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Duplex Al-Based Thermal Spray Coatings for Corrosion Protection in High Temperature Refinery Applications

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The application of thermal spray coatings has been effective in preventing corrosion of steel and iron products. It has been used in a wide range of applications spreading from the petroleum to the food industry. In this work, the performance and effectiveness of a two-layered aluminum-based thermal spray coating applied to an ASTM A387 G11 steel was evaluated. The coating structure was comprised of an inner Al-Fe-Cr layer and an outer layer of aluminum. Coated samples were tested in the reactor zone of a fluid catalytic cracking unit (FCCU) of a petrochemical plant for 2.5 years. The reactor zone temperature was about 793 K (520 °C) and the environment was a mixed gas containing sulfur, oxygen and carbon. Laboratory-scale tests were also conducted on the coated samples in order to gain a better understanding of the corrosive effect of the gaseous species present in the FCCU atmosphere. Porosity present in the thermal spray coatings allowed the penetration of the atmosphere corrodents, which instigated intergranular corrosion of the steel substrate. The presence of an inner Al-Fe-Cr layer did not prevent coating spallation, which further contributed to the internal corrosion process.

Keywords: *aluminum coatings, thermal spray coatings, high temperature corrosion, mixed-gas environments, petrochemical industry*

1. Introduction

Materials used in petrochemical plants are continuously exposed to the corrosive effects produced by the petroleum processing units. These effects are enhanced for processes operating at high temperatures, leading to a faster degradation of mechanical components[1, 2]. Therefore, material stability in corrosive high-temperature environments is of great importance with regard to industrial applications. Research, aimed at producing more resistant materials as well as protective coatings has been conducted to allow for the extended use of alloy components in severe corrosion conditions[3, 4, 5].

Mixed gas environments[6, 7, 8] are very characteristic of metallurgical and chemical processes, where the presence of molecular species such as oxygen, sulfur, carbon, hydrogen and nitrogen often requires the use of coatings to avoid the accelerated degradation these mixtures are able to promote[10,11].

The performance of aluminum-coated steel is beneficial for products that require the advantages of good corrosion resistance. For some products, the behavior of the aluminum-iron interfacial compound dictates the overall resistance of the coating system to oxidation, scale formation and abrasion. Aluminum-coated steel products are used successfully in corrosive (oxidizing, sulfidizing) environments in which the temperature ranges from that of outdoor exposure to 600 °C. Among the atmospheric corrodents to which these coated products are exposed, one can list high-sulfur containing industrial atmospheres, marine environments, organic acids in food waste, etc[12].

Methods of applying aluminum coatings include hot dipping, pack cementation, cladding, and thermal spraying, amongst others. The choice of one method is determined by the coating performance required, intended use

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of the product, shape, size, production volume and cost. Thermal-spray coatings have become an interesting alternative to the economical and efficient operation of many engineering components. Many industries have introduced this versatile technology into the manufacturing environment[13]. The main advantages of the process are:

- versatility with respect to feed materials (metals, ceramics and polymers in the form of wires, rods and powders);
- the capacity to form barrier and functional coatings on a wide range of substrates;
- the ability to create freestanding structures for near net-shape manufacturing;
- the rapid solidification synthesis of specialized materials.

One drawback of the coating is the oxide content generated during spraying[14,15]. A second drawback is the presence of open pores and crevices within the coating structure, through which the corrosive environment penetrates towards the substrate. And a third drawback is the degradation of coating materials during spraying. Some elements such as Cr and Al are partially oxidized and due to this phenomenon, chemical composition of the coating material changes[16].

However, during the last decades, many efforts and new technologies and techniques have been developed in order to minimize or prevent the adverse effects of these coatings[17]. The use of sealers and specially pre-heating treatments (when the dimensions of the product are not too wide) applied to thermal spray products, have often shown to be quite effective, for avoiding corrosion species penetration via porosity[13,17-19].

The present work evaluated the performance and effectiveness in corrosion resistance of an aluminum thermal spray coating applied to ASTM A387 G11 steel.

2. Experimental Methods

Substrate samples of ASTM A387 G11 were thermally sprayed using the arc spray technique to deposit a two-layered coating structure consisting of an outer layer of aluminum and an inner layer of Al-Fe-Cr. The main reason for the inner Al-Fe-Cr layer was to provide improved adhesion of the outer Al layer to the substrate[20,21].

The coated samples were tested following two different procedures. The first consisted of an *in-situ* degradation where the samples were exposed to a mixed environment in the reactor zone of a fluid catalytic cracking unit (FCCU) of a petrochemical plant for 2.5 years. The gas mixture inside the reactor consisted essentially of N_2, H_2, CO, CH_4, and H_2S, but proportions of those compounds within the mixture were not very well defined, as those amounts vary according to the type of fuel that is being processed at the time. It is believed though, according to the refinery periodical surveys, that the average composition of the mixture follow the fractions listed in Table 1. The average temperature of the process was 793 K (520 °C); the total pressure in the system was 1 atm. The partial pressures of sulfur and oxygen were in the order of 10^{-9} atm and 10^{-28} atm, respectively, and the carbon activity inside the reactor was close to unity.

The second procedure was carried out in laboratory, in a "simulated condition" of degradation. Samples of double layered coated steel (Al + Al-Fe-Cr) were corroded into a vertical furnace for 200 h, in a gas mixture consisting of the compounds listed in Table 1. The temperature of the process was 793 K (520 °C), the total pressure in the system was 1 atm, the equilibrium partial pressures of sulfur and oxygen were 2.31×10^{-9} atm and 2.73×10^{-28} atm, respectively, and the carbon activity inside the reactor was unity.

