High Temperature Oxidation of Fe-Cr-Al Coatings Prepared by Flame Spray Technique

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Abstract. In the present study, Fe-Cr and (Fe-Cr)-30at% Al coatings were prepared by a flame spray technique. The coated samples were then annealed in a vacuum furnace at 800°C for 2h. The high temperature cyclic oxidation test was performed at 800°C for up to 8 cycles to investigate its oxidation resistance. XRD and SEM-EDS were used to characterize the oxidized samples. The results showed that low carbon steel was susceptible to oxidation at this temperature. Thick Fe oxides layer was formed on the steel surface. On the contrary, Fe-Cr-Al coating showed an increase in oxidation resistance of low carbon steel. The FeCr coating with 30 at% Al content exhibited the lowest mass gain after exposure for 8 cycles at 800°C.

1. Introduction

Low carbon steel has several roles in industrial applications due to a number of advantages such as low production cost and good mechanical properties, but the low resistance against oxidation at high temperature makes the short lifetime of this material. To overcome such limitation, the deposition of protective coating on carbon steel becomes indispensable [1].

There are several techniques of surface coating that have been widely used to improve the oxidation resistance [1]. One of those techniques is flame spray (FS). The convenience of this methods due to the fact that FS has lower cost than others thermal spray method, FS is practical is use, and it also can produce thicker coatings using various kind of materials [2]. On the other hand, the other important factor in coating technique is in selecting the coating materials because some elements that have good oxidation resistance such as aluminum and chromium are needed to improve the resistance of low carbon steel against oxidation at high temperature. Both elements can act as reservoir for the formation of protective layers as known as Al₂O₃ and Cr₂O₃ which have high melting point of about 2040°C and 2435°C, respectively [4,5].

In this work, we study the deposition of Fe-Cr and Fe-Cr-Al coatings using a flame spray method. The effect of annealing on the coating structure and oxidation resistance was investigated by Optical Microscope, XRD and SEM-EDX. The obtained results are presented and discussed here.

2. Experimental Procedure

The commercial available low carbon steel with dimension of around 1 x 1 x 0.3 mm was used as substrate. The surface of substrate was polished using SiC papers for up to #1200 and then cleaned in ethanol solution using ultrasonic cleaner. After that, the low carbon steel was milled using a shaker mill (PPF-UG) to increase the adhesion between substrate and coating powder. For the powder...
preparation, the Fe, Al, and Cr powders were mixed in different nominal composition as shown in Table 1.

| Coating powders | Nominal Composition (at%) |
|-----------------|--------------------------|
|                 | Fe  | Cr  | Al  |
| Fe-Cr           | 80  | 20  | -   |
| Fe-Cr-Al        | 56  | 14  | 30  |

The coating deposition was carried out using Metallization MK74 Flame spray System with oxygen and acetylene as fuel of combustion. The oxygen and acetylene pressures were about 12 Psi and 30 Psi, respectively. The distance between sample and spray gun during coating process was maintained at around 170 mm. The combination of oxygen-acetylene gas was used as heat source due to the high temperatures offered by combustion of these gases [2,3]. The coated sample was then annealed at 800°C for 2h in a vacuum furnace. To evaluate the oxidation resistance of coating, the annealed samples were oxidized in a muffle furnace at 800°C for up to 8 cycles (1 cycle = 20h exposure and 4h cooling down).

The characterization of coating after oxidation test was studied by using X-ray Diffraclor (XRD SmartLab Rigaku) with Cu Kα radiation at 40 kV; 30 mA and Scanning Electron Microscope equipped with Energy Dispersive X-ray spectrometer (SEM Hitachi SU3500-EDX).

3. Results and Discussion

3.1. Microstructure and phase of Fe-Cr-Al coatings

Figure 1 shows the cross-sectional images of Fe-Cr and Fe-Cr-Al coatings taken by an optical microscope. It appears that both coatings are adhered to the substrate. The thickness of Fe-Cr coating is around 300 μm and the thickness of Fe-Cr-Al coating is around 600 μm. In addition, Fe-Cr-Al coating is thicker than Fe-Cr coating due to the fact that density of Al (2.7 gr/cm³) is lower than Fe (7.8 gr/cm³) and Cr (7.1 gr/cm³). So even if the weight of the coating powder is similar, the volume of Fe-Cr-Al coating powder is bigger than that of Fe-Cr coating. This results in the formation of a thicker coating layer [6].

X-ray diffraction patterns of Fe-Cr and Fe-Cr-Al coatings are shown in Figure 2. The XRD analysis shows that the Fe-Cr coating is composed of FeCr, FeO and Fe phases. Meanwhile, the Fe-Cr-Al coating consisted of FeCr, FeO, Fe and Al phases. The formation of FeO after coating process could be related to that some amount of iron reacts with oxygen when propelled by hot gas to form Fe oxide [2].

![Figure 1](image1.png)

**Figure 1.** Optical cross-sectional images of (a) Fe-Cr and (b) Fe-Cr-Al coatings.
Figure 2. X-ray diffraction patterns of (a) Fe-Cr and (b) Fe-Cr-Al coatings.

