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ARTICLE

# Effect of Be Content on Wear Behavior of Ti-Based Bulk Metallic Glass Composites

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**Abstract:** A series of Ti-based bulk metallic glass composites (BMGCs) and a Ti-based bulk metallic glass were prepared by arc melting, and the effect of Be contents on the wear performance was investigated. The results show that the decrease in Be content in the composites increases the volume fraction of dendrites in BMGCs; the increase in the volume fraction of dendrites reduces the coefficient of friction, but increases the wear ratio slightly. All the worn surfaces show abrasive wear, and the size of wear debris is decreased with increasing the volume fraction of dendrites.

**Key words:** bulk metallic glass composite; wear performance; volume fraction of dendrites

Due to the long-range disordered and short-range ordered atomic configurations at nanoscale, bulk metallic glasses (BMGs) have good mechanical properties at ambient temperature, such as high strength and large elastic area<sup>[1-6]</sup>. But the poor ductility at ambient temperature restricts their applications as structural material in commercial proliferation<sup>[7]</sup>. It is because the deformation essence of BMGs at room temperature is the generation of shear bands. Though shear band is a typical characteristic of plasticity, the amount of shear band is very restricted during the deformation, resulting in the fact that the shear strain of a single shear band is too high<sup>[8]</sup>. At last, the expansion of the restricted shear band leads to a catastrophic fracture without macroscopic plasticity. Therefore, there are many efforts devoted to improving the ductility of BMGs at ambient temperature<sup>[9-15]</sup>. The fabrication of bulk metallic glass composites (BMGCs) is an effective method. There are two phases in BMGCs: one is glassy matrix and the other is secondary crystalline phases. The main function of the secondary crystalline phases is absorbing and blocking the extension of shear band during deformation. Therefore, more shear bands are generated in the glassy matrix during deformation, and the macroscopic plasticity of

BMGCs is enhanced obviously.

Based on this theory, different kinds of BMGCs have been fabricated by different techniques. The most popular BMGCs of them are Ti-based and Zr-based BMGCs, which are reinforced by ductile  $\beta$ -phase dendrites<sup>[16,17]</sup>. The main focus of previous studies is the relationship between the microstructure and mechanical properties of BMGCs, or the microstructure evolution during deformation<sup>[18-22]</sup>. However, the influence of microstructure on tribological behavior of BMGCs was barely investigated.

It is well known that friction property is an important factor in the application of engineering materials, because wear and fracture are primary failure modes in engineering materials. Therefore, as an important potential engineering material, it is necessary to investigate the friction and wear properties of BMGCs. In this research, TiZr-based BMGCs were investigated due to their low density, high mechanical properties at ambient temperature<sup>[23-27]</sup>, and adjustable microstructure. Based on previous researches, there are two phases in TiZrNbCuBe BMGCs: one is the amorphous matrix, and the other is the secondary  $\beta$ -phase dendrite. The volume fraction of dendrite can be controlled by fine adjusting of the ratios of

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Ti to Be in the composite. Therefore,  $\text{Ti}_{50}\text{Zr}_{20}\text{Nb}_{12}\text{Cu}_5\text{Be}_{13}$ ,  $\text{Ti}_{46}\text{Zr}_{20}\text{Nb}_{12}\text{Cu}_5\text{Be}_{17}$ ,  $\text{Ti}_{42}\text{Zr}_{20}\text{Nb}_{12}\text{Cu}_5\text{Be}_{21}$ ,  $\text{Ti}_{38}\text{Zr}_{20}\text{Nb}_{12}\text{Cu}_5\text{Be}_{25}$ , and a pure TiZr-based BMG  $\text{Ti}_{36.2}\text{Zr}_{30.3}\text{Cu}_{8.3}\text{Fe}_4\text{Be}_{21.2}$  were selected as the research candidates and the reference, namely Ti50, Ti46, Ti42, Ti38, Ti-BMG, respectively. The friction properties of TiZr-based BMGCs of different dendrite percentages were investigated. The obtained results can evaluate the feasibility of TiZr-based BMGCs as potential engineering materials.

