Contents lists available at ScienceDirect



Journal of Materials Research and Technology

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



# Improvement of high-temperature wear resistance of Zr-based metallic glass by pre-oxidation treatment



Wenxue Wang<sup>a,1</sup>, Fei Sun<sup>b,1</sup>, Heting Zhang<sup>a</sup>, Jinbiao Huang<sup>a</sup>, Xiangyang Yu<sup>a</sup>, Jiang Ma<sup>a,c,\*</sup>

<sup>a</sup> Guangdong Key Laboratory of Electromagnetic Control and Intelligent Robots, Shenzhen University, Shenzhen, 518060, China

<sup>b</sup> Department of Materials Science and Engineering, Fujian University of Technology, 350118, Fuzhou, China

<sup>c</sup> Shenzhen Key Laboratory of High Performance Nontraditional Manufacturing, College of Mechatronics and Control Engineering, Shenzhen University, Shenzhen,

518060, China

### ARTICLE INFO

Handling Editor: P.Y. Chen

Keywords: Zr-based bulk metallic glasses Pre-oxidation treatment High-temperature wear resistance Wear mechanisms

# ABSTRACT

Zr-based bulk metallic glasses (BMGs) are promising for extensive industrial applications due to their superior mechanical properties, excellent glass formation ability (GFA), and low manufacturing costs. However, the wear resistance of Zr-based BMGs, especially when exposed to high-temperature service environments, is deficient and could lead to premature failure of critical components. Herein, we report an effective strategy that can significantly enhance the high-temperature wear resistance of Zr-based BMGs, referred to as pre-oxidation treatment (PT). At ambient temperature, the wear rate of the pristine Zr-based BMG samples was estimated to be ~173.7  $\times 10^{-6}$  mm<sup>3</sup> N<sup>-1</sup> m<sup>-1</sup>, whereas the PT samples subjected to the PT strategy showed no detectable volume loss. In addition, the wear rate of the PT samples at 250 °C was ~11.5  $\times 10^{-6}$  mm<sup>3</sup> N<sup>-1</sup> m<sup>-1</sup>. Intriguingly, even as the temperature surpassed the crystallization point of the BMG, the PT samples demonstrated a further enhancement in wear resistance, showcasing a wear rate of approximately ~7.29  $\times 10^{-6}$  mm<sup>3</sup> N<sup>-1</sup> m<sup>-1</sup>. Our work introduces a promising and convenient strategy to enhance the high-temperature wear resistance of Zr-based BMG components, thereby promoting their application in real-world engineering scenarios.

# 1. Introduction

Bulk Metallic glass (BMG) is a cutting-edge material with outstanding properties, such as superior strength, high hardness and excellent wear resistance [1–7]. Among which Zr-based BMGs are currently the most promising one to be used in engineering fields given their exceptional glass forming ability (GFA) and lower manufacturing costs [8–10]. These advantages enable them to prepare large-size BMG and widely employed in advanced scenarios [4,11–14]. For example, Zr-based BMGs are promising for application in the high-temperature precision molding of optical glass [15]. However, the wear resistance of Zr-based BMG is considered to be insufficient, especially in high-temperature environments [16]. The relatively low glass transition temperature ( $T_g$ ) leads to rapid failure of Zr-based BMG in high-temperatures for Zr-based BMG in high-temperatures region has both engineering significance and research interest.

Methods commonly used to improve the wear resistance of the metal

materials are various surface treatment techniques such as coatings [19–21], shot peening [22,23], ion nitriding [24,25], laser cladding [26, 27], oxidation treatments [28-33] and so on. Among those, oxidation treatment is a facile and low-cost surface treatment method, which can effectively enhance the wear resistance. Caron et al. performed nanoscale sliding wear experiments on pre- and post-annealed Ni<sub>62</sub>Nb<sub>38</sub> BMG and demonstrated the protective effect of thicker surface oxide layers against wear under multiple loads [34]. Jia et al. analyzed the wear mechanism of Zr-based BMG annealed under argon and oxygen atmospheres and found that oxidized Zr-based BMG exhibited the best wear resistance with increased hardness and stronger elastic recovery compared to pristine as-cast (AC) and structure-relaxed Zr-based BMG [35]. Zhou et al. reported that the thickness of the wear-resistant oxide layer of Zr-based BMG after oxidation treatment was increased by the addition of the rare earth element lutetium, which significantly enhanced the wear resistance of oxide-treated Zr-based BMG [36]. Many studies have been reported that the increased thickness of the oxide layer after oxide treatment can improve the wear resistance of BMG in

https://doi.org/10.1016/j.jmrt.2024.01.169

Received 18 December 2023; Received in revised form 5 January 2024; Accepted 18 January 2024 Available online 24 January 2024 2238-7854/© 2024 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/bync-nd/4.0/).

<sup>\*</sup> Corresponding author. Guangdong Key Laboratory of Electromagnetic Control and Intelligent Robots, Shenzhen University, Shenzhen, 518060, China. *E-mail address:* majiang@szu.edu.cn (J. Ma).

