High temperature behaviors of high velocity arc sprayed Fe-Al/Cr₃C₂ composite coatings

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Abstract: Fe-Al/Cr₃C₂ composite coatings were manufactured using high velocity arc spraying (HVAS) technology. The high temperature erosion, wear and corrosion resistance of the coatings were investigated. The coating properties such as bonding strength, porosity, hardness as well as microstructures were characterized. The results show that the coatings have relatively high heat tremble bond strength, hardness, and typical layer-shaped coatings' microstructures. With the rise of temperature, the coating erosion resistance increases too; the impingement angel does effects on erosion properties, and the erosion mechanism changes from ductile to brittle behaviors at 450°C. The coatings have good room temperature wear resistance and relatively good high temperature resistance. The wear mechanism of the coatings is peeling wear behavior. The coatings have excellent high temperature corrosion resistance because of the produce of oxides during corrosion.

Key words: Fe-Al/Cr₃C₂; coating; erosion; wear; corrosion

1 Introduction

High velocity arc spraying (HVAS) technology was developed on the basis of arc spraying (AS). It has some merits as high velocity and better atomizing of melted droplets, high bonding strength and low porosity [1]. From 1980s, Fe-Al intermetallics have received attentions for excellent high temperature oxidation and sulfuration resistance properties, corrosion resistance properties at different chemical mediums, good high temperature strength, low density, and low cost. It is considered as an ideally high temperature material. But low room temperature brittleness resistance greatly deteriorated its machinery properties. There are also some difficulties in using it in industry [2-5]. Using HVAS can obtain Fe-Al intermetallics coatings. It can not only fully exert the merits of Fe-Al intermetallics, but also can avoid the shortcomings, and can use Fe-Al intermetallics in industry early. Fe-Al intermetallics were manufactured into cored wires so as to spray it easily. Cr was added into the cored wires as it can improve the ductile properties of Fe-Al intermetallics. Cr₃C₂ has good abrasive resistance, it was added to elevate the high temperature wear resistance of the coatings.

The Fe-Al/Cr₃C₂ coatings were designed to repair firepower house boilers. The main wastage of those boilers is erosion. The purpose of the work is to assess the high temperature properties of the coatings so as to prove that the coatings are suited to industrial applications. In this paper, HVAS sprayed Fe-Al/Cr₃C₂ composite coatings were prepared by HVAS technology. The high temperature erosion, wear and corrosion behaviors of the coatings were investigated [6-15].

2 Experiment

2.1 Coating materials

The φ3 mm Fe-Al/Cr₃C₂ cored wires were used in HVAS, the shells used in producing the cored wires were mild steel metal bands 08F steel. The 08F metal bands have excellent ductile properties and can be machined easily without anneal heat treatment. The chemical composition is listed in **table 1**.

 Table 1 Chemical composition of the 08F steel
 wt%

 C
 Si
 Mn
 P
 S
 Ni
 Cr

 0.05-0.11
 ≤0.03
 0.25~0.50
 ≤0.035
 ≤0.035
 ≤0.25
 ≤0.10

The cored wires were manufactured using the welding wires production equipment, the wires were

excessive rolled and sequently pulled to reduce the diameter. The added elements into cored wires were Fe, Al, Cr and Cr₃C₂, the substrates were 20 grade steel.

2.2 Spraying process

HVAS was conducted with the CDM AS300 system and HAS-01 torch. All specimens were grit blasted with quartz sands and then were sprayed. The spraying parameters used in HVAS are: voltage, 32 V; current, 180 A; spray distance, 300 mm; and the pressure of compressed air, 0.43 MPa.

2.3 Bonding test

The heat tremble bonding strength samples were heated at a resistance stove. The samples were adhered by glue and heated at 80°C for 8 h and then be put into the stove. It was heated to 650°C and retained this temperature for 0.5 h a batch, then be put into cold water to cool, immediately they were cooled, and heated again. The bonding strength value of the coatings was the average of five measurements a batch.

