High Temperature Sulphidation of Composite Coatings on Cast Iron

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ABSTRACT

A cast iron retort used for producing carbon disulphide in the Charcoal-Sulphur process usually has a lifespan of less than one year due to high-temperature corrosion. In order to improve the lifespan, two thermal-sprayed coating systems were investigated. One was an inner coating of a Fe-Cr-Al alloy surmounted by a top coating of aluminum, and the other was a single aluminum coating. After 576 hours exposure under the operating conditions, the specimens with arc-sprayed composite coatings showed a good resistance to sulphur attack. On the other hand, the results of the specimens with a single aluminum coating were found not to be satisfactory. The coatings and the coating/substrate interface were characterized by SEM, EPMA and X-ray diffraction. The results showed the existence of a reliable bonding between the composite coatings and the substrate with formation of the intermetallic compound $AlCrFe_2$ which was beneficial against the sulphur attack.

Key words: Arc spray, Fe-Cr-Al alloys, Al coating, High temperature, Sulphidation

1. INTRODUCTION

The Charcoal-Sulphur process for producing carbon disulphide is still widely used in China. In this process, carbon disulphide is produced through the direct reaction of carbon with sulphur vapours at 1123～1173 K in the fuel-fired retorts, usually made of cast iron. The gaseous atmosphere resulting from this reaction, which consists of a mixture of carbon disulphide, sulphur and hydrogen sulphide, causes the retorts to be severely corroded. Because the formation of iron sulfide cannot prevent a further attack by sulphur, the lifespan of the iron retorts is normally not longer than one year. Moreover, the corrosion products interfere further with heat transfer and reduce the reaction space in the retort, which in turn increases the production cost. In order to solve the problem, many efforts have been made /1/. High chromium steel is one of the first selected candidates, but its high cost limits its application.

Protective coatings are another choice. There are several methods of applying protective coatings. Thermal spray coatings have been effective in protecting steel and iron alloys in corrosive (oxidizing, sulphidizing) environments in a wide temperature range spreading from the petroleum to the food industry /2,3/.

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Among the thermal spray techniques, arc spray is one of easy operation with low cost. In order to prolong the lifespan of the retorts, arc-sprayed composite coatings were investigated in this work. The performance and effectiveness of two coating systems applied on cast iron was tested and this includes a system of two-layered aluminum-based thermal spray coatings and a single aluminum coating.

2. EXPERIMENTAL

The specimens with a 150×100×30 mm size were made of cast iron of the same material as the retort used in the Charcoal-Sulphur process. The materials used for the arc spraying were wires of 3.0 mm in diameter. The chemical composition of the wires and substrate are listed in **Table 1**. After grit blasting, one group of specimens was sprayed with an inner coating 0.6-mm-thick Fe-Cr-Al and a top coating 1-mm-thick aluminum and the other group was sprayed with a coating of 1-mm-thick aluminum alone. An electric arc spray unit was used, which was equipped a spray gun with a "closed" atomizing nozzle. The parameters of the arc spraying process are listed in **Table 2.**

Table 1

Chemical composition of wires and substrate (mass %)

Material	Cr	Al	Fe	C	Si	Mn	S	P
Fe-Cr-Al	24.83	5.10	rest	0.03	--	0.42	<0.005	<0.025
Al	--	≥99.9	--	--	--	--	--	--
Cast iron	--	--	rest	3.62	0.25	0.54	<0.15	<0.10

Table 2

Arc spraying parameters

Material	Fe-Cr-Al	Al
Arc voltage (V)	33	32
Arc current (A)	220	200
Air pressure (MPa)	0.5	0.6
Spray distance (mm)	150	150

All the specimens were sealed with silicate flux to close the porosity in the coatings. Then they were exposed to the real environment in an operating retort of a Charcoal-Sulphur plant for 576 hours. The specimens were periodically taken out of the retort and prepared for observation with scanning electron microscopy (SEM), electron probe micro analysis (EPMA) and X-ray diffraction analysis.

3. RESULTS AND DISCUSSION

The gas mixture inside the retort for producing carbon disulfide at high temperature, which consists of carbon disulphide, sulphur and hydrogen sulphide, is known to be very corrosive. The iron sulfide grown on the cast iron specimen after exposure under to the operating conditions for 360 hours is more than 5-micrometers thick, as shown in **Fig. 1**. The iron sulfide scale is loose and is not protective to the underlying metal substrate.

