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Corrosion Resistance of Coating with Fe-based Metallic Glass Powders Fabricated by Laser Spraying

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Abstract: In order to improve their wearing resistance, some reinforced particles such as TiN and WC were usually inserted into Fe-based Metallic Glassy Coatings (Fe-MGC). In this study, a new Fe-MGC was fabricated with the powder mixtures of Fe-based metallic glass, NiCr alloy and WC particle by laser spraying. The corrosion resistance of Fe-MGC was investigated by potentiodynamic polarization tests in 1 M HCl, NaCl, H₂SO₄ and NaOH solutions, respectively. The microstructures were detected by X-ray diffraction and scanning electron microscope. The Fe-MGC of Fe_{68.5} C_{7.1} Si_{3.3} B_{5.5} P_{8.7} Cr_{2.3} Mo_{2.5} Al_{2.0}+NiCr+tungsten carbon exhibits low corrosion current density of 10.6 and 3.3 μA, high corrosion potential of 326.4 and 367.5 mV in HCl and NaCl solutions, respectively. The results indicate Fe-MGC presents low porosity and high microhardness implying superior wearing properties, moreover, exhibits excellent corrosion resistance and no inferior than that of full amorphous coatings in various solutions. The excellent corrosion resistance and wearing properties demonstrates that Fe-based metallic glassy matrix powder is a viable engineering material as practical anti-corrosion and anti-wear coating applications.

Key words: Metallic glass, coating, corrosion resistance, laser spraying

INTRODUCTION

Fe-based bulk metallic glasses (Fe-BMGs) are attractive for practical applications due to excellent corrosion resistances (Greer, 1995; Pang *et al.*, 2002; Scully *et al.*, 2007). Up to now, some Fe-based BMGs with high Glass Forming Ability (GFA) can be applied in practice as anti-wear or anti-corrosive coating materials for metallic components (Basu *et al.*, 2008; Majumdar *et al.*, 2004). However, the amorphous or nanostructured coatings fabricated through various coating methods using Fe-based BMG powders exhibited high wear loss or low corrosion resistance. In order to improve corrosion resistance and wear resistance, some Fe-based metallic glassy composite and composite coatings were developed (Zhang *et al.*, 2003; Cherigui *et al.*, 2004; Zhu *et al.*, 2007). In this study, the Fe-based metallic glassy coatings were fabricated by Laser Spraying (LS) method using Fe-based metallic glass Fe_{68.5} C_{7.1} Si_{3.3} B_{5.5} P_{8.7} Cr_{2.3} Mo_{2.5} Al_{2.0}, NiCr alloy and WC particle and the corrosion resistance is investigated in different aqueous media.

MATERIALS AND METHODS

Using amorphous powder mixtures synthesized with Fe-based metallic glass of Fe_{80.6} C_{1.8} Si_{2.0} B_{1.3} P_{5.7} Cr_{2.5} Mo_{5.1} Al_{1.2}, 25 wt.% NiCr alloy (Ni_{67.5} Cr₁₆ Si₄ B₄ Cu₃ Mo₃ Fe_{2.5} wt.%) and 25 wt.% tungsten carbide particle, the coating layers were fabricated by laser spraying. Laser spraying were carried out with a 2 kW fiber laser while powders were sprayed with a coaxial spraying gun. The spraying gun velocity was 500 mm min⁻¹ and the gun distance was 100 mm. The microstructural characterization of the coatings were identified from x-ray diffraction (XRD, Philip X'Pert diffractometer) with Cu radiation (Cu-Kα, λ = 0.1541 nm). The microhardness was measured using 401 MVD hardness test machine, the hold time is 10 sec and load force is 0.98 N. Electrochemical measurement were conducted by an EG and G Pinceton Applied. The microstructural characterization of the coatings were identified from x-ray diffraction (XRD, Philip X'Pert diffractometer) with Cu radiation (Cu-Kα, λ = 0.1541 nm). The microhardness was measured using 401 MVD hardness test machine, the hold time is 10 sec and load

force is 0.98 N. Electrochemical measurements. The potentiodynamic polarization curves were measured with a 50 mV min^{-1} potential sweep rate in 1 M HCl, NaCl, H_2SO_4 and NaOH solutions, respectively, open to air at 293 K after immersion for 30 min.