2.4 Erosion test

The GW/CS-MS (made by the National Key Laboratory for Remanufacturing) high temperature erosion apparatus was used to measure the coating's erosion properties. The equipment sketch map is shown in **figure 1**. The experimental conditions are as follows: atmosphere environment; from room temperature to 650°C; the erosion particles, the quartz sands of 250 µm; the velocity of the sands, 62 m/s; the impingement angles, 30° and 90°; the erosion time, 75-90 min; and the sand mass, 125-175 g.

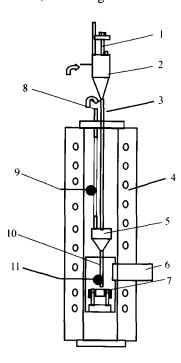


Figure 1 Digram of GW/CS-MS: 1—sand entry regulate shank; 2—sand filler; 3—sand entry tube; 4—resistance stove; 5—mix room; 6—exhaust tube; 7—sample; 8—warm-up tube; 9, 11—resistance; 10—spout.

2.5 Wear test

The specimens were tested using a high temperature THT07-135 apparatus made in Switzerland. The wear test schematic is shown in **figure** 2. The counter part was a φ3 mm fused Si₃N₄ ceramic ball. The wear conditions were: wear rate, 0.8 m/s; wear diameter, 5 mm; wear distance, 500 m. The test was done at room temperature, 200, 250, 300, 450, 550, and 600°C respectively. The samples and Si₃N₄ ceramic balls were cleaned before the wear test.

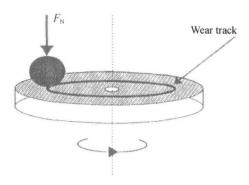


Figure 2 Schematic of the ball-on-disc apparatus.

2.6 Corrosion test

The corrosion solution was the Na₂SO₄+K₂SO₄ saturation solution with a molar ratio of 7:3, it was smeared on the surfaces of the sample and dried, then the dried samples were weighted and heated at 450, 650 and 800°C for 10 h a time. This process was repeated for times until total to 150 h. The corrosion rate can be calculated by:

$$\Delta W_i = [(W_{i+2} - W_i)/A] - [(W_{i+1} - W_i)/A] \times 0.6$$
 (1)

where W_i is the weight of the samples before corrosion; i the sequence; W_{i+1} the weight of the samples after corrosion; W_{i+2} the weight of the samples that had been heated; A the corroded surface square of the samples; 0.6 means the crystal water that will be heated out [8-10].

2.7 Morphology evaluation

Observations of the surface morphology of the coatings were conducted using a Philips Quant 200 scanning electron microscope (SEM) and an H-800 transmission electron microscope (TEM). Phases and compounds of the coatings were conducted using a D8-Advance X-ray apparatus made by German AXS Company.

3 Results and analysis

3.1 Phase characterization of the coatings

The typical cross-sectional microstructures and assprayed surface morphologies are shown in **figure 3**.

The cross sections show the porosity, unmelted particles, and the transverse cracks that are normal to the interfaces between the lamellae. The as-sprayed surface of the coatings shows solidification appearances. It is a typically HVAS sprayed coatings and the main combination style is mechanical combination. As the coatings are formed by layer overlap, they show different mechanical properties from cast materials. They combine densely between layers and layers, and the

grayness rigidity particles Cr₃C₂ diffuse evenly at the coatings. The melted droplets bumped to the substrate at a high velocity and then distorted to form lamellar. The crystal size is small because of the highly cooling velocity (>10⁵ K/s). Some even reach to nanosize (figure 3(d)). Those quickly cooled structure characterization made the lamellar hard. Small oxide particles can ensure the bonding strength and improve the erosion and abrasive resistance properties of the coatings.