Aluminum-sprayed coatings may be expected to offer good protection against aggressive environments containing oxygen and sulphur, due to their ability to form dense and homogeneous aluminum oxide scales. However, the specimens with a single aluminum coating used in this investigation did not behave well under the present conditions. After exposure, parts of the coating were degraded. Conversely, there was no evidence of local coating spallation and failure on the specimens of two-layered aluminum-based coatings after exposure for 576 hours under the same conditions, implying that the inner Fe-Cr-Al coating plays an important role. This coating sprayed onto a cast iron or steel substrate by the arc process possesses a self-bonding property, which makes it tightly adherent to the substrate. The arc-sprayed Fe-Cr-Al coating can bond to a clean and smooth steel surface. Therefore, Fe-Cr-Al coating is sometimes used as a self-bonding coating. Thus, an inner layer of Fe-Cr-Al provides improved adhesion of the outer Al layer to the substrate. In addition to that, the chromium in the coating also increases the resistance of the material to high temperature sulphur corrosion /4/.

Aluminum additions to iron-chromium alloys bring about increase in sulfidation resistance. It was reported that addition of 3~5 % Al (mass fraction) to Fe-17Cr alloys increased sulfidation resistance in H_2S environments with sulfur partial pressure (P_{S_2}) of 6 ×

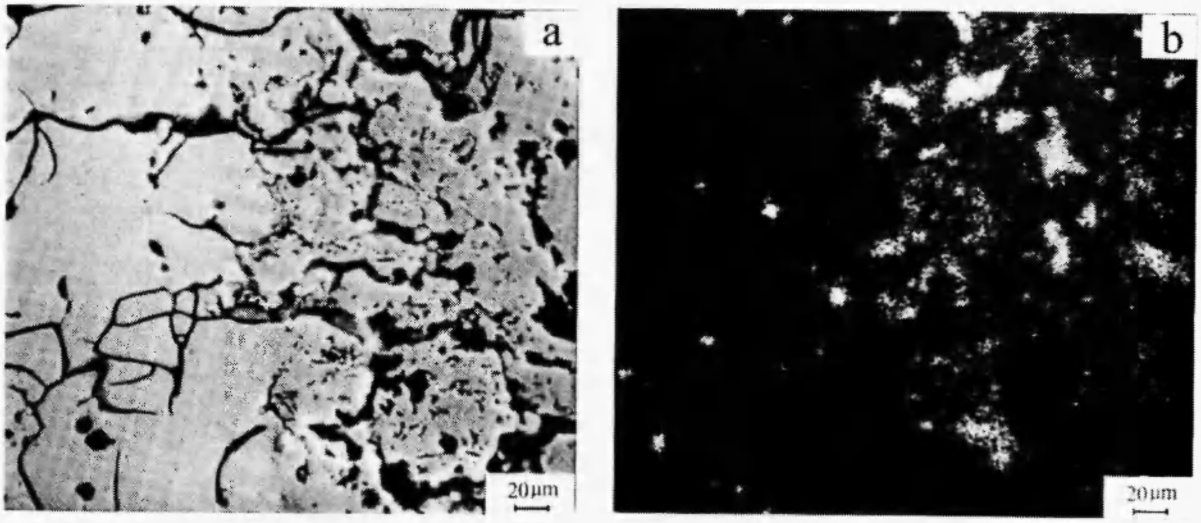

Fig. 1: Cross sectional view of iron sulphide (a) and X-ray image of S (b)

10^{-2} torr^{12}. Further increase in Al content, as iron aluminides, increased sulphidation resistance even more at 800 °C, and this was attributed to the formation of α-Al_2O_3 scale; the aluminium oxide layer formed on the alloy surface remains unattacked /5/. Also, the development of substantial oxide scales by preoxidation could significantly improve the subsequent sulphidation resistance for some alloys /6,7/. These oxide scales act as barriers to the environment and produce low rates of metal degradation. The protectiveness of the oxide scales is influenced markedly by a number of factors, particularly the type of oxide scale, with Al_2O_3 being much more effective than Cr_2O_3, the aggressiveness of the environment and the adhesion and mechanical integrity of the scale /8/. During arc spray process, Fe-Cr-Al wires are melted by electric arc and the molten metal is atomized by compressed air and then deposited on the substrate surface. The over heating of these droplets in the presence of air results in their partial oxidation. Numerous droplets, each covered by a thin and continuous oxide film, compose the coating. Due to their special microstructure, the coating exhibits better corrosion resistance at high temperature and the Al_2O_3 formed in coatings during arc-spraying process can prevent the penetration of sulphur.