<sup>&</sup>lt;sup>1</sup> These authors contributed equally to this work.



**Fig. 1.** (a) Schematic of wear experiment. (b) As-cast (AC) sample with positioning notch. (c) XRD and DSC curves of the  $Zr_{55}Cu_{30}Ni_5Al_{10}$  BMG. (d) Weight versus temperature curve of  $Zr_{55}Cu_{30}Ni_5Al_{10}$  BMG in the air. (e) Pre-oxidation treatment (PT) sample with positioning notch. (f) Backscattering morphology of cross section of PT sample.

room temperature (RT) environments, however, the effect of oxide treatment on the wear performance of BMG in higher temperature environments has rarely been reported.

In this work, the wear resistance of Zr-based BMG (Zr<sub>55</sub>Cu<sub>30</sub>Ni<sub>5</sub>Al<sub>10</sub>) was demonstrated to be significantly enhanced over a wide temperature range through pre-oxidation treatment (PT). At RT, the wear rate of original sample without any pretreatment is ~173.7 × 10<sup>-6</sup> mm<sup>3</sup> N<sup>-1</sup> m<sup>-1</sup>, whereas there was no detectable volume loss of PT sample. Furthermore, at the temperature of 250 °C, the wear rates of the AC and PT samples are ~253.2 × 10<sup>-6</sup> mm<sup>3</sup> N<sup>-1</sup> m<sup>-1</sup> and ~11.5 × 10<sup>-6</sup> mm<sup>3</sup> N<sup>-1</sup> m<sup>-1</sup>, respectively. Notably, the AC and PT samples also exhibit excellent wear resistance even the temperature beyond the crystallization temperature of 500 °C is ~17.71 × 10<sup>-6</sup> mm<sup>3</sup> N<sup>-1</sup> m<sup>-1</sup> and ~7.29 × 10<sup>-6</sup> mm<sup>3</sup> N<sup>-1</sup> m<sup>-1</sup>, respectively.

## 2. Experimental

### 2.1. Sample preparation

 $Zr_{55}Cu_{30}Ni_5Al_{10}$  alloy ingots were synthesized by arc melting pure Zr (99.95 at.%), Cu (99.99 at.%), Ni (99.99 at.%) and Al (99.9 at.%) in a high-purity argon atmosphere. The ingot was melted in five iterations to ensure a homogeneous mixture of alloy composition. Zr-based BMG plates measuring 1.5 mm  $\times$  20 mm x 50 mm were fabricated via casting of the molten alloy ingot into a water-cooled copper mold. Using a low-speed wire electrical discharge machining (WEDM; SODICK AP250L), Zr-based BMG plates were processed into 11 mm diameter disks with a positioning notch, as depicted in Fig. 1b.

## 2.2. Characterizations

The amorphous property of AC and PT samples was analyzed using X-ray diffraction (XRD; Rigaku MiniFlex 600) with Cu K $\alpha$  radiation. In addition, the thermal characteristics of original Zr-based BMG were evaluated by differential scanning calorimetry (DSC; PerkinElmer DSC-8000) with a heating rate of 20 °C/min. The weight change of Zr-based

BMG upon heating in air was measured using a thermalgravimetric analyzer (TG; NETZSCH TG 209F3). The micro-structure and elemental distribution of wear experiment samples were analyzed using a field emission scanning electron microscope (SEM, FEI QUANTA FEG 450) with energy dispersive spectroscopy (EDS) capability. The volume loss after wear experiments was evaluated using a white light interference profiler (Bruker ContourGT-X 3D). The hardness and modulus of AC and PT samples were measured using a nanoindenter (TI750 Hysitron Ltd) with a maximum load of 10 mN.

## 2.3. Wear test

The surface of AC and PT samples were tested for dry sliding wear at different temperatures using a ball-on-disk tribometer (Rtec MFT-5000, USA) under air atmosphere, and a schematic of the wear experiment is shown in Fig. 1a. A commercially available zirconium dioxide (ZrO<sub>2</sub>) ball with a diameter of 9.5 mm and a hardness of roughly 14 GPa was chosen as the corresponding counterpart. The load of 3.5 N was applied to all the wear test samples and slid for 30 min at a wear radius of 3 mm and a fixed sliding speed of 100 rpm. The temperature of the wear experiments of AC and PT samples were set to RT, 250 °C and 500 °C to investigate the effect of PT on wear behavior of Zr-based BMG over a wide temperature region. The wear rate  $\omega$  of AC and PT samples after wear at different temperatures can be calculated by the following equation [16,37]:

$$\omega = \frac{V_{loss}}{P * L},\tag{1}$$

Where  $V_{\text{loss}}$  is the total wear volume loss (mm<sup>3</sup>), *P* is the applied normal load (N) and *L* is the total sliding distance (m).