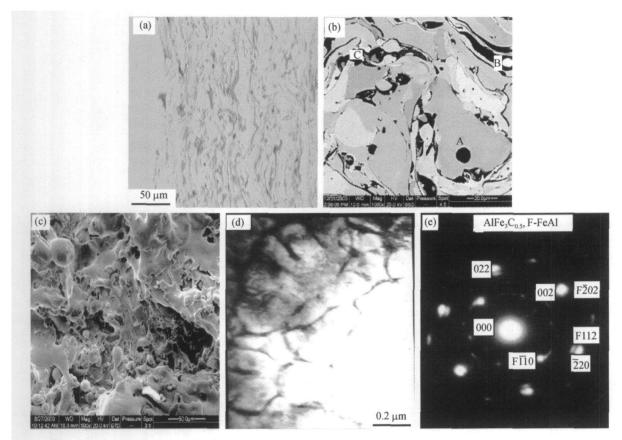


Figure 3 Micrographs of HVAS sprayed Fe-Al/Cr₃C₂ coatings: (a) cross section image; (b) back-scattering electron image; (c) as-sprayed surface morphology; (d) TEM image; (e) electron diffraction pattern of FeAl compound and derived compound $AlFe_3C_{0.5}$.

EDAX analysis show that the average component of the Fe-Al/Cr₃C₂ composite coatings is Fe-15.15Al-2.93C-11.26Cr-4.42O (wt%). The X-ray result of the coatings is shown in figure 4, it shows the compounds that contained in the coatings. Figure 3(e) shows that there have crystal relationships as (002) FeAl//(202) AlFe₃C_{0.5} between the phases, there also have (110) α - $Al(Fe)/(012) Fe_3C$, (110) $FeAl/(001) FeO \cdot Al_2O_3$, and (022) FeO·Al₂O₃//(102)Fe₃C relationships between the coatings, which can increase the combination powers of the coatings. EDAX tests show that the image of figure 3(b) exhibits the gray based Fe-Al composite phases (Fe₃Al, FeAl) and α phase (shown as A), the white rigidity compounds as Cr₃C₂, Fe₃C and $AlFe_3C_{0.5}(B)$. There are oxide particles as $FeO \cdot Al_2O_3$ and $Cr_2O_3(C)$, they localized on the gray boundaries.

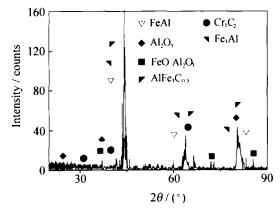


Figure 4 X-ray diffraction pattern of the coatings.

3.2 Mechanics properties

The heat tremble bonding strength of HVAS Fe-Al/ Cr_3C_2 coatings is shown in **figure 5**. With the

heating time going on, the bonding strength of the coatings increases evidently. It is because of the action of element Al. Al can combine with other elements and increase metallurgical bonding at the interface of the coatings at high temperature, thus elevate the bonding strength. But cold water erosion of more times can damage the mechanical bonding of coatings, thus lowered the bonding strength. The hardness of HVAS sprayed Fe-Al/Cr₃C₂ coatings is shown in figure 6, it is higher than that of the substrates, and there has an abnormally high hardness zone at the coatings. The reason is that Fe-Al intermetallics have high hardness, and the places that have oxides and rigid compounds have even higher hardnesses than Fe-Al. That also increased the abrasive properties of the coatings. The porosity of the coatings is lower than 2%.

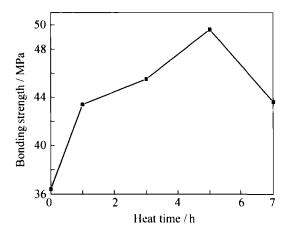


Figure 5 Bonding strength of HVAS sprayed Fe-Al/Cr₃C₂ coatings.

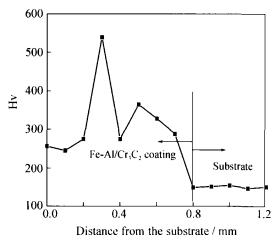


Figure 6 Hardness of HVAS sprayed Fe-Al/ Cr_3C_2 coatings.