Characterization of the corroded products for all samples was carried out using X-ray diffraction (XRD), optical microscopy and scanning electron microscopy (SEM) with X-ray dispersive analysis (EDS).

3. Results

Aluminum Coated Steel Corroded in the FCCU Reactor Zone

Analysis of samples by elemental X-ray mapping revealed the presence of corrodent species along the doubled layer coating, as shown in Fig. 1.

A large amount of oxygen was observed at the coating/substrate interface and also within the entire coating region, suggesting the presence of oxides throughout. Sulfur was mainly observed in the upper part of the Al coating and at the coating/substrate interface, in the area of the Al-Fe-Cr coating. Small traces of carbon could be observed in this latter region as well.

Cracks were present after exposure within the Al-Fe-Cr coating and spallation took place in this region. Small cracks and pores could also be observed in the upper layer (Al-coating).

Particles of oxides were observed dispersed along the subsurface of the substrate matrix, immediately under the coating region, indicating internal oxidation of the steel substrate. Closer observation of this region revealed the

Table 1. Gaseous species fractions.

Gaseous Species	Fraction (volume %)
N_2	53
H_2	25
CO	15
CH_4	5
H_2S	2

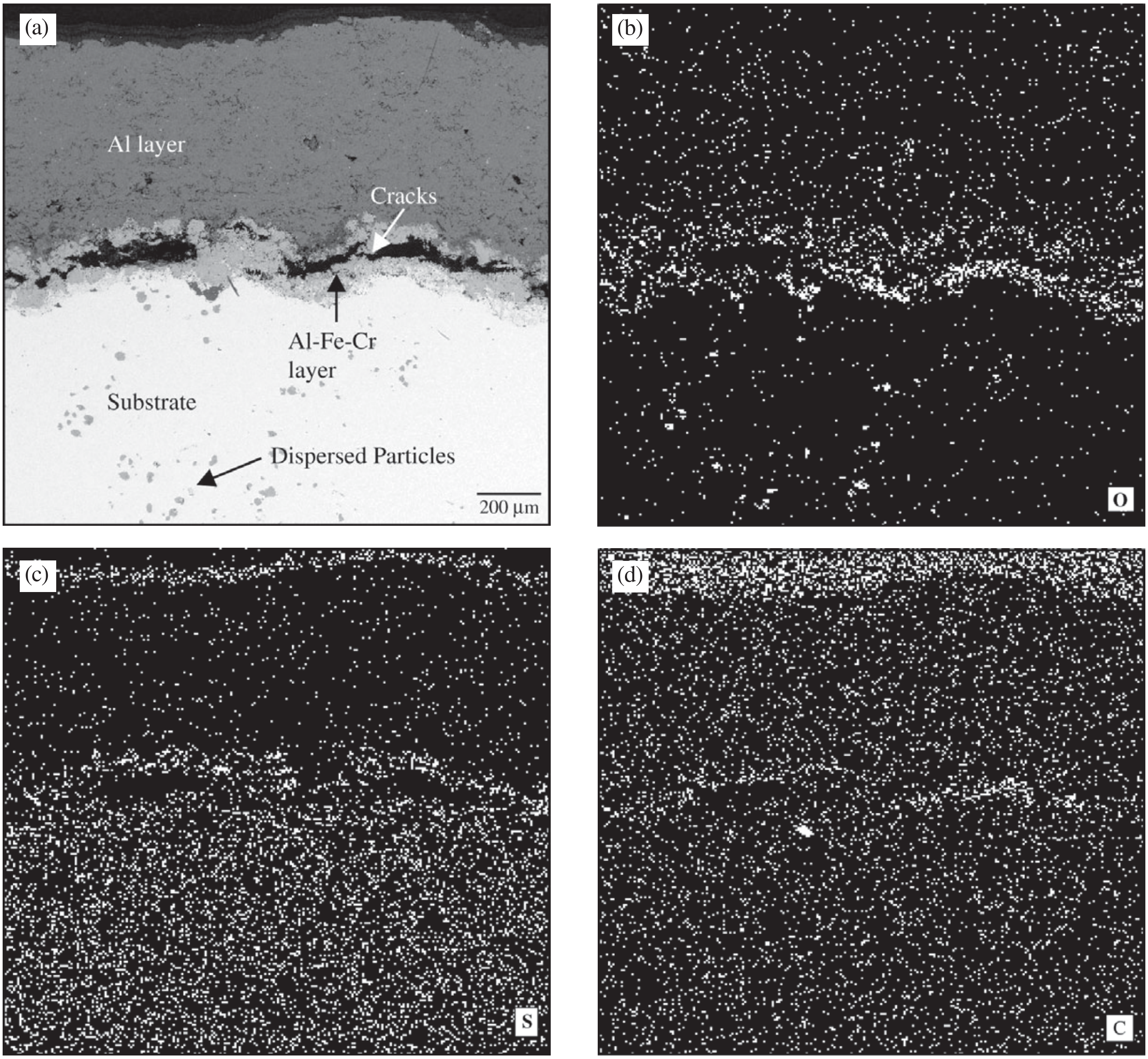

Figure 1. a) Cross section of corroded Al-coated steel; b) EDS maps of oxygen; c) sulfur; d) carbon in the region analyzed.

occurrence of intergranular corrosion, as depicted in Fig. 2. Analysis by EDS showed the presence of elements such as O and S in the intergranular product, suggesting the formation of oxides and sulfides.

Aluminum Coated Steel – Simulated Corrosion

The samples subjected to lab-scale simulated conditions exhibited similar corrosion products as those obtained in the FCCU. Sulfur and oxygen were mainly observed within the Al-Fe-Cr coating, as shown in Figs. 3 and 4 shows this region in greater detail. Cracks parallel to the coating/substrate interface were observed within the inner region of the coating. