

Corrosion resistance of Fe-based amorphous metallic matrix coating fabricated by HVOF thermal spraying

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Abstract: The Fe-based amorphous metallic matrix coating (Fe-AMMC) was fabricated with the powder mixtures of Fe-based metallic glass synthesized with industrial raw materials, NiCr alloy and WC particle by high velocity oxy-fuel (HVOF) spraying. The corrosion resistance of Fe-AMMC was investigated by potentiodynamic polarization tests in 1 mol/L HCl, NaCl, H₂SO₄ and NaOH solutions, respectively. The surface morphologies corroded were observed by SEM. The results indicate that Fe-AMMC exhibits excellent corrosion resistance, higher corrosion resistance than 304L stainless steel in the chloride solutions. The low corrosion current density and passive current density of Fe-AMMC with a wide spontaneous passivation region are about 132.0 $\mu\text{A}/\text{cm}^2$ and 9.0 mA/cm^2 in HCl solution, and about 2.5 $\mu\text{A}/\text{cm}^2$ and 2.3 mA/cm^2 in NaCl solution. The excellent corrosion resistance demonstrates that Fe-based amorphous metallic matrix powder is a viable engineering material in practical anti-corrosion and anti-wear coating applications.

Key words: Fe-based metallic glass; coating; corrosion resistance; HVOF spraying

1 Introduction

Fe-based metallic glasses are great interesting in practical application due to their unique physical, mechanical and chemical properties, especially in the excellent corrosion resistance in the form of the protective coatings [1–3]. The coatings have been fabricated by a variety of technologies, such as laser spraying, high velocity oxy-fuel spraying (HVOF), plasma spraying and electrospark deposition process [4–7]. HVOF is probably an economical and frequently-used method to produce surface coatings [8,9]. However, few fully amorphous coatings have been fabricated due to the low glass forming ability of the master alloy, which deteriorates corrosion resistance and wear properties of the coatings [8,10]. Therefore, in order to improve the glass forming ability, some Fe-based bulk metallic glasses have been developed with highly pure elements, even rare elements [11,12], while a productive cost will be increased greatly. In recent decade, some Fe-based metallic glasses with high glass forming ability have been synthesized successfully with

industrial raw materials [13–15], and the fully amorphous coatings were reported [16,17]. Moreover, the reinforced TiN and WC particles were inserted into Fe-based metallic glass coating to enhance the wear properties [18,19]. In this study, a Fe-based amorphous metallic matrix coating (Fe-AMMC) was produced with the powder mixtures of Fe-based metallic glass of $\text{Fe}_{80.6}\text{C}_{1.8}\text{Si}_{2.0}\text{B}_{1.3}\text{P}_{5.7}\text{Cr}_{2.5}\text{Mo}_{5.1}\text{Al}_{1.2}$ (mass fraction, %) synthesized with industrial raw materials, NiCr alloy and WC particle by HVOF thermal spraying and its corrosion resistance was investigated, compared with 304L stainless steel, in a practical application as anti-corrosive and/or anti-wear material in corrosive environments.

2 Experimental

Using the powder mixtures synthesized with Fe-based metallic glass of $\text{Fe}_{80.6}\text{C}_{1.8}\text{Si}_{2.0}\text{B}_{1.3}\text{P}_{5.7}\text{Cr}_{2.5}\text{Mo}_{5.1}\text{Al}_{1.2}$, 25 % NiCr alloy ($\text{Ni}_{67.5}\text{Cr}_{16}\text{Si}_4\text{B}_4\text{Cu}_3\text{Mo}_3\text{Fe}_{2.5}$, %) and 25% WC particle, the coating layers were fabricated by HVOF thermal spraying as described in Ref. [16]. The microstructural characterization of the

coatings was identified by X-ray diffraction (XRD, Philip X'Pert diffractometer) with Cu radiation ($\text{Cu K}\alpha$, $\lambda=0.1541 \text{ nm}$). Electrochemical measurements were conducted on an EG&G Princeton Applied Research PARSTAT 2273 potentiostat with EG&G Powersuit software (Princeton Applied Research, Oak, TN). The electrochemical cell contained a central inlet for the working electrode, a Luggin probe connected with a saturated calomel reference electrode (KCl), and a graphite counter electrode. The potentiodynamic polarization curves were measured with a 50 mV/min potential sweep rate in 1 mol/L HCl , NaCl , H_2SO_4 and NaOH solutions, respectively, and were opened to air at 293 K after immersion for 30 min . After polarization test, the surface morphology was observed using a scanning electron microscope (SEM, HITACHI 4300 SEM, 15 kV).