## 1 Experiment

The ingots of TiZr-based BMGCs and BMG were prepared by arc melting. The pure elements (purity > 99.95%) were prepared according to the nominal composition of BMGCs and BMG, then melted in a water-cooled copper crucible, and finally in situ suction cast in the copper mold under a purified argon atmosphere. Then the BMGCs and BMG rods with diameter of ~5 mm were fabricated. The ingots were all remelted several times before suction casting in order to ensure the homogeneity. The characteristic of phase composition was identified by X-ray diffraction (XRD) recorded on a diffractometer with  $2\theta = 20^\circ \sim 80^\circ$  and monochromatic  $\text{Cu K}\alpha$  radiation (Philips X'Pert Pro). The working condition was 40 kV and 30 mA for the X-ray tube and the scanning rate was  $0.02^\circ$  per step. The microstructures and worn surfaces of the specimens were analyzed by scanning electron microscopy (SEM, EVO 18, Zeiss, Germany) coupled with energy dispersive spectroscopy (EDS) at 30 kV. The specimens were etched by an etchant with volume ratio of  $\text{HNO}_3$ : HF: ethanol = 1: 1: 8 before the microstructure observation. Moreover, the wear performance of the specimens was evaluated by pin-on-disk wear tests (CETR-UMT-2, Bruker, America) under the dry sliding condition. The counterface material was martensitic stainless steel 440C (SS440C) disk. The pin specimens of 5 mm in diameter and 20 mm in length were cut from the as-cast cylinders by a wire-cut electrical discharge machine. Furthermore, the contacting surfaces of the pin specimens and counterface disks were well polished by 1500# SiC paper before the tests. The wear tests were performed under the condition of load of 5 N, sliding velocity of 0.1 m/s, and sliding distance of 300 m in air at ambient temperature. The wear factors were obtained by measuring the mass loss of pin specimens with the accuracy of  $\pm 0.1$  mg. Before the measurement, the pin specimens were ultrasonically cleaned with acetone for 10 min. Three separate tests were conducted for each specimen, and the average wear factors and coefficients of friction were obtained.

## 2 Results and Discussion

### 2.1 Phase and microstructures of as-cast alloy

The phase components and microstructures of the as-cast specimens were confirmed by XRD and SEM. Fig. 1 shows the phase components of the specimens. It can be clearly seen that there is only one broad diffraction peak for Ti-BMG, which is a typical characteristic peak for BMG. However, the

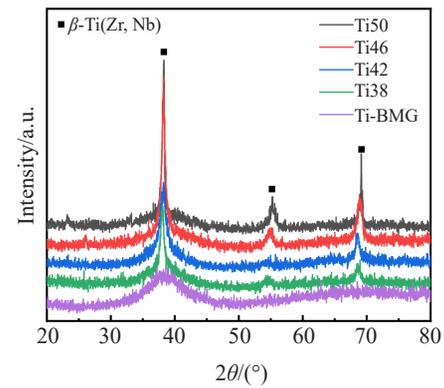


Fig.1 XRD patterns of Ti-BMG, Ti38, Ti42, Ti46, and Ti50 BMGCs

XRD patterns of BMGCs all exhibit three crystalline peaks (identified as  $\beta$ -Ti phase) superimposed on the broad diffraction peak, indicating that BMGCs are composed of  $\beta$ -Ti and amorphous phases. The XRD result is consistent with the idea of material design for BMGCs. It can also be noticed that the three crystalline peaks become sharper and sharper with the decrease of Be content in BMGCs, which implies that the  $\beta$ -Ti dendrite shows stronger diffraction intensity and the volume fraction of dendrite is increased with decreasing the Be content.

To further investigate the microstructures of as-cast BMGCs and BMG, SEM images of specimens' microstructures are shown in Fig. 2. The microstructure is homogeneous in BMG specimen, and no dendrite or crystal can be observed, as shown in Fig. 2a, which is a typical morphology of long-disordered atomic configurations in BMG. For BMGCs, the  $\beta$ -Ti dendrites are distributed evenly in the glassy matrix, as shown in Fig. 2b~2e. It can also be noticed that the volume fraction of dendrites is increased with a decrease in Be content in BMGCs. The volume fractions of dendrites are 18.81%, 37.74%, 43.80%, and 49.52% for Ti38, Ti42, Ti46, and Ti50 BMGCs, respectively, which is consistent with the XRD results. There are only a few dendrites of thin dendrite arms in Ti38 BMGC (Fig. 2b), but many dendrites of thick dendrite arms in other BMGCs (Fig. 2c~2e). Therefore, reducing the content of Be element can promote the forming and coarsening of  $\beta$ -Ti dendrites of BMGC in this research. The addition of Be element can increase the alloy viscosity in melting state, because the atomic volume of Be element is very small, which restricts the movement of other element atoms during melting state in the alloy. It also indicates that the alloy tends to retain the atomic arrangement during cooling procedure from melting state to solid state. This property of Be element is of significance for BMGs preparation. For TiZrNbCuBe BMGCs, raising Be content can restrict the forming of  $\beta$ -Ti dendrite during cooling procedure.