RESULTS AND DISCUSSION

The as-atomized powders with the composition of $\text{Fe}_{80.6} \text{C}_{1.8} \text{Si}_{2.0} \text{B}_{1.3} \text{P}_{5.7} \text{Cr}_{2.5} \text{Mo}_{5.1} \text{Al}_{1.2}$ exhibit a typical spherical morphology and the particle size is about $50 \mu\text{m}$, as shown in Fig. 1. Figure 2 shows optical images of the coatings synthesized by LS methods using the powders with composition of $\text{Fe}_{68.5} \text{C}_{7.1} \text{Si}_{3.3} \text{B}_{5.5} \text{P}_{8.7} \text{Cr}_{2.3} \text{Mo}_{2.5} \text{Al}_{2.0}$ (MG), $\text{Fe}_{68.5} \text{C}_{7.1} \text{Si}_{3.3} \text{B}_{5.5} \text{P}_{8.7} \text{Cr}_{2.3} \text{Mo}_{2.5} \text{Al}_{2.0} + \text{NiCr}$ (MG+Ni) and $\text{Fe}_{68.5} \text{C}_{7.1} \text{Si}_{3.3} \text{B}_{5.5} \text{P}_{8.7} \text{Cr}_{2.3} \text{Mo}_{2.5} \text{Al}_{2.0} + \text{NiCr} + \text{tungsten carbon}$ (MG+Ni+WC). The thickness of coatings exceeds $200 \mu\text{m}$ and no big pores are observed from cross-section and surface views. The cross-section and surface views of the LS coating layer shows a fairly dense coating layer well-bonded on substrate. Since a large amount of heat per unit area was imposed during LS coating process, powders as well as the surface of substrate are completely melted and then, solidified yielding the dense coating layer with dendritic microstructure (Wang *et al.*, 2012).

Figure 3 shows the XRD patterns for the coatings fabricated by LS. It can be observed that the coating synthesized only with Fe-based metallic glass is crystallized. Some crystal phases such as $\alpha\text{-Fe}$, Fe_3B , Fe_3C and Fe_3P are detected. Except for those crystal phases, Cr_2Ni_3 and WC phases can be found in other coatings.

Figure 4 presents a comparison of the microhardness profiles as a function of cross sectional depth from the surface for the LS coating layers. The microhardness for all coatings is higher than 500 Hv. A sharp decrease in hardness for the coating with addition of Ni alloy and an improvement for the coating with addition of WC can be observed, while the hardness of all coatings is higher than that of substrate and these coatings present excellent wearing resistances (Jang *et al.*, 2010).

As known, the quality of coatings such as microhardness and tribological coefficient are affected not only by the thermal spray techniques, but also by the microstructures. The NiCrBSi coatings were produced using the different thermal spray techniques: Flame, plasma and HVOF (Planche *et al.*, 2005). The sprayed