3 Results and discussion

Figure 1 shows SEM images on top surface and cross-section of Fe-AMMC. Generally, Fe-AMMC exhibits a dense layered structure, typical HVOF thermally sprayed deposits. Though many pores as very dark regions exist, some big pores locate between flattened droplets. WC particles with bright contrast that is attributed to the high atomic number of tungsten elements can be observed clearly on the surface. WC particles are deposited as bright cluster between flattened droplets, other than homogenous dispersion in the layer. The X-ray diffraction pattern of Fe-AMMC is shown in

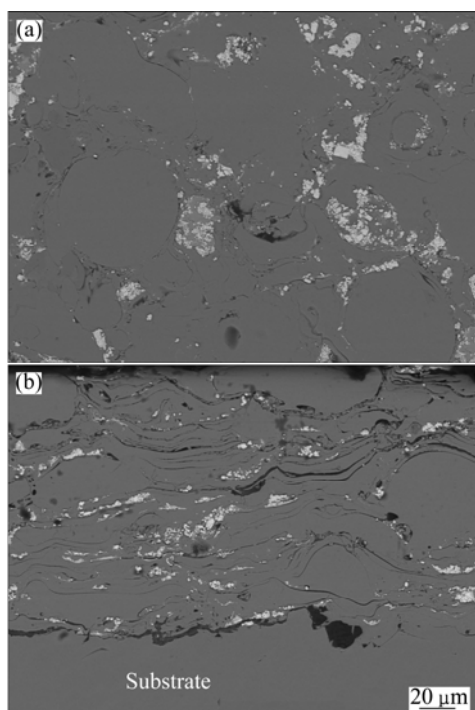


Fig. 1 SEM micrographs of Fe-AMMC: (a) Top surface; (b) Cross-sectional plane

Fig. 2. Except for the crystallized peak of WC particles, no other crystallized peaks are detected from Fe-AMMC, which is deduced an amorphous structure for the substrate.

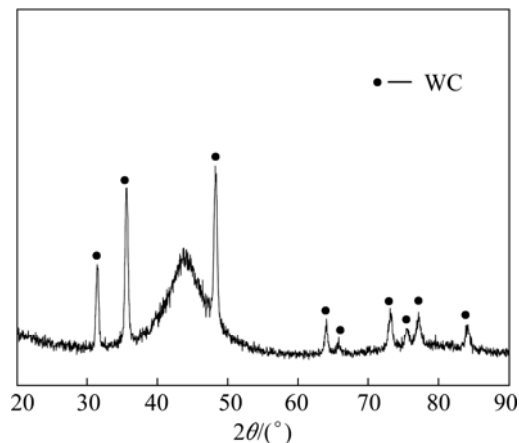


Fig. 2 XRD pattern of Fe-AMMC

Figure 3 shows the potentiodynamic polarization curves of Fe-AMMC in comparison with 304L stainless steel (SUS304) in 1 mol/L HCl solution. It can be observed that Fe-AMMC is spontaneously passivated with low passive current density and wide passive region, which suggests that Fe-AMMC possesses a prominent ability to resist localized corrosion [20]. The low corrosion current density, passive current density and corrosion potential of Fe-AMMC are about $132.0 \mu\text{A/cm}^2$, 9.0 mA/cm^2 and -340 mV , respectively. By comparison, expect a lower corrosion current density about $60.0 \mu\text{A/cm}^2$, SUS304 displays a low corrosion potential and undergoes active dissolution at a low potential without any distinct passivation, which indicates a low ability to withstand localized corrosion as pit for SUS304.

