Research Article

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Effect of Arc Power on the Wear and High-temperature Oxidation Resistances of Plasma-Sprayed Fe-based Amorphous Coatings

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Abstract: Atmospheric plasma spraying (APS) technique is employed to prepare Fe-based amorphous coatings on T91 steel substrate under various arc powers of 30 kW, 35 kW and 40 kW. The morphology and microstructure of both Fe-based powders and amorphous coatings are characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). In addition, the wear resistance and high-temperature oxidation resistance of the plasma-sprayed coatings at various arc powers are studied. It is found that with increasing the arc power, the content of the porosity and the amorphous phase in the coatings declines. Specifically, under 30 kW, 35 kW and 40 kW arc power, the porosity of the coatings is 7.96%, 6.13% and 5.75%. Correspondingly, the relative content of amorphous phase from the coatings is measured to be 96.07% (mass fraction), 73.89% and 65.54%. Moreover, under 40 kW arc power, it gives the coating the highest micro-hardness having more compact microstructure and more dispersive α -Fe grains. Besides, the coatings fabricated at high arc power exhibit less wear induced weight loss and less weight gain from high-temperature oxidation comparing with those fabricated at lower arc power.

Keywords: Plasma spraying; Amorphous coating; Microstructure; Wear resistance; Oxidation

1 Introduction

High temperature erosion is recognized as one of the main failure causes of utility boiler tubes. At present, an economical and effective way has been used to overcome this problem with the development of thermal sprayed protective coatings [1–3].

With high toughness and corrosion resistance [4, 5], the amorphous alloys are considered potential materials for multiple applications. Nevertheless, some limitations have been posed in the application of the amorphous alloys due to the challenges in the production of the amorphous structures [6]. High cooling rate is essential to form the amorphous structure from the liquid state. This leads to small thickness or cross sections in the resulting powders, ribbons or wires [7]. Consequently, the application of the amorphous alloys is hindered as structure materials. In addition, the higher cost also limits the application of the amorphous materials. Nevertheless, Fe-based amorphous alloys are generally known for their excellent hardness properties, superior corrosion and wear resistance, and relatively lower cost [8–10] among all amorphous alloys.

In order to proliferate the application of Fe-based amorphous alloys, thermal spraying technique is applied as potential fabrication technique for amorphous coatings considering the feature of rapid cooling [11, 12]. Recently, amorphous metallic coatings have been prepared by different spraying processes, such as high velocity oxygen fuel (HVOF) spraying [2, 13, 14] and plasma spraying (PS) [15–17]. In spite of the high cooling rate ($\sim 10^6$ K/s) of the droplet, obtaining a complete amorphous coating is still difficult because of the uneven heating of the powder particles in plasma jet and the uneven oxidation of the depositing droplet. Kishitake *et al.* [18] fabricated Fe-based amorphous coating by APS process, and found there is a mixture of amorphous and crystalline phases in the coating with good wear and corrosion resistances. Zhao *et al.* [19] fabricated Mo-based amorphous and nanocrystalline alloy coatings by APS using the Mo-based amorphous pow-

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Table 1: Composition of the spraying powders (wt%)

Component	Mo	Cr	Ni	P	Si	B	C	Fe
Content%	4.1	8.3	3.63	8.34	3.41	1.52	4.84	Bal.

der as the feedstock. It is found that the coating exhibited excellent wear resistance comparing with that of the substrate. Shi *et al.* [20] developed Fe-Si nano-particle composite coating (FSN) and Fe-Si micro-particle composite coating (FSM) via APS. The results show that the corrosion resistance of FSN was improved compared with that of FSM. Thus, it is reasonable to consider a hybrid coating with both amorphous and nano-crystalline structures to enhance corrosion and wear resistances.

In the present study, Fe-based amorphous powder was used as the spraying feedstock, and atmospheric plasma spraying (APS) system was used to deposit the Fe-based alloy coatings. The microstructure, wear behavior, and high-temperature oxidation resistances of Fe-based amorphous coatings were investigated with samples deposited under different arc powers.

2 Experimental

2.1 Material

Fe-based alloy powders were employed as thermal spray material, which were prepared by high pressure argon gas atomization, then sieved and divided into different size ranges. The powders used in this experiment are spherical with a size range from 40 to 60 μm . The nominal composition of the feedstock powders were shown in Table 1.