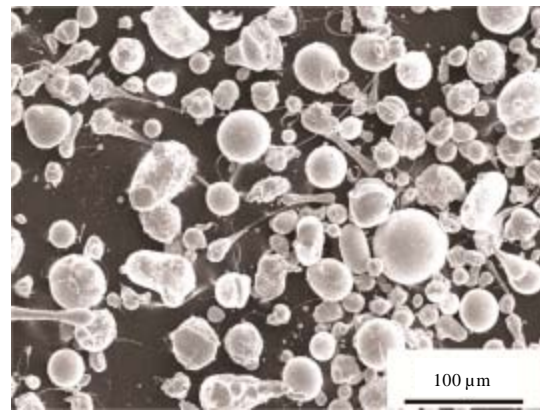


Fig. 1: Particle morphology of the as-atomized powder

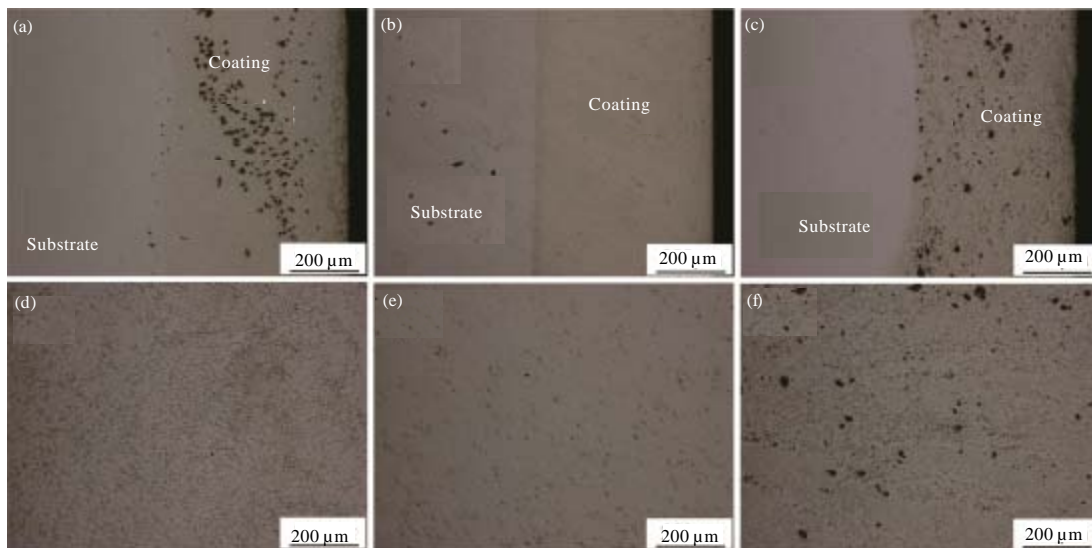


Fig. 2(a-f): Optical images for the coating with different composition, (a-b) MG, (c-d) MG+Ni and (e-f) MG+Ni+WC

coatings revealed the next best results that are related to its density of the coatings and associated high micro hardness of the coatings. The excellent results are attributed to the optimized parameters: The higher the particle speed lead to a better spreading and flattening of the particles onto the substrate which finally allows to produce good coating densities, then results in a higher coating hardness. The microhardness of Ni-WC coating is higher than that of Ni-Cr₃C₂, on average 300 Hv, due to the different solidified structure of the two coatings (Zhang and Zhang, 2005). The hardness were improved significantly on the Ni-based alloy reinforced by all kind of hard phases and the hardness increases with the increasing content of WC among the surface composition layer (Song *et al.*, 2007). So, the hardness of MG+Ni coating decrease than that of MG coating, maybe since the concentration of hard phases such as boride and carbide decreases and the improvement of MG+Ni+WC coating is attributed to the addition of WC particles.

Figure 5 shows the plots of potentiodynamic polarization for the coatings produced by LS method, measured in 1 M HCl, H₂SO₄, NaCl and NaOH electrolytes, respectively. The MG coatings exhibits the different corrosion behaviors compared with that of the coatings of MG+Ni and MG+Ni+WC. While the active dissolution and no passivation are observed in the polarization curves for the MG+Ni and MG+Ni+WC coatings, the MG coating is passivated spontaneously in 1 M NaOH solution. The corrosion potential, corrosion current density and passive current density attained from the plots in Fig. 5 are listed in Table 1. These results indicate an increase in corrosion potential and a decrease in corrosion current density occur for MG+Ni and MG+Ni+WC coatings. Furthermore, the sequences are evident in the same solution, that is, MG coating > MG+Ni coating > MG+Ni+WC coating in corrosion current density and opposite tendency in corrosion potential. The MG+Ni+WC coating possesses a relative lower passive current density. It might be inducted from these results that the corrosion resistances are improved with the addition of Ni and/or WC in the coatings.