3.3 High temperature erosion behavior

The erosion properties of HVAS Fe-Al/Cr₃C₂ coatings are shown in **figure 7**. The erosion surface of the coatings is shown in **figure 8**. Erosion impinge-

ment angle does effects on the erosion loss, the erosion loss at the impingement angle of 30° is higher than that at 90°. Temperature also influences the erosion loss of the coatings, with the increase of temperature, the erosion loss descends even to negative. The erosion behavior also changes with the increase of temperature, it is mainly ductile erosion behavior when below 450°C (figure 8(a)), and changes into brittle erosion behavior above 450°C (figure 8(b)). The coating image of erosion surface at 450°C is shown in figure 8(c). The surface has black and sequent oxidation films that can protect the coatings from being eroded. When the coatings are eroded from the substrates, uncovered places will be oxidized soon, and oxides protect the coatings from being eroded again. Therefore, the coatings have excellent erosion resistance because of the produce of oxides during erosion.

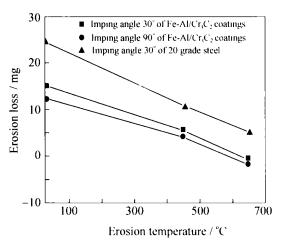


Figure 7 Erosion properties of HVAS sprayed Fe-Al/Cr₃C₂ coatings.

3.4 High temperature corrosion behavior

The heat corrosion results of HVAS sprayed Fe-Al/ Cr_3C_2 coatings are shown in **figure 9**. The corrosion rate of the coatings is low and increases with the rise of temperature, but increases slowly with the increasing of corrosion time. The coatings have better heat corrosion resistance properties than 20 grade steel at high temperature. It is found that there has an oxidation film at the surface of the coatings after corrosion, the existing of Cr_2O_3 can speed the produce of Al_2O_3 and thus protect the coatings from being corroded.

3.5 High temperature wear behavior

The wear properties of HVAS sprayed Fe-Al/Cr₃C₂ coatings are shown in **figure 10**. The coatings have relatively high wear resistance at room temperature, the wear resistance of the coatings descends with the increase of temperature from room temperature to

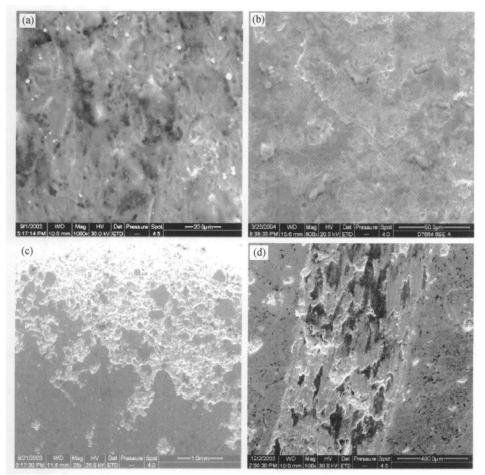


Figure 8 SEM images of the coatings: (a) erosion image of the coatings at room temperature; (b), (c) erosion images of the coatings at 450°C; (d) wear image of the coatings at 300°C.

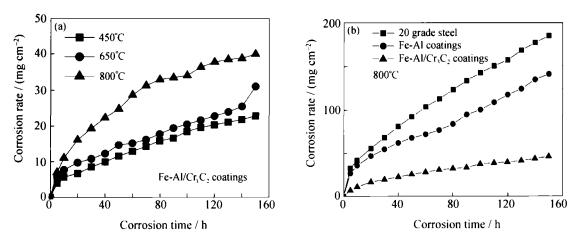


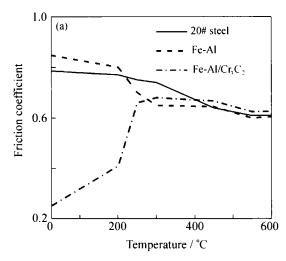
Figure 9 Corrosion properties of HVAS sprayed coatings and 20 grade steel: (a) the corrosion rate at different temperatures; (b) the corrosion rate of different materials.

