Micro-Crystalline Aluminide Coating Deposited on Fe-5Cr-Mo Steel by Vibrating Electro-Pulse Discharge

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ABSTRACT

Fe-Al intermetallic coatings of 100 μm thickness were deposited on the surface of Fe-5Cr-Mo steel samples by vibrating electro-pulse discharging. The coatings developed micro-crystalline structure due to the high cooling and solidification rate during deposition. The coatings also possess a strong metallurgical bonding to the steel substrate. Oxidation behaviour of these coated samples was investigated at 600°C in air for 200 h. Sulfidation resistance was also studied in a flowing SO_2 gas (99.98%) at 600°C. The results indicated that the oxidation and sulfidiation resistance of Fe-5Cr-Mo steel has been greatly improved by the aluminide coatings. The oxidation mechanisms of the coatings are studied based on SEM and XRD analysis.

Key words: Vibrating electro-pulse deposition, Micro-crystalline aluminide coating, Fe-5Cr-Mo steel, Oxidation, Sulfidation.

1. INTRODUCTION

Surface modification can significantly improve the performance of a work piece and prolong its service life under harsh environments. Among various coating processes, aluminide coatings are widely used to provide high temperature protection for iron, nickel, and cobalt-based alloys /1-4/. Conventional processing routes for aluminide coatings include pack cementation, hot dip aluminizing and chemical vapor deposition (CVD). These methods have their shortcomings. For instance, pack cementation uses a large amount of powder, which is environmentally unfriendly and expensive. The size of the crucibles and furnace often limit the application of hot dip aluminizing and pack cementation. As for the CVD method, the deposition efficiency is usually low and the fabrication cost is high. Furthermore, these techniques cannot be used to treat a part or component *in-situ*.

Electro-pulse (spark) deposition (ESD) is a convenient technique to overcome the above problems. It uses the electrical energy stored in the capacitors to generate electric sparks between the anode and cathode. The high temperature generated by the spark produces partial melting of the electrode and substrate materials. The thin layer of molten material solidifies rapidly to form a micro-crystalline coating with good bonding to the substrates. ESD can be applied to any size of work pieces at the engineering spot. The equipment and operation method are simple and easy /5-9/. The main shortcoming of this technique, however, has been the

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low deposition rate and the difficulty of obtaining a thick coating.

This paper reports our study on the processing technique of a vibrating electro-pulse discharger in order to obtain a thick coating, and the performance of aluminide coatings deposited by this method. Fe-5Cr-Mo steel was used as the coating substrate.

2. EXPERIMENTAL METHODS

Fe-5Cr-Mo steel specimens were cut to a size of 20×15×3 mm. All surfaces of the specimens were ground to 600-grit SiC paper and then cleaned ultrasonically in de-ionized water and alcohol.

The vibrating electro-pulse deposition equipment is schematically shown in Fig. 1. Electromagnetic force was generated when 50 Hz alternating current was passed through the loop of the electromagnets. The electromagnetic force periodically attracted the iron plate, which held the aluminium electrode. In this way, the Al electrode contacted with the sample and discharge took place periodically, partially melting the electrode and sample surface. The molten Al and sample then solidified on the surface of the steel, forming an aluminide coating. Ar gas flowed at the tip of the electrode to avoid oxidation. An *a.c.* source of a welding machine was used to provide a voltage of 30 – 35 V. In order to obtain a dense coating, depositing was performed on a sample twice.

High temperature oxidation of the coated specimens was carried out in a furnace at 600°C in air for 200 h. The specimens were weighed with an electronic balance with an accuracy of 10^{-5} g after every 10 h exposure. Oxidation kinetics curves were plotted using both mass gain and spallation mass-loss *vs.* exposure time.

High temperature sulfidation of the specimens was performed in flowing gas of 99.98% SO_2 at 600°C for 50 h. The specimens were weighed before and after exposure, and the mass gain and spallation were measured accordingly.