The Cr concentration will increase with the addition of NiCr alloy. The existence of larges of passive elements such as chromium and molybdenum promotes the passivation for Fe-based metallic glasses (Long *et al.*,

2007). Moreover, Pang *et al.* (2002) and Im *et al.* (1995) suggested the addition of phosphorous and boron in the metallic glass steels can also improve the automatic passive ability. NiCr/WC composite coating having good wear and corrosion resistance has been widely used in numerous industries (Wang *et al.*, 1996; Wu *et al.*, 2003; Danisman and Cansever, 2010). The NiCr/WC coating produced by AC-HVAF spraying enabled to improve the corrosion resistance of 0Cr13Ni5Mo stainless steel (Liu and Zheng, 2009).

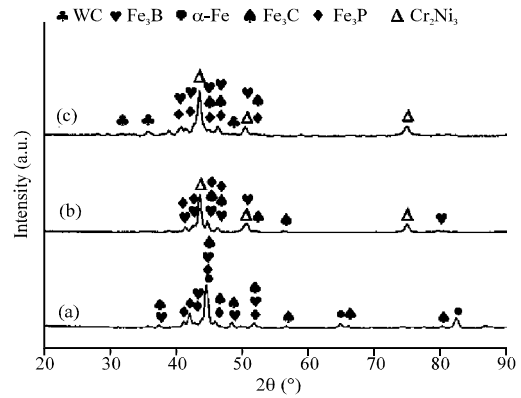


Fig. 3(a-c): XRD patterns of Fe-based metallic glassy coatings with different composition: (a) MG, (b) MG+Ni and (c) MG+Ni+WC

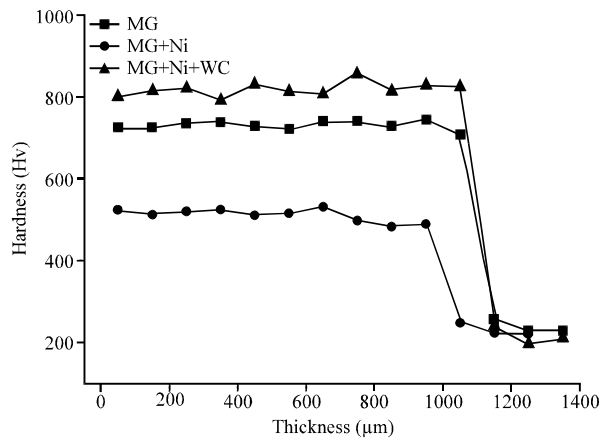


Fig. 4: Microhardness in thickness of Fe-based metallic glassy coatings

Table 1: Results of potentiodynamic polarization for LS coatings in different solutions

Type	HCl			H ₂ SO ₄			NaCl			NaOH		
	E _{corr} (mV)	I _{corr} (μA)	I _{pass} (mA)	E _{corr} (mV)	I _{corr} (μA)	I _{pass} (mA)	E _{corr} (mV)	I _{corr} (μA)	I _{pass} (mA)	E _{corr} (mV)	I _{corr} (μA)	I _{pass} (mA)
MG	397.0	2092.7	92.2	400.0	6507.8	71.3	519.2	32.1	89.2	848.0	13.8	17.9
MG+Ni	371.1	17.4	234.6	324.3	31.6	12.4	389.6	8.6	272.2	663.2	5.0	---
MG+Ni+WC	326.2	10.6	89.9	320.4	20.7	16.7	367.5	3.3	97.7	697.1	2.8	---

E_{corr}: Corrosion potential, I_{corr}: Corrosion current density, I_{pass}: Passive current density

