Characterisation of the Microstructure of Fe–Al/Cr3C2 Composite Coatings

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Abstract. An Fe–Al/Cr3C2 composite coating is investigated to assess its suitability for treating high-temperature components in a power plant. The coating exhibits excellent high-temperature properties including good corrosion, erosion and friction-wear resistance at high temperatures. To deduce the formation of the Fe–Al/Cr3C2 composite coating and to provide an adequate theoretical basis for its extensive application, its structures and microstructures are investigated. Scanning electronic microscopy (SEM) is used along with energy-dispersive X-ray analysis (EDAX) to analyse the surface of the coating. Energy-dispersive spectroscopy (EDS) is used to analyse the cross-section of the coating. Further, X-ray diffraction (XRD) and transmission electron microscopy (TEM) are used to analyse the phases and microstructural features within the coating. The results reveal that the basic phases are two orderly intermetallic compounds (Fe3Al and FeAl) and that the reinforcement includes two oxides (Al2O3 and Cr2O3) as well as substantial quantities of Cr3C2. Al2O3 is formed using two mechanisms: oxidation of aluminium in the coating and separation of Al2O3 crystals from Fe3Al and FeAl. The grain size of Al2O3 and Cr2O3 in the coatings is nanometric. These two oxides may increase the corrosion–erosion and wear resistances of the coating when they are used as reinforcements.

1. Introduction

Iron aluminide intermetallics (including FeAl and Fe3Al) are intermetallic compounds that depict excellent anti-erosion properties at high temperatures. Therefore, these materials can be potentially applied to manufacture cheap high-temperature structural materials. However, the room-temperature brittleness of iron aluminide intermetallics results in shaping difficulties and limits their industrial application[1–4]. High-velocity flame spraying (HVFS), which is a flame-spraying technology developed in the 1980s, is especially beneficial for spraying composite coatings because of its high spray velocity and diminished temperature effect on the substrate[5–7]. HVFS technology has been further used to produce FeAl intermetallic coatings containing powder materials on AISI 1020 steel. This technology not only eliminates the problems that are encountered while fabricating these alloys into useful shapes but also enables the effective use of their outstanding high-temperature characteristics. Adding Cr3C2 as reinforcement to iron aluminide intermetallic coatings can yield an Fe–Al/Cr3C2 composite coating, which exhibits several excellent properties. Chromium is the only...
element that is renowned to improve the room-temperature mechanical properties of iron aluminide intermetallics[8–10].

Further, an Fe–Al/Cr$_3$C$_2$ composite coating was prepared using high-velocity arc spraying (HVAS) technology. However, the sprayed materials were observed to be cored wires. The Cr$_3$C$_2$ content was limited to 20 wt% because of the coating rates of these cored wires. However, the authors could not exploit the complete potential of the material properties of Cr$_3$C$_2$ in order to influence the properties of the as-fabricated material. In contrast, the spraying materials that were used in HVFS technology were powders. Thus, the Cr$_3$C$_2$ content can be adjusted in accordance with the necessary requirement.

In the current study, we sprayed an Fe–Al/Cr$_3$C$_2$ alloy powder onto AISI 1020 steel using HVFS technology, resulting in an Fe–Al/Cr$_3$C$_2$ composite coating containing a Cr$_3$C$_2$ content of 45 wt%. We subsequently used scanning electron microscopy (SEM) along with energy-dispersive X-ray analysis (EDAX) to analyse the surface of the Fe–Al/Cr$_3$C$_2$ composite coating. Further, energy dispersive spectroscopy (EDS) was used to analyse the cross-section of the Fe–Al/Cr$_3$C$_2$ composite coating, whereas X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used to analyse the phase composition and microstructural features of the composite coating.