Scanning electron microscopy (SEM) was used to observe the surface morphology of the oxide scales and to make an elemental map of cross-section after oxidation for 200 h and sulfidation for 50 h at 600°C. The composition and phases of the corrosion products were analyzed by EDS and XRD.

3. EXPERIMENTAL RESULTS

Figure 2 shows the surface and cross-section morphology of coatings produced by vibrating electro-pulse deposition. It can be seen that the grains of the aluminide coatings are very small (< 1 μm); and the thickness of the coating is larger than 100 μm. There is no obvious boundary between the coating and the substrate, evidence of a good metallurgical bonding. EDS analysis shows that the main contents of the coatings are Fe and Al, with a small amount of Cr (Fig. 3). No oxygen could be detected, indicating good

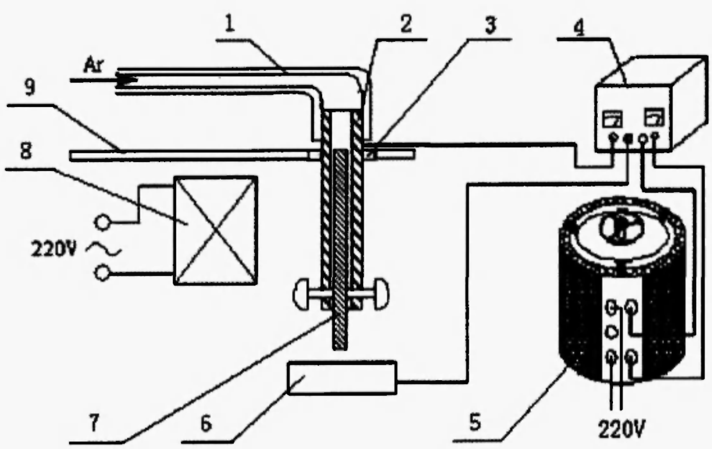

Fig. 1: Vibrating electro-pulse deposition equipment: 1. Ar tube, 2. Cu tube, 3. Insulating cushion, 4. An *a.c.* welding machine, 5. Booster, 6. Specimen, 7. Al electrode, 8. A loop, and 9. An iron plate.

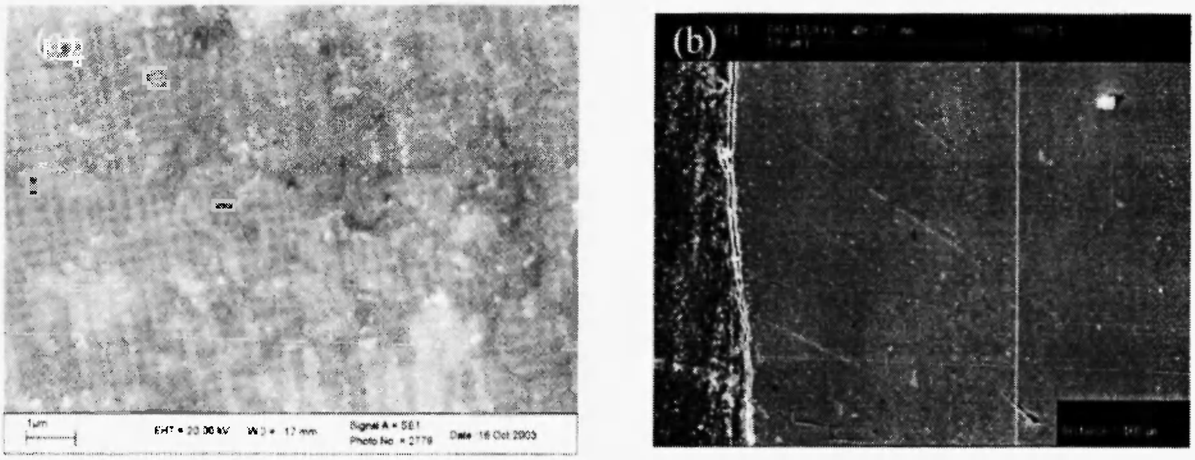

Fig. 2: SEM surface and cross-section morphologies of an aluminide coating: (a) Surface morphology, (b) cross-section morphology.

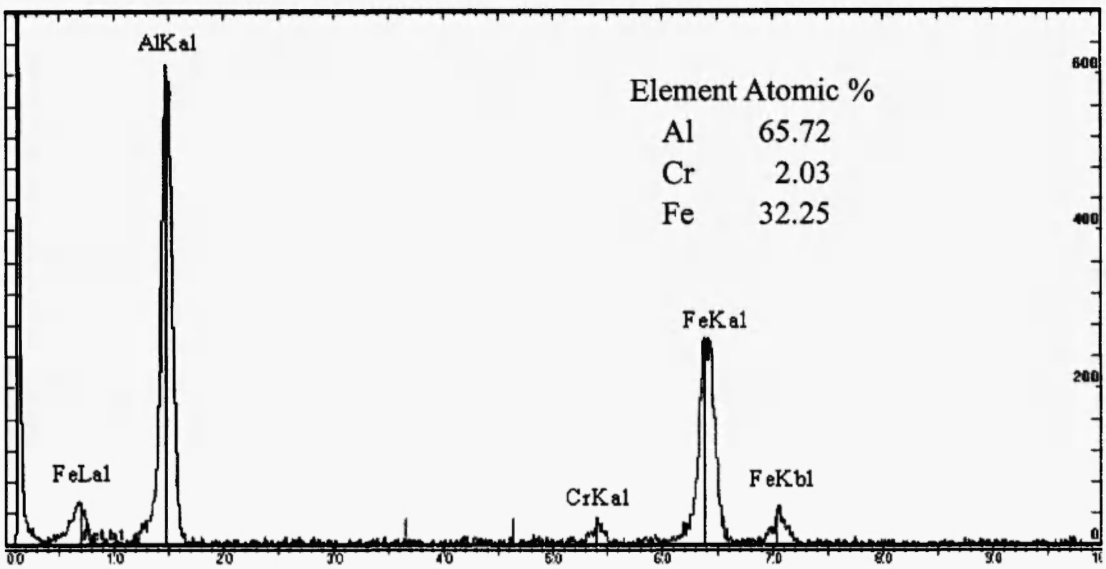

Fig. 3: EDS analysis of aluminide coating.

protection by the flowing Ar gas during deposition.

Figure 4a shows the oxidation kinetics of Fe-5Cr-Mo steel in air at 600°C. It can be seen that the oxidation resistance of the steel has been improved significantly by the aluminide coatings. The specimen without coating produced a mass gain of ~4 mg/cm^2 after oxidation at 600°C for 200 h in air, while the specimens with aluminide coatings showed mass gains of 0.3 – 0.4 mg/cm^2. The spallation resistance was also improved by the coatings, from the uncoated steel of 0.15 mg/cm^2 to the coated samples of ~0.06 mg/cm^2 as shown in Fig. 4b. therefore, aluminide coatings showed significant improvement to the oxidation resistance. The results also indicated that the deposition voltages (30 or 35 V) did not have a significant effect on the properties.

The results of sulfidation are shown in Fig. 5. After exposure in SO_2 at 600°C for 50 h, the mass gain and spallation mass of the samples with aluminide coatings