A general view of the cross section of the composite coatings after corrosion for 216 hours under the production conditions is shown in **Fig. 2**. On the other hand, **Fig. 3** is the SEM picture with X-ray images of

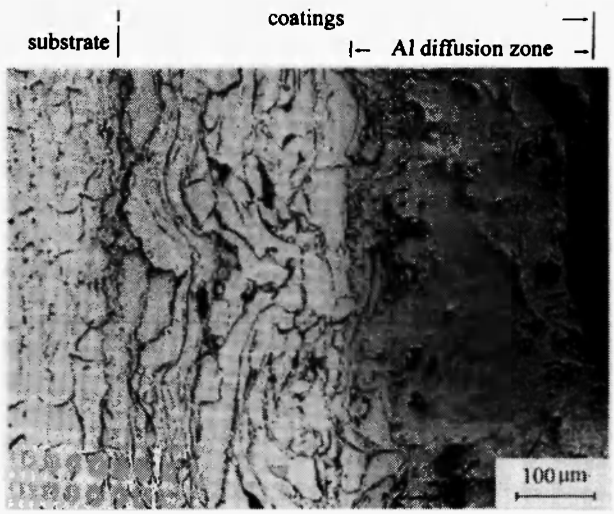

Fig. 2: A general cross sectional view of the composite coatings after testing for 216 hours

the outer part of the composite coatings. Aluminum has diffused into the inner coating and formed a layer of Fe-Al intermetallic compound. There are many pores and oxides in the arc-sprayed coatings. It is generally agreed that the formation of pores and oxide in the coatings are two main drawbacks of the are spraying technique. Pores in the coatings may act as penetration paths for the oxidants, resulting in corrosion inside or even beneath the coating. The working temperature of the retort is from 1123 K to 1173 K, which is much above the melting point of aluminum. At these temperatures,

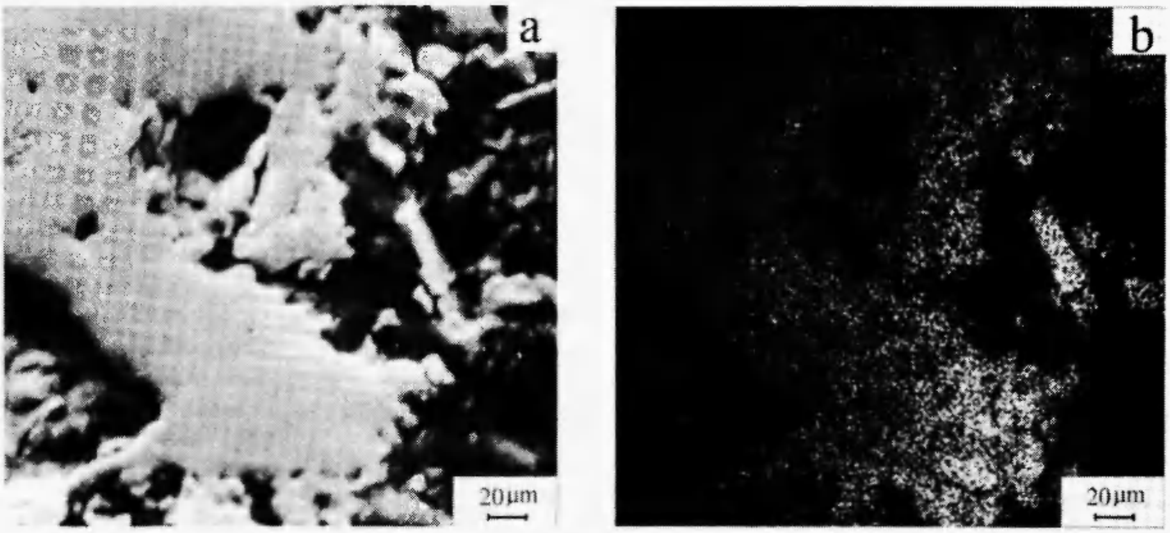

Fig. 3: SEM photograph (a) of the Al diffusion zone of the composite coatings, after testing for 216 hours and X-ray image of Al (b).

