

# Study on microstructure and properties of high velocity arc sprayed Fe<sub>3</sub>Al intermetallic coating<sup>\*</sup>

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**Abstract** Coating structural materials with Fe<sub>3</sub>Al based intermetallics may rapidly lead to industrial application of their environment and wear resistant features. In the present study , high velocity arc spraying ( HVAS ) was used to in-situ synthesize Fe<sub>3</sub>Al intermetallic coating. The microstructural characterization and properties of the coating have been investigated. The microstructure was found to consist of Fe<sub>3</sub>Al based intermetallic ( DO<sub>3</sub> and B2 ) and  $\alpha$ -Fe regions together with fine oxide (  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> ) layers. TEM images of coating show that the solidified lamellae are polycrystalline and have a grain size of the order of about 150 nm , and there also exists amorphous state in some areas . It can be concluded that a very high cooling rate has been obtained during HVAS process . Moreover , the coating has relatively higher adhesion strength and microhardness , as well as lower density and porosity .

**Key words** Fe<sub>3</sub>Al intermetallics , high velocity arc spraying , coating , microstructure , property

## 0 Introduction

Wire arc spraying is an efficient , economical method of applying metal coatings to substrate materials. The wire feeder feeds two wires to the gun. The wires are melt in the high heat zone by the arc , and the molten droplets are blown onto the prepared substrate by high velocity compressed air. The molten droplets impact on the substrate at high speed , spread out to form lamellae , and rapidly solidify. The bulk coating develops through the formation of successive layers of lamella<sup>[1]</sup>. In recent years , high velocity arc spraying ( HVAS ) has been developed to produce well bonded , low porosity coatings. The atomized metal droplets can be accelerated up to 350 m / s by the “ supersonic ” compressed air before impact. This is thus possible to minimize the droplet reaction with the gas stream. Consequently using HVAS can result in much improvement in properties of the coatings such as density , hardness and strength , as well as in wear-and corrosion-resistance<sup>[2]</sup>.

Fe<sub>3</sub>Al based intermetallics are excellent candidates for use in high temperature environment in view of the combination of low cost , lower density , remarkable resistance to high-temperature sulfidization and oxidization. Moreover , they

have high hardness with an excellent erosion resistance<sup>[3]</sup>. However , industrial application of these alloys has been very limited due to their poor ductility and fracture toughness at room temperature as well as difficulty to shaping. Studies have demonstrated that coating structural materials with Fe<sub>3</sub>Al based intermetallics may rapidly lead to industrial application of their environment-and wear-resistant features. But the production of iron aluminides based on Fe<sub>3</sub>Al by thermal spray deposition has not been widely reported.

The purpose of the present paper is to in-situ synthesize Fe<sub>3</sub>Al intermetallic coatings using cored wire and high velocity wire arc spraying , and to characterize the microstructure as well as property of the coating.

## 1 Experiment procedures

### 1.1 Cored wire

Cored wire 3 mm in diameter was used to produce Fe<sub>3</sub>Al intermetallic coatings. The high-quality low-carbon steel strip 08F was selected as material making up the base of the cored wire filler. Besides Al , a little Cr and REM powder was added to the cored wire charge to improve structure and properties of the coatings.

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## 1.2 Coating process

The cored wires were sprayed onto grit blasted and degreased low carbon steel coupons (25 mm × 16 mm × 5 mm) to a thickness of approximately 0.4 mm using lately designed HAS-01 high velocity wire arc spraying gun and CDM AS3000 system. Processing parameters were optimized as follows<sup>[2]</sup>: spray voltage 32 V, spray current 180 A, air pressure 0.43 MPa, and spray distance 300 mm.