### 2.2 Tribological behavior

The coefficient of friction (COF) of BMGCs and BMG as a function of sliding distance is shown in Fig. 3. It shows clearly that COF at steady state is decreased slightly with increasing

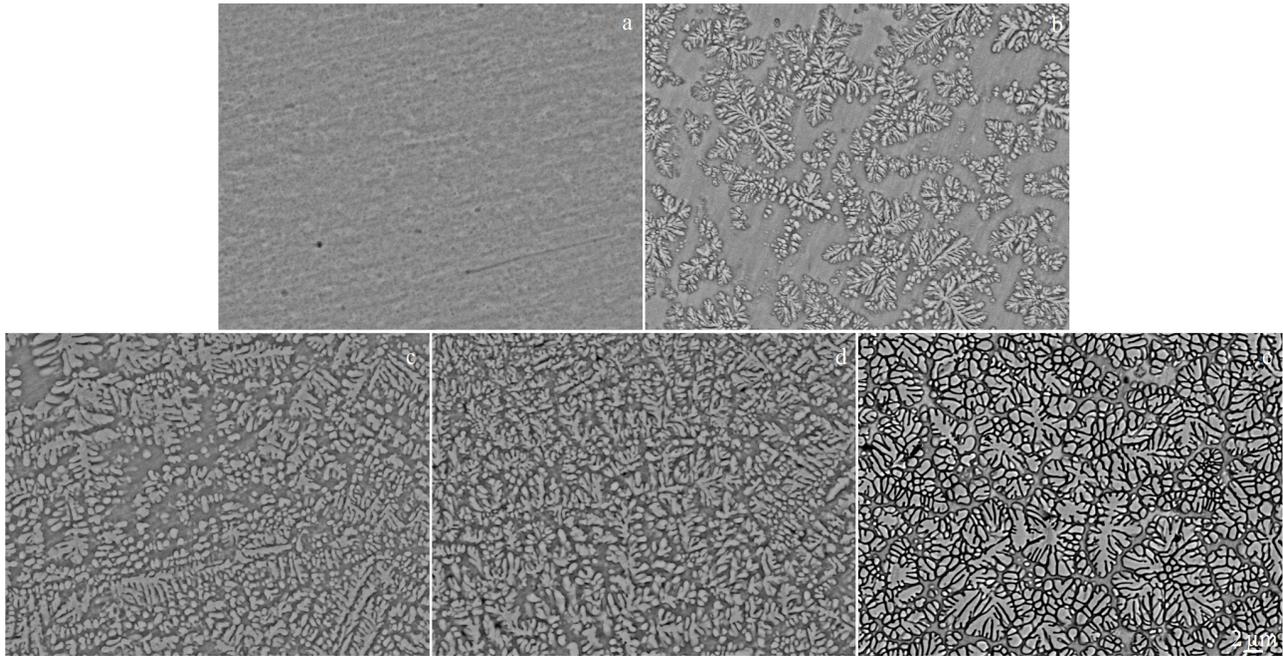


Fig.2 SEM images of microstructures of different specimens: (a) Ti-BMG, (b) Ti38, (c) Ti42, (d) Ti46, and (e) Ti50

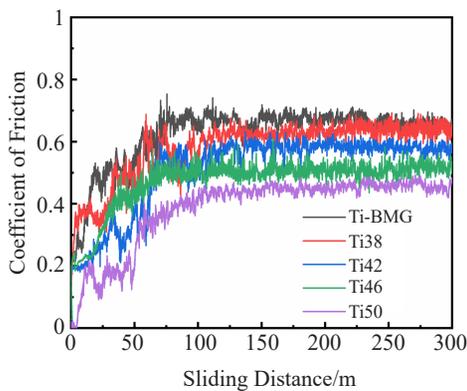


Fig.3 Coefficient of friction of as-cast Ti-BMG, Ti38, Ti42, Ti46, and Ti50 BMGCs (sliding against SS440C disk under the load of 5 N and sliding velocity of 0.1 m/s)

the volume fraction of dendrites. For example, COFs at steady state are 0.66, 0.62, 0.58, 0.52, and 0.45 for Ti-BMG, Ti38, Ti42, Ti46, and Ti50 BMGCs, respectively. The wear loss of BMG and BMGCs are listed in Table 1. The result shows that the increasing volume fraction of  $\beta$ -Ti dendrites reduces the COF but increases the wear loss.