2. Materials and Methods

2.1. Experimental Materials

The substrate material that was used in this study was an AISI 1020 steel. The sprayed material was an Fe–Al/Cr$_3$C$_2$ composite powder composed of Fe, Al, Cr$_3$C$_2$ and a small amount of Ni. Overcoming the limit of a reinforcement-phase content of 15 wt% that was caused due to a low cladding ratio, we increased the content of the Cr$_3$C$_2$ reinforcement phase in this experimental material to reach 45 wt%. The contents of the basic phases Fe, Al and Ni were observed to be 35, 15 and 5 wt%, respectively. The powder was prepared using water atomising technology, and the particle diameters were observed to be sufficiently small for all of the particles to pass through a 200-mesh sieve.

2.2. Experimental Methods

The materials were sprayed onto the surface of the AISI 1020 carbon substrate using an HVFS system that was equipped with a CP-5000 high-velocity spray gun. The specimen dimensions were 25 mm (diameter) × 5 mm (length), and the materials were sprayed on one end-face. The process parameters were as follows: an oxygen pressure of 0.8 MPa, acetylene pressure of 1.1 MPa, an air pressure of 0.4 MPa and a spray stand-off distance of 300 mm.

The cross-section microstructure of the Fe–Al/Cr$_3$C$_2$ composite coating was observed using a Philips Quant200 scanning electron microscope (Field Electron and Ion Company, USA). The experimental parameters included a resolution of 3.5 nm, an amplification multiple of $7 \times 10^6$, an accelerating voltage of 30–200 kV, a maximum beam current of 2 A and a sample-chamber pressure ranging from 6×10$^{-6}$ to 2600 Pa.

The phase compositions of the Fe–Al/Cr$_3$C$_2$ composite coating were analysed using a D8 Advance X-ray diffractometer (Bruker AXS Company, Germany) that was equipped with a Cu Kα radiation source, having a wavelength, λ, of 0.154157 nm. The source was operated at a voltage of 40 kV and a current of 20 mA. Further, samples were scanned using a step length of 0.02°.

The microstructures of coatings were observed using an H800 transmission electron microscope (Hitachi Ltd., Japan), which exhibits high resolution and can provide information about the microstructure and crystal defects of the Fe–Al/Cr$_3$C$_2$ composite coating. The main technical parameters include a point resolution of 0.45 nm, a lattice resolution of 0.204 nm, an acceleration voltage of 35, 75, 100, 150 or 200 kV, amagnification of 100 to 500,000× and an electron-diffraction camera length of 0.4, 0.8, 1.2, 1.6 or 2 m. The process of sample thinning was divided into three steps. First, the sample was cut from the substrate using a linear cutting
machine and mechanically thinned to 300μm. The sample was further thinned to 120μm using a metallographic sand paper. AGL-6960 ion-beam thinner was subsequently used to thin the perforated sample. Further, the angle between the surface of the sample and the ion beam was gradually decreased from 30° to 15°.

3. Results

3.1. Structure and Microstructure of the Coating

Figure 1 depicts the microstructure of the Fe–Al/Cr₃C₂ composite coating. Figure 1(a) illustrates the even distribution of the Cr₃C₂. Figure 1(b) exhibits that the binding method that was applied between the coating and substrate involved mechanical jointing. Mechanical jointing can be explained as follows: a molten metal drop impacts the treated substrate surface where it spreads out as a thin liquid film and adheres to the rough substrate surface. The drops further penetrate and form a mechanical joint with the rough substrate surface.

![Figure 1. Microstructure of the Fe–Al/Cr₃C₂ composite coating: (a) cross-section and (b) junction of the coating.](image)

Figure 2 depicts the cross-sectional morphology and EDS spectra of the Fe–Al/Cr₃C₂ composite coating. The coating was observed to be stratified or lamellar. The oxyacetylene heat source that is used during the HVFS process partially oxidised the sprayed materials to form ferrous, chromic and aluminium oxides.

