Oxidation induced ductility enhancement of Zr based metallic glass ribbons in vicinity of glass transition temperature

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Abstract: Zr-based metallic glasses (MGs) possess a wide supercooled liquid region, which gives a wide processing window for superplastic forming to make microdevices with demanding size accuracy and surface finishing. The existence of oxygen may have an influence on the thermoplastic deformation process. Therefore, the effect of oxidation on the mechanical behavior of the MGs in the vicinity of glass transition temperature is of great significance for practical forming of MG components. In the present study, the effect of oxidation on tensile properties of $Zr_{50}Cu_{40}Al_{10}$ metallic glass was investigated. The tested samples were characterized by XRD and SEM analysis. For the samples tested in air, the strength decreases 187 MPa, 61 MPa and 59 MPa and the ductility increases 0.31, 0.36, and 0.77 at 420 °C, 430 °C, and 440 °C, respectively, compared with those tested in flowing argon. ZrO_2 preferentially formed during the tensile testing at 420 °C, and both ZrO_2 and Al_2O_3 oxides formed at 430 °C. The dilution of Zr elements in the remaining amorphous matrix caused by preferential oxidation on the surface layer attributes to the decrease in strength and enhancement in ductility of the $Zr_{50}Cu_{40}Al_{10}$ metallic glasses.

Keywords: metallic glass; mechanical properties; tensile test; preferential oxidation; high temperature

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1 Introduction

Compared to traditional polycrystalline alloys, bulk metallic glasses (BMGs) exhibit unique physical, chemical, and mechanical properties and have attracted much attention for opening opportunities for fundamental research and practical engineering applications^[1-3]. Super plastic deformation could be achieved in the super cooled liquid region, therefore, metallic glasses are engaged to make sub-micrometer-sized gears^[4], linear actuators and other microdevices by high temperature near net shape forging^[5]. Open air forging is preferred if the oxygen in air has little deteriorative effect on the final products during the forming processes. Therefore,

it is necessary to investigate the mechanical behavior of BMGs at elevated temperatures from the point of processing consideration and practical applications.

Zr-based metallic glasses are one of the most promising alloy systems in MGs, as they possess high thermal stability, outstanding glass forming ability, a large supercooled liquid region and excellent mechanical properties. During the past decades, some studies on the oxidation of Zr-based glasses have been performed; yet the results were lack of consistency and sometimes controversial conclusions were proposed between different researchers^[6-8]. Köster et al.^[9] conducted the oxidation of a Zr-based bulk metallic glass (BMG) and its nanocrystalline counterpart and found that the oxidation kinetics could be influenced by the difference of the free enthalpy; glassy alloy has a much higher enthalpy than the crystalline alloy, thereby leading to faster oxidation kinetics. Other studies on the oxidation of Zr-Cu-Al^[10], Zr-Al-Ni^[11] and Zr-Al-Ni-Cu^[12] metallic glasses have concluded preferential oxidation of Zr and Al elements. Liu et al.^[13] studied the oxidation effect on mechanical properties of a $Zr_{64}Cu_{16}Ni_{10}Al_{10}$ BMG characterized by nano-indentation, wedge

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indentation and compression tests. It was shown that the oxidized Zr-based bulk metallic glass exhibited about 9% compression plasticity before failure. The results suggest that the Zr-based BMG still keeps the amorphous nature and its good mechanical properties after surface oxidation.

To date, most of the studies on the effect of oxidation on mechanical properties were carried out by compression or nano-indentation tests^[13, 14]. Compression or indentation has quite different deformation, crack propagation, and fracture mechanisms with tensile tests. However, the effect of oxidation on in situ tensile tests of amorphous alloys have seldom been studied.

In the present study, to elucidate the oxidation effects on mechanical properties and deformation behavior, the flowing Ar protection and air atmosphere tensile tests were carried out, respectively. To amplify the effect of oxidation on the mechanical behavior, amorphous ribbons, rather than bulk samples, were employed, since the oxidized layer would have a higher volume fraction of the whole sample.

2 Experimental procedure

Zr₅₀Cu₄₀Al₁₀ (at.%) master alloys were prepared by arc melting pure Zr, Cu, and Al elements in a Ti-gettered Ar atmosphere and remelted 4–5 times to ensure the composition homogeneity. Melt spinning was performed using a laboratory-scale single roller melt-spinner operated in a purified Ar atmosphere. The amorphous structure was identified by X-ray diffraction (XRD-7000 (S/L), Shimadzu). The initial thermal properties of the alloy were studied using a differential scanning calorimetry (DSC-1, Mettler Toledo) at a constant heating rate (20 K·min⁻¹). The samples with ~4 mm in width and 50 μm in thickness were used in the tensile tests. An electronic servo universal testing machine (WDW-1D, SUNS) equipped with an electric furnace with temperature accuracy of ±1 K and a pair of twin drum jigs was used for tensile tests, and the gauge length was set as 25 mm. The initial strain rate was set as 3.33×10⁻⁴ s⁻¹ at displacement control mode. High temperature tensile tests were carried out at two surrounding conditions, that is, in a purified flowing Ar protection or air atmosphere, respectively. The samples were heated to the preset temperature and held for 10 min before loading. The fracture surfaces of the samples were observed with a table scanning electron microscope (TM 3030, Hitachi).