## 3. Results and discussion

The XRD pattern and DSC curve of the original  $Zr_{55}Cu_{30}Ni_5Al_{10}$  BMG are shown in Fig. 1c. A broad diffraction peak can be observed in the XRD pattern, indicating that the as-cast Zr-based BMG is completely amorphous. Based on the DSC curve, it can be determined that the  $T_g$ 

#### Table 1

The statistics of coefficient of friction, cross-section area and wear rate of AC and PT samples at RT, 250  $^\circ C$  and 500  $^\circ C.$ 

Samples	Wear environment	Coefficient of friction	Cross- section area (µm <sup>2</sup> )	Wear rate ( $\times$ $10^{-6}\ mm^3$ $N^{-1}\ m^{-1}$ )
As-cast	RT	0.087	1824	173.7
	250 °C	0.124	2659	253.2
	500 °C	0.389	285	27.1
Pre-oxidation	RT	0.044	-	-
treatment	250 °C	0.06	121	11.5
	500 °C	0.351	74	7.04

and  $T_x$  of the Zr-based BMG are approximately 420 °C and 480 °C, respectively. In addition, Fig. 1d illustrates the TG result of Zr-based BMG in air. It can be found that the weight of Zr-based BMG starts to increase at approximately 380 °C. Based on the results of DSC and TG, the temperature and duration of PT were chosen as 380 °C and 90 min, respectively, in order to avoid crystallization and achieve a thicker oxide layer. As shown in Fig. 1e, the surface of PT sample appears black. The cross-sectional morphology of PT sample was observed by backscattering as shown in Fig. 1f. It can be observed that a differential layer with a thickness of about 1.28  $\mu$ m exists after PT.

# 3.1. Wear behavior at 250 $^{\circ}C$ and 500 $^{\circ}C$

To provide a more comprehensive analysis, the wear behavior of BMG samples at RT were firstly investigated. The coefficient of friction (COF) of AC and PT samples at RT are shown in Fig. S1 (a, d), respectively. During the initial wear stage, it is evident that the COF experiences a rapid increase followed by a stabilization phase, commonly referred to as the "running-in" stage [31,37,38]. As summarized in Table 1, the average COF values of AC and PT samples at RT are approximately 0.087 and 0.044, respectively. The corresponding 3D morphology of wear tracks of AC and PT samples at RT are shown in Fig. S1 (b, e). We can find that apparent wear tracks are observed belong to AC sample, and no wear tracks are observed in PT sample. The results demonstrate that the oxidized samples exhibit significantly enhanced

wear resistance at RT compared to the original samples. The cross-sectional morphology of AC and PT samples are shown in Fig. S1 (c, f), respectively. The cross-sectional area of the wear track of the former can be obtained by the integration method to be about 1824  $\mu m^2$ , while the PT sample exhibited almost a linear wear tracks profile, indicating no obvious volume loss. The wear rate ( $\omega$ ) of the AC sample at RT can be calculated as  $\sim 173.7 \times 10^{-6} \mbox{ mm}^3 \mbox{ N}^{-1} \mbox{ m}^{-1} (\omega_1)$  based on Eq. (1), and the PT sample shows an extremely low wear rate without significant wear.

To investigate the benefit of PT on high temperature wear resistance, the AC and PT samples were subjected to wear experiments at 250 °C. The COF of AC and PT samples at 250 °C are displayed in Fig. 2 (a, d), respectively. We can find that the COF mutation of AC sample was more severe in the stable wear stage. And the average COF of AC sample was higher than that of PT sample, which were about 0.12 and 0.06, respectively. The 3D morphology of AC and PT samples at 250 °C are displayed in Fig. 2 (b, e), respectively. It can be found that the PT sample shows less wear compared to the AC sample, which assumes that the preoxidation treatment enhances the wear resistance even at high temperatures. The corresponding cross-sectional profiles of AC and PT samples were presented in Fig. 2 (c, f), we can calculate that the area of the wear tracks of AC and PT samples at 250 °C are about 2659  $\mu$ m<sup>2</sup> (S<sub>2</sub>) and 121  $\mu$ m<sup>2</sup> (S<sub>3</sub>), respectively. And the wear rate of AC and PT samples are  $\sim 253.2 \times 10^{-6} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$  ( $\omega_2$ ) and  $\sim 11.5 \times 10^{-6} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$  $(\omega_3)$ , respectively.

Finally, to investigate the wear behavior of AC and PT samples at higher temperatures, the wear experiments at 500 °C were performed. The COF of AC and PT samples at 500 °C are shown in Fig. 3 (c, d), respectively. It can be observed that the COF of the PT sample remains very stable in the steady state, while the COF of the AC sample gradually increases before stabilizing. And there is no significant abrupt change in the COF of both samples throughout the stable wear stage, which the mean COF values at 500 °C of AC and PT sample are about 0.39 and 0.35, respectively. In addition, the 3D morphology of the wear tracks of AC and PT samples at 500 °C are presented in Fig. 3 (b, e) and the corresponding cross-sectional profiles of wear tracks are shown in Fig. 3 (c, f). It can be obtained that the cross-sectional areas of wear track of AC and PT samples at 500 °C are 285  $\mu$ m<sup>2</sup> (S<sub>4</sub>) and 74  $\mu$ m<sup>2</sup> (S<sub>5</sub>), respectively.



