Oxidation of a $\text{Zr}_{46}\text{Cu}_{46}\text{Al}_7\text{Gd}_1$ bulk metallic glass detected *via* optical characterizations

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ABSTRACT Oxidation of metallic glasses has been shown to be different from crystalline alloys due to the disordered atomic structures and far-from-equilibrium state, and quick characterization is required to reveal their early stage oxidation. In this study, we investigated the oxidation behavior of a $\text{Zr}_{46}\text{Cu}_{46}\text{Al}_7\text{Gd}_1$ bulk metallic glass by measuring the changes of optical constants *via* spectroscopic ellipsometry. Characterizations with X-ray diffraction, scanning electron microscopy, and thermogravimetric analyzer confirmed that the changes of pseudo-optical constants reflected not only the onset temperature at which the alloys underwent obvious oxidation, but also the subtle oxidation which was tedious to characterize. Our study suggests a more efficient and accurate approach to understand the oxidation of metallic glasses with temperature, time and compositions.

Keywords: metallic glasses, spectroscopic ellipsometry, oxidation

INTRODUCTION

Bulk metallic glasses (BMGs) have attracted great interests both fundamentally and technologically owing to their remarkable properties including high strength, high hardness [1], remarkable corrosion resistance [2], unique thermoplastic forming ability [3], and catalytic activity [4]. These properties make BMGs potential candidates in areas such as clean energy, aerospace, coating, biomedical instruments, and even as high temperature structural materials [1,5–9].

Due to the high chemical activity of metals, oxide layer can form on the surfaces of BMGs [10,11], which leads to the variation in mechanical, physical, and chemical properties. On one hand, oxidation has to be avoided in

many applications to prevent degradation of components [10]. On the other hand, it has been found that the oxide layer can be helpful for enhanced properties, in particular, for the strengthening of micro devices, because it can prevent the micro devices from failure upon friction [12–14]. Therefore, understanding the oxidation behavior of BMGs is critical and will be helpful for the control of oxidation process.

Typically, thermogravimetric analysis (TGA), X-ray diffraction (XRD), and transmission electron microscopy (TEM) are the most widely used methods to characterize the oxidation of BMGs [10]. However, these methods are either time consuming or incapable to capture the process of early stage oxidation. Approaches that can quickly and precisely identify oxidation are thus required, because BMGs exhibit more complex oxidation behavior arising from their non-equilibrium structure. Optical characterizations have been proven to be valid for the identification of oxide phases in Ni–Al–Cr alloys [15]. Compared with crystalline materials, metallic glasses are structurally homogeneous without grain boundaries or dislocations [16], which makes it convenient to perform spectroscopic ellipsometry (SE) measurements.

In this study, we use SE to study the oxidation of a $\text{Zr}_{46}\text{Cu}_{46}\text{Al}_7\text{Gd}_1$ BMG by measuring the polarization of the light reflected from the surface, which is fast, non-contact and precise. We found that the optical constants can capture early stage oxidation that is beyond the resolution of XRD, and their changes exhibit a tendency similar to TGA so that the onset temperature where the BMG undergoes significant oxidation can be precisely identified. Our study indicates that SE measurements can

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be potentially used for fast characterization of BMG oxidation, which benefits not only controlled formation of oxide layer, but also the development of oxidation resistant BMGs within a vast number of alloys by high-throughput experiments.