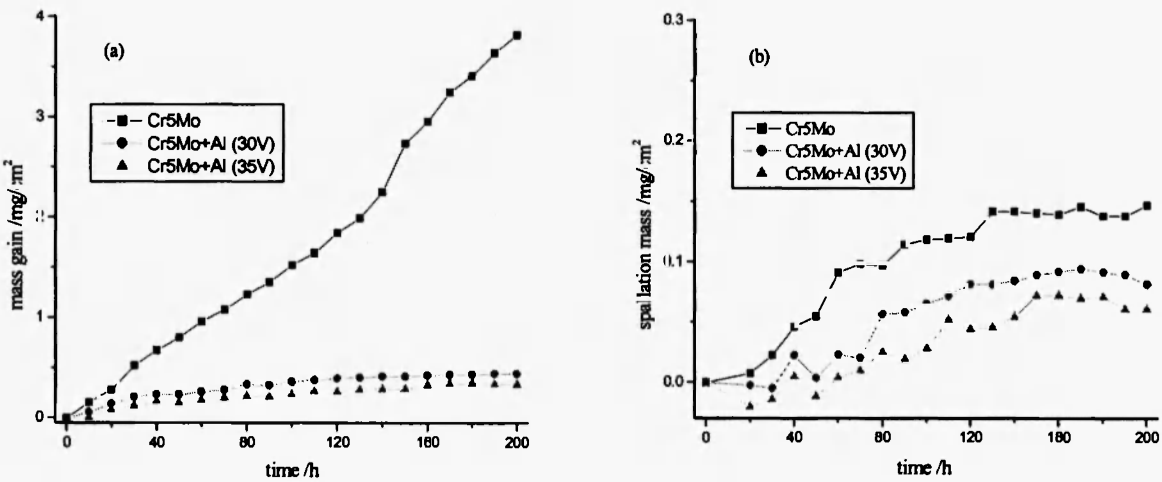

Fig. 4: Oxidation kinetics at 600°C in air for 200 h; the samples were deposited with aluminide coatings: (a) mass gain *vs* time, and (b) oxide spallation *vs* time.

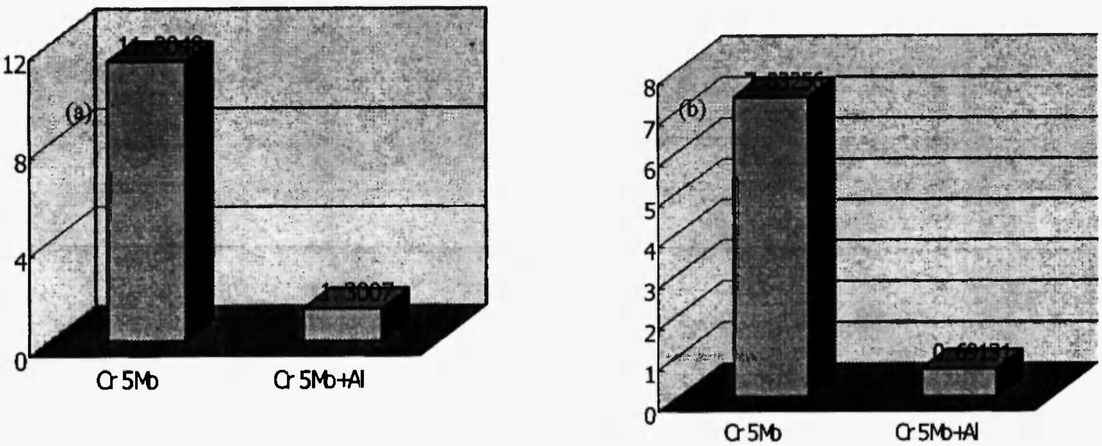

Fig. 5: Sulfidation experiment results at 600°C in SO_2 for 50 h: (a) mass gain *vs* time, and (b) spallation *vs* time.

is only about 1/10 of the steel. Even the colour of the samples is different: The steel samples showed a brown colour, while the coatings kept a metallic sheen. The sulfidation resistance of the aluminide coatings has also been significantly improved.

The SEM surface morphology of the oxide scales after oxidation and sulfidation is shown in Fig. 6. It is interesting to see that the oxide scale formed on Fe-5Cr-Mo samples exhibits a whisker shape. The width of the whisker is smaller than 100 nm and the maximum length is about 10 μm. The formation of this type of whisker oxide leads to a high mass gain, but relatively low scale spallation, perhaps because the whisker-shaped oxides do not break from the scale layer by layer.

