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ARTICLE

# Tribological and Corrosive Mechanism of Fe-based Metallic Glassy Composite Coatings Sprayed by Plasma Spraying

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**Abstract:** A novel gas multiple-tunnel plasma spraying technology was adopted to fabricate amorphous Fe-based composite coatings with various contents of $ZrO_2$. By this way, the $ZrO_2$ particles were distributed homogeneously in the matrix and the proportion of the two phases in the composite coatings can be regulated. During the wear process, the wear resistance is improved for the composite coatings. Meanwhile, the introduction of $ZrO_2$ improves both the corrosion resistance and porosity. Therefore the best corrosion resistance is obtained for the composite coating with 50 wt% $ZrO_2$.

**Key words:** coating; amorphous; plasmas spraying; tribology mechanism; corrosion resistance

As well as known, bulk metallic glasses (BMGs) exhibit unique properties, including high mechanical strength, high hardness, superior corrosion resistance and so on[1-3]. Nevertheless, the limiting condition of glass-forming ability (GFA) that the thickness (or diameter) of BMGs is usually small, restricts their application as engineering material. Fortunately, they can be made to coatings by spraying. It means that we just need to obtain powders with micrometer size, and then we can enlarge the size in 3 dimensions. Furthermore, metallic glassy coating can take advantage of the superior properties of BMGs and it can widen the application fields of BMGs.

Zhou[4] reported the Fe-based coatings possess high micro-hardness and low porosity with an optimizing process. Shen[5] reported the Fe-based metallic glassy coating had higher corrosion resistance in aggressive $H_2SO_4$ solution than 921A navy steel and Ti6Al4V. Kobayashi[6] obtained Fe-based metallic glassy coating and researched the mechanical properties. The results indicated that the Vickers hardness of metallic glassy coating was similar to that of the original powder and the abrasive wear resistance was higher than that of the stainless steel substrate. However, as far as coating materials, the metallic glassy coating is brittle, which results in the brittle spall of the coatings during wear. Hofmann et al[7] pointed that in order to optimize the wear performance of gears, the toughness should be maximized. It means the coatings with superior wear resistance should not only possess high hardness but also be with high toughness. In order to obtain high toughness, high strength and high plasticity should be possessed simultaneously for the materials. As pointed above, there is high strength for BMGs. So the key issue is how to improve the plasticity of the metallic glassy coatings. Some papers reported the method of introducing the crystalline phases into the metallic glassy matrix coating can improve the wear resistance. Liu [8] obtained Fe2B and (Fe, Cr)B in the Fe-based coatings by heat treatment above 873 K, and the wear loss was reduced obviously. Lan[9] reported the micro-hardness and wear resistance were improved

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significantly due to the formation of composite coating. But the wear rate does not linearly reduce with the increase of the crystalline phase fraction. Suresh[10] reported the higher crystalline content in Ni-metallic glass composite coating resulted in more abrasive wear. Yugeswaran[11] research also indicated that the composite coating with 36% crystalline content exhibited minimum wear rate.

It is worthy to note that the deformation mechanism of BMGs is different from the crystalline alloy. At the atomic scale, the plastic deformation of crystalline alloys is regarded as the cumulative effect of numerous dislocation slip and/or twining. Meanwhile, the accommodation of shear strain in metallic glass under an applied stress is believed to occur via local rearrangement of atoms in a narrow volume element called the shear transformation zone (STZ) [12, 13]. Therefore, for the composite coatings with crystallization, the deformation mechanism is related to the crystallization fraction, which affects the shear bands' initiation and development.

In the present study, the Fe-based metallic glass and $ZrO_2$ composite coatings with various contents were fabricated by atmospheric plasma spraying. The wear mechanism of the composite coatings was investigated systematically. For the coating materials to protect the substrate, another property is corrosion resistance. Therefore, the corrosion resistance properties of composite coatings in NaCl solution and $H_2SO_4$ solution were investigated.

## 1 Experiment

Commercially available Fe-based amorphous powders ($Fe_{45}Cr_{16}Mo_{16}C_{18}B_5$, atomic ratio) with a size of 10~50 μm were prepared by gas atomization. The size of ceramic $ZrO_2$ powders is 20~40 μm. The carbon steel (0.14 wt%~0.22 wt% C) substrate was machined into samples of 10 mm ×10 mm ×10 mm. The composite metallic glassy coatings were fabricated by multiple-tunnel feeding plasma spraying equipment, which is manufactured by Taixing Yeyuan Device Company in China. In order to avoid crystallization during spraying, the $ZrO_2$ powders were fed into the spraying gun to reach the flame flow with the highest temperature, and the Fe-based metallic glassy powders were fed out of the spraying gun.