![Figure 2. The cross-sectional morphology of the Fe–Al/Cr₃C₂ composite coating and the corresponding results of EDS analysis.](image)
Figures 3 and 4 present an SEM micrograph depicting the morphology of the Fe–Al/Cr$_3$C$_2$ composite coating and the corresponding EDAX spectrum. Figure 4 illustrates the XRD pattern of the coating. The surface of the coating depicts dense aggregation, as evident in Figure 3. EDAX analysis illustrates that the coating contained Fe, Al, Cr, C, O and Ni. Further, the XRD pattern in Figure 4 indicates the presence of α-Fe, FeAl, Fe$_3$Al and Cr$_3$C$_2$ in the coating. The grey basic phases in Figure 1 are observed to be iron aluminide intermetallics (FeAl and Fe$_3$Al), whereas the white phases are reinforcements. Further, we observe that the black Al$_2$O$_3$ phase is embedded in the tabular grains. The diffraction peaks of the phases containing elemental C were unnoticeable in these XRD patterns because the Cr$_3$C$_2$ content in the coating was relatively high and this phase underwent less decomposition.

![Figure 3. SEM micrograph depicting the morphology of the Fe–Al/Cr$_3$C$_2$ composite coating; its corresponding EDAX spectrum is also depicted.](image)

![Figure 4. XRD pattern of the Fe–Al/Cr$_3$C$_2$ composite coating.](image)

Several phases were formed because HVFS imposes a rapid cooling rate. Further, numerous chemical reactions occur causing inhomogeneity during molten-drop alloying. The relations governing the behaviour of interactions between phases were observed to be complicated. Fe–Al/Cr$_3$C$_2$ composite coatings are typically used in industrial applications. Therefore, this investigation about the microstructure of an Fe–Al/Cr$_3$C$_2$ composite coating was deemed to be important.

### 3.2. Experimental Results and Microstructural Analysis of the Composite Coating
Figures 5 and 6 depict the TEM micrographs and SAED patterns that are used for crystallographic phase matching of the Fe₃Al and FeAl phases, which formed the main basic phases of the Fe–Al/Cr₃C₂ composite coating. In Figure 5, an amorphous structure is indicated by the diffraction ring, which was caused due to Fe₃Al. Nano particles that precipitated from the Fe₃Al are further observed in the TEM micrograph. The FeAl content was determined by calibrating against the aforementioned diffraction ring, as depicted in Figure 6. Similarly, the FeAl phase additionally contained nanoparticles formed by rapid cooling. By analysing the crystallographic phase matches, we observed that two types of orderly intermetallics were inside the flat granules (Fe₃Al and FeAl), among which the basic phases were observed to be anisotropic.

![Figure 5. TEM micrograph and SAED pattern depicting the Fe₃Al and corresponding crystallographic phases.](image1)

![Figure 6. TEM micrograph and SAED pattern depicting the FeAl and corresponding crystallographic phases.](image2)

Figures 7 and 8 depict the TEM micrographs and results of crystallographic phase matching between the formation and precipitation of oxides during the coating process.

In Figure 7, an amorphous diffraction ring can be observed in the Fe₃Al phase. After calibration, it was determined that Al₂O₃ was precipitated from Fe₃Al.

In Figure 8, the Al₂O₃ content was determined by calibration, which separated the crystalline phases from the Fe₃Al, exhibiting high hardness and good high-temperature stability. The grain size in the Al₂O₃ phase was observed to be nanometric. As a reinforcement, Al₂O₃ exhibited high compatibility with the basic phase that was observed, thereby further improving the performance of the Fe–Al/Cr₃C₂ composite coating.
Figure 7. TEM micrographs depicting the results of Fe$_3$Al/Al$_2$O$_3$ and crystallographic phase matching.

Figure 8. TEM micrographs depicting the results of FeAl/Al$_2$O$_3$ and crystallographic phase matching.

In Figure 9, a lath structure is observed in the basic phase. After calibration, it was observed to be Al$_2$O$_3$. Its formation mechanism can be described as follows: Relatively small droplets of aluminium are oxidised to form Al$_2$O$_3$. When the droplets collide with the base metal during spraying, the solidified droplets becomes perhlical, whereas those that are semi-molten become flat, as depicted in Figure 5. The melting point of Al$_2$O$_3$ is 2030°C, and it crystallises in a trigonal system. Al$_2$O$_3$ exhibits excellent high-temperature oxidation and sulphur corrosion resistance. Further, it does not produce volatiles at high temperatures because of its high thermal stability. The oxidation process for aluminium is observed to be the same as that for iron. First, the oxygen gas molecules are adsorbed onto the surface of the composite coating and decomposed into oxygen atoms. The oxygen atoms are further ionised, and the oxygen ions, which are the product of this ionisation process, react with the aluminium ions to form Al$_2$O$_3$. At the start of the oxidation process, no diffusion of cations, anions or electrons was observed to occur. Thus, the oxidation process is controlled solely by the rate of the chemical reaction. After the formation of the Al$_2$O$_3$ oxide film, which exhibits good adhesion, diffusion of Al$^{3+}$ and O$^2-$ becomes the main factors that drive the oxidation process.