The grains of the aluminide coating after oxidation are fine and smaller than 1 μm, while the grains after sulfidation show a nano-structure. Neither scales show scale spallation. Figure 7 shows the elemental distribution maps of the cross-section coating after oxidation at 600°C for 200 h. It can be seen that Al was rich in the coating, and the thickness of the coatings was about 100

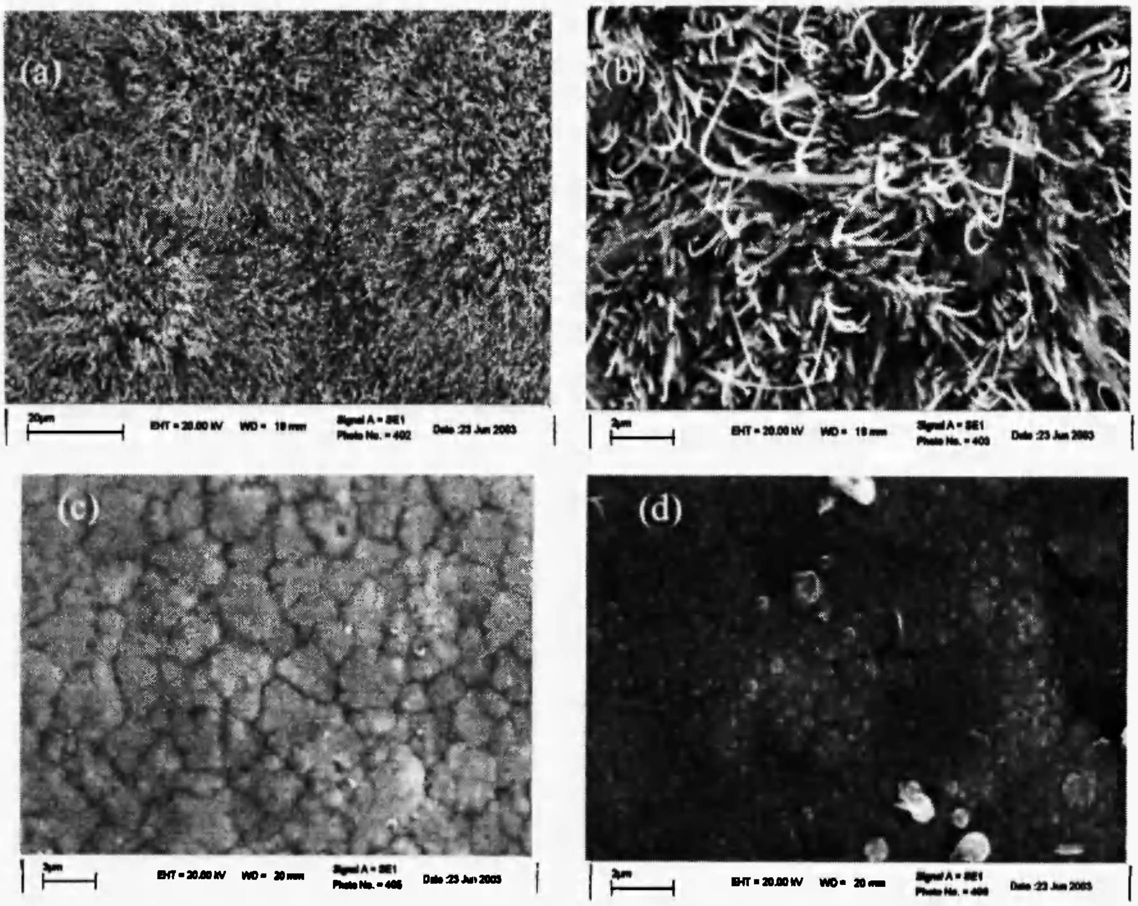

Fig. 6: SEM surface morphologies after oxidation and sulfidation at 600°C: (a) uncoated steel, (b) high magnification of (a), (c) aluminide coating after oxidation, and (d) aluminide coating after sulfidation.

μm.