The surface morphology and microstructure of coatings were investigated with a scanning electron microscopy (SEM, S-4800, Hitachi, Japan). The phase constitution of the metallic glassy powders and the composite coatings was analyzed by X-ray diffraction (XRD, Philips X'-Pert MPD) with Cu Kα radiation. A ball-on-disc friction-wear tester (SFT-2M, Zhongkekaihua, Technology Development Co., Ltd, China) was adopted to evaluate the tribological properties of the Fe-based metallic glassy coating and the composite coatings sliding against commercially obtained $Si_3N_4$ balls (5 mm in diameter) in air. The tests were carried out using applied loads 50 N. The sliding speed was selected at a constant value of 800 r/min and the duration time of sliding was 15 min. The electrochemical corrosion test was performed in a three electrode cell (graphite rod as the counter electrode, saturated calomel electrode as the reference electrode and the coating sample as the working electrode). The model of equipment used in the electrochemical corrosion test is shown in Fig.1.

## 2 Results and Discussion

### 2.1 Phase structure and morphology of coatings

The phase structures and morphologies of coatings are tested by XRD and SEM. The results are shown in Fig.2. The Fig. 2a displays the patterns of multiple-tunnel plasma sprayed composite coatings, $ZrO_2$ ceramic coating and Fe-based metallic glassy coating. The results indicate that the Fe-based metallic glassy coating is fully amorphous phase. For the composite coatings, besides the amorphous phase, $ZrO_2$ peaks were detected, and no other phase is precipitated from the glassy metallic phase. Furthermore, intensity of $ZrO_2$ peaks increases with fraction percentage of $ZrO_2$ increasing.

The surface of sprayed coating is shown in Fig.2b. And the original and polishing SEM morphology of the composite coating with 20 wt% $ZrO_2$ as an example is shown in Fig.2c and 2d, respectively. The Fe-based metallic glassy feeding powders and $ZrO_2$ powders were deposited on the substrate as a disk-type pattern, which indicates the feeding powders were melted adequately. The surface morphology of the coating (as shown in Fig.2d) shows that $ZrO_2$ particles are homogeneously dispersed in the glassy matrix.

### 2.2 Mechanical properties of coatings

The $ZrO_2$ materials possess high hardness but low ductility, so the $ZrO_2$ coating shows fatigue wear. The wear rate of the composite coating is related to the content of $ZrO_2$. According to the previous study[14], the best wear resistance property for the composite coatings is with 20 wt% $ZrO_2$. In the present study, the wear failure mechanism at different stages during the wear process at applied loading 50 N was investigated. Fig. 3 shows the friction coefficient value of the composite coating with 20 wt% $ZrO_2$ and wear morphologies at 50 N load. Firstly, the friction coefficient value increases rapidly and then decreases