Figure 4 shows the surface morphologies of Fe-AMMC and SUS304 after potentiodynamic

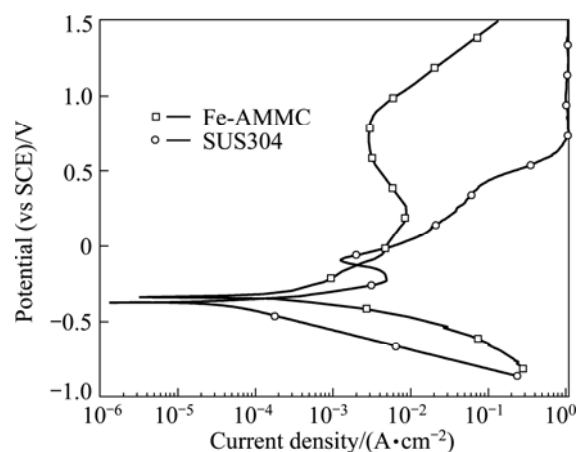


Fig. 3 Potentiodynamic polarization curves in 1 mol/L HCl solution

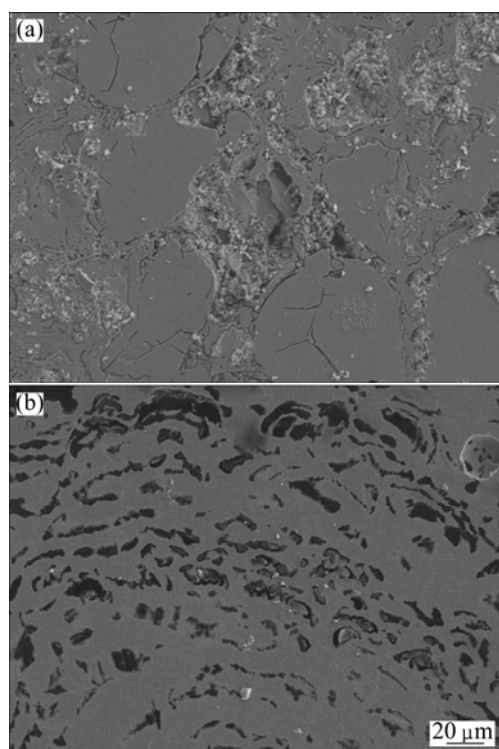


Fig. 4 Surface morphologies after potentiodynamic polarization in 1 mol/L HCl solution: (a) Fe-AMMC; (b) SUS304

polarization measurement. As expected, Fe-AMMC does not suffer obvious pitting and exhibits general corrosive morphologies, though some WC clusters are sloughed off from the matrix, resulting from the dissolution at the interface between WC particles and the matrix [21]. However, SUS304 is obviously subjected to pitting corrosion.

The potentiodynamic polarization curves obtained in 1 mol/L NaCl solution are shown in Fig. 5. Similar to those in 1 mol/L HCl solution, Fe-AMMC exhibits a low corrosion current density and a wide passive region. The corrosion potential and transpassive potential of Fe-AMMC are about -645 mV and 935 mV, and the low corrosion current density, passive current density are about $2.5 \mu\text{A}/\text{cm}^2$ and $2.3 \text{ mA}/\text{cm}^2$, respectively. While no spontaneous passivation and many peaks of current density jump are observed in polarization curve of SUS304, which signifies the suffering of pitting corrosion. The pitting corrosion is also demonstrated in the surface morphology after potentiodynamic polarization measurement, as shown in Fig. 6. Compared with the as-cast surface (Fig. 1), a similar surface morphology of Fe-AMMC can be discovered after potentiodynamic polarization test. Therefore, it might be proposed that the corrosion resistance of Fe-AMMC is superior to that of SUS304 in the corrosive environments containing chloride ions to induce pitting corrosion, such as HCl and NaCl solutions.