Figure 8 shows the XRD spectra of three types of specimens after oxidation in air at 600°C for 200 h and sulfidation in SO_2 at 600°C for 50 h. The oxide scales formed on the surface of Fe-5Cr-Mo steel was mainly composed of Fe_2O_3 and Cr_2O_3, while the surfaces of aluminide coatings mainly show Fe-Al intermetallic compound, indicating the aluminide coatings have been formed by vibrating electro-pulse deposition; and the formation of Fe and Cr oxides was suppressed.

4. DISCUSSION

Electro-pulse deposition techniques were developed using a special power supply /6-9/. Capacitance and resistance of the power supply can be adjusted to change the pulse frequency and discharging energy of each pulse. Alloy, aluminide or alloy-oxide composite coatings have been deposited on the surface of metal samples. However, the deposition efficiency is generally low due to the interaction of electrode and surface. The thickness of aluminide coatings is generally lower than 40 μm.

The improved ESD equipment uses a loop to create electromagnetic force to drive a vibrating electrode. An industrial *a.c.* power supply with 50 Hz frequency is sufficient for deposition operation. This power source permits a large current to pass, so that the energy of one pulse can be quite high. Moreover, Ar gas can protect the oxidation of coating during deposition. As a result, an aluminide coating about 100 μm thick can be deposited on the steel surface, and the deposition efficiency is high.

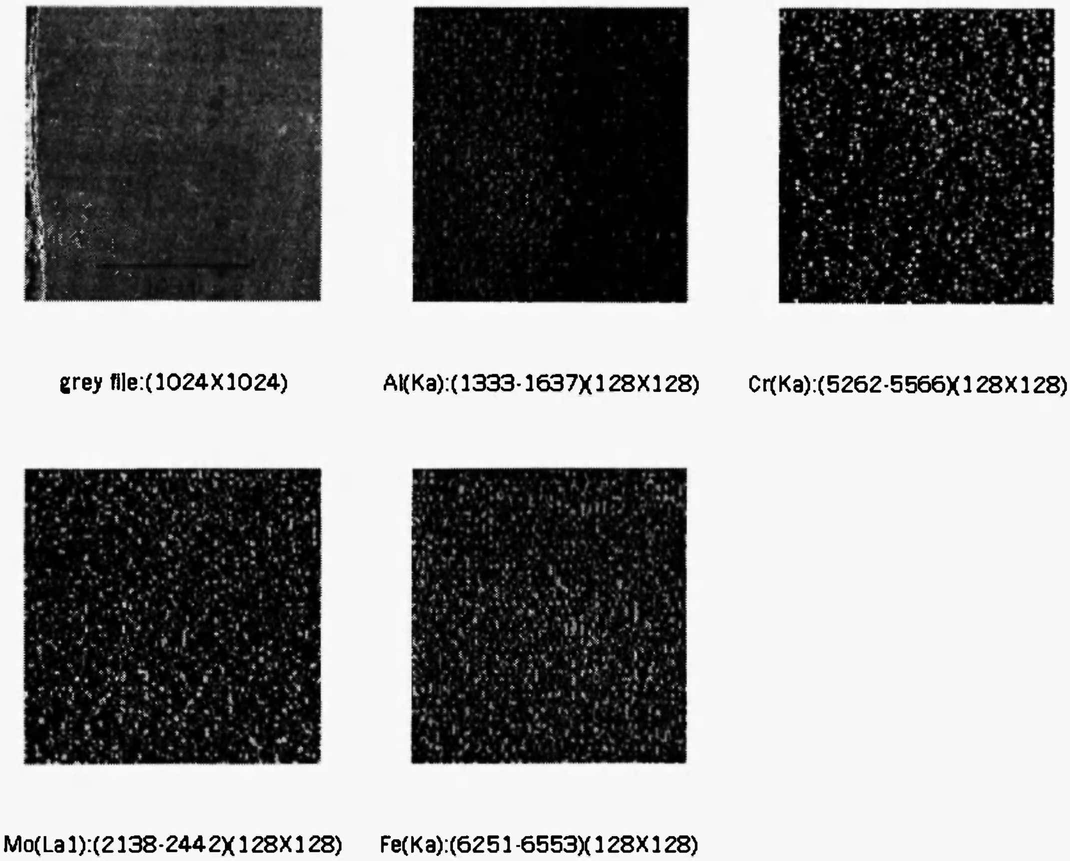

Fig. 7: SEM element mapping of the cross-section of Fe-5Cr-Mo steel with aluminide coating after oxidation at 600°C for 200 h.