EXPERIMENTAL SECTION

The ingots with a nominal composition of $\text{Zr}_{46}\text{Cu}_{46}\text{Al}_7\text{Gd}_1$ were prepared by arc-melting a mixture of pure Zr (99.9%), Cu (99.9%), Al (99.9%) and Gd (99.9%) in argon atmosphere. Copper-mould suction casting was used to fabricate rod samples with a diameter of 5 mm. The rods were then cut into discs of thickness of 1.43 mm and polished to mirror-surface. The discs were annealed in air for 10 min at different temperatures ranging from 130 to 410°C. The amorphous nature of the samples and oxide phases formed after annealing were identified with a Bruker D8 X-ray diffractometer using Cu K α ($\lambda=0.15406$ nm) radiation. The thermal properties of the samples were measured with differential scanning calorimetry (DSC; TA DSC8000) at a heating rate of 20°C min⁻¹. The glass transition temperature, T_g and crystallization temperature, T_x , of the $\text{Zr}_{46}\text{Cu}_{46}\text{Al}_7\text{Gd}_1$ BMG were measured to be 423 and 490°C, respectively. Mass changes upon annealing were measured by using TGA (MT GC301) at a heating rate of 5 K min⁻¹. Morphology characterizations were performed by using scanning electron microscopy (SEM; Phenom XL), and chemical analyses were performed by using energy dispersive X-ray spectrum attached to the SEM. SE (J.A. Woollam RC2-XI) experiments were carried out to measure the optical constants. Upon oxidization, the changes in the value of ellipsometric parameters, Ψ and Δ , were detected in air by SE at incidence angles of 70° in the wavelength range of 200–2500 nm as a function of annealing temperature. The interval was 1 nm at short wavelength and 6 nm at long wavelength. The pseudo-optical constants were determined through the calculation of Ψ and Δ using B-spline method. Nineteen knots were chosen with a spacing of 0.3 eV in the measured range when the Kramers-Kronig relation was used to ensure a physical solution and to reduce the number of fitting parameters. In the calculation, the extinction coefficient, k , was kept to be non-negative. The calculation was performed using the commercial software installed in the SE instrument (Complete EASE 5.26 from J. A. Woollam Co., Inc.).

RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of the as-prepared Zr_{46} -

Figure 1 XRD patterns of $\text{Zr}_{46}\text{Cu}_{46}\text{Al}_7\text{Gd}_1$ BMGs upon different annealing temperatures.

$\text{Cu}_{46}\text{Al}_7\text{Gd}_1$ BMG along with those annealed at different temperatures in air. The XRD patterns only exhibit broad humps when the annealing temperature is lower than 350°C, indicating that the samples remain amorphous and no crystalline oxides can be detected. However, obvious Bragg peaks appear in the XRD spectra for the samples annealed at 380 and 410°C. Because the annealing temperatures are all below T_g and the annealing time is only 10 min, the peaks are not derived from the crystallization of BMG. Instead, they indicate the formed oxides that are mainly composed of ZrO_2 . This is confirmed by the XRD spectra after the oxide layer is removed (see Fig. 1).

In Fig. 2, obvious color change of the samples annealed under different temperatures can be seen with increasing annealing temperatures, even below 380°C. This indicates that the samples annealed below 380°C had experienced oxidation, but the behavior was beyond the resolution of XRD characterizations, probably because only a thin layer of oxide had formed or the oxide was amorphous [10]. However, the change of color implies the variation in

Figure 2 Appearances of the $Zr_{46}Cu_{46}Al_7Gd_1$ BMG samples annealed at different temperatures in air for 10 min.

optical properties upon oxidation, which may reflect the degree of oxidation. We therefore measured the pseudo-optical constants by using SE. For simplicity, the dielectric function of alloys is assumed to be unchanged below T_g . As an example to show the variation of optical properties upon oxidation, Fig. 3 displays the changes of the refractive index, n , as a function of annealing temperature. It can be seen that the curves exhibit similar shapes when the annealing temperature is lower than 350°C, i.e., a clear valley around the wavelength of 400 nm followed by monotonic increase above the wavelength of 500 nm. However, distinctly different curve shapes can be seen when the annealing temperature is higher than 350°C. The valley around 400 nm rises sharply and a broad peak occurs at the wavelength around 550 nm. These differences indicate significant changes in optical properties of the BMG annealed above 350°C, suggesting that the oxidation process is detectable with SE.

We chose the optical constants at the wavelength of 700 nm for further analyses, by which the tendency of oxidation with the increase of annealing temperature can

Figure 3 Refractive index n as a function of wavelength for samples annealed at different temperatures.

