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Abstract

The present investigation addresses surface hardening and the oxidation behavior of $(\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5)_{98}\text{Er}_2$ bulk-metallic glass (BMG) during gaseous oxidizing *below* the glass transition temperature ($<T_g$). The BMG was thermochemically surface engineered in controlled gaseous atmospheres imposing either an extremely low or an extremely high oxygen partial pressure. The hardened oxygen-containing case developing during oxidizing the BMG was characterized with X-ray diffraction, (electron) microscopy, energy dispersive spectroscopy and micro-hardness indentation. It was observed that oxidizing at a high p_{O_2} resulted in the formation of an internal and an external oxidized zone; the latter can be minimized by applying a low p_{O_2} . The inner oxide zone (IOZ) consisted mainly of a nano-crystalline dispersion of tetragonal ZrO_2 , while a porous CuO_x network developed in the outer oxide zone (OOZ). The formation of copper oxide islands at the surface is interpreted as the result of outward diffusion of metallic Cu driven by a compressive stress gradient in the IOZ caused by volume expansion associated with ZrO_2

(and Al_2O_3) formation. The results demonstrate that a hardened case (the IOZ) with a maximum hardness of ~12 GPa can be achieved. The depth distribution of oxygen is explained in terms of a concurrent crystallization of the BMG below T_g .

Key words: ZrCu-based bulk metallic glass; Internal and external oxidation; Oxidizing; Thermochemical treatment; Surface hardness

1. Introduction

Bulk metallic glasses (BMGs), have attracted considerable scientific and technological interest for their potential use in different functional and engineering applications, recognizing their peculiar combination of high strength and high elastic limit [1–9]. On the other hand, the application of BMGs is restricted by their intrinsic low fracture toughness [10–11]. Therefore, introducing appropriate techniques for enhancing the plasticity of these fragile materials is crucial with respect to their structural performance. Previously, efforts were reported to promote the plasticity of metallic glasses via altering their Poisson ratio (ν) [12–14] or synthesizing metallic glass composites with a precipitated second phases [15–20]. Despite, the significant improvements of the fracture toughness achieved by increasing the Poisson ratio or making amorphous matrix composites, it is of interest to develop a practical technique to improve metallic glass plasticity without changing their initial metallic composition and sacrificing their unique properties. Recently, several surface treatments [21] were investigated in order to enhance the surface toughness of metallic glasses by effectively mitigating the propagation of shear bands and crack nucleation at the surface. These surface modification techniques, including mechanical surface treatment [22–25], surface coating [26–28] and thermal surface treatment [29–30], prevent shear band propagation through the introduction of compressive residual stresses in the surface region.

Surface engineering by thermochemical treatment is widely applied to improve the performance of alloys and metals [31]. Thermochemical treatment entails changing the surface composition at elevated temperatures to obtain a hardened case, typically by the incorporation of interstitial elements. Low-temperature thermochemical surface treatment of metallic components can enhance the resistance against surface-initiated failure mechanisms, such as fatigue, wear and corrosion.

It is noted that, heretofore, several research activities have been performed to study the oxidation behavior of amorphous alloys in the air atmospheric conditions [32–35]. Nevertheless, thermochemical post-processing of metallic glasses in controlled oxidizing atmospheres has so far received limited attention. In this study, the low temperature surface hardening of $(\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5)_{98}\text{Er}_2$ BMG using gaseous oxidizing is investigated. It is anticipated that the presence of Zr and Al, which both have a high affinity for oxygen and a strongly negative Gibbs energy for oxide formation, enable the dissolution of an appreciable amount oxygen in the BMG, leading to a volume expansion that introduces compressive residual stress in the surface zone.