**Fig. 2.** Characterization of AC and PT samples at 250 °C. (a) COF versus time curve of AC sample at 250 °C. (b) Wear morphology of AC sample at 250 °C. (c) Cross-sectional profile of AC sample at 250 °C. (d) COF versus time curve of PT sample at 250 °C. (e) Wear morphology of PT sample at 250 °C. (f) Cross-sectional profile of PT sample at 250 °C. (c) Cross-sectional profile of PT sample at 250 °C. (c) Cross-sectional profile of AC sample at 250 °C. (c) Cross-sectional profile of PT sample at 250 °C. (c) Cross-sectional profile of



**Fig. 3.** Characterization of AC and PT samples at 500 °C. (a) COF versus time curve of AC sample at 500 °C. (b) Wear morphology of AC sample at 500 °C. (c) Cross-sectional profile of AC sample at 500 °C. (d) COF versus time curve of PT sample at 500 °C. (e) Wear morphology of PT sample at 500 °C. (f) Cross-sectional profile of PT sample at 500 °C. (c) Cross-sectional profile of PT sample at 500 °C. (c) Cross-sectional profile of AC sample at 500 °C. (c) Cross-sectional profile of PT sample at 500 °C. (c) Cross-sectional profile of



Fig. 4. Wear patterns of AC and PT samples at 250 °C. (a–b) The wear morphology and magnification of AC sample at 250 °C. (c–d) The wear morphology and magnification of PT sample at 250 °C.

And the corresponding wear rates are about  ${\sim}17.71 \times 10^{-6} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$  ( $\omega_4$ ) and 7.29  $\times$  10<sup>-6</sup> mm<sup>3</sup> N<sup>-1</sup> m<sup>-1</sup> ( $\omega_5$ ). Both samples exhibit significant reductions in wear rates, and the reasons behind this phenomenon will be explained in the Discussion section.

# 3.2. Wear appearance

The wear morphology of AC and PT samples at RT are shown in Fig. S2 (a, b), respectively. It can be observed that the wear morphology of PT sample is consistent with the 3D morphology result, showing no significant wear. However, the AC sample shows severe wear. This can be seen from the wear morphology, which exhibits plastic deformation,

# Table 2

T	he statistics of	e	lemental	loxyge	en content	of.	AC an	d PT	samp	les ir	ı dif	fferent	regions	at 250	0 °C and	1 500	°C.

Position Element	$P_1$	P <sub>2</sub>	P <sub>3</sub>	P <sub>4</sub>	P <sub>5</sub>	P <sub>6</sub>	P <sub>7</sub>	$P_8$
O (at.%)	4.59	37.95	49.88	61.25	47.90	59.93	50.56	58.75



Fig. 5. Wear patterns of AC and PT samples at 500 °C. (a–b) The wear morphology and magnification of AC sample at 500 °C. (c–d) The wear morphology and magnification of PT sample at 500 °C.

tribological layer (tribo-layer), pores and grooves.

#### 3.2.1. Wear appearance at 250 °C

Fig. 4a displays the detailed morphology of wear track of AC sample after being subjected to wear at 250 °C, and obvious plastic deformation can be observed. This can be attributed to the frictional heat generated during the reciprocating sliding process surpassing the  $T_{g}$ , resulting in a reduction in the viscosity and formation of a softened layer on the AC sample [39,40]. Moreover, during the wear process, a localized accumulation caused by plastic deformation leads to the development of tribo-layer in the presence of sustained loading, which is a typical characteristic of adhesive wear [37]. The crack and peeling of the tribo-layer can be observed in the local magnified Fig. 4b. Under the action of cyclic stress, localized tribo-layer are prone to develop microcracks, which further propagate and lead to the delamination of the tribo-layer. This indicates the presence of fatigue wear in the wear process. It is concluded that the severe plastic deformation of the AC sample accelerated the formation and delamination of the plate-like tribo-layer, which ultimately leads to increased wear. In order to further investigate the wear mechanism of the AC sample at 250 °C, the distribution of oxygen content in different characteristic areas on the wear tracks was analyzed by EDS. As summarized in Table 2, the oxygen content in the non-wear region (P1) and the locally accumulated tribo-layer region (P2) is 4.59 % and 37.95 %, respectively, which indicates oxidation in the tribo-layer region. Therefore, the wear mechanisms of the AC sample at 250 °C are predominantly plastic deformation-dominated adhesive wear, fatigue wear, and slight oxidative wear.