2.2 Spraying process

The rectangular T91 steel plates with the dimension of 15 mm $\times$ 15 mm $\times$ 5 mm were used as substrates. In order to obtain clean and rough surface for improving the bonding strength between the coating and substrate, the substrates were immersed in acetone to eliminate grease and other organic matter followed by drying at room temperature, and then grit-blasted for about 30 seconds with alumina particles before spraying.

In this paper, the Fe-based amorphous coatings were fabricated by an atmospheric plasma spraying system (GP-80, Taizhou, China) with variable power levels. The detailed spraying parameters for the APS process are presented in Table 2. During spraying process, in order to ob-

tain an enhanced glass forming ability (GFA), the substrate should be cooled continuously by compressed airflow.

Table 2: The parameters of APS for Fe-based amorphous coatings

Parameters	Values		
Spraying powers (kW)	30	35	40
Spraying distance (mm)	110		
Powder feed rate (g/min)	10		
Primary gas pressure (Ar), MPa	0.8		
Auxiliary gas pressure (H_2),	0.4		
Primary gas flow (L/min)	26		
Auxiliary gas flow (L/min)	5		

2.3 Characterization

Scanning electron microscopy (SEM) (S-4800, Hitachi, Japan) was used to understand the morphology and the cross section microstructure of as-deposited coatings. Furthermore, the worn surface of the specimens was also studied by SEM. The apparent porosity of coatings was quantitatively characterized using image analysis technique using at least three micrographs of coatings. The phase transformation during each process were investigated using X-ray diffraction (XRD) (D/max 2500PC, Rigaku, Japan) with Cu $K\alpha$ radiation in a 2θ range between 15° and 85° at $10^\circ \text{ min}^{-1}$. Furthermore, the relative crystallinity of the Fe-based amorphous coatings was calculated by means of the XRD diffraction patterns.

2.4 Hardness and wear test

The micro-hardness on the cross section of the amorphous coatings were measured using an optical microscope (OM) equipped with Vickers under 1N load applied over a period of 15 s (XH-1000TM/LCD). The dry wear test was carried out using a ring on block type tester (M-2000). During the testing process, the surface of the amorphous coatings was contact well with the surface of the GCr15 high carbon steel ring. The mass loss of the coatings was measured by

an electronic precision balance (BS400-WE, Sartorius AG, Germany) with the accuracy of 0.1mg.

2.5 High-temperature oxidation test

To examine the high-temperature oxidation resistance of the coatings, the as-sprayed coatings were oxidized at 700°C for 84 h in air atmosphere. During the oxidation process, the mass gain of the coatings was measured by an electronic precision balance (BS400-WE, Sartorius AG, Germany) with the accuracy of 0.1 mg. The phase composition of the coatings was analyzed by X-ray diffraction (XRD) (D/max 2500PC, Rigaku, Japan) with Cu K α radiation in a 2θ range between 20° and 80° at 10° min⁻¹.

3 Results and discussion

3.1 Surface morphology and cross-sectional structure of the coatings

Figure 1 and Figure 2 show the surface morphology and cross-sectional structure of the amorphous coatings deposited under different arc powers. As shown in Figure 1a, the coating obtained with a low arc power of 30 kW presents many unmelted particles and pores on the surface. It has been revealed that the low arc power is not sufficient to completely melt the powder particles, resulting in a loose coating. When the arc power increased to 35 kW and 40 kW, the amount of unmelted particles reduced, together with the size and amount of the voids in the coating decreased (see Figure 1b and 1c). The results show that the 40 kW plasma arc power produces the most compact microstructure compared with the coatings obtained at lower arc powers of 30 kW and 35 kW.