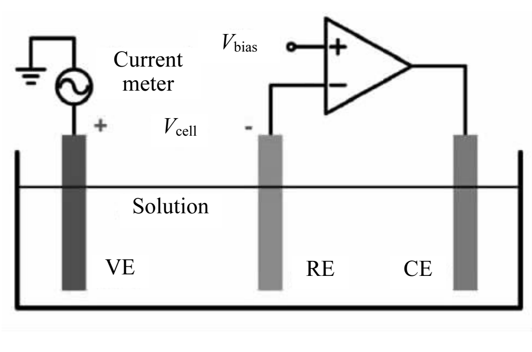


Fig.1 Diagram of the three-electrode system

at the first 2 min. Because the wear sample was polished, the surface of the wear test sample is smooth. However, at early stage, the surface of the sample becomes rough. So firstly the friction coefficient increases rapidly. Meanwhile, the contact surface of $Si_3N_4$ against to the coating is small at the beginning. And then the contact surface of $Si_3N_4$ against is enlarged during the initial wear process. Therefore, the friction coefficient decreases slowly. At the next stage, the friction coefficient increases slightly during the wear test 2 ~5 min. The reason is that the coating experiences large deformation, which results in the increase of frictional resistance. Fig. 3a shows the worn morphology of the coating after 3 min tribological test. A smooth surface with some scar regions is seen at the abrasive initial stage. However, many shear bands are observed in the magnified image of marked circle in Fig.3a (as shown in Fig.3b). Generally, shear bands are regarded as plastic deformation in metallic glass [15]. Therefore, it means the coating experiences intense plastic deformation. After that a bit of decrease follows it during 5 min to 6 min in the friction coefficient curve. It is attributed to the increase of frictional heat, which results in the viscous flow of the glassy matrix at a high temperature. Fig. 3c shows the worn surface morphology of the coating after 9 min tribological test. At the abrasive mid-term stage, spalling regions are expanded. It is formed due to the formation of a large number of shear bands followed by viscous flow. The worn surface of the coating after viscous flow is shown in Fig. 3d. The worn surface morphology after 15 min wear test is shown in Fig. 3e. At the abrasive late stage, micro-crack is formed followed by viscous plastic deformation (as shown in Fig.3f). With the spall of the coating, the roughness of coating increases. Therefore, the friction coefficient value increases gradually.

As reported by Hofmann group[7], the excellent wear property is related to the toughness of the materials. The bending fracture morphologies of the coatings were observed, and the results are shown in Fig. 4. Fig. 4a is the fracture morphology of the Fe-based metallic glassy coating. Because the deformation of the metallic glass which is dependent on the development of shear bands is different from the crystallization. The fracture morphology is smooth and long ribbon shape is observed as shown in Fig. 4a. The fracture surface of the composite coating with 20 wt% $ZrO_2$ is rough as shown in Fig.4b. And the morphology that $ZrO_2$ around the Fe-based metallic glassy is observed as shown in Fig. 4b. Compared with the metallic glassy coating, long ribbon shape is changed into coarse morphology in the composite coating fracture surface as shown in Fig. 4b. The reason is that the deformation of the metallic glass is related to the development of shear bands. The initiation and rapid development of the shear bands result in the failure of the coating. Therefore, smooth fracture morphology is observed in the metallic glassy coating. On the other hand, due to the introduction of $ZrO_2$ in the composite coating the development of shear bands in the metallic glass is prevented. So the fracture toughness of the coating is improved.

### 2.3 Corrosion resistance properties of coatings

The potentiodynamic polarization curves of Fe-based glassy coating and composite coatings in 3.5 wt% NaCl solution and 0.5 mol/L $HSO_4$ solution are shown in Fig. 5. The data of the polarization are summarized in Table 1 and Table 2. It is worthy to note that the corrosion resistance of Fe-based

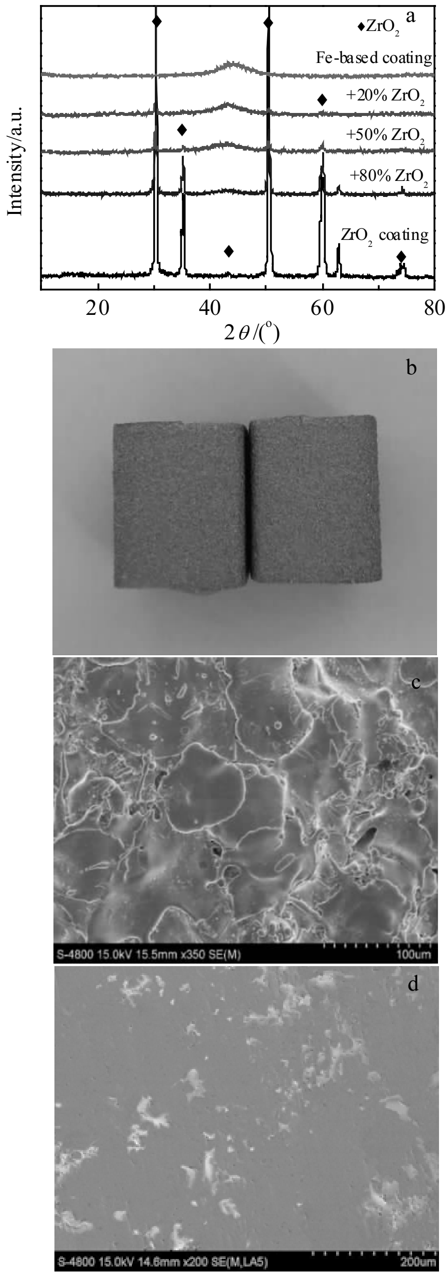


Fig.2 Phase structures and morphologies of coatings: (a) XRD patterns of sprayed coatings; (b) surface of sprayed coating; SEM morphology of composite coating with 20 wt% $ZrO_2$: (c) original surface and (d) polished surface