3 Results

3.1 DSC characterization

As shown in Fig. 1, the DSC curve of the as-spun sample shows the glass transition temperature (T_g) of 428 °C and the onset of crystallization temperature (T_x) of 505 °C, providing a super-cooled liquid region of 77 °C. Therefore, the tensile testing temperatures in the vicinity of the T_g were set as 420 °C, 430 °C, 440 °C, respectively, to study the effect of oxidation at different temperatures on tensile property of Zr-based amorphous alloys.

Fig. 1: DSC curve of as-spun Zr₅₀Cu₄₀Al₁₀ metallic glass

3.2 Tensile test

The stress-strain curves of the tensile tests of Zr₅₀Cu₄₀Al₁₀ metallic glass, which were carried out in air and Ar atmosphere, at different temperatures are shown in Fig. 2. It shows that the fracture strength of the sample protected by flowing Ar is obviously higher than that tested in air at all corresponding testing temperatures, while the ductility decreases remarkably. The tensile strength is ~506 MPa and the corresponding fracture strain is ~0.103 in Ar at 420 °C. Under the same conditions except in air atmosphere, the strength decreases to ~319 MPa and the final strain increases to ~0.409. At 430 °C, the tensile strength is ~330 MPa and ~269 MPa in Ar and in air, respectively. The corresponding fracture strain is ~0.162 in Ar and ~0.518 in air. At 440 °C, the samples also show lower strength and larger fracture strain due to the oxidation exposed to air, as shown in Fig. 2(c). The strength is ~175 MPa and the final strain is ~0.296 in Ar, while the strength

Fig. 2: Tensile stress-strain curves of samples in air or Ar at different temperatures: (a) 420 °C; (b) 430 °C; (c) 440 °C

is ~116 MPa and the strain is ~1.066 in air. This indicates that the oxidation during high temperature testing enhances the ductility at all these temperatures, but reduces the strengths.

According to the above tensile stress-strain curves, tensile strengths and fracture strains are shown in Fig. 3. The tensile strength in air decreased 187, 61, 59 MPa at 420 °C, 430 °C and 440 °C, respectively, compared with that in Ar, indicating that the tensile strength is more sensitive to oxidation below the

glass transition temperature. Oxidation also affects the ductility of the amorphous materials at tensile conditions. At 420 °C, the fracture strain tested in air increases 0.31 compared with that in Ar. With the increase of temperature, the ability of oxidation-induced plasticity increases more remarkably, and the fracture strain increases 0.77 compared with that tested in Ar at 440 °C. Therefore, the plastic deformation ability of the tensile samples is more sensitive to oxidation above the glass transition temperature.

Fig. 3: Strength and final strain of $Zr_{50}Cu_{40}Al_{10}$ metallic glasses varies with temperature in air and Ar: (a) tensile strength; (b) fracture strain

Figure 4 exhibits the X-ray diffraction patterns for $Zr_{50}Cu_{40}Al_{10}$ samples after tensile tested in Ar and air and the as-spun specimen. The XRD profile of the as-spun sample shows an obvious broad peak, which confirms the amorphicity of the prepared alloy. It is clearly seen that a few small sharp diffraction peaks overlap on the broad hump for the samples tensile tested at 420 °C and 430 °C both in air and in Ar. These peaks are indexed as ZrO_2 and Al_2O_3 . No other metal oxides or intermetallics are detected. Only ZrO_2 diffraction peaks are found on the sample tested at 420 °C. For the sample tested at 430 °C, the intensity of ZrO_2 peaks is obviously stronger than those tested at 420 °C. And Al_2O_3 peaks which are absent at 420 °C are also detected for the samples tested at 430 °C. At 420 °C, the diffraction peaks tested in air are comparable with those tested in Ar. At 430 °C, the corresponding diffraction peaks tested in air are mostly higher than those tested in Ar, except that the second peak and the third peak of ZrO_2 are a little lower in air than those tested in Ar, which proves that flowing Ar protected the sample from oxidation to some extent. However, the samples could not be fully excluded from oxidation by the flowing Ar atmosphere, and oxidation may also occur after fracture due to opening the furnace. To further compare the oxidation severity of the samples tested in air and in Ar, the fracture surfaces of the samples tested in air or in Ar are characterized by using scanning electronic microscopy.

