)], in which much larger dark clusters (about dozens of nanometers in diameter) were densely distributed. Note that the internal amorphous nature of the six samples was verified by the inset area diffraction (SAD) images, as no crystalline spot was observed in them, as well as the high resolution TEM (HRTEM) images. For typical instance, with reference to Fig. 3(f), the inset HRTEM image of the dark cluster as indicated by the rectangle exhibited no crystalline phase.

The contrast fluctuations in Fig. 3(d)–(f) could be attributed to elemental fluctuations. To explore this, EDS scanning was performed on 12 randomly selected points in Fig. 3(f): the yellow points 1–6 were located in the dark clusters while the blue points 7–12 were located in the bright regions. Relatively speaking, according to the results summarized in Table 1, the dark clusters were Cu-rich and the bright regions were Zr-rich. This indicated that, upon annealing, decomposition processes, i.e., formation of nano-scaled Zr- and Cu-rich regions, happened in all the coated and uncoated BMG samples. The result was in accord with many previous works [20–25], which showed that Zr-Cu based MGs had a strong tendency to decompose into Zr- and other element (e.g., Cu)-rich regions, since the decomposed state was more stable than the uniformly distributed state for Zr–Cu based MGs (i.e., the decomposition processes happened mainly due to the thermodynamic driving force to lower the system's Gibbs free energy). Furthermore, the decomposition processes were slightly enhanced by the amorphous CuZr coating, while significantly enhanced by the crystalline W coating. As the internal FV would run off from the uncoated BMG upon annealing [3,4] and FV might be a necessary condition for atom transport [26–28], the decomposition process in uncoated BMG should be suppressed by the running off of FV, resulting in the slightly inhomogeneous structure of BMG$_{\text{annealed}}$ [Fig. 3(d)].

In comparison, for the W-coated BMG, the crystalline coating could effectively inhibit the running off of FV from the BMG upon annealing [29], and the maintained FV would persistently contribute to atom transport, thus leading to the significant decomposition state in W/BMG/W$_{\text{annealed}}$ [Fig. 3(f)]. Besides, the persistent thermal stress in the W-coated BMG during annealing due to distinct thermal expansion mismatch between crystalline W and BMG [19] might also contribute