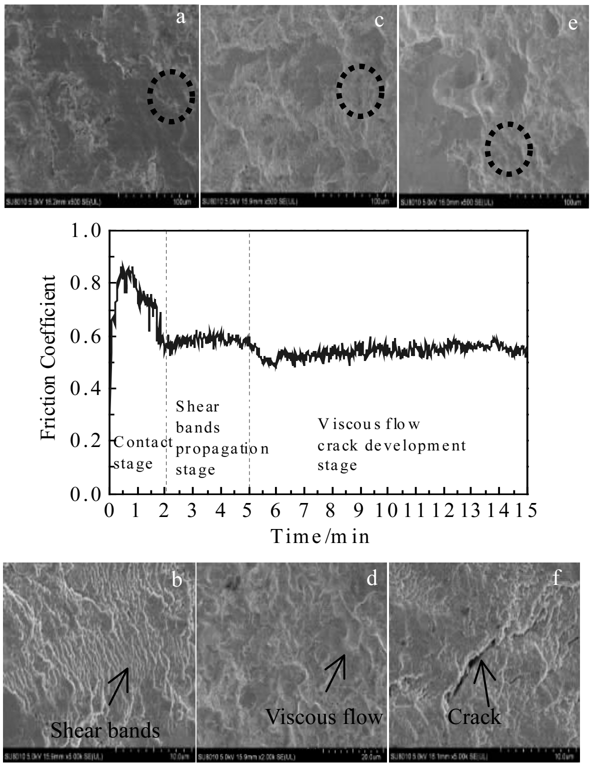


Fig.3 Friction coefficient value and worn surface morphologies of composite coating with 20 wt% $ZrO_2$ at 50 N load: (a) morphology of the coating after 3 min tribological test; (b) the magnified image of marked circle in Fig.3a; (c) morphology of the coating after 9 min tribological test; (d) the magnified image of marked circle in Fig.3c; (e) morphology of the coating after 15 min tribological test; (f) the magnified image of marked circle in Fig.3e

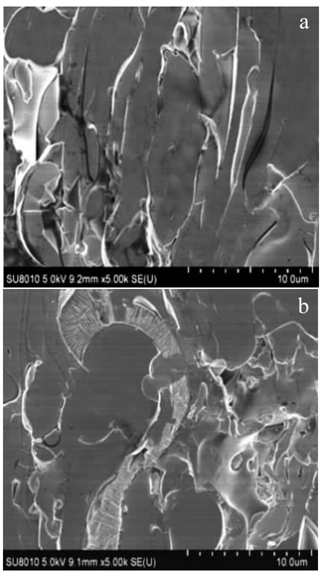


Fig.4 Bending fracture morphologies of the coatings: (a) metallic glassy coating and (b) composite coating with 20 wt% $ZrO_2$

metallic glassy coating in salt solution and acid solution is different. The Fe-based metallic glassy coating is spontaneously passivated with a passive current density of about $10^{-4}$ A/cm$^2$ in $H_2SO_4$ solution. The reason is the element chromium which provides a high passivating ability of Fe-Cr-Mo-Metalloid metallic glasses[16, 17]. As reported by Pang[18], a chromium-rich passive surface film is formed on the surface after immersion in acid solution. Meanwhile, due to the introduction of molybdenum, which prevents dissolution of chromium during passivativation, the corrosion resistance and passivating ability is improved in acid solution[19].

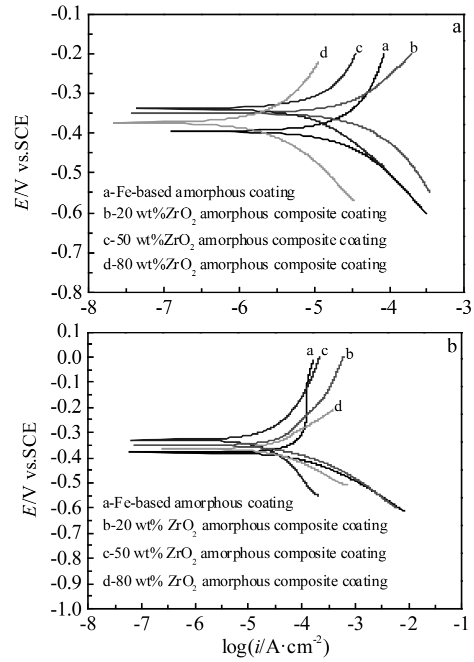


Fig.5 Potentiodynamic polarization curves of Fe-based glassy coating and composite coatings in 3.5 wt% NaCl solution (a) and 0.5 mol/L $H_2SO_4$ solution (b)