3.3 Fracture surface morphology

Fracture surfaces are shown in Fig. 5. It can be seen that oxides form at all the samples tested in air and Ar, which is consistent with the XRD results. But the widths of oxidized layers on the samples surface displayed by fracture cross section are quite different [as indicated in Fig. 5]. As shown in Figs. 5(a) and (b),

Fig. 4: XRD patterns for as-prepared, tensile tested $Zr_{50}Cu_{40}Al_{10}$ metallic glasses in air and Ar atmosphere

the single side width of oxides for the cross section of fracture surface is ~8.0 μm in the air and ~4.0 μm in Ar at 420 °C. At 430 °C, the whole fracture surface tested in air is covered by oxides; while the oxide layer tested in Ar is only about 6 μm . This further proves that the flowing Ar protection reduces the oxidation during the high temperature deformation and fracture processes, but the sample could not be completely protected from oxidation by flowing Ar.

As shown in Fig. 5, widths of the fracture cross section were measured to be 40.7 μm and 52.7 μm corresponding to those tested in air and in Ar atmosphere at 420 °C, respectively. And at 430 °C, the widths are 34.3 μm and 38.7 μm in air and Ar atmosphere, respectively. The reduction in cross section of the fracture surfaces is consistent with the ductility acquired from the tensile plastic deformation, as indicated in Fig. 2,

Fig. 5: SEM images of fracture surfaces of $Zr_{50}Cu_{40}Al_{10}$ metallic glass at different temperature: (a) 420 °C in air; (b) 420 °C in Ar; (c) 430 °C in air; (d) 430 °C in Ar

that is, higher plastic strain corresponds to smaller width of the fracture surface, except that the width of the sample tested in Ar at 420 °C is a little higher than the original thickness. The values less than 50 μm , which is the original width of the ribbon, are primarily due to plastic deformation and partially due to necking. The increase of the fracture cross section tested in air at 420 °C may be ascribed to oxides formation induced dilatation with limited plastic deformation.

The oxides distribution indicates the cracks initiate from both sides of the ribbons and propagate towards the center, rather than a single shear event through the whole cross section of the ribbon.

According to the SEM observation of the fracture surface, the flowing Ar atmosphere has an obvious protection for the sample from oxidation during tensile testing. The oxide layers tested in Ar are much thinner than those tested in air. The X-Ray scanned not only the top surface layer of the samples and the depth of atoms that X-ray interacted with producing diffraction pattern is in a range of several micrometers, so the obtained XRD profiles involve contributions of the top oxidized layer and some atoms beneath. The oxides on the top surface of the tested sample have an only partial influence on the diffraction peaks. Consequently, less differences of XRD profiles compared with SEM observations was observed for the samples tested in air and Ar at the same temperature.

4 Discussion

On the basis of the experimental results, it is clear that oxidation affects the tensile performance of $Zr_{50}Cu_{40}Al_{10}$ samples at temperatures near glass transition. The XRD results show that ZrO_2 starts to form below the glass transition temperature, and both ZrO_2 and Al_2O_3 form above the glass transition temperature. The oxides concentrate on the fracture surface of the sample, as shown in Fig. 5. Kai et al.^[12] studied the oxidation mechanism of the $Zr_{55}Cu_{30}Al_{10}Ni_5$ BMG alloy using a platinum marker and found that the marker was always located on the outside after oxidation. Therefore, they suggested that the oxidation of bulk metallic glass was mainly due to the inward diffusion of oxygen. In the present experiments, Zr and Al elements are preferentially oxidized to form corresponding oxides in oxygen diffusion mode. Oxidation vulnerability is related to the intrinsic properties of the components of the metallic glass. The physical parameters of component elements of the $Zr_{50}Cu_{40}Al_{10}$ metallic glass are summarized in Table 1. The data show that Zr and Al elements have lower electro negativity and are easier to bond with other elements with higher electro negativity. Barin^[15] et al. studied the heat of formation of different oxides at 600 K and found that the heat of formation of ZrO_2 and Al_2O_3 was much higher than those of Cu oxides. It indicates that Al and Zr elements are much easier to form corresponding oxides. The oxidation of Zr element often involves

Table 1: Properties of component elements in $Zr_{50}Al_{40}Cu_{10}$ metallic glass