## 1.3 Characterization

Cross section of the coating samples was examined by CSM-950 scanning electron microscope (SEM) coupled with EDS. Composition analysis was performed in the SEM using a EDS system. In order to determine the crystallography of phases present in coating, XRD analysis was carried out on a Philips X-ray diffractometer with CuK $\alpha$  radiation operating at 40 kV and 20 mA. Transmission electron microscopy (TEM) was conducted at 200 kV on H-800 to get fine scale features of the microstructures.

The coating adhesion strength was determined according to ASTM C633-79. Microhardness measurements were performed on PIMT-3 microhardness tester. And ISA4 image analysis system was employed to measure the content of oxide and porosity.

## 2 Results and discussion

### 2.1 Morphology and phase analysis of the coating

Fig. 1 is a SEM image of the coating cross section showing the typical aspect of thermal sprayed material structure. The individual lamellae are clearly visible within the coating, with layers of oxide (approximately 1 ~ 5  $\mu\text{m}$  in thickness) at lamella boundaries. Some small near-spherical particles are also visible. The morphology and the coloration of these lamellae could be well different from one to the other. The difference in coloration in the microstructure results from difference in chemistry<sup>[4]</sup>. Fig. 2 shows XRD spectrum of the coating surface, and Table 1 shows chemical composition of different areas in coating by means of EDS. Combining SEM, XRD and EDS results, the phases of the coating can be identified. The very dark contrast corresponds to porosity and fine oxide ( $\alpha\text{-Al}_2\text{O}_3$ ) layers. The majority phases of the deposit were Fe<sub>3</sub>Al-based intermetallics (D0<sub>3</sub> and B2) and  $\alpha\text{-Fe}$ : the

deeper gray contrast corresponds to D0<sub>3</sub>-Fe<sub>3</sub>Al, the lighter gray to B2-Fe<sub>3</sub>Al, and the white to  $\alpha\text{-Fe}$ . Image analysis results show that oxide content is 14.38%, and porosity is approximately 1.83%. Thus there are about 84.11% iron aluminides (D0<sub>3</sub> and B2) and  $\alpha\text{-Fe}$  in the coating.

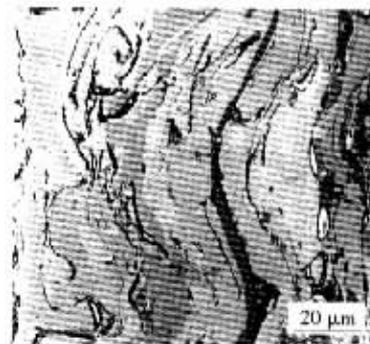


Fig. 1 SEM image of the coating cross section

Table 1 Chemical composition (at. %) of the coating by EDS

| Element | Composition of different areas |             |              |       |
|---------|--------------------------------|-------------|--------------|-------|
|         | Very dark                      | Deeper gray | Lighter gray | White |
| Fe      | 0.41                           | 73.52       | 59.00        | 88.32 |
| Al      | 41.07                          | 26.15       | 40.41        | 11.68 |
| O       | 58.52                          | 0.33        | 0.59         | —     |

### 2.2 Fine scale features of the microstructure

TEM of coating was undertaken to obtain more detailed information on the microstructure. The result shows that the solidified lamellae were polycrystalline and had a grain size of the order of about 150 nm. Fig. 3 shows a bright-field TEM image of a region of a typical coating and a selected area diffraction pattern that exhibits a fine scale microstructure of the as-deposited coating. The results of TEM also indicate to partial amorphous state in some areas. Fig. 4 shows a bright-field TEM image and a selected area diffraction pattern that exhibits an amorphous microstructure in the coating.

### 2.3 Formation of the coating microstructure

When depositing cored wire coatings, the steel fillers and wire charge components (Al, as well as Cr and REM) interact with each other and with environment. A heterogeneous structure is formed in the coating, consisting of Fe<sub>3</sub>Al-based intermetallic matrix, thin oxide layers and some small particles.