To investigate the wear mechanism of PT samples at 250 °C, we observed the detailed morphology of wear trace. The morphology of the wear tracks of PT sample after being subjected to wear at 250 °C is presented in Fig. 4c. Compared to the AC sample, it is evident that the PT sample exhibits narrower wear tracks, smoother wear surfaces, and milder wear severity, indicating superior wear resistance of the PT sample. Furthermore, the presence of slight plastic deformation, cracks, and delamination on the wear marks can be observed from the locally magnified morphological details in Fig. 4d, which demonstrates the existence of adhesive wear and fatigue wear. For further investigation, as summarized in Table 2, the oxygen content of the non-wear region (P<sub>3</sub>) of the PT sample is 49.88 %, which indicates the presence of an oxide layer on the surface of the PT sample. The existence of a hard oxide layer can enhance the ability of BMG to resist the embedding of the abrasive ball, thereby improving the wear resistance of the Zr-based BMG at 250 °C [41]. However, the oxygen content of the locally accumulated tribo-layer area ( $P_4$ ) is 61.25 %, attributed to the further oxidation of the PT sample due to reciprocating friction, indicating the existence of oxidative wear. Therefore, the wear mechanism of the OT sample at 250 °C involves adhesive wear, fatigue wear, and oxidative wear.

## 3.2.2. Wear appearance at 500 $^{\circ}C$

To investigate the excellent wear resistance exhibited by both samples at higher temperatures, their wear morphology was studied. The wear morphology of the AC sample after worn at 500 °C is displayed in Fig. 5a. It can be found that the wear track surface is relatively smooth, but grooves can be observed, which is a typical characteristic of abrasive



Fig. 6. Characterization of the oxide layer (a) Cross-sectional morphology of PT sample at 250 °C. (b) Cross-sectional morphology of AC sample at 500 °C. (c) Crosssectional morphology of PT sample at 500 °C. (d) Oxygen elemental analysis of the cross section. (e) XRD analysis of the oxide layer. (f) Comparison of nanoindentation results for Zr-based BMG and oxide layer.

wear [37]. The smooth surface of the wear track implies that the AC sample exhibits relatively excellent wear resistance at 500 °C. From the local magnified image of the wear track area in Fig. 5b, it can be observed that there are tiny pores, micro cracks, and peelings in smooth tribo-layer, which indicates the presence of adhesive wear and minor fatigue wear. It is noteworthy that, as summarized in Table 2, the oxygen content of the non-wear region ( $P_5$ ) is 47.9 %, which indicates that the entire AC sample was severely oxidized at an ambient temperature of 500 °C. Moreover, the oxygen content in the layered tribo-layer region ( $P_6$ ), which is 59.93 %, which indicates further oxidation occurring during reciprocating friction, providing evidence of oxidative wear. Therefore, the wear mechanism of the AC sample at 500 °C involves adhesive wear, fatigue wear, and oxidative wear, all of which occur in conjunction with severe oxidation.

To study the wear mechanism of the PT sample with excellent wear resistance at 500 °C, the corresponding morphology of wear track is displayed in Fig. 5c. It can be clearly noticed that the non-wearing region presents a rough morphology, while the wear region, however, presents a smooth morphology. And the wear track width of the PT sample is narrower than that of the AC sample, and the wear track surface is smoother, demonstrating the superior wear resistance of the PT sample at 500 °C. Moreover, as shown in Fig. 5d–a smooth surface is still observed in the locally magnified image of the wear track, with only a small number of micro cracks and pores being observed, indicating very slight fatigue wear. This suggests that there was minimal fatigue wear present of the PT sample. In addition, as summarized in Table 2, the oxygen content in the rough non-wear region (P<sub>7</sub>) is 50.56 %, while the oxygen content in the smooth wear track region (P<sub>8</sub>) is 58.75 %. This

indicates that the PT sample continues to undergo oxidation in the 500 °C environment, and the oxidation is more severe at the wear track area. In summary, the wear mechanism of the PT sample at 500 °C involves a combination of mild fatigue wear and oxidative wear, with the participation of an oxide layer and further oxidation.

# 3.3. Discussion

To investigate the reasons for the improvement of wear resistance of Zr-based BMG in high-temperature due to PT, the wear tracks crosssection was analyzed using backscattering pattern and EDS. The wear tracks cross-sectional morphology of PT sample at 250 °C, and the AC and PT samples at 500 °C are shown in Fig. 6(a-c), respectively. It can be found that all these samples exhibit differential layers of varying thickness. As shown in Fig. 6d, EDS analysis revealed that the differential layers are oxygen-rich zone, thus confirming that these differential layers are oxide layers. According to Fig. 6a, it can be observed that the PT sample exhibits an oxide layer with a thickness of approximately 1.03 µm after being subjected to wear at 250 °C. However, as shown in Fig. 6b, the AC sample exhibits an uneven oxide layer with a thickness of approximately 3.01 µm after being subjected to wear at 500 °C. Additionally, the oxide layer exhibits an inhomogeneous interface with the substrate. As shown in Fig. 6c, the PT sample exhibits a thicker and more homogeneous oxide layer than AC sample, with a thickness of approximately 4.61  $\mu m.$  Therefore, based on the above results, it can be concluded that both AC and PT samples undergo severe oxidation with a significant increase in the thickness of the oxide layer during the wear experiment at 500 °C. This is consistent with the results of TG as shown



