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Wear behavior of a Zr-based bulk metallic glass and its composites

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ABSTRACT

The wear behaviors of $Zr_{52.5}Cu_{17.9}Al_{10}Ni_{14.6}Ti_5$ metallic glasses with different contents of crystalline phases were studied by using a pin-on-disc test. The results indicate that the friction coefficient of the metallic glass with a steel counterpart is in the range of 0.24–0.32. Both surface softening and crystallization occur on the surface of the metallic glass during wear, and the wear curve is not as stable as the crystalline materials due to the interaction of the two processes. The wear mechanism of the metallic glass may change with wear conditions and the crystallinity. The fully amorphous material shows an abrasive wear at a low load, then adhesive wear at a high load. Increasing the crystallinity results in more abrasive wear. The wear behaviors of the metallic glass and its crystalline composites do not follow the Archard's equation. Only a good combination of the hardness and the toughness can the metallic glass be wear resistant.

1. Introduction

Bulk metallic glasses (BMGs) have been emerging as a type of very attractive materials, due to their high strength [1,2], corrosion resistance [3,4] and other excellent physical and chemical properties [5,6]. Thus, BMGs have great potentials for applications in high strength mechanical parts, sporting, biomedical instruments, molding and information technologies [7–9]. Much effort has also been made on increasing the glass forming ability of metallic glasses [10,11], and BMGs with diameters as large as tens of millimeters have been widely developed in Zr-, Fe-, Cu- and Ni-based systems [12–14]. Therefore, some BMGs are almost ready for industrialization [15].

Recently, the wear resistance of bulk metallic glasses has been paid more and more attentions [16–18]. Two applications show that bulk metallic glasses have a much longer lifetime in wear applications. One example used a Ni-based bulk metallic glass as micro-sized gears, which have a lifetime of 2500 h compared with 8 h for SK-steel [19], the other used a Zr-based bulk metallic glass for bearings, which also exhibit a higher wear resistance than GCr15 steel [20]. In fact, in both applications rolling friction is involved. However, the studies of the sliding friction of bulk metallic glasses do not show such a significant increase of wear resistance compared with steels [19,21]. Under lubrication conditions, the wear rate of BMG is even much higher than those of conventional steels [22].

In scientific view, bulk metallic glasses, which have a high hardness and no work hardening, should have a completely different wear behavior other than conventional crystalline materials [16]. Studies indeed show that the wear behavior of bulk metallic glasses do not follow the empirical Archard's wear equation [23,24], which indicates a positive increase of wear resistance with the hardness. Furthermore, bulk metallic glasses are of brittle nature, and usually deform and crack through highly localized shear bands, which are different from the failure of crystalline metallic materials. However, as the wear resistance is not an inherent property of materials, and strongly depends on wear conditions and processing history of materials, the data in different work are contradictory. For example, some studies show there is no crystallization in the friction surface of bulk metallic glass [25,26], while others show crystallization [27]. Some show a positive effect of nanocrystalline phase on wear resistance [27], while others show a negative effect [16]. The reason may be that since bulk metallic glasses are in a non-equilibrium state, a slight variation in test conditions and local chemical compositions will change microstructures, and results in different wear behaviors. Thus more insightful understandings on wear behaviors of bulk metallic glasses both under rolling and sliding conditions are still needed.

This work aims to characterize the wear behavior of Zr-based bulk metallic glasses under dry sliding conditions, and then to study the effect of crystallization on the wear behavior by using amorphous-crystalline composites with different crystallinity.

2. Experimental

The Zr-based alloy with a nominal composition of $Zr_{52.5}Cu_{17.9}Al_{10}Ni_{14.6}Ti_5$ was prepared by arc melting the mixtures of pure Zr (99.8 wt.%), Cu (99.9 wt.%), Al (99.99 wt.%), Ni (99.9 wt.%) and Ti (99.9 wt.%) in a Ti-gettered argon atmosphere

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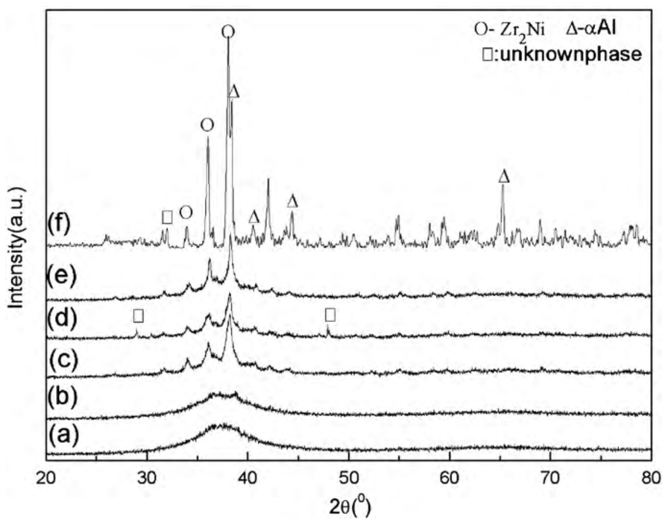