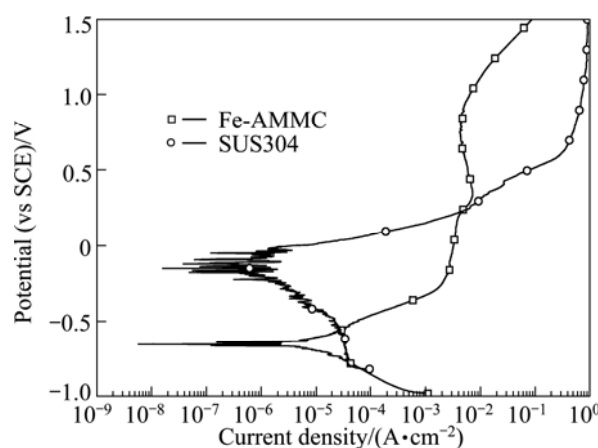


Fig. 5 Potentiodynamic polarization curves in 1 mol/L NaCl solution

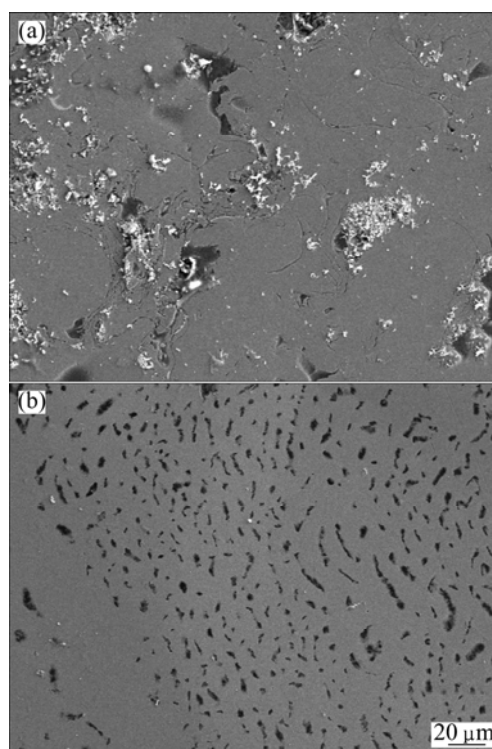


Fig. 6 Surface morphologies after potentiodynamic polarization in 1 mol/L NaCl solution: (a) Fe-AMMC; (b) SUS304

Figure 7 shows the results of potentiodynamic polarization in 1 mol/L H_2SO_4 solution. The results indicate that excellent passivation ability with a low passive current density and a wide passive region are presented for Fe-AMMC and SUS304. The corrosion current densities of Fe-AMMC and SUS304 are about $260 \mu\text{A}/\text{cm}^2$ and $96 \mu\text{A}/\text{cm}^2$, respectively. The passive current densities of Fe-AMMC and SUS304 are about $3.2 \text{ mA}/\text{cm}^2$ and $0.3 \text{ mA}/\text{cm}^2$, respectively. It is evident that the corrosion current density and passive current density of Fe-AMMC are both larger than those of SUS304, as the existence of WC cluster located between

flattened droplets, poor interparticle bonding and more pores in the layer might be formed easily, which allows electrolyte penetrations [8].

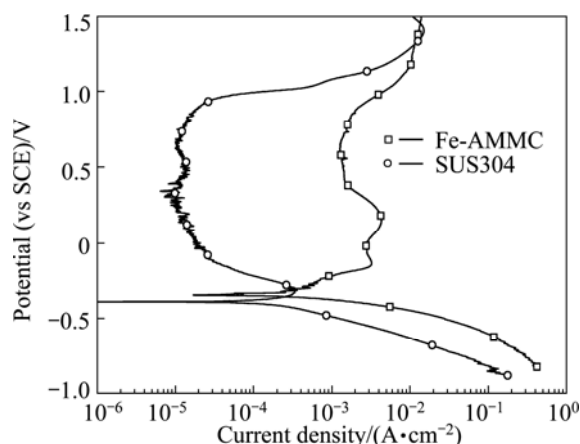


Fig. 7 Potentiodynamic polarization curves in 1 mol/L H_2SO_4 solution

The surface morphologies of Fe-AMMC and SUS304 after potentiodynamic polarization test in 1 mol/L H_2SO_4 solution are shown in Fig. 8. Fe-AMMC exhibits the characteristic of general corrosion without obvious difference from that in NaCl solution. Except for the formation of some pits also implied in polarization curve, SUS304 presents nearly smooth surface.