Figure 4 The evolution of (a) reflectivity R ; (b) index of reflection n ; (c) extinction coefficient k ; (d) mass change; (e) oxygen content with annealing temperatures. The optical constants of the unannealed sample were plotted at 20°C.

be quantitatively revealed. As shown in Fig. 4a–c, although reflectivity, R , remains nearly constant, both refractive index, n , and extinction coefficient, k gradually decrease, suggesting incremental oxidation with the increase of annealing temperatures even below 350°C. However, such oxidation behavior cannot be identified by the XRD patterns which are featured by broad humps and indistinguishable from each other. Above 350°C, abrupt changes take place for all optical constants, i.e., both reflectivity and extinction coefficient significantly decrease,

while refractive index increases, indicating that significant oxidation has taken place. Therefore, from the variation of optical constants, the temperature where significant oxidation happens can be identified to be between 310–350°C.

To confirm that the evolution in optical constants reflects the oxidation process of the BMG, we measured the mass changes with annealing temperatures by using TGA. As shown in Fig. 4d, below 350°C, the mass gain only slightly increases with the increment of temperature, but substantial mass gain takes place around 350°C. The behavior is well consistent with the variation of reflectivity, refractive index, and extinction coefficient, demonstrating that optical constants are capable to reveal the tendency of oxidation. We also measured the oxygen content of the annealed BMGs *via* EDX. As shown in Fig. 4e, only subtle increase in the amount of oxygen can be observed below 350°C. However, the oxygen content exhibits a drastic increase above 350°C, indicating the acceleration of oxidation at high temperatures. It should be mentioned that the measured oxygen content is only for qualitative analysis. The tendency in oxygen content with annealing temperatures is similar to that of reflectivity, refractive index, and extinction coefficient, confirming the feasibility of using optical constants to characterize the early stage oxidation of the BMG. In Fig. 5, we plot the evolution of reflectivity, refractive index, and extinction coefficient at different wavelengths. The overall tendency of the optical constants with the increasing annealing temperature is similar for the wavelength of 500, 700, 1300, 1700 nm, indicating that the variation tendency of optical constants is independent on the wavelength selected to obtain the onset temperature of significant oxidation.

The changes of optical constants for the BMG are accompanied with the evolution in surface morphologies upon oxidation. As shown in Fig. 6, the sample annealed at 190°C displays a featureless surface (Fig. 6a). This suggests that oxidation is not obvious at low annealing temperature, consistent with the results of XRD, TGA, and SE measurements. With the increase of annealing temperature, some particles appear on the surface (Fig. 6b) and the number of such particles significantly increases when the annealing temperature is above 350°C (Fig. 6c). We found that Gd can only be detected in the particles, indicating that the oxidation process of the $\text{Zr}_{46}\text{Cu}_{46}\text{Al}_7\text{Gd}_1$ BMG includes the formation of homogeneous ZrO_2 layer and inhomogeneous formation of Gd oxide. However, the Gd oxide cannot be revealed by XRD characterization because of the low content of Gd in the

Figure 5 (a) Oxidation-induced changes in reflectivity, R , (b) refractive index, n , and (c) extinction coefficient, k , calculated with the wavelength of 500, 700, 1300 and 1700 nm, respectively.

studied BMG. From the evolution of surface morphologies, it can be seen that both the formation sequence of oxides and oxidation kinetics are temperature-dependent. Although the oxygen affinity of Gd is the highest among the constituent elements [10,17,18], the formation of Gd oxide may require long-range diffusion that prevents its formation at lower temperature. Therefore, Zr is easier to react with oxygen to form ZrO_2 layer over the surface by inward diffusion of oxygen [19–21].

It is known that the thickness increase of oxide layer has a positive correlation with oxidation rate constant obeying the Arrhenius law: $k = k_0 \exp(-Q/k_B T)$, where k_0 is a constant, k_B is the Boltzmann factor and Q is the activation energy related to diffusion pathway [22]. As ex-

Figure 6 Evolution of surface morphologies of $\text{Zr}_{46}\text{Cu}_{46}\text{Al}_7\text{Gd}_1$ after annealing at (a) 190°C; (b) 310°C; (c) 380°C. The rectangles in the images indicate the regions where compositional mapping by EDS was performed.

pected, the increased annealing temperature will result in increased thickness of oxide layer. Therefore, the pseudo-optical constants obtained in this study reflect the coupled effect of both MG substrate and oxide layer. At the early stage of oxidation when the annealing temperature is relatively low, e.g., < 350°C, the measured optical constants are dominated by the BMG substrate, but are gradually influenced by the oxide film with the increase of oxide thickness. When the temperature is higher than 350°C, the oxide film becomes thick enough and can substantially affect optical properties. As shown in Fig. 6, the surface of the oxide layer becomes rougher at higher annealing temperature, which can also influence the optical constants. The drastic change of refractive index n , extinction coefficient k , and reflectivity R can be ascribed to the combined effect of thickness-induced energy absorption during light propagation and surface roughness-induced light scattering.