As shown in Fig. 3, all COF curves are serrated in shape. The main reasons are as follows: (1) the periodic contact vibration of two friction surfaces, i. e., the sudden jerky

Table 1 Wear loss of Ti-BMG, Ti38, Ti42, Ti46, and Ti50 BMGCs ( $\times 10^{-4} \text{ mg}\cdot\text{N}^{-1}\cdot\text{m}^{-1}$ )

Ti-BMG	Ti38	Ti42	Ti46	Ti50
5.43	5.45	5.48	5.51	5.54

response to an external driving force (the amplitude is not obvious due to the high precision of the equipment used in this work); (2) the sudden stress drop or strain jump in almost all the solid metals when an external stress (compressive, tensile, shear) is applied. Moreover, this internal serrated behavior can be affected by many factors (applied strain rate, temperature, and specimen geometry), i. e., the serration magnitude is usually decreased with increasing the strain rate and temperature. Based on previous researches<sup>[28]</sup>, although the serrated behavior can be observed in all kinds of solid metals, the internal causes are totally different. For BMGCs in this research, the internal cause of the serrated behavior is a superposition result of several aspects, which is different from other serration forming theories, because BMGCs are in-situ metallic glass composites with two phases (glassy matrix and  $\beta$ -Ti dendrite).

When an external stress is applied on the  $\beta$ -Ti dendrites, the deformation depends on the movement of internal defect, i. e., dislocation motion. Then the diffusive solute atoms are aggregated at the front of the dislocations during the deformation in order to hinder the propagation of dislocations. Thus, the pinning dislocations need more energy to break free from the pinning, and the alloy is strengthened. Subsequently, the external stress rises to the critical value, the dislocation motion is initiated again, and the diffusive solute atoms are regrouped at the front of the dislocations. This strengthening phenomenon caused by the repeated interaction between the diffusive solute atoms and the moving dislocations is dynamic strain aging (DSA), which is the micro-mechanism of the serrated behavior of  $\beta$ -Ti dendrites.

For the glassy matrix in BMGCs, the deformation depends on the movement of shear bands. There are many "weak points", namely free volumes in metallic glass, which can

become stress concentration points under an applied external stress. The shear bands can be initiated in these free volumes when the applied stress exceeds the critical value; thereby the sliding shear bands can occupy the position of these free volumes. With increasing the external stress, new free volumes are generated at the front of the shear bands which keep sliding to occupy the position of these new free volumes. The propagation of shear bands along with the repeated generations of free volumes is the micro-mechanism of the serrated behavior in the metallic glass matrix. In conclusion, the internal cause of the serrated behavior of BMGCs in this research is a superposition result of three aspects: (1) the periodic contact vibration of two friction surfaces; (2) the repeated interaction between diffusive solute atoms and the moving dislocations; (3) the propagation of shear bands and repeated generation of free volumes.

In order to reveal the wear mechanism, the worn pin surfaces and wear debris were examined in detail, as shown in Fig. 4. The worn surface of BMG specimen is very smooth, and the shallow ploughed grooves are parallel to the sliding direction (SD). Only a few peel-off parts can be observed and are marked by white circle. The worn surface shows the characteristic features of abrasive wear. The worn surface of Ti38 specimen exhibits the similar morphology only with a little bit more peel-off parts, as shown in Fig. 4b. Fig. 4c shows the EDS spectra of the two areas marked in Fig. 4b. EDS analysis confirms that besides the base material, the peel-off parts are the mechanical mixture of pin and disk caused by wear. The morphologies of worn surfaces of Ti42, Ti46, and Ti50 are shown in Fig. 4d~4f, respectively. The number of peel-off parts is increased with increasing the volume fraction

of dendrites, but the wear mechanism is still the abrasive wear.

When the materials of pin and disk have the similar hardness in a friction condition, the peel-off occurs at the micro-cracks in the worn surface, and the micro-cracks extend under the friction press and vibration condition during the whole wear experiment. When the cracks are large enough, part of material peels off from the worn surface. If the specimen material has homogeneous single phase and high hardness, less micro-cracks occur in the worn surface, such as BMGs, which is consistent with the results. By contrast, the BMGCs have two phases: the harder metallic glass matrix and the relatively softer  $\beta$ -Ti dendrite phase, suggesting that the plastic deformation occurs more easily in the  $\beta$ -Ti dendrite phase. Therefore, the metallic glass matrix hinders the plastic deformation of the dendrites during the wear process, and the boundary of two phases becomes the stress concentration area where the cracks are generated easily. Based on this analysis, the number of micro-cracks is increased with increasing the volume fraction of dendrites. On the other hand, the peel-off parts are generated more easily in BMGCs with high volume fraction of dendrites. Moreover, the increasing volume fraction of dendrites reduces the volume of peel-off parts due to the reducing dendritic distance.