Fig. 1. XRD patterns of $Zr_{52.5}Cu_{17.9}Al_{10}Ni_{14.6}Ti_5$ with different crystallinity. (a) 0%; (b) 6.38%; (c) 10.72%; (d) 34.27%; (e) 62.82%; (f) 100%.

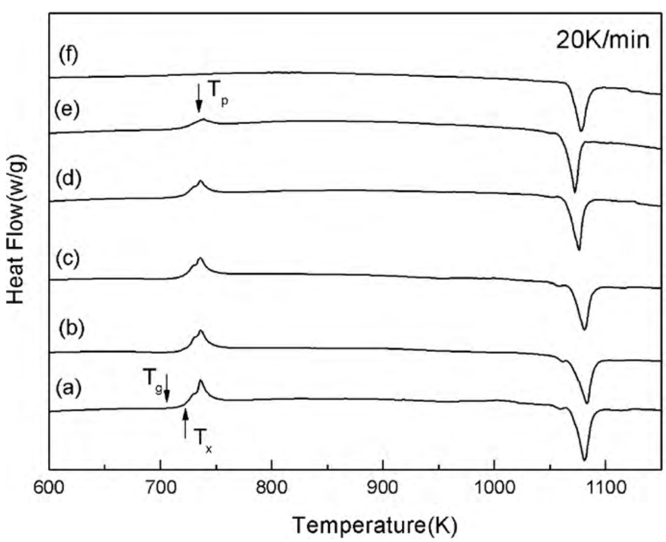

Fig. 2. DSC curves of $Zr_{52.5}Cu_{17.9}Al_{10}Ni_{14.6}Ti_5$ with different crystallinity. (a) 0%; (b) 6.38%; (c) 10.72%; (d) 34.27%; (e) 62.82%; (f) 100%.

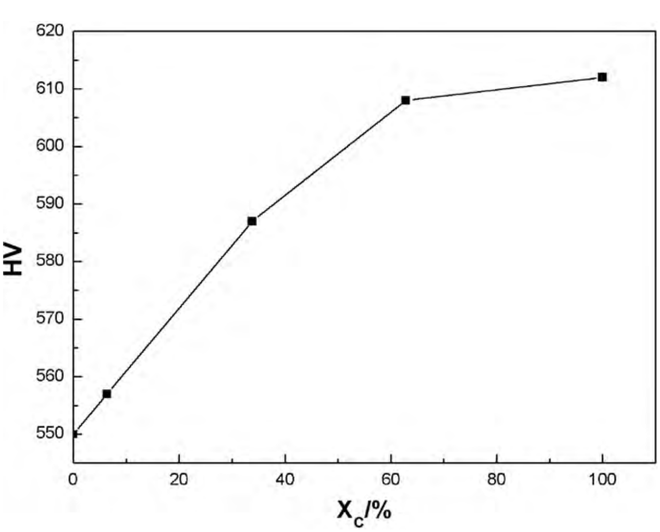

Fig. 3. Microhardness of $Zr_{52.5}Cu_{17.9}Al_{10}Ni_{14.6}Ti_5$ with different crystallinity.