Estimation according to Fig. 4 indicates that the variation of refractive index n , extinction coefficient k , reflectivity R , and mass change for the sample annealed at 310°C relative to the unannealed sample is ~21%, ~10%, ~0.6% and ~0.006%, respectively. This suggests that refractive index n is very sensitive to early stage oxidation of the BMG. Therefore, the optical constants, in particular, refractive index, can be adopted as a fast probe with high sensitivity to detect oxidation of BMGs, and also be extended as a high-throughput characterization approach to map oxidation behavior of many glass forming alloys within a combinatorial materials library [1,15,23].

CONCLUSION

In conclusion, the oxidation of a $\text{Zr}_{46}\text{Cu}_{46}\text{Al}_7\text{Gd}_1$ BMG was studied using SE combined with XRD, SEM, and TGA. The pseudo-optical constants obtained by SE can well reflect the change of the oxygen content upon oxidation. Based on the variation of optical constants, the onset temperature at which the $\text{Zr}_{46}\text{Cu}_{46}\text{Al}_7\text{Gd}_1$ BMGs undergo significant oxidation is determined to be in the

range of 310–350°C, consistent with the information derived from mass change. Compared with XRD and TGA, the SE characterization exhibits much higher sensitivity and the formation of thin oxide layer at the initial stage of oxidation can be detected. Our results indicate that the optical constants, in particular, refractive index, is a fast probe to study the BMG oxidation. Paired with combinatorial fabrication, SE can be potentially extended as a high-throughput characterization approach to map oxidation of many alloys within a vast compositional space.

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- 1 Li MX, Zhao SF, Lu Z, *et al.* High-temperature bulk metallic glasses developed by combinatorial methods. *Nature*, 2019, 569: 99–103
- 2 Gerard AY, Lutton K, Lucente A, *et al.* Progress in understanding the origins of excellent corrosion resistance in metallic alloys: From binary polycrystalline alloys to metallic glasses and high entropy alloys. *Corrosion*, 2020, 76: 485–499
- 3 Kumar G, Tang HX, Schroers J. Nanomoulding with amorphous metals. *Nature*, 2009, 457: 868–872
- 4 Wang Z, Li M, Yu J, *et al.* Low-iridium-content IrNiTa metallic glass films as intrinsically active catalysts for hydrogen evolution reaction. *Adv Mater*, 2020, 32: 1906384
- 5 Inoue A. Stabilization of metallic supercooled liquid and bulk amorphous alloys. *Acta Mater*, 2000, 48: 279–306
- 6 Inoue A, Nishiyama N. New bulk metallic glasses for applications as magnetic-sensing, chemical, and structural materials. *MRS Bull*, 2007, 32: 651–658
- 7 Inoue A, Kong FL, Zhu SL, *et al.* Multicomponent bulk metallic glasses with elevated-temperature resistance. *MRS Bull*, 2019, 44: 867–872
- 8 Li HF, Zheng YF. Recent advances in bulk metallic glasses for biomedical applications. *Acta Biomater*, 2016, 36: 1–20
- 9 Chu JP, Jang JSC, Huang JC, *et al.* Thin film metallic glasses: Unique properties and potential applications. *Thin Solid Films*, 2012, 520: 5097–5122
- 10 Xu Z, Xu Y, Zhang A, *et al.* Oxidation of amorphous alloys. *J Mater Sci Tech*, 2018, 34: 1977–2005
- 11 Louzguine-Luzgin DV, Chen CL, Lin LY, *et al.* Bulk metallic glassy surface native oxide: Its atomic structure, growth rate and electrical properties. *Acta Mater*, 2015, 97: 282–290
- 12 Chen X. Structure and hardness evolution of the scale of a Zr-based metallic glass during oxidation. *J Non-Cryst Solids*, 2013, 362: 140–146
- 13 Nie XP, Yang XH, Chen LY, *et al.* The effect of oxidation on the corrosion resistance and mechanical properties of a Zr-based metallic glass. *Corrosion Sci*, 2011, 53: 3557–3565
- 14 Kang SJ, Rittgen KT, Kwan SG, *et al.* Importance of surface oxide for the tribology of a Zr-based metallic glass. *Friction*, 2017, 5: 115–122
- 15 König D, Eberling C, Kieschnick M, *et al.* High-throughput investigation of the oxidation and phase constitution of thin-film Ni-Al-Cr materials libraries. *Adv Eng Mater*, 2015, 17: 1365–1373
- 16 Wang W. Roles of minor additions in formation and properties of bulk metallic glasses. *Prog Mater Sci*, 2007, 52: 540–596