In 1 mol/L NaOH solution, Fe-AMMC shows a low corrosion current density about $38 \mu\text{A}/\text{cm}^2$ and low

passive current density about $1.2 \text{ mA}/\text{cm}^2$, while the transpassive potential just about 500 mV is lower than that in other solutions, as shown in Fig. 9. The low transpassive potential indicates that a passive film can be formed on the surface whereas it is broken easily in a low potential, that is, the corrosion resistance of Fe-AMMC decreases in 1 mol/L NaOH solution. It can also be demonstrated in Fig. 10. A severely corrosive morphology instead of smooth surface can be observed. In comparison, SUS304 exhibits a lower corrosion current density, a higher corrosion potential and smoother surface except a few tiny pits after polarization test. It can be induced that SUS304 presents a superior corrosion resistance to Fe-AMMC in alkaline solution.

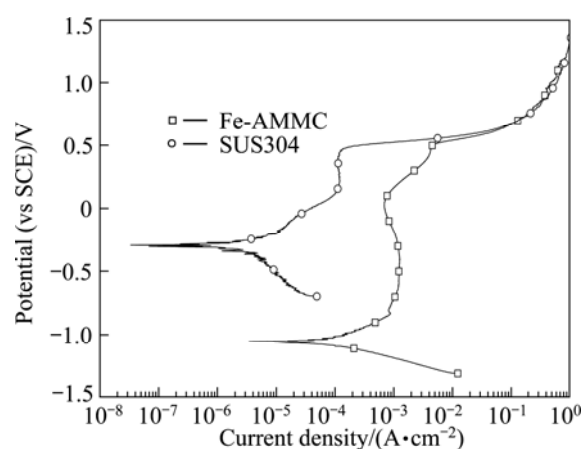


Fig. 9 Potentiodynamic polarization curves in 1 mol/L NaOH solution

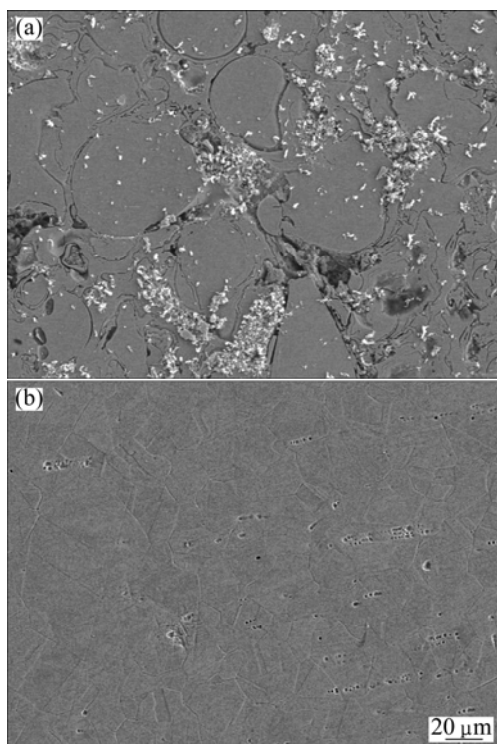


Fig. 8 Surface morphologies after potentiodynamic polarization in 1 mol/L H_2SO_4 solution: (a) Fe-AMMC; (b) SUS304

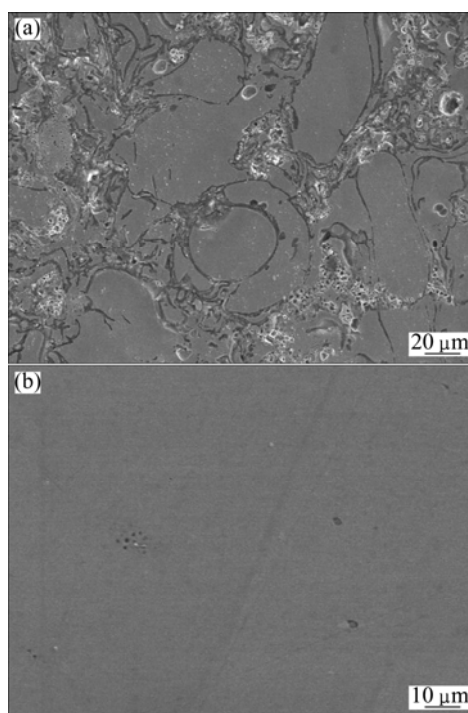


Fig. 10 Surface morphologies after potentiodynamic polarization in 1 mol/L NaOH solution: (a) Fe-AMMC; (b) SUS304