2. Materials and methods

As-cast Zr-based BMG with chemical composition $(\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5)_{98}\text{Er}_2$ (at.%) was provided by the Jiangxi Academy of sciences in China. The initial ingots were prepared using vacuum arc melting of high purity (99.9 wt. %) elemental constituents in a Ti-gettered argon atmosphere. The synthesized ingots were re-melted several times to ensure compositional homogeneity. The homogenous ingots were subsequently cast into $2 \times 10 \times 60 \text{ mm}^3$ plates using a copper mold casting method (Rapid Quench Machine System VF-RQT50, Makabe Co. Ltd. Japan). The glass transition (T_g) and the onset crystallization temperatures (T_x) were measured to

700 K and 740 K, respectively as determined by differential thermal analysis in a Netzsch STA 449C thermal analyzer for a heating rate of 10 K.min⁻¹ under a flow of argon at a flow rate of 50 cm³.min⁻¹. Gaseous oxidizing was carried out 10 K below the glass transition temperature in a proprietary gas mixture with either an extremely low ($p_{O_2}=10^{-26}$ bar) or an extremely high oxygen partial pressure ($p_{O_2}=1648$ bar). The oxygen partial pressures were realized chemically at a total gas pressure of 1 bar. Samples of 3×3×1 mm³ were treated for 4 and 16 hours at 690 K (i.e. 10 K lower than T_g) in a thermogravimetric analyzer (Netzsch STA 449 F3). The samples were carefully polished to 1 μm diamond and then cleaned with ethanol before thermochemical treatment. The amorphous and thermochemically oxidized samples were characterized with X-ray diffractometry (XRD) using a Bruker D8 Discover equipped with CuK_α radiation ($\lambda=0.15406$ nm). Diffractograms were recorded in the 2θ range 25°-90° (2θ) at a step size of 0.04° and a counting time of 8 s per step. The surface topography and the cross-section microstructure of the thermochemically oxidized samples were examined using scanning electron microscopy (SEM, JEOL JSM-5900) equipped with Oxford (Inca X-act) energy dispersive spectroscopy (EDS). The microstructure of the cross-section of the surface-treated BMG samples were investigated using a Neophot 32 (Zeiss, Jena) reflected light microscope. A JEOL 3000F transmission electron microscope (TEM) coupled with EDS detector was employed for supplementary characterization of the various zones formed in the oxidized BMG specimen treated at 690 K for 16 hr in a high p_{O_2} atmosphere. An electron transparent TEM foil was prepared using a FEI Helios Nanolab with focused ion beam (FIB) milling using Ga⁺ ions and an Omniprobe micro-manipulator. Initial rough FIB milling was carried out with a 30 kV ion beam acceleration voltage and 20 nA ion current. It should be noticed that the region of interest on the sample surface was protected from the excessive ion damage with the Pt-deposited layer. Thereafter, the lamella was lifted out

with the Omniprobe and then mounted to a TEM Cu grid. The thinning process was performed using an ion beam current of 90 pA-0.9 nA on both sides of the extracted lamella. Finally, a low acceleration voltage (2 kV) cleaning was done with a 24 pA ion beam current to remove the residual Ga^+ ion damage on the lamella. To evaluate the hardened case, Vickers micro-hardness indentations (standard E 384-17) were determined on the cross-section of the thermochemically oxidized samples, using a FutureTech FM-700 Vickers indenter with 5 gf load and a dwell time of 10 s.

3. Results and Interpretation

3.1. X-ray diffraction of as-cast and thermochemically oxidized BMG

The X-ray diffractograms of the as-cast $(\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5)_{98}\text{Er}_2$ BMG and the specimens thermochemically oxidized in low and high oxygen partial pressure are shown in Fig. 1. The as-cast material has a broad peak at $2\theta \approx 38^\circ$, indicating that it is amorphous without detectable crystalline phases. The XRD results exhibit that after isothermal heating at 690 K for 4 hr in a low oxygen partial pressure atmosphere, the amorphous phase devitrifies and forms crystalline Zr-Cu, Zr-Cu-Al and Zr-Ni intermetallic phases, while oxidation results in the formation of tetragonal- ZrO_2 (t- ZrO_2), which is ascribed to the high affinity of Zr for O. Prolonging the treatment to 16 hr, the intensity of t- ZrO_2 is amplified and only a small fraction of other crystalline phases can be detected. Evidently, the intermetallic compounds are located beyond the information depth of the applied X-rays. Further, the oxidation at a high chemical partial pressure of oxygen under identical isothermal heating condition leads to the formation of t- ZrO_2 and three types of copper oxides: CuO, Cu_2O , and Cu_4O_3 . Interestingly, in addition to the copper

oxides formed during the thermochemical treatment, also diffraction peaks of pure copper are distinguished in the diffractograms. For the specimens oxidized at high p_{O_2} , no intermetallic phases were found in the X-ray diffractogram, implying that the oxide layer is relatively thick as compared to the information depth of the applied X-radiation. From the intensity reduction of the main t-ZrO₂ peak ($2\theta \approx 30^\circ$) on prolonged oxidizing at high p_{O_2} atmosphere it is concluded that the amount of CuO_x at the surface increases with oxidizing time.