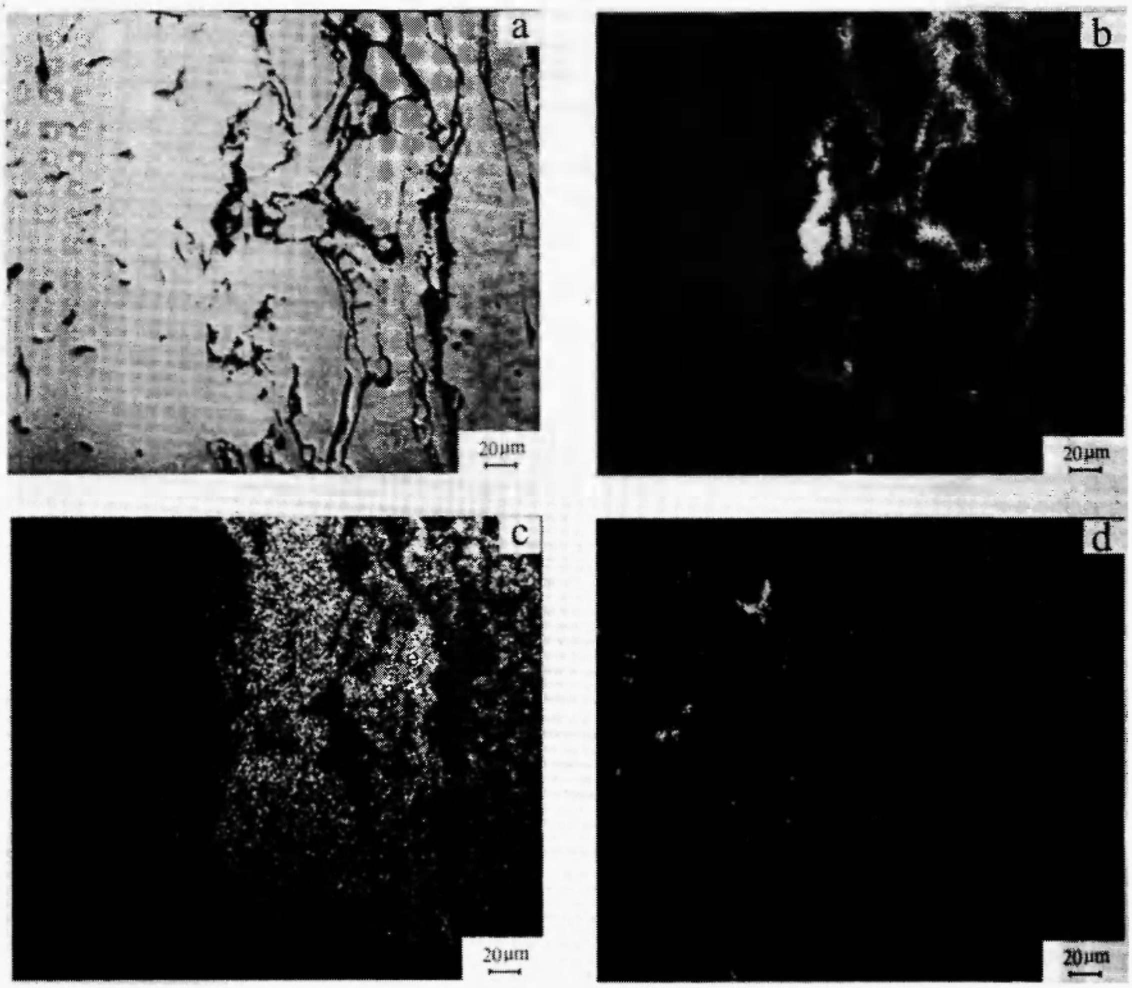

Fig. 4: SEM photograph (a) and X-ray images of Al (b), (Cr (c) and S (d) near the interface of coating/substrate of the specimen after testing for 216 hours

the aluminum top coating is molten and aluminum generally diffuses into the Fe-Cr-Al coating. According to thermodynamics, aluminum in alloy oxidizes preferentially with respect to chromium. **Fig.4-a** shows the SEM picture of the coating/substrate interface of the specimen. The oxide (black area in Fig.4-a) is mainly composed of aluminum oxide (Fig. 4-b), while chromium exists in the coating in solid solution (Fig. 4-c). As aluminum melts and diffuses, the pores in the inner coating are sealed. Moreover, most of the aluminum is concentrated in the oxide and its vicinity (Fig. 4-c). Small traces of sulphur could be observed in the coating and a few of sulphide particles formed in the substrate (Fig. 4-d). In spite of this, the two-layered coatings showed effective resistance to sulphur corrosion.