**Table 1 Electrochemical parameters from potentiodynamic polarization curves of Fe-based glassy coating and composite coatings in 3.5 wt% NaCl solution**

| Samples | $E_{corr}$/mV | $i_{corr}$/μA·cm$^{-2}$ |
|---|---|---|
| Fe | −412.7 | 5.747 |
| +20 wt% $ZrO_2$ | −361.2 | 5.332 |
| +50 wt% $ZrO_2$ | −349.8 | 5.271 |
| +80 wt% $ZrO_2$ | −386.6 | 5.581 |
| $ZrO_2$ | −457.2 | 6.143 |

**Table 2 Electrochemical parameters from potentiodynamic polarization curves of Fe-based glassy coating and composite coatings in 0.5 mol/L $H_2SO_4$ solution**

| Samples | $E_{corr}$/mV | $i_{corr}$/μA·cm$^{-2}$ |
|---|---|---|
| Fe | −372.2 | 4.679 |
| +20 wt% $ZrO_2$ | −343 | 4.332 |
| +50 wt% $ZrO_2$ | −329.4 | 4.126 |
| +80 wt% $ZrO_2$ | −353.7 | 4.228 |
| $ZrO_2$ | −497.3 | 7.713 |

In the salt solution, the concentration of $Cl^-$ is high, which depresses the formation of passive film[20]. Therefore, there is no passivation phenomenon during the potentiodynamic polarization test. Although the passivated behavior does not be observed in the composite coatings, the property of corrosion resistance is increased with the increase of $ZrO_2$ content, and the composite coating with 50 wt% $ZrO_2$ shows the best corrosion resistance both in salt solution and aggressive solution among all the coatings. While the $ZrO_2$ content reaches 80% in the composite coating, the corrosion resistance is reduced. As generally, the ceramic material possesses high corrosion resistance [21]. Therefore, the corrosion resistance is improved with the introduction of $ZrO_2$. On the other hand, the high content of $ZrO_2$ results in the increase of the porosity of the composite coating.

The corrosion resistance property of the composite coating is related to the intrinsic corrosion property of materials and also to the structure of the composite coating. During potentiodynamic polarization test, the solution penetrates into the coating and then contacts with the substrate, and finally generates the charge transfer reactions at metal-electrolyte interface. It means that the channel of the solution penetrating into the substrate is increased with higher porosity. In other words, for the composite coating, the introduction of $ZrO_2$ gives positive and passive effect at the same time. $ZrO_2$ ceramic material improves the corrosion resistance of the coating. On the other hand, the increase of porosity due to the introduction of $ZrO_2$ is not beneficial to the corrosion resistance. Therefore, it is necessary to control and regulate the proportion of the two phases in the composite coating.

## 3 Conclusions

1) The amorphous Fe-based matrix composite coatings with various $ZrO_2$ particles contents are obtained by gas multiple-tunnel plasma spraying technology.

2) With the addition of $ZrO_2$, the wear resistance and corrosion resistance of amorphous Fe-based matrix coatings are improved. The wear mechanism of the composite coating is due to initiation and propagation of shear bands at the early stage, and then to the viscous flow in the glassy matrix because of frictional heat. Both of them improve the plastic deformation of the glassy matrix. Therefore, the wear resistance of the coating is improved.

3) The elements Cr and Mo improve the corrosion resistance of Fe-based metallic glassy coating. Ceramic material $ZrO_2$ further improves the corrosion resistance of the composite coatings. And the best corrosion resistance is obtained for the composite coatings with 50 wt% $ZrO_2$.

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# 等离子喷涂 Fe 基非晶复合涂层的磨损和腐蚀机制的研究


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**摘　要**：采用一种新型的气体多通道送粉等离子喷涂技术制备得到了含有不同质量分数的 $ZrO_2$/Fe 基非晶复合涂层。采用该技术可成功制得 $ZrO_2$ 颗粒均匀分布于非晶基体的复合涂层，且可实现第二相颗粒的比例调控。磨损实验表明，复合涂层的磨损性能较单一的 Fe 基涂层有了很大提高。同时，$ZrO_2$ 颗粒的添加可提高耐蚀性能，降低孔隙率。经实验表明，质量分数 50%$ZrO_2$ 复合涂层的耐蚀性能最佳。



**关键词**：涂层；非晶；等离子喷涂；摩擦学机制；耐蚀性



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