3.2. Cross-sectional hardness measurement

Microhardness-depth profiles obtained after oxidizing at 690 K for 4 hr and 16 hr in the thermogravimetric analyzer are given in Fig. 2. The effective case depths after oxidizing for 4 and 16 hr at low p_{O_2} are $\sim 2 \mu\text{m}$ and $\sim 10 \mu\text{m}$, respectively, while at high p_{O_2} case depths of $\sim 18 \mu\text{m}$ and $\sim 34 \mu\text{m}$ were reached (see dotted vertical lines in Fig. 2). The hardness of the treated BMG reaches approximately $\sim 12 \text{ GPa}$ close to the surface, and decreases gradually until it reaches a steep drop to the hardness value of the un-oxidized BMG at the case-to-core transition. Evidently, changing the oxygen partial pressure has a large influence on the thickness of the hardened case depth.

3.3. Microstructure characterization of the oxidized zones

Microscopical investigations were carried out on the BMG that was thermochemically oxidized at 690 K for 16 hr in a high p_{O_2} atmosphere. A secondary electron micrograph of the surface topography is presented in Fig. 3a. A gray porous oxide network appears to cover the surface. The chemical composition of the oxide network was probed with EDS point-to-point analyses

and showed copper and oxygen, while other elements were virtually absent, indicating that the porous oxide network is formed by copper oxides. A light-optical image of a cross-section over the hardened case is provided in Fig. 3b and shows the presence of island-like (Cu/CuO) particles lying on the top of the sample surface. Also, a Cu-colored line directed perpendicularly to the surface is identified (see white arrow). This feature is interpreted as a Cu-filled crack (see discussion). For further cross-sectional inspection of the oxidized $(\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5)_{98}\text{Er}_2$ BMG Fig. 3c shows a back-scatter electron (BSE) micrograph and Fig. 3d EDS maps of the area marked in Fig. 3c. In addition, Fig. 3e shows composition-depth profiles determined with EDS. In the quantification of these profiles only the metallic components were considered, while the oxygen profile represents oxygen intensity relative to the maximum value. In Fig. 3c-3e, the case is subdivided in an inner oxide zone (IOZ) and an outer oxide zone (OOZ), based on the fraction of Cu revealed by EDS. The OOZ consists of island-like particles lying on the surface and of the top surface of the sample, appearing dark in Fig. 3c. Additionally, the IOZ is subdivided in three distinct zones denoted as I, II and III. The EDS results (Figs. 3d-e) show that the OOZ only contains copper and some oxygen. In the entire IOZ, the oxygen content decreases gradually while zirconium and aluminum are more or less homogeneously distributed. It is anticipated that the trend of increasing Zr and Al contents towards the surface in the IOZ, is a consequence of changes in density caused by internal oxidation and omitting O in the quantification of the EDS intensities of the metallic components. Zones I and II in the IOZ are closest to the surface and are depleted in copper. A sharp discontinuity in the Cu and Ni contents marks the transition between zones II and III in the EDS profile (marked by white arrow in Ni map). The oxygen content is highest in zone I and slightly lower (and constant) in zone II. In zone III the oxygen content shows a maximum at the location where the Cu content goes through a minimum and thereafter

decreases with distance to the surface. Along with the decrease in oxygen content the BSE micrograph in Fig. 3c becomes brighter, indicating an increase in atomic density. The gradient in oxygen content is interpreted as a reduction of the amount of Zr (and Al) available for internal oxide formation, because of the development of intermetallic compounds of Zr and Al prior to the arrival of oxygen. Although oxide formation eventually will prevail thermodynamically, the nucleation of ZrO_2 is likely to be delayed, because i) the driving force for oxide formation is reduced if Zr is present in an intermetallic compound and ii) the reduction in free volume associated with devitrification and crystallization enhances strain energy evoked by internal oxidation. The transition from IOZ to oxygen-free BMG is very sharp, consistent with a sharp case-core transition in the hardness profile in Fig. 2b.