The results can be further confirmed by the morphologies of wear debris shown in Fig. 5. The wear debris of Ti-BMG and Ti38 specimens shows big flakes of the largest size of 110~120  $\mu\text{m}$  at the same scale. The size of wear debris is decreased with increasing the volume fraction of  $\beta$ -Ti dendrites, and the wear debris of Ti50 specimen only shows very small flakes of the largest size of about 20  $\mu\text{m}$ .

In general, the worn surfaces of Ti-BMG and Ti38

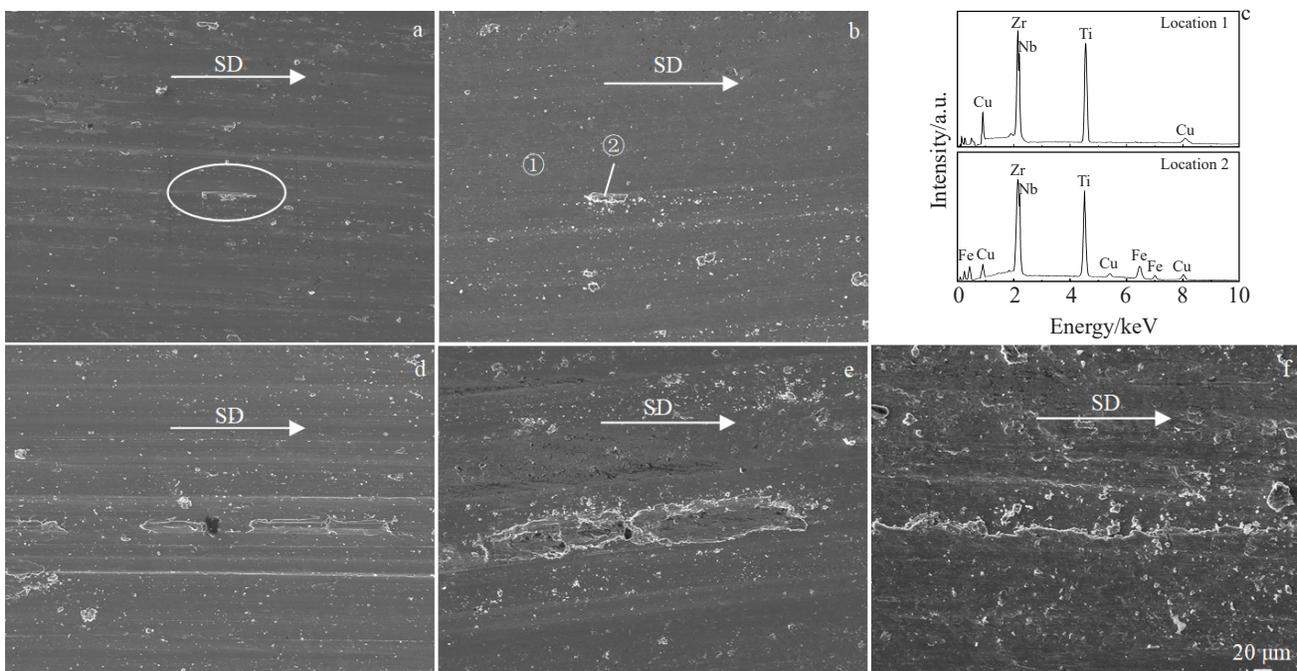


Fig.4 SEM morphologies of worn pin surfaces of Ti-BMG (a), Ti38 (b), Ti42 (d), Ti46 (e) and Ti50 (f) BMGCs after sliding against SS440C disk for 300 m under load of 5 N and velocity of 0.1 m/s; EDS spectra of location 1 and 2 in Fig.4b (c)