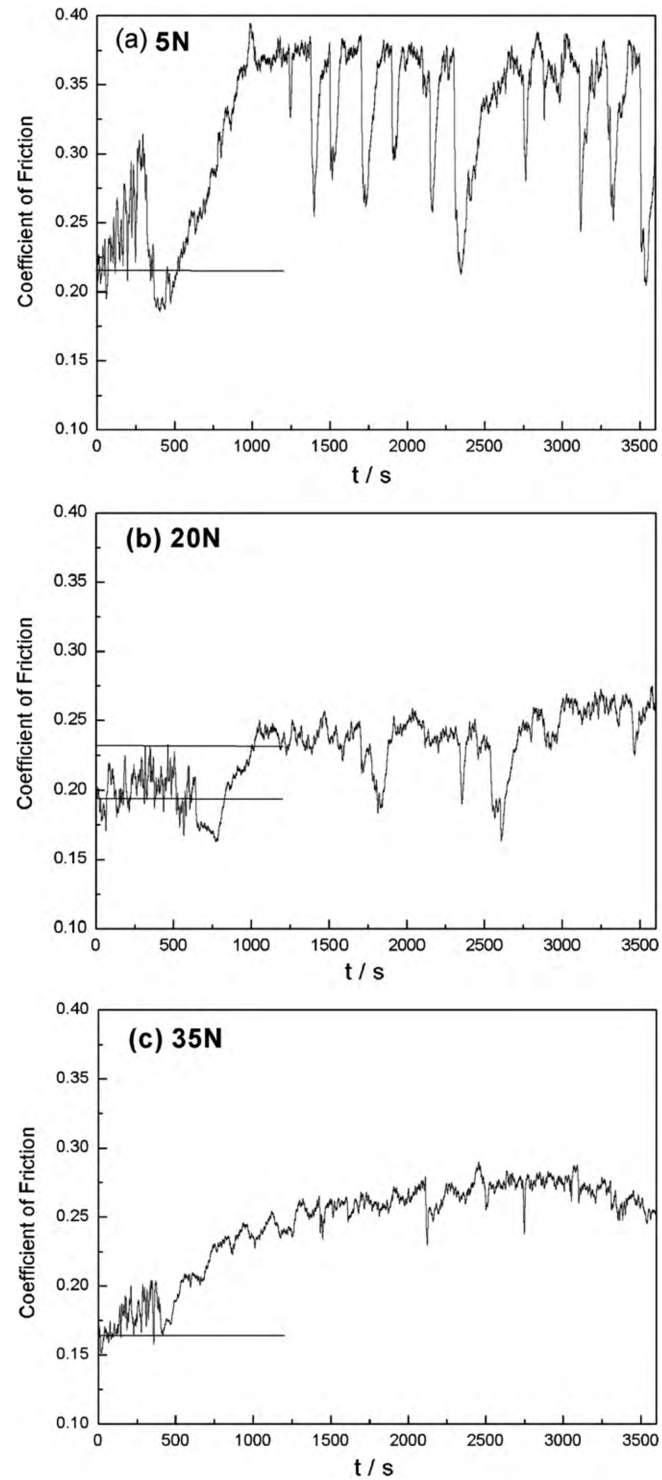

Fig. 4. Friction behaviors of $Zr_{52.5}Cu_{17.9}Al_{10}Ni_{14.6}Ti_5$ bulk metallic glasses at different loads. (a) 5 N; (b) 20 N; (c) 35 N.

and each ingot was arc-melted at least four times. Bars of 5 mm in diameter were prepared by casting the ingots into water-cooled copper molds. The bars were also heat treated at a temperature above T_x for different time to obtain materials of different crystallinity. The amorphous and crystalline structures were analysed by using a Siemens D500 diffractometer with CuKα radiation. DSC measurements were performed under a purified argon atmosphere in an SDTQ600V8.0DSC-TGA Instrument. The specimens were scanned from 473 K to 973 K at a constant heating rate of 20 K/min. The Vickers microhardness HV was measured with Matsuzawa Digital Microhardness Tester HD9-45 at a load of 100 g (0.98 N). Abrasive wear tests were conducted by using UMT-3 equipment (WAZAU model TRM 5000) with a pin-on-disc manner in air at room temperature. The applied nor-

Table 1
Friction coefficients and wear loss of $Zr_{52.5}Cu_{17.9}Al_{10}Ni_{14.6}Ti_5$ bulk metallic glasses at different loads.

Load/N	Load/N	Wear loss/mg
5	0.321	1.93
20	0.240	5.33
35	0.261	5.05

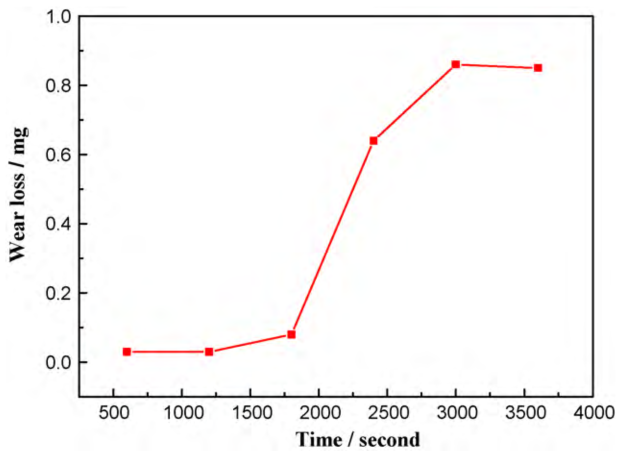

Fig. 5. Variation of wear loss of $Zr_{52.5}Cu_{17.9}Al_{10}Ni_{14.6}Ti_5$ bulk metallic glass with time.