3.2. Microstructure and phase of Fe-Cr-Al coatings after annealing at 800°C

Figure 3 shows X-ray diffraction patterns of Fe-Cr and Fe-Cr-Al coatings after annealing at 800°C for 2h. Phases of Fe-Cr coating after annealing as shown in Figure 3(a) are composed of FeCr and FeO. Disappearing of Fe phase occurs because Fe has reacted with Cr and O to form FeCr and FeO phases. Meanwhile, phases of Fe-Cr-Al coating as shown in Figure 3(b) are composed of FeCr, FeAl, and FeO. The Al diffraction is not found due to that Al element is completely reacted with iron to form FeAl.

The cross sectional BSE images of Fe-Cr and Fe-Cr-Al coatings after annealing at 800°C for 2h are shown in Figure 4(a) and (b). The images show that the coating contains some pores that might be caused by movement of atom during annealing process. This results in vacancy formation. The presence of pores in the coating will reduce the oxidation resistance [2].

Figure 3. XRD patterns of (a) Fe-Cr and (b) Fe-Cr-Al coatings after annealing at 800°C for 2h.
Figure 4. Cross-sectional BSE images and corresponding EDX elemental maps of (a) Fe-Cr and (b) Fe-Cr-Al coatings after annealing at 800°C for 2h.

EDX elemental maps in Figure 4 show the distribution of Fe, Cr, Al and O in the coating after annealing. The Fe distribution can be clearly seen in the substrate and coating. While the Cr and Al are distributed in the coating. Corroborating XRD results as shown in Figure 3, EDX mapping also founds the distribution of oxygen in the coating. This indicates that some iron was oxidized during coating process.

3.3. Oxidation kinetic and structure of Fe-Cr-Al coatings after high temperature oxidation test

The oxidation resistance of low carbon steel and annealed samples was studied at 800°C up to 8 cycles. The curve of mass gain per surface area versus number of cycle, namely oxidation kinetic curve is shown in Fig. 5

Figure 5. Oxidation kinetic curve of low carbon steel and Fe-Cr-Al coatings.
It can be seen that the low carbon steel has lowest oxidation resistance as it yields the highest mass gain. For Fe-Cr coating has a lower mass gain than low carbon steel without coating. According to XRD results as shown in Figure 6(a), the Fe-Cr coating is composed mainly of Fe\textsubscript{2}O\textsubscript{3} and small fraction of FeCr\textsubscript{2}O\textsubscript{4} phases. The FeCr\textsubscript{2}O\textsubscript{4} layer is able to withstand the diffusion of oxygen [7], so that the oxidation resistance of Fe-Cr coating is better than low carbon steel without coating. The formation of FeCr\textsubscript{2}O\textsubscript{4} may occur through the following reaction [8]:

\[
Cr_2O_3 + O_2 + Fe \rightarrow FeCr_2O_4
\]  

From Fig. 5, it can be seen that the Fe-Cr-Al coating shows the smallest mass gain (Fig. 5). The existence of Al can make the coating more protective than Fe-Cr coating. According to the results of XRD analysis as shown in Fig. 6, the Fe-Cr-Al coating forms Fe\textsubscript{2}O\textsubscript{3} and Al\textsubscript{2}O\textsubscript{3} after exposure at 800°C for 8 cycles. The formation of Al\textsubscript{2}O\textsubscript{3} appears to improve the oxidation resistance of Fe-Cr-Al coating. This is due to that Al\textsubscript{2}O\textsubscript{3} exhibits an excellent oxidation and corrosion resistance [9]. The Al\textsubscript{2}O\textsubscript{3} formation may occur through the following reaction [10]:

\[
Al + O_2 \rightarrow Al_2O_3
\]  

**Figure 6.** XRD patterns of (a) Fe-Cr and (b) Fe-Cr-Al coatings after high temperature oxidation test.
Figure 7. Cross-sectional BSE images and corresponding EDX elemental maps of annealed (a) Fe-Cr and (b) Fe-Cr-Al coatings after high temperature oxidation test.

The cross-sectional BSE images of Fe-Cr and Fe-Cr-Al coatings after high temperature oxidation test can be seen in Figure 7 (a) and (b), respectively. The figure shows that the total thickness of coating and oxide is around 1300 µm for Fe-Cr coating and 800 µm for Fe-Cr-Al coating. Combining the results of XRD and EDX analysis as presented in Fig. 7, it can be predicted that since the distribution of Fe and O elements can be found at the outer layer, the formation of Fe₂O₃ is likely to occur in the aforesaid location. For the FeCr₂O₄ and Al₂O₃ phases, the results of EDX analysis comprises the distribution of Fe, Cr and O of Fe-Cr coating and Fe, Cr, Al and O for Fe-Cr-Al coating in the inner layer. It seems that FeCr₂O₄ and Al₂O₃ are found in the inner layer at the outer/substrate interface. Comparing the structure of oxide layer formed on both coating, the Fe-Cr coating forms more porous and thicker oxide layer compared to that of Fe-Cr-Al coating. This strongly suggests that Al element in the coating plays a role in increasing the coating oxidation resistance.

4. Conclusions and Suggestions
The flame sprayed Fe-Cr coatings with and without Al have been successfully deposited into surface of low carbon steel and then annealed for 2h at 800°C. After high temperature oxidation test at 800°C for 8 cycles, the kinetic oxidation curve shows that low carbon steel without coating is susceptible to oxidation and Fe-Cr with Al has good oxidation resistance. The increase of high temperature oxidation resistance of Fe-Cr-Al coating is due to the presence of Al which plays a role to make the coating more protective by forming Al₂O₃.
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