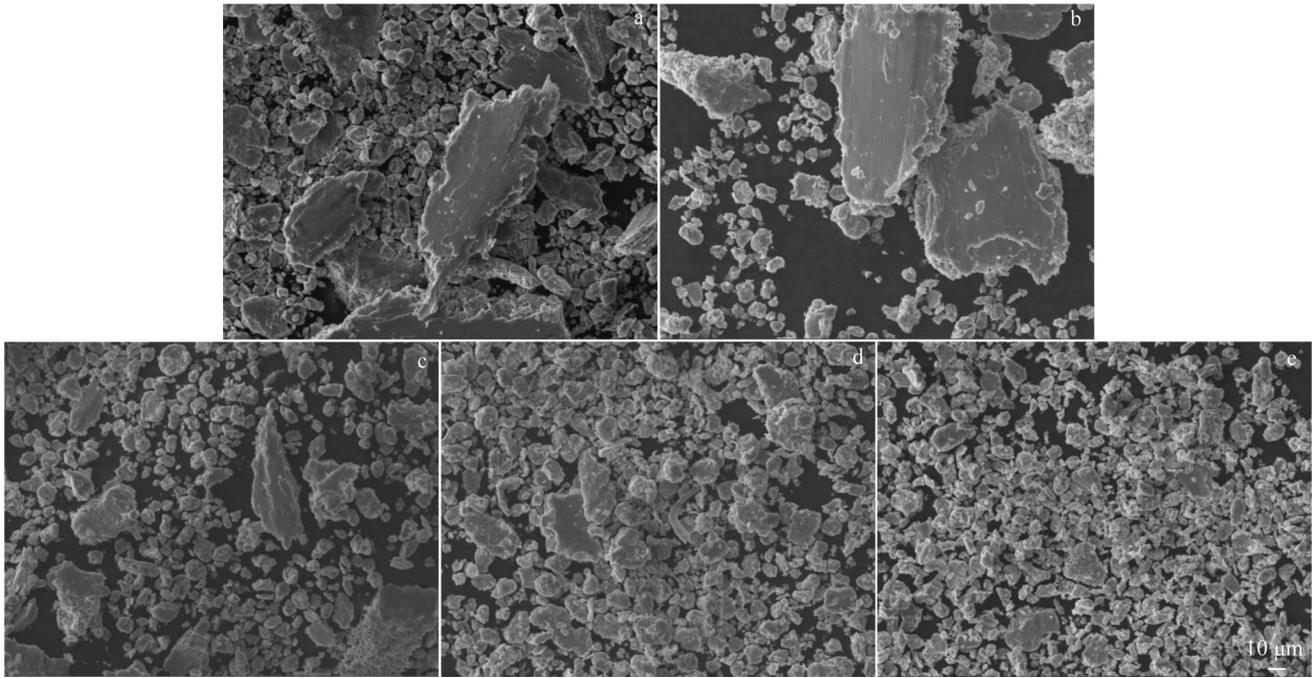


Fig.5 SEM images of the wear debris of Ti-BMG (a), Ti38 (b), Ti42 (c), Ti46 (d) and Ti50 (e) BMGCs after sliding against SS440C disk for 300 m under load of 5 N and velocity of 0.1 m/s

specimens only have a few peel-off parts, and the number of peel-off parts is increased with increasing the volume fraction of  $\beta$ -Ti dendrites in Ti42, Ti46, and Ti50 specimens, indicating that the volume fraction of  $\beta$ -Ti dendrites can accelerate the peel-off behavior. Therefore, a large amount of wear debris is participated in the wear process, and the wear mechanism changes from pure abrasive wear to three-body abrasive wear. Besides, the participation of small hard debris changes the wear state from pure sliding friction to rolling friction, which can also explain the decrease in COF in Fig.3.

### 3 Conclusions

1) The decrease in Be content increases the volume fraction of dendrites in the Ti-based bulk metallic glass composites (BMGCs).

2) The pin-on-disk wear tests show that the increase of volume fraction of  $\beta$ -Ti dendrites reduces the coefficient of friction, but increases the wear loss slightly.

3) All specimens show the abrasive wear mechanism. The size of wear debris is decreased with increasing the volume fraction of dendrites.

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## 铍含量对钛基非晶复合材料摩擦行为的影响

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**摘要:** 通过真空电弧熔炼制备了一系列钛基非晶复合材料和钛基非晶合金, 研究了合金中铍元素的含量对整体合金摩擦行为的影响。随着合金中铍元素的减少, 非晶复合材料中的枝晶体积分数逐渐增加, 整体合金的摩擦系数降低, 但是合金的磨损率升高。所有材料的磨损表面都展现出了磨粒磨损的磨损机制, 并且磨屑的尺寸随着枝晶体积分数的升高而逐渐降低。

**关键词:** 非晶复合材料; 摩擦行为; 枝晶体积分数

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