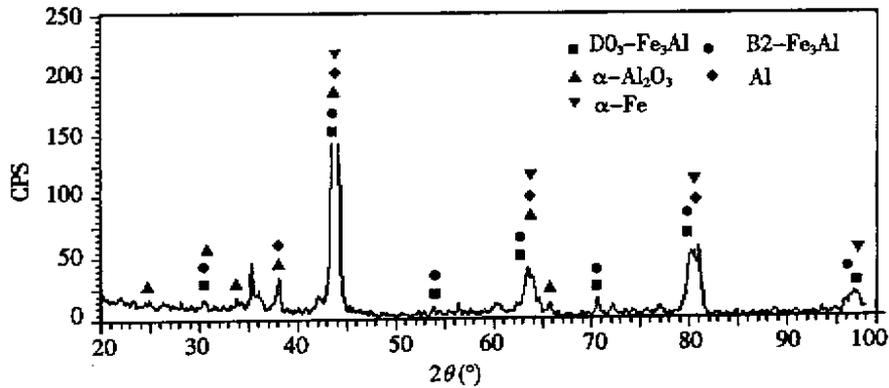
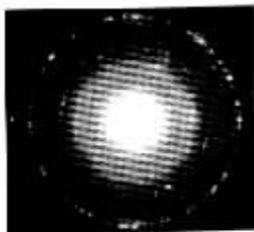


Fig.2 XRD spectra of the Fe-Al coating

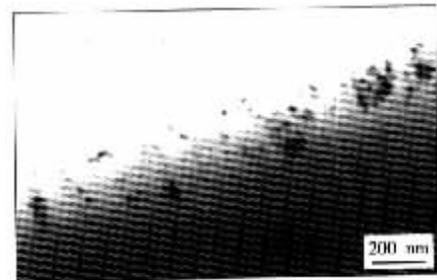


(a) Bright-field

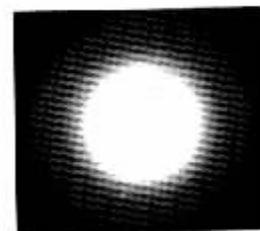


(b) A selected area diffraction pattern

Fig.3 TEM images exhibiting a fine scale microstructure of the coating



(a) Bright-field image



(b) A selected area diffraction pattern

Fig.4 TEM images exhibiting an amorphous microstructure of the coating

Considering firstly the intermetallic phases, it is clear from XRD that Fe<sub>3</sub>Al-based intermetallics (DO<sub>3</sub> and B<sub>2</sub>) are the major phases in the coating. In HVAS process, two wires meet at an intersection point and produce an arc temperature up to 4 000 K. Thus the cored wires are melt in the high heat zone, then Al drop interacts with the steel filler and forms solution. For iron aluminides with 24 ~ 32at. % Al, disordered α-Fe solid solution is the stable phase at high temperature. With temperature falling, these iron aluminides undergo a continuous transformation from α disordered structure to B<sub>2</sub> partial ordered structure between 1 020 K and

1 220 K, and this transformation is so rapid that cannot be stopped by quenching. At about 820 K, a continuous transformation from B<sub>2</sub> partial ordered structure to DO<sub>3</sub> ordered structure arises, and this transformation is a very slow one. Even anneal 5 days at 820 K highly ordered DO<sub>3</sub> structure can be obtained<sup>[5]</sup>. In HVAS condition, poor distribution of alloy elements in the droplets and restraint of B<sub>2</sub>→DO<sub>3</sub> transformation due to rapidly atomizing and depositing result in that DO<sub>3</sub> and B<sub>2</sub> coexist in the Fe<sub>3</sub>Al based coating. TEM results of fine grain sizes (about 150 nm) in these regions, even of the amorphous microstructure, indicate a rapid solidification rate

within the lamellae. Calculations show that the cooling rates of the droplets during range from  $10^4$  K/s to  $10^6$  K/s, reflecting the feature of rapid solidification process<sup>[6]</sup>.