mal loads used were 5, 20 and 35 N respectively. The counterpart was a Cr-12 steel with a hardness of HRC62, and run in a to-and-forth manner at a frequency of 20 Hz. Scanning electron microscopy was used to observe the wear surface and wear debris. The wear loss of bulk metallic glasses was measured by using an analytical balance before and after the wear test. Nanoindentation was also conducted on the CSM Model UNHT Nanoindenter to measure the elastic moduli of specimens before and after wear tests, and the maximum load was 500 mN.

3. Results

Fig. 1 shows the starting materials of different crystallinity. The crystallinity can be determined by calculating the crystallization enthalpy in the DSC curves (as shown in Fig. 2) according to the following equation [28]:

$$Xc = \frac{\Delta H_0 - \Delta H}{\Delta H_0} \times 100\%,$$

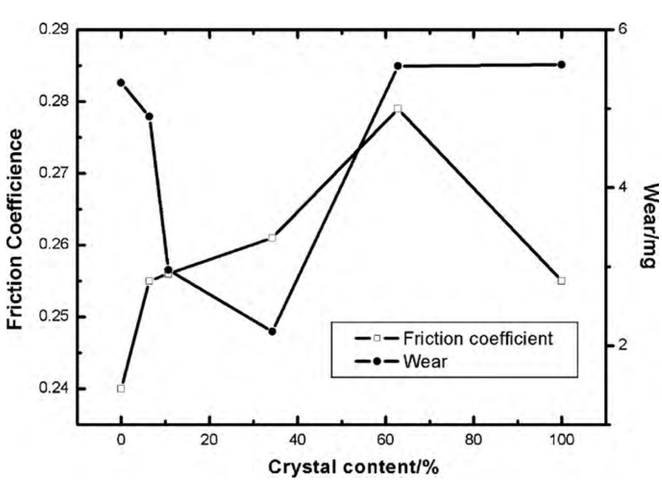

Fig. 6. Friction coefficients and wear loss of $Zr_{52.5}Cu_{17.9}Al_{10}Ni_{14.6}Ti_5$ with different crystallinity.

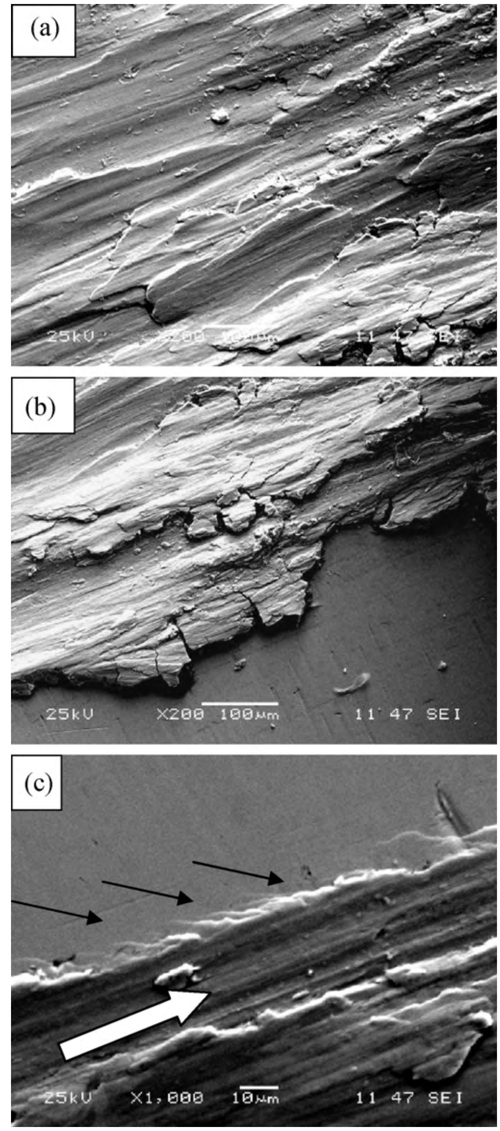

Fig. 7. Wear surface of $Zr_{52.5}Cu_{17.9}Al_{10}Ni_{14.6}Ti_5$ bulk metallic glass. (a) Grooves and plastic deformation; (b) crack; (c) shear bands.

where ΔH_0 is the crystallization enthalpy of the fully amorphous materials, and ΔH is that of partially crystallized materials. The microhardness of different materials is also measured, as shown in Fig. 3. It indicates that the hardness increases with the content of crystalline phases increasing.