The voids in a plasma-sprayed coating will seriously affect the overall performance of the coating [21]. From Figure 2, the coating exhibits a porous, layered structure with no microcracks observed. The Fe-based amorphous coating presents a typical lamellar structure with pores, interplat cracks and unmelted or incompletely melted particles. The presence of unmelted and incompletely melted particles increases the porosity of the coating. Consequently, this weakens the bonding between the splats in the coating. The porosity of the coatings obtained at different arc powers is 7.96% (30 kW), 6.13% (35 kW), and 5.75% (40 kW) respectively. With large arc power, the temperature of the plasma arc increases, and sufficient heating of the powder particle is expected. As a result, good melting

Figure 1: SEM images of surface of the amorphous coatings deposited under different spraying power levels (a) 30kW, (b) 35kW and (c) 40kW, respectively.

of the powders leads to sufficient spreading of the molten particles, which counters the formation of the pores during deposition [22]. The pores in the coating are generally considered as original sites of cracking when the internal stress exists.

Figure 2: SEM images of the cross section of the amorphous coatings deposited under different spraying power levels (a) 30kW, (b) 35kW and (c) 40kW, respectively.

3.2 XRD analysis of the coatings

Figure 3 shows the XRD patterns of the amorphous powder and the coatings prepared with three arc powers. There is a broad halo peak at about 44° with no crystallization

Figure 3: XRD patterns of the powders and coatings deposited under different spraying power levels.

peak in the XRD pattern of the powder, indicating the presence of amorphous phase. For the deposited amorphous coatings, the wide halo peaks indicate appearance of the amorphous phases, while the low intensity of diffraction peaks at about 44° indicates the formation of nanoscale α -Fe crystals in the coating. These demonstrate that the powder exhibits amorphous structure, while the coating is a partially amorphous with a small amount of α -Fe crystal phase [23]. Moreover, the intensity of α -Fe peak in the coating decreases with increasing arc power, which indicates that the high arc power could be favorable to the formation of α -Fe phase in the coating [24, 25]. Therefore the content of the amorphous phase decreases as the arc power increases. By calculations based on XRD patterns, the relative contents of the amorphous phase of the coatings prepared at 30 kW, 35 kW, and 40 kW were calculated as 96.07 wt%, 73.89 wt%, and 65.54 wt%, respectively. Therefore, with the increased plasma spraying power, the content of amorphous phase in the sprayed Fe-based amorphous coating decreases, which may be due to the transformation of partial amorphous phases into crystalline phase during plasma spraying [24]. As the coating power increases, the partial transformation of amorphous phase in the coating is closely related to the deposition characteristics of the molten particles. During spraying, the powder particles are heated and transferred to molten or semi-molten state. The molten or semi-molten particle spreads, solidifies on the substrate surface to finally form splats. It is well known that there is a high cooling rate of the molten particle in the solidification process, which effectively prevents the crystallization tendency of the molten particle and thus ensures a high degree of amorphization [26]. Con-

sidering the above analysis, the content of the amorphous phase largely depends on the cooling and oxidation of the molten particle, as well as the heat accumulation in the coating [27]. As the arc power increases, the temperature of the plasma arc elevates and preheats the substrate surface or deposited splat surface which slows the cooling rate of the molten particles. The oxidation of the particles also reduces the cooling rate of the molten particles due to the lower thermal conductivity of the metallic oxides. Moreover, the latent heat released during crystallization also hinders the cooling of the molten particles. As a result, the amorphization process is suppressed and the crystallization process is encouraged.

3.3 Wear resistance of the coatings

Figure 4 shows the microhardness profiles along the cross-section of the coatings. It is found that the Fe-based amorphous coatings exhibit a higher hardness (650–770 HV) than the substrate (~250 HV). Furthermore, with the increase in plasma arc power, the microhardness value of the coating increases accordingly. The raw material powders were fully melted in the plasma jet with a higher power, which allows more sufficient spreading of the droplets. Consequently, the amount of pores is greatly reduced and the compactness of the splats in the coating is improved [28], which is in favor of the enhancement in the hardness of the coating.

Figure 5 shows the weight loss of the coatings under dry friction conditions. With the increase of plasma arc power, the wear loss of amorphous coatings decreases. When the wear time is 80 minutes, the mass loss of the coating prepared at 40 kW is 6.6 mg, which is less than

the wear loss of the coating prepared at 35 kW (7.8 mg) and 30 kW (10.5 mg) for the same duration. As described by the Archard wear equation, the wear rate of the material is inversely proportional to its hardness [29]. Due to the higher microhardness [30], the coating prepared at higher arc power exhibits better wear resistance and its weight loss is less than that deposited at low power.