250°C and it changes little above 250°C. Table 2 shows the EDS results of the worn surface of coatings, there have C and some element acted as lubricant in the process of wear testing. With the increase of temperature, C is burnt down and worn scraps become more, thus the wear friction coefficient increases. At high temperature, the produce of Cr₂O₃ can speed the produce of Al₂O₃ and then lessen the wear loss of the coatings [11]. TEM analysis indicates that the coatings have tightness structures. The good physical and

chemical amalgamations between additive reinforcements and based phases iron aluminum intermetallics also increase the ductile of the coatings [12]. Researches show that Cr is the only element that can advance the room temperature ductile properties of iron aluminum intermetallics [13], the adding of Cr_3C_2 into the cored wires enhances the room temperature properties of the coatings. The proper working temperature of ceramic reinforcement Cr_3C_2 is 550-980°C [14]. In this range, the coatings have relatively good wear re-

sistance. Figure 6 shows that the coatings have high hardness. That can enhance the wear resistance of the coatings. Figure 8(d) shows the worn image of the coatings. There produced oxides during wear testing,

and presented peeling shape at the image. Newly appeared oxides can protect the coatings from being more worn, and the main wear behavior of the coatings at high temperature is peeling wear behavior.



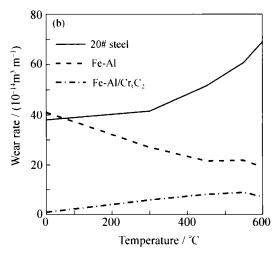


Figure 10 Wear properties of HVAS sprayed Fe-Al/Cr₃C₂ coatings at different temperatures: (a) friction coefficient; (b) wear rate. The wear distance: 0.5 km; the wear force: 5 N; the wear rate: 0.8 m/s.

Table 2 EDS analysis of worn and non-worn surfaces of Fe-Al/Cr₃C₂ coatings wt%

Item	С	О	Al	Cr	Fe
Worn Place	7.07	6.35	13.56	11.56	61.86
Non-Worn Place	2.93	4.42	15.15	11.26	66.24

4 Conclusions

(1) Using HVAS to obtain Fe-Al/Cr₃C₂ coatings can solve the application problems of Fe-Al intermetallics. HVAS sprayed Fe-Al/Cr₃C₂ coatings have equally 39.6 MPa heat tremble bonding strength. The bonding strength of the coatings elevates with the increase of heat tremble time, it is mainly because of the increase of Al combined with other elements, as a result, metallurgical combination increases. The coatings posess high hardness and low porosity, with lamellar structure and small oxide particles. The phases that the coatings consist of are: based FeAl and Fe3Al phases, reinforcement phases as Cr₃C₂, Fe₃C and AlFe₃C_{0.5}, and oxidation phases as FeO·Al₂O₃, Cr₂O₃. There are crystal relationships as (002) FeAl//(202) AlFe₃C_{0.5}, (110) α -Al(Fe)//(012) Fe_3C , (110) FeAI/(001) $FeO \cdot Al_2O_3$, and (022) $FeO \cdot Al_2O_3//(102)$ Fe_3C between phases, which can increase the combination power of the coatings.

(2) The erosion resistance at an impingement angle of 30° is lower than that at 90°. The erosion resistance enhances with the increase of temperature. The erosion mechanism changes at 450°C, from ductile behavior below 450°C to brittle behavior over 450°C. The coatings have relatively high temperature corrosion properties. The corrosion resistance increases lit-

tle with the rise of temperature, and the main reason is the oxidation Cr_3O_2 . The coatings posess high room temperature wear resistance and relatively good high temperature wear resistance. The main wear style at room temperature is C lubrication, and the main wear mechanism at high temperature is peeling wear mechanism.

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