- 17 Fu H, Wang H, Zhang H, *et al.* The effect of Gd addition on the glass-forming ability of Cu–Zr–Al alloy. *Scripta Mater*, 2006, 55: 147–150
- 18 Sharma SK, Strunskus T, Ladebusch H, *et al.* Surface oxidation of amorphous $\text{Zr}_{65}\text{Cu}_{17.5}\text{Ni}_{10}\text{Al}_{7.5}$ and $\text{Zr}_{46.75}\text{Ti}_{8.25}\text{Cu}_{7.5}\text{Ni}_{10}\text{Be}_{27.5}$. *Mater Sci Eng-A*, 2001, 304–306: 747–752
- 19 Liu L, Chan KC. Oxidation of $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$ bulk metallic glass in the glassy state and the supercooled liquid state. *Appl Phys A*, 2005, 80: 1737–1744
- 20 Wang B, Huang DY, Prud'homme N, *et al.* Diffusion mechanism of Zr-based metallic glass during oxidation under dry air. *Intermetallics*, 2012, 28: 102–107
- 21 Xu Y, Jeurgens LPH, Huang Y, *et al.* Effect of structural order on oxidation kinetics and oxide phase evolution of Al–Zr alloys. *Corrosion Sci*, 2020, 165: 108407
- 22 Tam CY, Shek CH. Oxidation behavior of $\text{Cu}_{60}\text{Zr}_{30}\text{Ti}_{10}$ bulk metallic glass. *J Mater Res*, 2005, 20: 1396–1403
- 23 Ding S, Liu Y, Li Y, *et al.* Combinatorial development of bulk metallic glasses. *Nat Mater*, 2014, 13: 494–500

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Author contributions Liu Y conceived and led the research; Wang C, Xie W and Li M designed the experiments; Cao J fabricated the samples; Xie W and Li M performed the experiments with the assistance from Hu L; Xie W, Li M and Wang C contributed to the analyses of data; Xie W, Wang C and Liu Y wrote the paper with the input from Wang W and Li M; All authors contributed to the general discussion.

Conflict of interest These authors declare no conflict of interest.

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$\text{Zr}_{46}\text{Cu}_{46}\text{Al}_7\text{Gd}_1$ 块体非晶合金氧化过程的光学表征

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摘要 相比于晶态合金, 非晶合金表现出显著不同的氧化行为, 其氧化过程受无序原子结构和非平衡状态的影响。为揭示非晶合金的早期氧化过程, 需要对其氧化行为进行快速表征。本文以 $\text{Zr}_{46}\text{Cu}_{46}\text{Al}_7\text{Gd}_1$ 块体非晶合金为对象, 通过测量光学常数的变化对氧化行为进行表征。与X射线衍射、扫描电子显微镜和热重分析测得的结果相比, 光学常数不仅可以反映非晶合金发生明显氧化的起始温度, 还可以反映难以用传统方法表征的早期氧化过程。本研究结果说明光学常数是反映氧化行为的灵敏参数, 将有助于认识非晶合金氧化过程随温度、时间和组分变化的演化过程。