Fig. 7. Schematic of the wear mechanism at 250 °C and 500 °C. (a) Wear mechanism of AC sample at 250 °C. (b) Wear mechanism of PT sample at 250 °C. (c) Wear mechanism of AC sample at 500 °C. (d) Wear mechanism of PT sample at 500 °C.

in Fig. 1d, indicating that the rate of weight gain of Zr-based BMG reaches its maximum at 500 °C. The oxide layer of both AC and PT samples grows rapidly during the wear process at 500 °C and dominates the wear process. In the initial stage of wear at 500 °C, the AC sample undergoes wear predominantly on the surface of the crystalline matrix, resulting in inhomogeneous wear tracks. However, in the steady wear stage, the continuously growing oxide layer mainly participates in the wear process. Therefore, this is the reason for the presence of an inhomogeneous interface between the oxide layer and the substrate of the AC samples. The composition of the oxide layer was analyzed using XRD. As

shown in Fig. 6e, the result indicates that t-ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> are the predominant constituents of the oxide layer. These hard oxides contribute to the improved wear resistance of Zr-based BMG [42]. Fig. 6f displays the results of nanoindentation, which indicate that the original BMG possesses an average hardness and modulus of 5.5 GPa and 57.7 GPa, respectively. Conversely, the oxide layer displays an average hardness of 15.5 GPa and modulus of 200.8 GPa, respectively. Therefore, the PT samples have a hard oxide layer that protects the substrate during the wear process, significantly improving the wear resistance of Zr-based BMG in high-temperature environment.

To facilitate the understanding of the wear mechanisms of AC and PT samples in different high-temperature environments, Fig. 7 shows the corresponding schematic of the wear mechanisms. As shown in Fig. 7a, the AC sample without an initial protective oxide layer experiences a frictional heating temperature exceeding the  $T_g$  during wear at 250 °C, resulting in the formation of a softening layer on the wear surface. Therefore, the wear mechanisms of AC sample are adhesive wear, fatigue wear, and slight oxidative wear dominated by plastic deformation of softened layer. However, as shown in Fig. 7b, the initial hard oxide layer of PT sample participates in wear during both the "running-in" stage and the stable wear stage. The corresponding wear mechanisms involve adhesive wear, fatigue wear, and oxidative wear dominated by the oxide layer. In addition, during the wear experiment at 500 °C, the ambient temperature exceeded the  $T_x$  of Zr-based BMG, resulting in its crystallization. As shown in Fig. 7c, during the "running-in" stage, the low-hardness crystalline state of original Zr-based BMG experiences wear. However, at this stage, the extremely high oxidation rate leads to the protection of the crystalline matrix by the newly formed hard oxide layer during stable wear. Therefore, the wear mechanisms of AC sample at 500 °C is dominated by severe oxidation-induced adhesive wear, slight fatigue wear and oxidation wear. In contrast, as shown in Fig. 7d, the PT sample exhibits involvement of the oxide layer in the wear process in both stages, thereby protecting the crystallized substrate. In conclusion, despite the fact that crystallization can cause the Zr-based BMG to lose its excellent properties, PT can significantly enhance the high-temperature wear resistance of Zr-based BMG.

## 4. Conclusions

In this paper, a pre-oxidation treatment strategy was developed to significantly enhance the wear resistance of Zr-based BMGs in the temperature range from RT to 500 °C (above  $T_x$ ). At RT, the original BMG sample exhibited drastic wear with a wear rate of  $\sim 173.7 \times 10^{-6}$ mm<sup>3</sup> N<sup>-1</sup> m<sup>-1</sup>. In contrast, the PT sample showed significantly enhanced wear resistance with no observable volumetric wear. Correspondingly, at higher temperatures of 250 °C and 500 °C, the PT samples exhibited a noticeable enhancement in wear resistance, with values of  $\sim 11.5 \times 10^{-11.5}$ 6 mm<sup>3</sup> N<sup>-1</sup> m<sup>-1</sup> and  $\sim$ 7.29  $\times$  10<sup>-6</sup> mm<sup>3</sup> N<sup>-1</sup> m<sup>-1</sup>, respectively. The results showed that the designed pre-oxidation treatment successfully formed robust ZrO<sub>2</sub> oxide layers on the surface of Zr-based BMGs, thus preventing the drastic wear of the BMG substrate at high temperatures. As a result, our findings offer a cost-effective and practical method to improve the suitability of Zr-based BMG components in challenging high-temperature environments, thus broadening their applications in real-world engineering.

## Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

## Credit author statement

Wenxue Wang: Methodology, Validation, Formal Analysis, Investigation, Data curation, Writing-Original Draft, Visualization. Fei Sun: Investigation, Methodology, Validation, Data curation. Heting Zhang: Methodology, Investigation. Jinbiao Huang: Investigation, Methodology, Investigation, Methodology. Xiangyang Yu: Investigation, Methodology. Jiang Ma: Writing-Review & Editing, Supervision.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgements

The work was supported by the National Key Research and Development Program of China (Grant No. 2018YFA0703605), the Key Basic and Applied Research Program of Guangdong Province, China (Grant Nr. 2019B030302010), the NSF of China (Grant Nr. 52122105, 51971150) the Science and Technology Innovation Commission Shenzhen (Grants No. 20220804091920001). The authors also thank the assistance on microscope observation received from the Electron Microscope Center of the Shenzhen University.

# Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jmrt.2024.01.169.

#### References

- Klement W, Willens RH, Duwez P. Non-crystalline structure in solidified goldsilicon alloys. Nature 1960;187(4740):869–70.
- [2] Schuh CA, Hufnagel TC, Ramamurty U, No Overview. 144 mechanical behavior of amorphous alloys. Acta Mater 2007;55(12):4067–109.
- [3] Chen M. Mechanical behavior of metallic glasses: microscopic understanding of strength and ductility. Annu Rev Mater Res 2008;38:445–69.
- [4] Schroers J. Processing of bulk metallic glass. Adv. Mater. 2010;22(14):1566–97.
  [5] Zhang JY, Zhou ZQ, Zhang ZB, Park MH, Yu Q, Li Z, et al. Recent development of chemically complex metallic glasses: from accelerated compositional design, additive manufacturing to novel applications. Mater. Futures 2022;1(1):012001.
- [6] Ma J, Yang C, Liu XD, Shang BS, He QF, Li FC, et al. Fast surface dynamics enabled cold joining of metallic glasses. Sci Adv 2019;5(11):9.
- [7] Hua D, Zhou Q, Shi Y, Li S, Hua K, Wang H, et al. Revealing the deformation mechanisms of (110) symmetric tilt grain boundaries in CoCrNi medium-entropy alloy. Int J Plast 2023;171:103832.
- [8] Li N, Xu XN, Zheng ZZ, Liu L. Enhanced formability of a Zr-based bulk metallic glass in a supercooled liquid state by vibrational loading. Acta Mater 2014;65: 400–11.
- [9] Zhang QS, Zhang W, Inoue A. Ni-free Zr-Fe-Al-Cu bulk metallic glasses with high glass-forming ability. Scr. Mater. 2009;61(3):241–4.
- [10] Wang Q, Shang Y-H, Yang Y. Quenched-in liquid in glass. Mater. Futures 2023;2 (1):017501.
- [11] Li N, Chen Y, Jiang MQ, Li DJ, He JJ, Wu Y, et al. A thermoplastic forming map of a Zr-based bulk metallic glass. Acta Mater 2013;61(6):1921–31.
- [12] Huang S, Sun F, Ruan W, Ren S, Zhang Z, Liang X, et al. Design of near-zero thermal expansion composites with superior mechanical properties in a wide temperature region. J Mater Res Technol 2023;25:2166–76.
- [13] Zhang C, Ouyang D, Pauly S, Liu L. 3D printing of bulk metallic glasses. Mater Sci Eng R Rep 2021;145:100625.
- [14] Ren Y, Huang Z, Wang Y, Zhou Q, Yang T, Li Q, et al. Friction-induced rapid amorphization in a wear-resistant (CoCrNi)88M012 dual-phase medium-entropy alloy at cryogenic temperature. Composites Part B 2023;263:110833.
- [15] Sun F, Yang J, Fu J, Wang B, Ma J, Shen J. Hierarchical macro to nano press molding of optical glasses by using metallic glasses. J Non-Cryst Solids 2022;594: 121821.
- [16] Sun F, Deng ST, Fu JA, Zhu JH, Liang DD, Wang PF, et al. Superior hightemperature wear resistance of an Ir-Ta-Ni-Nb bulk metallic glass. J Mater Sci Technol 2023;158:121–32.
- [17] Sun F, Yu X, Fu J, Zhu Y, Wang W, Sun R, et al. High-temperature wear behavior of a Zr-based metallic glass. J Alloys Compd 2023;960:170703.
- [18] Jones MR, Kustas AB, Lu P, Chandross M, Argibay N. Environment-dependent tribological properties of bulk metallic glasses. Tribol Lett 2020;68(4):123.
- [19] Hsieh JH, Tan ALK, Zeng XT. Oxidation and wear behaviors of Ti-based thin films. Surf Coat Technol 2006;201(7):4094–8.
- [20] Zhang C, Liu L, Chan KC, Chen Q, Tang CY. Wear behavior of HVOF-sprayed Febased amorphous coatings. Intermetallics 2012;29:80–5.
- [21] Zhou Q, Luo D, Hua D, Ye W, Li S, Zou Q, et al. Design and characterization of metallic glass/graphene multilayer with excellent nanowear properties. Friction 2022;10(11):1913–26.
- [22] Menezes MR, Godoy C, Buono VTL, Schvartzman MMM, Avelar-Batista Wilson JC. Effect of shot peening and treatment temperature on wear and corrosion resistance of sequentially plasma treated AISI 316L steel. Surf Coat Technol 2017;309: 651–62.
- [23] Bagherifard S, Guagliano M. Review of shot peening processes to obtain nanocrystalline surfaces in metal alloys. Surf Eng 2009;25(1):3–14.
- [24] Selvabharathi R, Muralikannan R. Influence of shot peening and plasma ion nitriding on tensile strength of 2205 duplex stainless steel using A-PAW. Mater. Sci. Eng. A 2018;709:232–40.
- [25] Ooi S, Bhadeshia HKDH. Duplex hardening of steels for aeroengine bearings. ISIJ Int 2012;52(11):1927–34.
- [26] Raghuram H, Katsich C, Pichelbauer K, Koschatzky K, Gachot C, Cihak-Bayr U. Design of wear and corrosion resistant FeNi-graphite composites by laser cladding. Surf Coat Technol 2019;377:124897.