The high corrosion resistance of Fe-AMMC in chloride solution is primarily attributed to the homogeneity of compositions and microstructure without crystalline defects such as grain boundary, precipitates and segregations which are sensitive to chloride ions absorption [2]. The homogeneity reduces the tendency of the formation of corrosion micro-cells and facilitates the formation of structurally homogeneous stable passive films. The existence of passive elements such as chromium and molybdenum promotes the passivation for Fe-based metallic glasses [21]. Moreover, PANG et al [2] and IM et al [22] suggested that the addition of phosphorous and boron in the metallic glass steels can also improve the automatic passive ability.

In sulfide and alkaline solutions, the chromium-rich oxide film becomes more stable without the attack of chloride ions, so the contribution of homogeneity in chemical composition and microstructure of Fe-AMMC become minor factors, even the negative effect of incompact structure for Fe-AMMC prevails [20]. Moreover, HOCHSTRASSER et al [23] reported that WC is unstable in alkaline solution due to the detrimental local galvanic coupling at the interface. The WC decomposition is considered to consist of two steps: the oxidation of W to WO_3 when WC is in contact with the solution and the chemical dissolution of W oxide at higher pH. Therefore, Fe-AMMC presents inferior corrosion resistance to SUS304 in alkaline solution.

4 Conclusions

1) The Fe-based amorphous metallic matrix coating (Fe-AMMC) was successfully fabricated with the powder mixtures of Fe-based metallic glass of $Fe_{80.6}C_{1.8}Si_{2.0}B_{1.3}P_{5.7}Cr_{2.5}Mo_{5.1}Al_{1.2}$, NiCr alloy and WC particle by HVOF thermal spraying.

2) Fe-AMMC presents superior corrosion resistance to 304L stainless steel in the chloride solutions, but it exhibits inferior corrosion resistance in NaOH solution.

3) Excellent corrosion resistance of Fe-AMMC demonstrates the viability of the Fe-based metallic glass of $Fe_{80.6}C_{1.8}Si_{2.0}B_{1.3}P_{5.7}Cr_{2.5}Mo_{5.1}Al_{1.2}$ as a potential coating material for extensive practical anti-corrosive and anti-wear applications.

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铁基非晶基涂层的 HVOF 制备及耐腐蚀性能

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摘 要: 以工业原材料制备的铁基非晶合金、镍铬合金、碳化钨颗粒的混合粉末为原材料, 采用高速火焰喷涂技术制备铁基非晶基涂层。通过分析铁基非晶基涂层分别在 1 mol/L 盐酸、氯化钠、硫酸和氢氧化钠溶液中的动态极化特性, 研究其腐蚀阻抗。采用扫描电子显微镜(SEM)分析涂层的腐蚀形貌。结果表明: 铁基非晶基涂层具有优良的耐蚀性能, 而且在含氯离子溶液中, 表现出比 304L 奥氏体不锈钢更高的腐蚀阻抗。在 1 mol/L 盐酸溶液中, 铁基非晶基涂层的腐蚀电流密度和钝化电流密度分别为 $132.0 \mu\text{A}/\text{cm}^2$ 和 $9.0 \text{ mA}/\text{cm}^2$, 在 1 mol/L 氯化钠溶液中分别为 $2.5 \mu\text{A}/\text{cm}^2$ 和 $2.3 \text{ mA}/\text{cm}^2$, 且表现出一个宽的自钝化区间。其优异的耐蚀性能表明铁基非晶基粉末可以作为一种耐腐蚀、耐磨损的工程材料。

关键词: 铁基非晶; 涂层; 腐蚀性能; 高速火焰喷涂技术(HVOF)

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