Another feature observed in the cross-section BSE micrograph in Fig. 3c is the presence of cracks perpendicular to the surface in zone I (dark lines marked by white arrows). Such cracks hint at a tensile stress imposed onto zone I.

Cross-sectional TEM bright-field images and their corresponding selected area electron diffraction (SAED) patterns are shown in Fig. 4 for the OOI and in zone II of the IOZ. Closest to the surface the SAED patterns show the presence of monoclinic CuO and tetragonal Cu_4O_3 , while zone I in the IOZ contains nano-crystalline t- ZrO_2 .

4. Discussion

The results obtained on oxidizing $(\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5)_{98}\text{Er}_2$ BMG at a temperature below T_g show that the incorporation of oxygen leads to the development of an IOZ consisting of nano-crystalline t- ZrO_2 within the BMG and an OOI consisting of Cu-based oxides. Although the

oxidizing temperature was chosen 10 K below T_g , the development of crystalline intermetallic phases was observed for the sample oxidized at a low p_{O_2} for 4h, where the thinnest IOZ has developed. It is likely that such crystallization also occurred for the other oxidizing condition, but it remained unobserved because of the limited information depth of the applied X-radiation. Nevertheless, under the present oxidizing conditions the developing IOZ is the result of a competition between the crystallization of intermetallic compounds and internal oxidation of strong oxide forming alloying elements.

The strongest oxide formers in the investigated BMG are Zr and Al. The Gibbs energy for oxide formation (per mol O_2) is slightly more negative for ZrO_2 than for Al_2O_3 . Hence, for the present BMG, which contains ~55 at.% Zr and ~10 at.% Al, ZrO_2 is the thermodynamically most stable oxide, which could explain why it is the only oxide present after oxidation at a low p_{O_2} for 4h (Fig. 1). As no indications for the development of Al_2O_3 were found, not even after prolonged oxidation or at higher p_{O_2} , it is concluded that Al_2O_3 is either amorphous or it is dissolved in ZrO_2 [36].

The case depth of the IOZ was observed to depend strongly on the p_{O_2} in the oxidizing gas (Fig. 2 and section 3.2). For the low p_{O_2} , the hardened case depth is increased about 4 times on prolonging the oxidizing treatment by a factor 4; for the high p_{O_2} , the hardened case depth is about doubled when the duration is quadrupled. These observations suggest that for the oxidizing conditions at low p_{O_2} , growth of the case depth (the IOZ) is not diffusion controlled, but rather controlled by the surface reaction, i.e. the transfer of oxygen from the gas to the solid. On the other hand, the observations for the high p_{O_2} are consistent with diffusion-controlled growth of

the IOZ. The diffusing species that governs the thickness of the IOZ for the high p_{O_2} is most likely atomic oxygen.

The development of an OOOZ consisting of Cu-based oxides and a redistribution of Cu in the IOZ (especially zones I and II) is explained as follows. The development of nano-crystalline t-ZrO₂ in the IOZ leads to a volume expansion. This volume expansion is accommodated by compressive stress in the IOZ, which leads to a higher chemical potential for the components in IOZ than in the unaffected regions, i.e. the surface and the interior of the BMG. Consequently, a driving force for diffusion out of the IOZ is established and those components which are not bound to oxides, mainly Cu and Ni, will diffuse out of the IOZ. For oxidizing at high p_{O_2} the Cu arriving at the surface will oxidize to Cu-oxide and develop the porous network that forms the OOOZ, while Cu does not oxidize at low p_{O_2} . Also the observation of metallic Cu in microcracks can be explained by the outward diffusion of Cu towards a free (crack) surface (Fig. 3b). If no oxidation occurs of Cu it implies that the local p_{O_2} is not sufficiently high to stabilize Cu-oxide. Thus, microcracks can in principle be “repaired” by this self-healing mechanism. This phenomenon has also been recently reported for air-oxidation of the noble-metal containing Zr-based BMG by the present authors [37].