Fig. 4 shows the friction behaviors of $Zr_{52.5}Cu_{17.9}Al_{10}Ni_{14.6}Ti_5$ bulk metallic glass at different loads. It indicates that there is a small bump of the friction coefficient during the first 500–600 s, possibly due to the adaptation of the metallic glass surface to that of the steel counterpart. Then, the friction coefficient increases fast to a flat platform in about 100 s. However, the curves of the metallic glass are very unstable with numerous waves, compared with conventional friction materials. The phenomenon is more serious at loads of 5 N and 20 N than that at 30 N. The friction coefficients at the platform are shown in Table 1. The values of friction coefficients are between 0.24 and 0.32, which is a little smaller than those in other work [25,29]. It is also interesting to note that the friction coefficient decreases with the load increasing from 5 N to 20 N, and does not change much at 35 N. The wear loss increases with the load increasing from 5 N to 20 N, and does not change at 35 N either. Fig. 5 shows the wear loss with time at a load of 20 N,

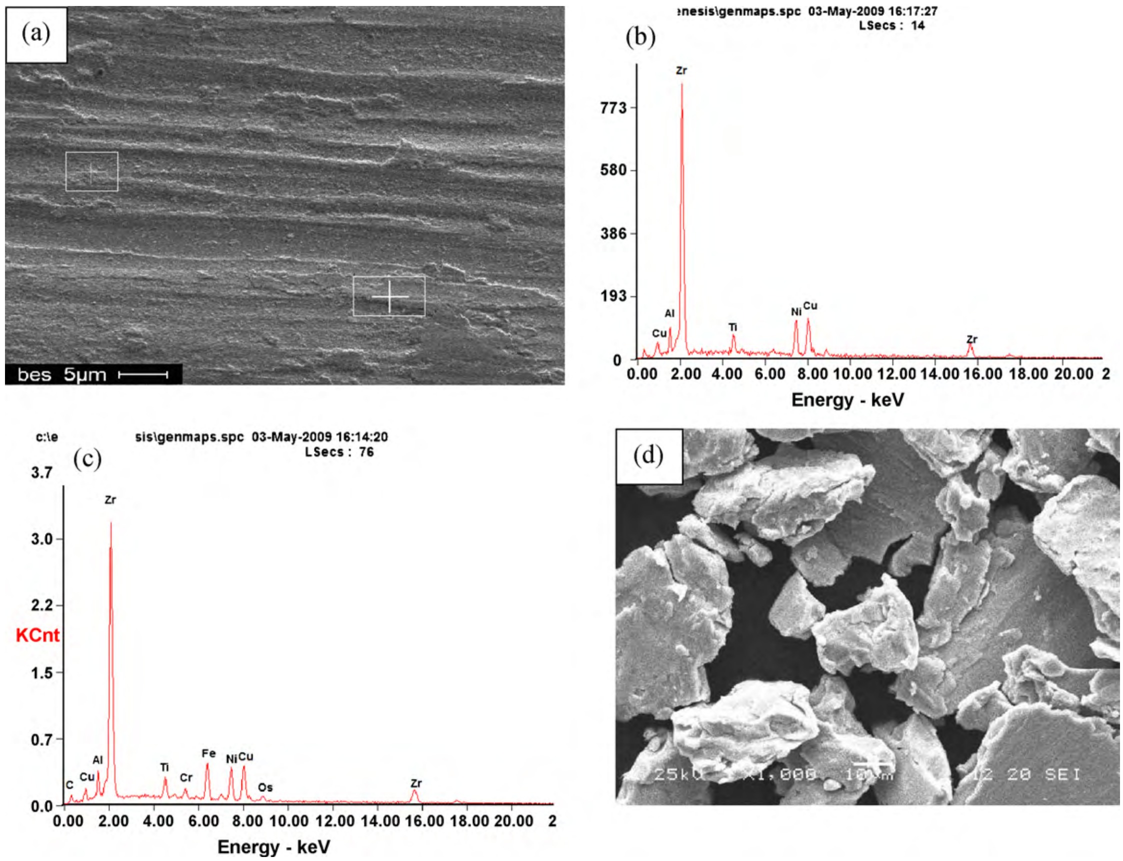

Fig. 8. Chemical analysis of wear surface and wear debris. (a) Wear surface; (b) chemical compositions of small particles; (c) chemical compositions of plastic deformation zone; (d) wear debris.

it is very small in the first 30 min, then increases very fast, finally becomes stable at 50 min. The drop of wear loss in the end may be due to transfer of the metal counterpart to the bulk metallic glass surface.