A general view of the cross section of the composite coatings after corrosion for 576 hours is shown in **Fig. 5**. The specimens corroded for 576 hours have a surface morphology similar to that of specimens corroded for 216 hours. The coatings are adherent to the substrate without any visible degradation. **Fig. 6-a** illustrates the micrograph of a cross section close to the coating/substrate interface. A comparison of Fig 4-b with Fig 6-b shows that in the former case aluminum concentrates just in the oxide and in its vicinity, while in the latter case aluminum is formed to diffuse into nearly almost the whole Fe-Cr-Al coating and some has even entered into the cast iron substrate. In the coating, each sprayed droplet is covered by a thin and continuous oxide film, while numerous droplets compose the coating which has a layered structure because the droplets strike against the substrate and become flat. The oxide films are the boundary of particles where some pores exist. Though almost all the pores in the inner coatings were sealed by aluminum, there were some micro faults inside the oxides and at their boundaries. On one hand, the oxide layer in the coatings acts as a barrier to prevent the penetration of sulphur inside the particles and limits the diffusion of the metal ions. On the other hand, the faults of the oxide become the ducts which provide the diffusion paths for sulphur and the metal ions, so that there are more aluminum and sulphide inside and around the oxides (see Figs. 6-b and 6-d). At longer times, more sulphur diffuses into the coating and the substrate, but there is no sign of crack in

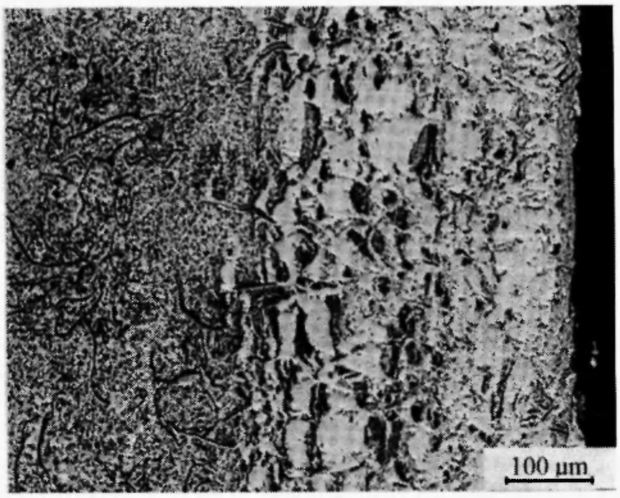

Fig. 5: A general cross sectional view of the composite coatings after testing for 576 hours

the coatings. Fig. 6-c shows that the distribution of chromium in the coating is almost unchanged.

Cunha Rocha *et al.* /9/ investigated the corrosion of duplex coating specimens at 793 K under a mixed gas environment which contained sulphur, oxygen and carbon. After exposure, cracks were present within the Al-Fe-Cr coating and spallation took place in those regions, which weakened the corrosion resistance of the coatings. Although the coating investigated in this paper is similar to that of Cunha Rocha *et al.* /9/, there are some differences between the two cases. Firstly, the coating used in the present study is thicker than that of the previous work /9/, especially for the present inner layer of the coating, which is three times thicker than the previous case. Secondly, the present coating was sealed before testing, which is considered as the first barrier to prevent the penetration of sulphur before the formation of the Al-Cr-Fe intermetallic compound. Finally, the present testing temperature is higher, which results in the melting of the top aluminum coating and the diffusion of aluminum into the inner coating, forming a layer of the Fe-Cr-Al intermetallic compound. X-ray diffraction analysis showed that $AlCrFe_2$ was the main phase present in the coatings after 576 hours exposure under the production conditions (see **Fig. 7**). The X-ray pattern also shows the presence of two more phases, Al_2S_3 and α-Al_2O_3, in the coating, especially close to the coating surface. Some Al_2O_3 was formed in

