Influence of the size of spraying powders on the microstructure and corrosion resistance of Fe-based amorphous coating

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ABSTRACT

The Fe-based amorphous coatings with the composition of $Fe_{48}Cr_{15}Mo_{14}C_{15}B_6Y_2$ were successfully sprayed on mild steel substrate by the high velocity oxygen fuel (HVOF) spraying process with different feedstock powder sizes (i.e., powder A: $-33+20\,\mu m$, powder B: $-45+33\,\mu m$, powder C: $-55+45\,\mu m$). The coatings were characterized for its morphology, microstructure and thermal stability by using X-ray diffraction (XRD), differential scanning calorimetry (DSC), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The corrosion behavior of the coatings in 3.5 wt% NaCl solution was studied with potentiodynamic and potentiostatic polarization test. It was found that the particle size of the feedstock powders had a significant influence on microstructure and corrosion resistance of the resultant coatings. The coatings sprayed with the finest powders show the most compact structure; while the coating with the coarser powders exhibits a better corrosion resistance. It is found that the corrosion resistance of the coatings is closely related to the wetting behavior which is affected by the oxygen content and the roughness of coatings. The coatings with hydrophobicity exhibit a better corrosion. The present result demonstrates that the amorphous coatings with hydrophobicity and excellent corrosion resistant are promising for industrial application in marine environment.

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1. Introduction

An increasing interest has been paid in Fe-based amorphous coating in recent years because of their combinations of excellent properties including exceptional hardness, superior corrosion and wear resistances, and relatively low material cost [1–6]. Such characteristics make the Fe-based amorphous coating well suited for industrial applications in aggressive environments [6–8].

Various methods have been used to fabricate Fe-based amorphous coating, such as plasma spraying [4], kinetic spraying [9], flame spraying [10] and spark plasma sintered [11] and high velocity oxygen fuel (HVOF) [6–8,12,13]. Among them, HVOF spray process is superior to others because coatings prepared by HVOF usually exhibit excellent quality with low porosity, high hardness, high adhesion and compression stress [14,15]. The principle of HVOF is that the fuel (mostly using kerosene) and oxygen with a desired mass ratio combust to create a high temperature and high pressure exhaust gas, which then passes through a narrow nozzle to obtain a high speed of gas flow. In front of the nozzle, powders are introduced radially, thereby experiencing a high acceleration to supersonic velocities; upon impacting the substrate, the powders spread out thinly to form a well-bonded dense coating. The detailed process of HVOF was described in Ref. [16]. Liu et al. [6] has successfully prepared dense and hard FeCrMoCBY coatings with almost fully amorphous structure by HVOF, which exhibit the wear resistance several times higher than electroplated Cr and Ni-based amorphous coating. Regarding the corrosion behavior of amorphous coatings, Farmer et al. and Branagan et al. [8,17] reported that $Fe_{49.7}Cr_{17.7}Mn_{7.4}Mo_{1.6}W_{1.6}B_{15.2}C_{3.8}Si_{2.4}$ amorphous coating prepared by HVOF is more resistant to pitting than nickel-based alloy (C-22) coating in seawater solutions and the salt fog environment. They argued that the excellent corrosion resistance of the Fe-based amorphous coating studied is attributed to the structural and compositional effect. First, amorphous alloys with homogenous structure at atomic level and without crystal defects such as grain boundaries and dislocations could highly reduce the sensitive sites for pitting initiations; Secondly, the Fe-based amorphous coatings containing a large amount of valve elements, such as Cr, Mo and W, could easily form a dense and stable passive film to prevent the coatings from Cl^- attacks [18].

On the other hand, the spraying parameters also have an important effect on the structure and performance of amorphous coatings. Zhou et al. [12] studied the effect of spraying parameters, i.e., ratio of fuel and deposition rate, on the structure and corrosion resistance of the coatings with the same composition as ours. The result revealed that optimal spraying parameters could

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improve the corrosion resistance of Fe-based amorphous coatings due to the reduction of porosity and increase in the amorphous fraction. In addition to the spray parameters stated above, the feedstock powder size also plays a crucial role in the manufacturing and quality of coating as it affects the deposition efficiency, porosity, oxygen content, and eventually the properties of the coatings [19]. Farmer et al. [8] found that powder size has an effect on the corrosion performance of $Fe_{49.7}Cr_{17.7}Mn_{7.4}Mo_{1.6}W_{1.6}B_{15.2}C_{3.8}Si_{2.4}$ amorphous coating in seawater. For example, the passive film of the coating prepared with coarse powders is more stable than that of the coating prepared with fine powders. However, the mechanism for such an effect has not been understood so far.

In the present work, the influence of the size of spraying powders on the microstructure and corrosion resistance in 3.5 wt% NaCl solution of $Fe_{48}Cr_{15}Mo_{14}Y_2C_{15}B_6$ amorphous coatings was studied. It is found that the structure and corrosion performance of the coatings is closely related to the particle size of the spraying powders.

2. Experimental procedure

$Fe_{48}Mo_{14}Cr_{15}Y_2C_{15}B_6$ powders were produced by high pressure Ar gas atomized, then sieved into three kinds of size ranges: i.e., powder A: $-33+20\,\mu m$; powder B: $-45+33\,\mu m$; powder C: $-55+45\,\mu m$. The mild steel (0.45 wt% C) was selected as substrate with a size of 60 mm × 40 mm × 5 mm. The coatings using three particle sizes were fabricated by HVOF thermal spray system under the identical spraying condition. The detailed spraying parameters are the following: kerosene and oxygen flow are $22\,L\,h^{-1}$ and $32\,m^3\,h^{-1}$, respectively; the spraying distance is 350 mm and the powder feed is $30\,g\,min^{-1}$. All the spraying experiments were conducted in open air. In addition, an amorphous rod with 2 mm diameter with the same nominal composition was prepared by copper mould casting [20] for comparative study.