#### W. Wang et al.

#### Journal of Materials Research and Technology 29 (2024) 2166-2174

- [27] Liu X, Bi J, Meng Z, Li R, Li Y, Zhang T. Tribological behaviors of high-hardness Cobased amorphous coatings fabricated by laser cladding. Tribol Int 2021;162: 107142.
- [28] Bajpai S, Nisar A, Sharma RK, Schwarz UD, Balani K, Datye A. Effect of fictive temperature on tribological properties of Zr44Ti11Cu10Ni10Be25 bulk metallic glasses. Wear 2021:486–7. 204075.
- [29] Jin HW, Ayer R, Koo JY, Raghavan R, Ramamurty U. Reciprocating wear mechanisms in a Zr-based bulk metallic glass. J Mater Res 2011;22(2):264–73.
- [30] Zhang M, Yao D, Cao Z, Li P, Zhou P, Wang X. Influence of oxidation on the performance of Zr55Cu30Al10Ni5 BMG. Intermetallics 2016;79:20–7.
- [31] Chen Z, Sun F, Wang W, Chen J, Ren S, Ruan W, et al. Improved wear resistance of metallic glacier glass. J Non-Cryst Solids 2023;619:122582.
- [32] Fu X, Li C, Li X, Li C, Zhao Y, Ding Y, et al. Effect of heat treatment on the frictional wear properties of Zr-based amorphous alloy. J Mater Eng Perform 2023. https:// doi.org/10.1007/s11665-023-08191-y.
- [33] Hua N, Qian Z, Lin B, Liao Z, Wang Q, Dai P, et al. Formation of a protective oxide layer with enhanced wear and corrosion resistance by heating the TiZrHfNbFe0.5 refractory multi-principal element alloy at 1,000 °C. Scr. Mater. 2023;225:115165.
- [34] Caron A, Sharma P, Shluger A, Fecht HJ, Louzguine-Luzguin DV, Inoue A. Effect of surface oxidation on the nm-scale wear behavior of a metallic glass. J Appl Phys 2011;109(8):083515.

- [35] Jia Q, He WH, Hua DP, Zhou Q, Du Y, Ren Y, et al. Effects of structure relaxation and surface oxidation on nanoscopic wear behaviors of metallic glass. Acta Mater 2022;232:117934.
- [36] Zhou K, Chen C, Liu Y, Pang SJ, Hua NB, Yang W, et al. Effects of lutetium addition on formation, oxidation and tribological properties of a Zr-based bulk metallic glass. Intermetallics 2017;90:81–9.
- [37] Zou YM, Qiu ZG, Zheng ZG, Wang G, Yan XC, Yin S, et al. Ex-situ additively manufactured FeCrMoCB/Cu bulk metallic glass composite with well wear resistance. Tribol Int 2021;162:107112.
- [38] Wang W, Wong PL, Zhang Z. Experimental study of the real time change in surface roughness during running-in for PEHL contacts. Wear 2000;244(1–2):140–6.
- [39] Rahaman ML, Zhang LC, Ruan HH. Effects of environmental temperature and sliding speed on the tribological behaviour of a Ti-based metallic glass. Intermetallics 2014;52:36–48.
- [40] Ji XL, Alavi SH, Harimkar SP. High-temperature sliding wear behavior of Zr-based bulk amorphous alloys. JOM 2015;67(7):1578–84.
- [41] Liu LF, Zhang HA, Shi C. Sliding tribological characteristics of a Zr-based bulk metallic glass near the glass transition temperature. Tribol Lett 2009;33(3):205–10.
- [42] Attia MH, de Pannemaecker A, Williams G. Effect of temperature on tribo-oxide formation and the fretting wear and friction behavior of zirconium and nickelbased alloys. Wear 2021;476:203722.