The development of micro-cracks perpendicular to the surface was only observed in zone I of the IOZ, and indicates that tensile stresses have been present in this region. In order to understand how these tensile stresses were introduced in zone I of the IOZ it is important to explain the subdivision of the IOZ in zones I, II and III. The subdivision is most likely associated with the competition between internal oxidation and the nucleation of intermetallic compounds and devitrification in the core. Clearly, the volume changes in the various zones

within the IOZ will be different. Apparently, zone I has experienced a volume expansion imposed by the underlying zones II and III while they expanded on internal oxidation. This is suggested to be caused as follows. Presuming that no intermetallic compounds formed in zone I prior to internal oxidation of Zr (and Al), the devitrification deeper in the material will lead to additional compressive stress imposed onto zone I, resulting in an additional flux of Cu out of this region to comply with these stresses and reduce them. Then, on subsequent formation of ZrO_2 deeper in the (partly) devitrified and crystallized BMG, the occurring volume expansion leads to imposing tensile straining of zone I, causing crack initiation perpendicular to the surface.

Obviously, the hardness profiles in Fig. 2 correlate with the oxygen content in the IOZ (Fig. 3e). The highest oxygen content corresponds to the highest hardness in zone I. In zone II the hardness is constant at about 1060 HV, while the hardness decreases gradually in zone III along with the reduction in oxygen content, to fall abruptly at the transition from IOZ to oxygen-free alloy.

5. Conclusion

The effect of gaseous oxidizing as a thermochemical treatment of $(\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5)_{98}\text{Er}_2$ BMG below the glass transition temperature (T_g) was investigated for different treatment durations in low and high oxygen partial pressure (p_{O_2}). It was demonstrated that for oxidizing at a low oxygen pressure internal oxidation of Zr to tetragonal ZrO_2 occurs in competition with crystallization of the BMG, despite an oxidizing temperature below T_g . The growth kinetics of the inner oxide zone (IOZ) for low p_{O_2} appears to be linear, suggesting that the oxygen transfer to the BMG is rate determining. For high p_{O_2} two different oxide zones formed at the surface: an outer oxide zone (OOZ) consisting of porous CuO_x islands and an IOZ which is subdivided in

three subzones. The presence of copper oxides in the OOO is attributed to the outward diffusion of copper from the inner oxide zone as a result of compressive growth stresses induced by the formation of ZrO_2 . The subdivision of the IOZ is suggested to be the outcome of the competition between internal oxidation of Zr (and Al) and devitrification and crystallization of the BMG. Parabolic growth kinetics of the IOZ appears to apply, indicating (oxygen) diffusion controlled growth.

The dissolution of oxygen into the MG substrate effectively enhances the surface hardness by forming the ZrO_2 in the IOZ. The hardness in the oxygen-containing case increased significantly from approximately ~ 600 HV in the core of un-oxidized BMG to ~1200 HV.

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Figure captions:

Figure 1. The X-ray diffractograms of the as-cast and thermochemically oxidized $(\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5)_{98}\text{Er}_2$ (at.%) BMG.

Figure 2. Microhardness profiles as a function of depth for $(\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5)_{98}\text{Er}_2$ BMG thermochemically oxidized at 690 K for 4 and 16 hr in (a) low (b) high oxygen partial pressure atmospheres (p_{O_2}).

Figure 3. (a) Secondary electron (SE) micrograph of surface morphology of $(\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5)_{98}\text{Er}_2$ BMG thermochemically oxidized at 690 K for 16 hr in high p_{O_2} atmosphere; (b) Optical image of the cross-section view demonstrating a self-healed microcrack with metallic Cu; (c) Cross-sectional BSE micrograph of the oxide zones formed on $(\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5)_{98}\text{Er}_2$ BMG after oxidizing treatment at 690 K for 16 hr (d) EDS mapping of

1 the selected area in c; (e) atomic fraction of metallic components (left vertical scale) and
2 oxygen intensity profile (right vertical scale).

3 Figure 4. Cross-sectional TEM bright-field image of thermochemically oxidized
4 $(\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5)_{98}\text{Er}_2$ BMG after applying the treatment at 690 K for 16 hr and their typical
5 corresponding SAED patterns which have been obtained from different positions: (a) position 1
6 (b) position 2 (c) position 3.

7

Highlights

1. Surface hardness of Zr-based BMG can be enhanced by oxidizing treatment below T_g .
2. Oxygen dissolution in BMG (high p_{O_2}) results in the formation of two oxide zones.
3. CuO_x formation is ascribed to outward stress-induced diffusion of Cu.
4. The growth of the inner oxide zone is accompanied by the partial devitrification.