Fig. 6 shows the variation of the friction coefficient and the wear loss with crystallinity. The friction coefficient increases with the crystallinity, and drops at a crystallinity of 64%, while the wear loss decreases with the crystallinity, and raises at a crystallinity of 34%. Apparently both the wear loss and the friction coefficient do not have a linear relationship either with the hardness or the crystallinity.

Fig. 7 shows the wear surface of the bulk metallic glasses at a load of 20 N. The surface morphology is due to a typical abrasion wear, with long grooves induced by ploughing, as shown in Fig. 7(a). Plastic deformation and microcracks can also be observed in Fig. 7(b). Shear bands can form at the edge of the worn area, which was also discovered by other studies [30,31], as shown in Fig. 7(c).

EDX analyses on the worn surface (Fig. 8(a)) of bulk metallic glass show the small particles in the groves contain Zr, Cu, Ni, and Al elements (Fig. 8(b)), and thus belong to the glass matrix; while in the plastic deformation zone, there are other elements like Fe and Cr (Fig. 8(c)). It is deduced that elements in the steel counterpart transferred or diffused into the metallic glass surface due to severe plastic deformation. Fig. 5 also indicates the drop of wear loss in the end of the test. The wear debris (Fig. 8(d)) collected after the wear test is of flake-like shape and in a diameter of about 40 μm, and mirco-cracks and small particles can be also observed among them. It seems that the debris could be peeled off from the surface in a very brittle manner.

The phase constitutions in the surface of bulk metallic glass before and after the wear test at 20 N are shown in Fig. 9. Apparent crystallization occurred after the wear test, due to temperature rising. It is also possibly due to plastic deformation, which is called strain-induced crystallization, as reported in other work [32].

Different load results in different surface morphology on the bulk metallic glass, as shown in Fig. 10. At 5 N and 20 N, the worn surface mainly shows an abrasion wear manner with a small

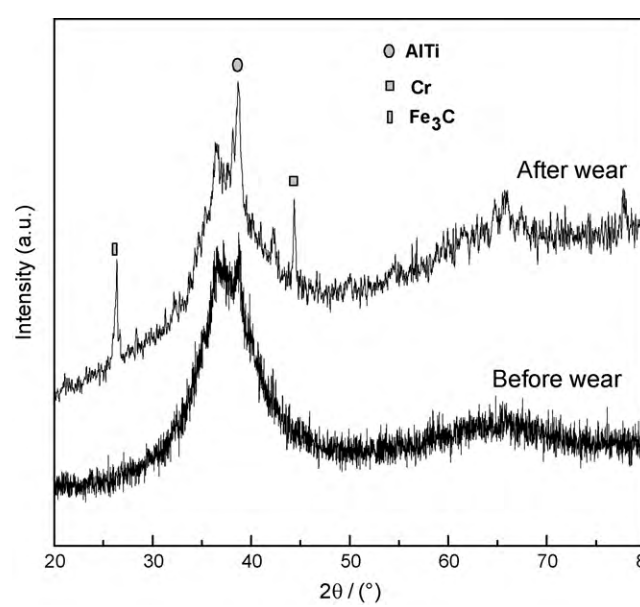

Fig. 9. XRD patterns of wear surface (a) before wear test; (b) after wear test.