In case of the high-temperature oxidation behaviour of Fe–Cr–Al alloy, researchers assumed that oxides with high iron and chromium contents were present on the surface of the alloy and that Al$_2$O$_3$ was present within these oxides at the onset of oxidation. Thus, there arrangement of the oxides was observed to occur in accordance with their thermodynamic stability over time. Huntz speculated that the formation of Al$_2$O$_3$ was driven by the short-range diffusion of aluminium and that the short-range diffusion of oxygen was a key factor along with the nature of the crystal boundaries, microscopic cracks and shrinkage.
In Figure 10, the oxide is observed to be an amorphous basic phase. However, after calibration, it was observed to be Cr$_2$O$_3$. Meanwhile, nanoparticles were observed to precipitate from Cr$_2$O$_3$. Further, we observe that the melting point of Cr$_2$O$_3$ is 2035°C and that its crystalline structure is trigonal. In the crystalline structure of Cr$_2$O$_3$, each Cr$^{3+}$ is surrounded by six O$^{2-}$ ions, and each O$^{2-}$ is bonded to four Cr$^{3+}$ in fixed positions. The fine granular structure enhances the combination of the coating materials, thereby improving the performance of the coating. Aluminium and chromium could prevent the basic metal (elemental Fe) from oxidising. We observe that aluminium and chromium are more easily oxidised than iron. Thus, the basic metal can be prevented from corroding. However, iron oxide can be reduced by aluminium and chromium, enabling proper control of the iron content. When a dense oxide film forms on the metal surface, the corrosion medium can be isolated from the base metal so that the corrosion–erosion resistance of the coating can be enhanced. During the growth of the oxide films of Al$_2$O$_3$ and Cr$_2$O$_3$, outward diffusion of aluminium and chromium and inward diffusion of oxygen can both occur. Additionally, boundary diffusion also plays a key role in this process by forming new oxides on the crystal boundaries. Because of the high concentration of oxygen in the outer layer, the diffusion effects of aluminium and chromium are enhanced, resulting in the growth of new oxides near the outer surface of the oxide film. Thus, we observe that the film becomes more uniform and can better protect the base metal.

**Figure 10.** TEM micrographs depicting the results of Cr$_2$O$_3$, and crystallographic phase-matching.

### 4. Conclusions

The Fe–Al/Cr$_3$C$_2$ composite coating was mechanically bonded with its substrate. The compound phases in the Fe–Al/ Cr$_3$C$_2$ composite coating were Fe$_3$Al, FeAl and Cr$_3$C$_2$. Further, we observed that the coating had a lamellar structure and that the Cr$_3$C$_2$ reinforcement was uniformly distributed. The
finer-grained Fe–Al/Cr$_3$C$_2$ composite coating was amorphous. The interior of the coating was composed of two types of orderly intermetallics (Fe$_2$Al and FeAl) and anisotropic basic phases.

Al$_2$O$_3$ was formed using two mechanisms that can be given as follows: the oxidation of aluminium in the coating and precipitation of Al$_2$O$_3$ from Fe$_2$Al and FeAl. The formation of Cr$_2$O$_3$ was observed to be beneficial for the formation of an Al$_2$O$_3$ phase with a compact structure. The grain size of the Al$_2$O$_3$ and Cr$_2$O$_3$ particles in the coating was observed to be nanometric. These two oxides acted as reinforcements in the coating, which may have improved its properties, including its corrosion–erosion and wear resistances.

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