Figure 5: The wear losses of Fe-based amorphous coatings plasma-sprayed under different spraying power levels.

In order to understand the difference in wear mechanism of the coatings prepared under different arc powers, a further investigation on the wear surface was performed using SEM. As depicted in Figure 6, the main types of wear include wearing, delamination peeling and plough grooves. Layering and debris can be easily found in the coatings because of its layered structure and voids. The wear debris from the coating surface acts as the abrasive to produce more wear tracks on the surface of the coating, leading to an increased mass loss. For the coating deposited under 30 kW, partial surface of the substrate exposed after wear testing due to poor interlayer bonding and coating-substrate adhesion, as shown in Figure 6a. Moreover, the wear surface of the coating deposited under low plasma arc power is rougher than that deposited under high power, as indicated by severe wear of the coating surface.

3.4 High-temperature oxidation resistance of as-sprayed coatings

Figure 7 shows the variations in mass gains of the coatings oxidized at 700°C for 84 h. It is clear that the curves of the mass gain versus oxidation time for all coatings present a

Figure 4: Micro-hardness profiles of plasma-sprayed Fe-based amorphous coatings.

Figure 6: Worn surface of Fe-based amorphous coatings deposited under different spraying power levels (a) 30kW, (b) 35kW and (c) 40kW, respectively.

parabolic shape. This indicates the oxidation of the coatings in air follows the parabolic diffusion rule. As shown in Figure 8, the composite oxide $(\text{Fe,Cr})_2\text{O}_3$ produced in the oxidized coating prepared under arc power of 35 kW. The

Figure 7: The mass gains of Fe-based amorphous coatings after oxidation at 700°C for 84 h.

Figure 8: XRD pattern of the oxidized coating prepared under arc power of 35 kW.

same phase is also found in the oxidized coatings prepared under arc powers of 30 kW and 40 kW.

According to Wagner theory of oxidation [31], chrome (Cr) atom in the coatings possesses high diffusion coefficient due to its small atomic diameter. Moreover, at low temperature, both iron and chrome oxides form because of comparative diffusion coefficient of iron and chrome atoms in the metal. As the temperature is high, the diffusion coefficient of chrome atom become higher than that of iron atom, resulting in the formation of chrome oxides in bulk, which cover the matrix or already formed iron oxides surfaces and form a dense oxidation film. At the early stage of oxidation of the coatings, the fast oxidation can be observed from Figure 7, which corresponds to the formation of the dense Cr_2O_3 film. As the protective Cr_2O_3 film is formed, the oxygen cannot diffuse into the coating

to make it oxidized because the Cr_2O_3 film acts as a barrier for the oxygen diffusion. As a result, in the subsequent oxidation time from 12 h to 84 h, an obvious reduction in the oxidation rate is observed. As the arc power increases from 30 kW to 40 kW, the mass gain exhibits a significant decrease. As aforementioned in section 3.1, the porosity of the coatings presents a decreased tendency from 7.96% to 5.75% with the increase of the arc power from 30 kW to 40 kW. Although the same surface area was used for measurement of oxidation mass gain, the real oxidation area was significantly with increase of the porosity because of more oxygen channels provided by increased pores. Therefore, a distinct decrease in mass gain of oxidized coatings could be found with increasing the arc power.

4 Conclusions

The Fe-based alloy coatings were prepared on T91 steel substrate by atmospheric plasma spraying under different spraying powers. The influences of plasma spraying power on microstructure, porosity, amorphous phase content as well as wear resistance of Fe-based amorphous coatings were investigated. It was demonstrated that with the increasing of plasma spraying powers, the porosity and the amorphous phase content of coatings declined. This is attributed to the particles with high temperature and velocity would generate sufficient deformation after the impact on the substrate, which results in compact microstructure and low porosity. The coating deposited at 40 kW power with amorphous and nano-scale α -Fe phase composite structure exhibited good wear resistance for the more compact structure and the higher micro-hardness. The wear of as-sprayed amorphous coatings under dry friction condition is dominated by abrasion, delamination and grooves mechanisms. Moreover, the oxidation mass gain of the coatings in air follows the parabolic diffusion rule because of the formation of dense oxide film and reduces with the increase of the arc power due to the decreased real oxidation area.

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