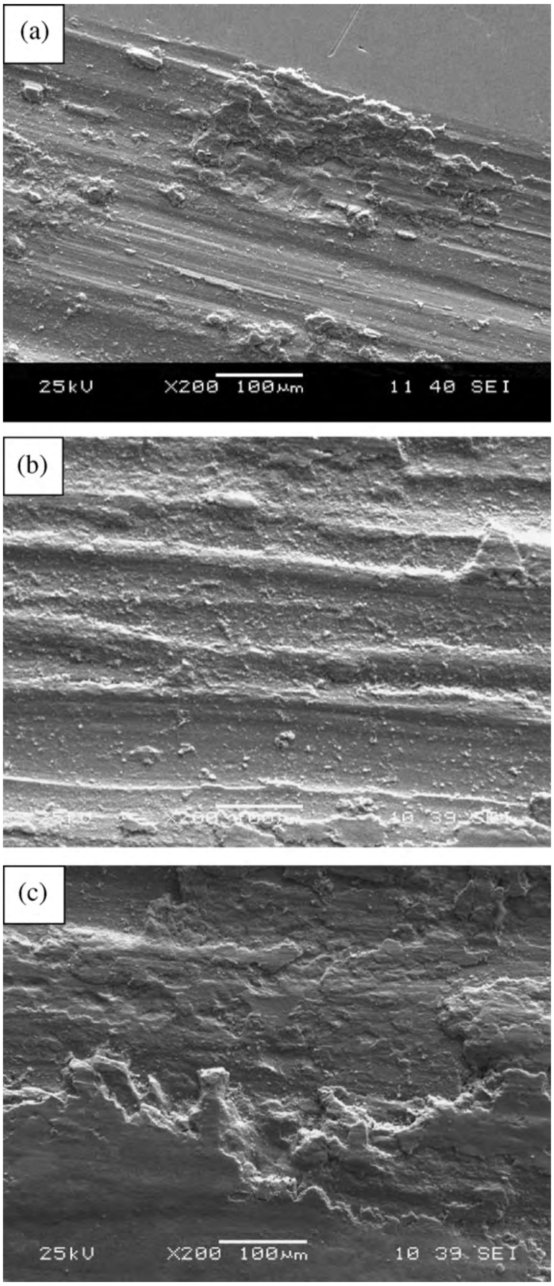

Fig. 10. Wear surface of $Zr_{52.5}Cu_{17.9}Al_{10}Ni_{14.6}Ti_5$ bulk metallic glass at (a) 5 N; (b) 20 N; (c) 35 N.

amount of adhesive wear. The interspacing of grooves seems to increase from 5 N to 20 N. However, at the load of 35 N, pronounced plastic deform areas appear on the worn surface, and no grooves can be found, thus, the adhesive wear becomes the main mechanism. The crystallinity also changes the worn surface morphology at a load of 20 N. With 10% crystalline phase, the worn surface shows a mainly adhesive manner, and some small particles possibly of crystalline nature can be seen. As the crystallinity increases to 34%, grooves and many small particles appear, indicating an abrasive wear manner. In the fully crystalline materials, the long parallel grooves show a typical abrasive manner, and debonding of crystals from the surface can be observed (Fig. 11).

It is worthwhile to note that after the wear test, the elastic modulus of the bulk metallic glass specimens in positions close to the worn region decreases by about 10%, while that of the crystalline specimen increases very little, as shown in Table 2.

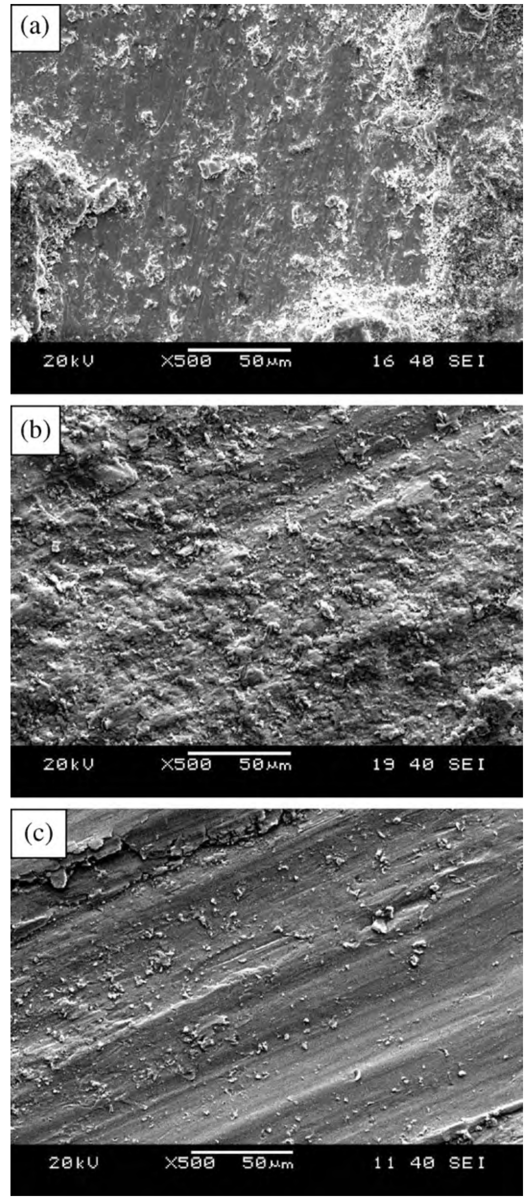

Fig. 11. Wear surface of $Zr_{52.5}Cu_{17.9}Al_{10}Ni_{14.6}Ti_5$ with different crystallinity. (a) 10%; (b) 34%; (c) 100%.

Table 2
Elastic moduli of specimens before and after wear tests.