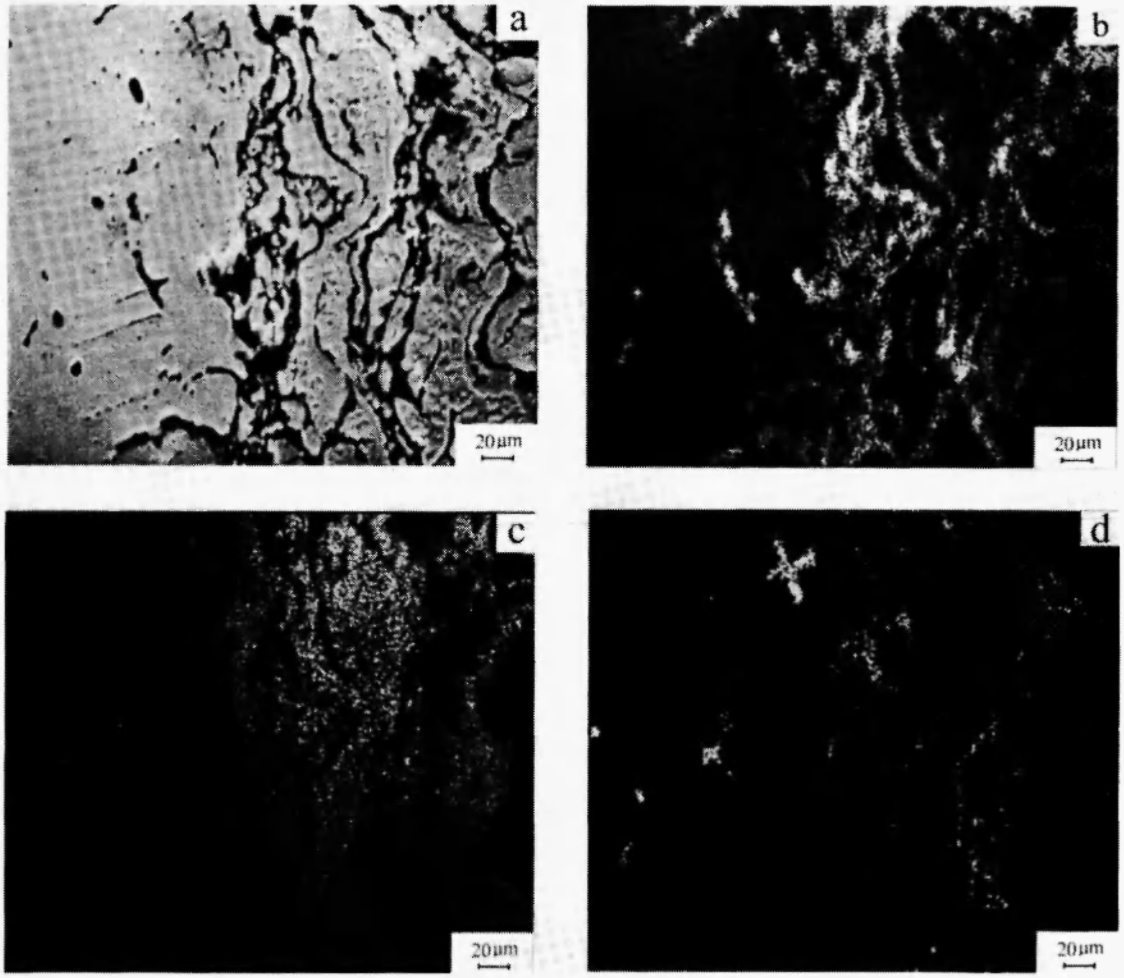

Fig. 6: SEM photograph (a) and X-ray images of Al (B), Cr (c) and S (d) near the interface of coating/substrate of the specimen after testing for 576 hours