Element	Surface binding energy (eV)	Electro negativity ^[21]	Oxide formula	Moh's hardness	Heat of formation at 600 K (kJ·mol ⁻¹) ^[15]
Zr	6.25	1.33	ZrO ₂	5	-1,094.97
Cu	3.49	1.9	CuO/Cu ₂ O	3.0	-154.01/-169.95
Al	3.39	1.50	Al ₂ O ₃	2.75	-1,675.35

a simultaneous dissolution of oxygen into the crystal lattice of Zr ^[16], which can promote the formation of the ZrO₂. In a recent study of ternary $Zr_{60}Al_{15}Ni_{25}$ metallic glass, Sun et al. ^[17] also found similar phenomena. During oxidation, the active elements of Zr and Al are preferentially oxidized, which is consistent with the current research. Louzguine-Luzgin et al. ^[18] studied the atomic structure, oxidation states and electrical conductivity of the naturally formed surface oxides on a Cu-Zr-Al BMG formed at ambient conditions. Their results showed that the naturally formed oxide layer on the BMG surface consists of the dominant Al₂O₃ and ZrO₂ amorphous oxides, which is also consistent with the present results.

According to the results of high temperature tensile tests, oxidation leads to a decrease in the strength of the $Zr_{60}Al_{15}Ni_{25}$ metallic glass, but significantly increases the ductility. The fracture strength is more sensitive to oxidation at 420 °C, which is decreased by 187 MPa due to oxidation. When the testing temperature is higher than the glass transition temperature ($T_g=428$ °C), the strength only descends ~60 MPa. Available experimental data already reveal that alloying of metallic elements could greatly influence glass formation and mechanical properties of metallic glasses ^[19]. In the present study, the XRD results show that ZrO₂ oxides are preferentially formed at 420 °C, which results in the decrease of Zr content in the residual amorphous matrix. As shown in Table 1, the Moh's hardness of Zr is higher than that of Cu and Al. During the oxidation process, the ZrO₂ formation dilutes the content of Zr in the amorphous matrix, which may consequently lead to the decrease of the strength of the residual amorphous matrix.

As shown in Fig. 4, the XRD intensity of ZrO₂ oxide phase at 430 °C is higher than that at 420 °C, indicating more Zr atoms precipitate from the matrix. When the testing temperature is above the glass transition temperature, the Al₂O₃ forms and the component Al element with the lowest hardness in the remaining amorphous is also oxidized. The Al dilution in the remaining amorphous matrix weakens the softening effect caused by ZrO₂ precipitation. Therefore, the tensile strength of samples in air decreased only 61 MPa at 430 °C, while the tensile strength decreased 187 MPa at 420 °C. Huang et al. ^[20] studied the mechanical properties of Al₈₇Gd₆Ni₇, Al₈₆Gd₆Ni₇Fe₁, and Al₈₆Gd₆Ni₇Co₁ amorphous alloys. It was found that the fracture strength of samples gradually increased to 1,050 MPa and 1,065 MPa after adding Fe and Co with higher the Moh's hardness to Al-Gd-Ni (950 MPa). It indicates that the addition of elements with larger Moh's hardness can effectively improve

the fracture strength of amorphous alloys. This is consistent with the results of the present study that the dilution of Zr with higher Moh's hardness softens the amorphous alloys.

According to Fig. 3(b), the preferential elemental oxidation leads to an obvious increase in the ductility. Generally speaking, the tendency of ductility and hardness (or strength) of an alloy is on the opposite direction. Improvement in strength induces lower ductility, and vice versa. The proportion of Al and Cu in the residual amorphous matrix increases with a large amount of Zr precipitates to form oxides, which downgrades the strength, but improves the tensile ductility.

The state of the oxide layer may also influence the strength of the materials. However, in the present study, the ZrO₂ layer formed during the lower (420 °C) temperature tensile testing is not in a dense state. Although Al₂O₃ layer in most commonly used Al alloys' surface is very dense and resistant to further oxidation, in the present testing environment, however, it comes to form later than ZrO₂, a dense layer is not expected due to the formation of hybrid oxides. Therefore, the oxide layer could hardly contribute to the strength of the alloy at high temperatures.

5 Conclusions

The oxidation seriously affects the high temperature mechanical properties of Zr-Cu-Al amorphous ribbons. The strength tested in air decreases compared with that tested in Ar, and the ductility remarkably increases. Compared with those tested in Ar protection, the strength of $Zr_{50}Cu_{40}Al_{10}$ amorphous ribbons decreases 187 MPa, 61 MPa and 59 MPa and the ductility increases 0.31, 0.36, and 0.77 tested in air at 420 °C, 430 °C and 440 °C, respectively. ZrO₂ preferentially forms during the tensile procedure at 420 °C, and both ZrO₂ and Al₂O₃ forms at 430 °C. The precipitation of Zr in the form of Zr dioxide leads to the dilution of higher Moh's hardness elements in the amorphous matrix, which is attributed to the improvement of ductility and decline of tensile strength.

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