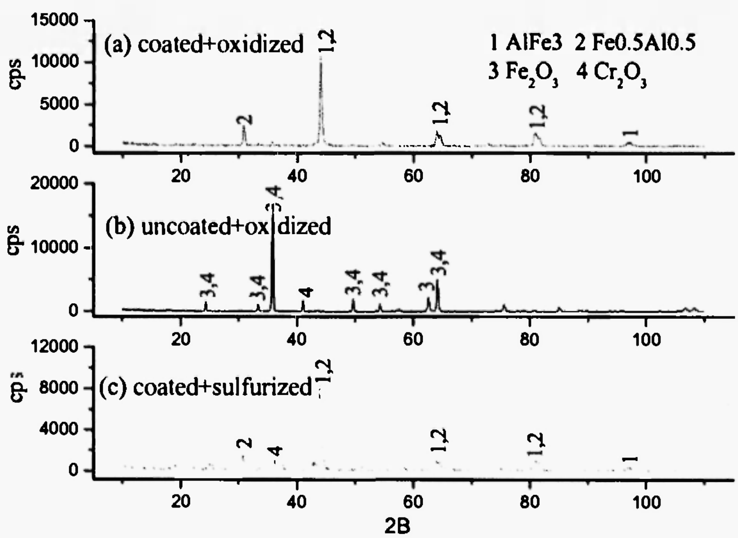

Fig. 8: XRD spectra of the specimens after oxidation and sulfidation at 600°C (a) coating after oxidation, (b) steel after oxidation, and (c) coating after sulfidation.

The aluminide coating has significantly improved the high temperature corrosion resistance of the steel. The reasons can be suggested below:

1. The aluminide coating has a strong bonding to the steel substrate. It can stop the growth of Fe-based oxide, avoiding fast high temperature corrosion. Fe-Al intermetallic compounds have good oxidation resistance, and can withstand oxidation up to ~1200°C, forming Al_2O_3 scale /10-12/. The exposure temperature in the present tests was 600°C, much lower than that level. Therefore, the Al oxide formed on the coating must be very thin, and is difficult to be detected by XRD.
2. Fe-Al intermetallic compounds also have excellent resistance to sulfidation in sulfur-containing atmosphere due to the fast formation and protection of a compact Al_2O_3 layer /13/.
3. The coatings have micro-crystalline structure due to the high cooling and solidification rate. According to Wagner's oxidation theory /14,15/, surface micro-crystalline structure can effectively enhance the diffusion of the solute element in the alloy, thus promoting the formation of a selective oxide scale. Therefore, micro-crystalline aluminide coatings possess excellent high temperature corrosion resistance.

5. CONCLUSIONS

The deposition efficiency of the newly-developed vibrating electro-pulse discharger is much improved compared to the conventional electro-pulse deposition. Micro-crystalline aluminide coatings of 100 µm thick with metallurgical bonding to the substrate have been produced on steel samples by the vibrating electro-pulse deposition.

The aluminide coatings have micro-crystalline structure due to the fast solidification. Exposure tests indicated that these coatings possess superior oxidation and sulfidation resistance at 600°C. SEM and XRD results indicated that the aluminide coatings can suppress the formation of Fe-based oxide. Micro-crystalline structure promotes the formation of a protective oxide layer.

The vibrating electro-pulse coating technique has the advantages of simple and portable equipment, easy operation and high deposition rate. It is a potential method that can be used *in-situ* to improve high temperature corrosion resistance for steel parts.

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