The presence of thin oxide layers is expected since oxidation takes place at the surface of particles in flight and, on impact with the substrate, droplet flattening and spreading occurs giving lamellae covered with thin oxide sheets. XRD shows that these oxide layers are  $\alpha$ - $\text{Al}_2\text{O}_3$ . Although the precise temperature-time histories of individual particles cannot be easily determined, calculations show that most particles would have been expected to be molten for at least several milliseconds before hitting the substrate<sup>[6]</sup>. Thus, the surface of molten particles should be oxidized by compressed air. According to Ellingham diagram data on standard free energies

of formation of oxide<sup>[7]</sup>, the thermodynamic stability of oxides will increase in the order Fe, Cr and Al. The preferential formation of aluminides is thus to be expected on thermodynamic grounds.

Some visible small near-spherical particles in SEM probably may result from either earlier solidified droplet (iron aluminide or oxide), or incomplete melting of added charge particles (Al) during spraying.

## 2.4 Properties of the coating

Table 2 is the properties of  $\text{Fe}_3\text{Al}$ -based intermetallic coating prepared by HVAS. The result shows that  $\text{Fe}_3\text{Al}$ -based intermetallic coating has relatively higher adhesion strength and microhardness, as well as lower density and porosity.

Table 2 Properties of  $\text{Fe}_3\text{Al}$  coating

| Properties | Adhesion strength<br>$\sigma/\text{MPa}$ | Microhardness<br>HV 0.1 | Density<br>$\rho/\text{kg}\cdot\text{m}^{-3}$ | Oxide content<br>O( % ) | Porosity<br>P( % ) |
|------------|--|-------------------------|---|-------------------------|--------------------|
| Value      | 24.5                                     | 238.9                   | 5 073   | 14.38                   | 1.83               |

## 3 Conclusions

(1) The majority phases of the coating prepared by HVAS are  $\text{Fe}_3\text{Al}$ -based intermetallics ( $\text{D0}_3$  and B2) and  $\alpha$ -Fe, together with fine oxide ( $\alpha$ - $\text{Al}_2\text{O}_3$ ) layers.

(2) TEM images of coating show that the solidified lamellae were polycrystalline and had a grain size of the order of about 150 nm, and also indicate to partial amorphous state in some areas. It can be concluded that a very high cooling rate has been obtained during HVAS process.

(3)  $\text{Fe}_3\text{Al}$ -based intermetallic coating has relatively higher adhesion strength and microhardness, as well as lower density and porosity.

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## References

- [1] Steffens H D, Dvorak M. Arc and plasma spraying today and in the 90<sup>th</sup>. Trans. of JWRI, 1988, 17: 57 ~ 62
- [2] Xu B S, Tian B H, Ma S N. Studies on particle velocity and atomizing characterization of HVAS. Chinese Journal of Mechanical Engineering, 2000, 36(1): 38 ~ 42 (in Chinese)
- [3] McKamey C G, Devan J H, Tortorelli P F, et al. A review of recent developments in  $\text{Fe}_3\text{Al}$ -based alloys. Journal of Materials Research, 1991(6): 1779 ~ 1785
- [4] Grosdidier T, Liao H L, Tidu A. X-rays and TEM characterization of nanocrystalline iron aluminide coatings prepared by HVOF thermal spraying. Proceedings of 2000<sup>th</sup> NTSC, 2000: 1341 ~ 1344
- [5] Du G W, Wang Z, Xiao J M. Phase transformations in Fe-28Al alloys. Acta Metallurgica Sinica, 1995, 31(4): A151 ~ 155 (in Chinese)
- [6] Edris H, McCartney D G, Sturgeon A J. Microstructural characterization of high velocity oxy-fuel sprayed coatings of Inconel 625. Journal of Materials Science, 1997, 32: 863 ~ 872
- [7] Gaskell D R. Introduction to metallurgical thermodynamics. New York: McGraw Hill, 1973.