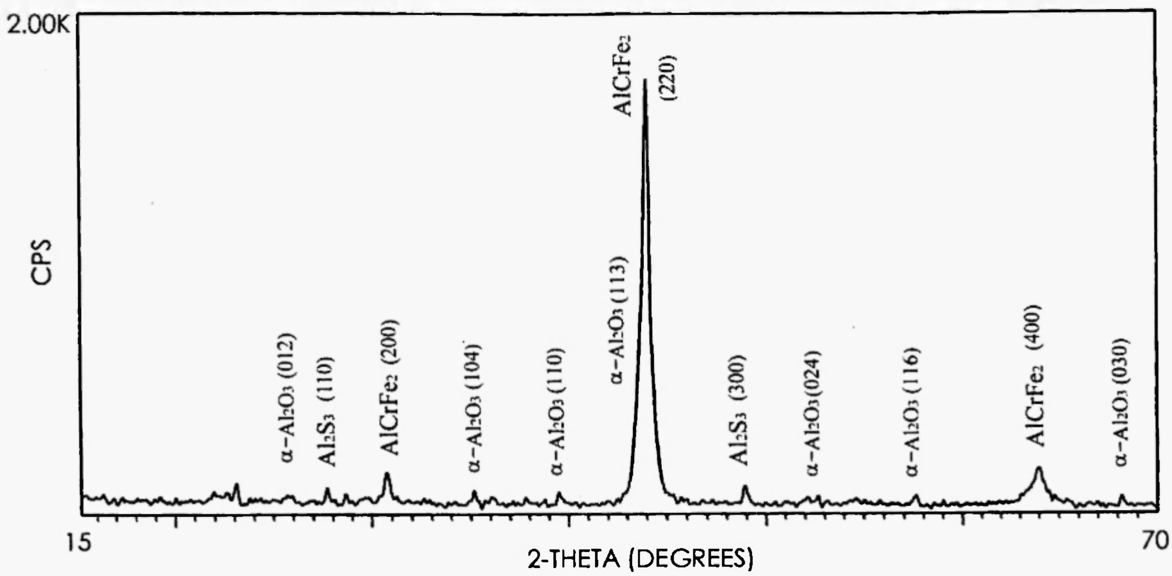

Fig. 7: X-ray diffraction pattern of the coating after 576-hour exposure

the process of arc spraying, while some was formed during the corrosion test. In fact, according to the stability diagrams for the aluminum-oxygen-sulphur system, alumina is stable under very low oxygen even in the presence of rather high sulphur pressure conditions /10,11/ and alumina is quite likely to act as a good barrier for preventing the penetration of sulphur. Thus, it is concluded that the intermetallic compound $AlCrFe_2$, formed in the coating by diffusion at high temperatures, can play an important role in decreasing the penetration of sulphur through the coating.

4. CONCLUSIONS

The following conclusions have been drawn:

1. Spraying an inner Fe-Cr-Al coating more than 0.5mm thick enables us to increase the adherence of a top aluminum coating to the substrate.
2. The single aluminum coating is not a good choice for preventing the cast iron substrate from high temperature sulphur corrosion.
3. During high temperature exposure, aluminum melts and diffuses into the Fe-Cr-Al coating, so that it can seal its pores and convert part of coating into an Al-Cr-Fe intermetallic compound.
4. A composite coating system composed of an inner Fe-Cr-Al coating and a top aluminum coating can effectively prevent the substrate from rapid degradation in sulphur-containing atmosphere.

REFERENCES

1. R. E. Kirk and D. F. Othmer, *Encyclopedia of Chemical Technology*, 4th ed., vol. 5, John Wiley & Sons, Inc., (1993), p.53-72.
2. K. Ishikawa, M. Seki, S. Tobe and Y. Kiamura, Proc. *13th Int. Therm. Spraying Conf.*, Orlando, FL (1992), p.859-864.
3. L.N Moskowitz. *Proc. 13th Int. Therm. Spraying Conf.*, Orlando, FL (1992), p.611-618.
4. M. Li. *High Temp. Corros. Met.*, Metallurgy Press of China, Beijing, (2001), p.293-295.
5. M. F. Pillis and L. V. Ramanathan. *Materials Research*, **7**, 97-102 (2004).
6. H. Qi and R. Zhu. *Corrosion Science and Protection Technique*, **6**, 41-46 (1994).
7. T.T. Huang, Y.C. Lin, D.A. Shores and E. Pfender. *J. Electrochem. Soc.*, **131**, 2191-2196 (1984).
8. J. Xing, W. Wang and Y. Gao. *Journal of Xian Jiaotong University*, **29**, 57-62 (1995).
9. A. da Cunha Rocha and F. Rizzo. *Materials Research*, **7**, 189-194 (2004).
10. F.H. Stott, S.W. Green and N.J. Wood, in *Oxidation of High-Temperature Intermetallics*, T. Grobstein and J. Doychak (Eds.), TMS, Warrendale (1988), p.117-126.
11. W. Kai, G.W. Fan, P.C. Chen and Y.T. Lin, *Oxid. Met.*, **61**, 439-461 (2004).