The microstructure of the powders and coatings (named as coating A, B and C for powder A, B and C, respectively) were characterized by scanning electron microscopy (SEM, Quanta 200) coupled with energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD, χ'Pert PRO). The oxygen content in powders and coatings was measured using an oxygen determinator (Leco Ro-416DR). Thermal behavior for the powders and corresponding coatings was investigated by differential scanning calorimetry (DSC, Netzsch Sta 449C) in a flow of argon atmosphere with a heating rate of $0.33\,°C\,s^{-1}$. Further details of the microstructure of the coatings were examined by transmission electron microscopy (TEM, Jeol-2010). The hardness of the coatings was measured using a micro-indenter with the load of 100 g and a dwell time of 15 s. At least 10 measurements were done for each sample to ensure the data repeatability. The porosity of the coatings was evaluated by analyzing SEM micrographs with the Image Pro-Plus 6.0 software.

The corrosion properties of the coatings were evaluated by electrochemical measurements. Prior to the corrosion test, all samples were wet ground up to 2000 SiC paper and polished to mirror finish, followed by ultrasonically cleaning in acetone, washed in distilled water and dried in warm air. Potentiodynamic polarization was performed at room temperature in a three electrode cell with platinum net counter-electrode and saturated calomel reference electrode (SCE). Specimens for corrosion test were closely sealed with epoxy resin, leaving only an end-surface (with a surface area of about 1 cm²) exposed for testing. The electrochemical behavior was characterized by recording a Tafel plot at a potential sweep rate of $0.5\,mV\,s^{-1}$ from −100 mV to 1500 mV (vs. OCP) in 3.5 wt% NaCl aqueous solution open to air after immersing the specimens for an hour, when the open-circuit potential became almost steady. Each test was repeated three to five times for repeatability and relia-

Table 1
Thermal stability of the coatings as compared with the powders and the as-cast rod, as well as the microhardness of the coatings and the as-cast rod.

	$T_g/°C$	$T_x/°C$	$\Delta H_{x,total}/J\,g^{-1}$	$H_{V100\,g}$
Powder A	–	633	18.57	–
Powder B	–	632	19.45	–
Powder C	–	633	19.83	–
Coating A	–	629	17.89	984 ± 43
Coating B	–	631	19.85	1054 ± 24
Coating C	–	630	21.25	1045 ± 68
As-cast rod	582	632	21.84	1524 ± 115

bility. In addition, potentiostatic test was applied to investigate the stability of passive film under the potential of 300 mV (in the region of passivation) for 10 h and the potential of 1500 mV (in the region of transpassive dissolution) for 500 s of the coatings in 3.5 wt% NaCl solution. After polarization, the corroded surface of the sample was examined by SEM.

The wetting behavior of the amorphous coating was investigated through the contact angle (CA) measurements with distilled water using an optical contact-angle meter at ambient temperature. All coating samples were wet ground to 2000 SiC paper and polished using 1-μm suspension of diamond in water, followed by ultrasonically cleaning in alcohol and dried in warm air. For CA measurements, 2 μL water droplets were dropped carefully on to the polished surfaces with a syringe at a very low flow rate from an outlet of a vertical thin tube. The outlet is set parallel to the surface, 2 mm above it. A typical droplet grows slowly and reaches the dry surface within a minute. At least, ten measurements were done for each sample to ensure the data reproducibility.

3. Results

3.1. Characterization of powders and as-sprayed coatings

The morphology of the powders with three dimensional ranges is shown in Fig. 1(a)–(c). It can be seen that all powders are spherical with smooth surface, indicative of good fluidity. Fig. 1(d) shows the XRD patterns of powders A, B and C, demonstrating a fully amorphous structure of all powders with different sizes. The DSC curves of the three types of powders are shown in Fig. 1(e), which display very similar thermal reaction behaviors with three exothermic signals at almost the same temperature ranges from 630 to 750 °C. The onset temperature (T_x) for crystallization and the total exothermic enthalpy ($\Delta H_{x,total}$) of the exothermic reactions for the three powders are listed in Table 1. It can be seen that the values of T_x and ($\Delta H_{x,total}$) are almost identical for the three powders, demonstrated that the powders A, B and C have almost the same structure and amorphous fraction although they have quite different particle size.

Fig. 2(a) and (b) shows the XRD patterns and DSC curves, respectively, of three coatings sprayed from powders A to C and the as-cast rod. The appearance of only broad diffraction hump at the angle of $2\theta = 43°$ and the absence of any Bragg peaks associated with crystalline phases indicate that the three coatings prepared from different powders as well as the rod are basically amorphous within the resolution limit of XRD. In the DSC curves, it is found that the three coatings demonstrate a very similar thermal behavior as to the spraying powders, i.e., three exothermic crystallization peaks at almost the same temperature ranges with nearly identical crystallization temperature around 630 °C (see Table 1). The amorphous rod, however, exhibits a distinct glass transition event at 582 °C, which was not observed for the powders and coatings. In addition, the three exothermic peaks of the rod are slightly shifted to lower or higher temperature regions as compared with the coatings and powders. This difference may result from the difference in