Specimens	Before test/GPa	After test/GPa
Amorphous	110.97	96.19
Crystalline	117.50	118.58

4. Discussion

4.1. Wear mechanism of bulk metallic glass

Due to the disordered atomic structure, the wear mechanism of bulk metallic glasses is different from that of crystalline materials. Metallic glass is intrinsically brittle, thus for sliding wear, the main damage mechanism is abrasive wear, started with a smoothing effect and followed by ploughing and/or cracking [16], as shown in Figs. 7(a) and 10(a). However, plastic deformation also occurs during wear of metallic glasses, in the form of shear bands, as shown in Fig. 7(c). The shear bands usually can be observed beside the wear track, and sometimes beneath it in sectioned samples [33]. The localized shear deformation may result in softening of metallic glasses due to the formation of more free volume [34]. The decrease of elastic modulus at positions close to the wear track after the wear test also indicates this behavior. On the other hand, crystallization may occur during the wear process [16]. Although the crystallization behavior during wear is not often observed, it did occur in this work, as shown in Fig. 9. Crystallization can be resulted from transient temperature rising between the steel counterpart and the metallic glass, which may occur on the whole wear track or some specific sites. However, it is difficult to measure *in situ* the heat generating process in wear, and there is no exact theoretical calculation either. The other possible mechanism for the formation of crystalline phases is stress-induced crystallization. During nanoindentation, the formation of nanocrystalline particles can be detected underneath the indents [32]. A certain amount of crystallization will increase the strength and the hardness of metallic glasses, and resulted in a higher friction coefficient. Thus, during the wear of metallic glasses, there could be two competitive processes: the softening process induced by plastic deformation and the hardening process induced by the crystallization. The concurrence of the two processes leads to a very unstable wear, as shown in Fig. 4, and a large vibration of the friction coefficient occurs. With the load increasing, there is a better contact between the two counterparts, and more homogenous distribution of plastic deformation and crystallization may occur, thus, the wear process becomes more stable. At a high load, more plastic deformation occurs in the wear surface, and possibly resulting in more softening and materials can be easier to be pushed away from the wear track. So the friction coefficient of the metallic glass decreases with the load, unlike that of crystalline materials, as shown in Table 1. Interaction between the steel counterpart and the surface of the metallic glass at a high load may happen due to the severe plastic deformation, and there is a material transfer in the surface, as shown in Fig. 8(c). The damage mechanism thus transits from the abrasive wear to the adhesive wear, and large wear debris is peeled off from the surface, as shown in Figs. 8(d) and 10(c).

4.2. *Effect of crystallinity*

The relaxation and crystallization will change the amorphous state of metallic glasses. The change in the structure may lead to a significant influence in the properties, for example, the viscosity and the hardness. For conventional materials, the wear behavior follows the Archard's equation:

$$dV = \frac{KP}{H}dx,$$

where dV is the wear loss, P and H are load and hardness, respectively, K is called the wear resistance factor and dx is the wear distance. The harder the material, the better the wear resistance will be. However, for the bulk metallic glass and its crystalline composites, the equation seems not to apply. There is a minimum wear loss at a crystal content of about 34%, then the wear loss increases with crystallinity, and is the highest for the fully crystalline material. A certain amount of crystalline phase will increase both the hardness and the toughness of metallic glass, thus the wear resistance will increase [35,36]. However, too many crystals will embrittle the glass matrix, and will induce the nucleation and growth of cracks during wear [17,37]. Therefore, the wear behavior of metallic glass depends both on hardness and toughness, a good balance between the hardness and toughness will increase the wear resistance, otherwise, will deteriorate it. Other studies also showed that 30–40% crystal content may be the optimum structure for wear resistant metallic glasses [16,27]. The crystallization also changes the morphology of the wear surface. The crystalline phase can be debonded from the surface by the shear force during wear, and then "three-body wear" may occur, leaving behind long parallel grooves by ploughing. The wear mechanism thus changes from an adhesive manner to an abrasive one.

5. Conclusions

(1) The friction coefficient of the metallic glass with a steel counterpart is in the range of 0.24–0.32.
(2) Both surface softening and crystallization occur on the surface of the metallic glass during wear, and the wear curve is not as stable as that of crystalline materials due to the interaction of the two processes.
(3) The wear mechanism of the metallic glass may change with wear conditions and the crystallinity. The fully amorphous material shows an abrasive wear at a low load, then adhesive wear at a high load. Increasing the content of crystalline phases results in more abrasive wear.
(4) The wear behaviors of the metallic glass and its crystalline composites do not follow the Archard's equation. Only a good combination of the hardness and the toughness can the metallic glass be wear resistant.

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