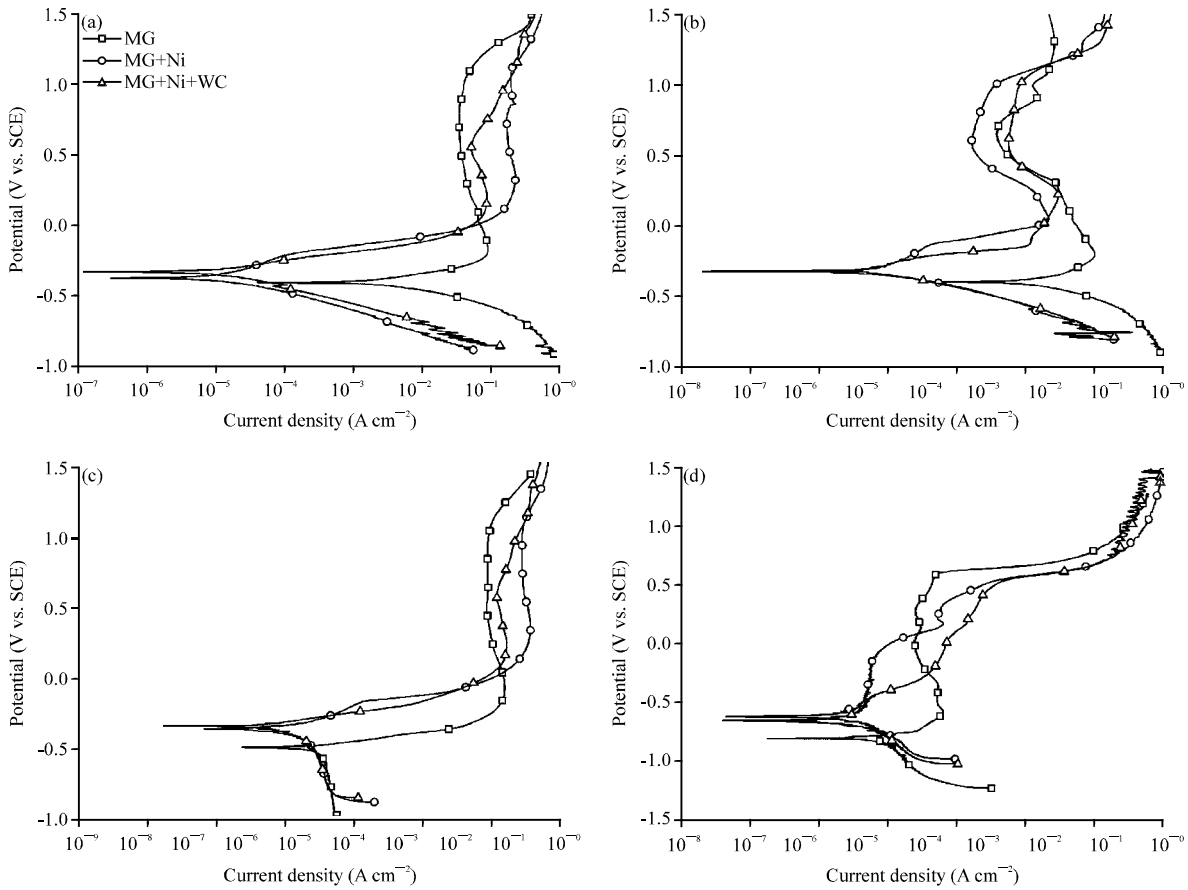


Fig. 5(a-d): Potentiodynamic polarizations of LS coatings in different solutions at room temperature (a) HCl, (b) H₂SO₄, (c) NaCl and (d) NaOH

CONCLUSION

Coatings with the nominal composition of Fe_{68.5}Cr_{7.1}Si_{3.3}B_{5.5}P_{8.7}Cr_{2.3}Mo_{2.5}Al_{2.0} with or without the addition of NiCr and WC particles were fabricated by LS methods. The corrosion behaviors are investigated in 1 M HCl, H₂SO₄, NaCl and NaOH solutions at ambient temperature. Some conclusions can be attained:

- The high dense coatings can be synthesized by laser spraying and the coatings were crystallized and compose of borides and carbides
- The microhardness is higher than 500 Hv and increase with addition of NiCr and WC particles
- The coatings exhibit excellent corrosion resistance and the corrosion resistance can be improved with the addition of Ni and/or WC in the coating

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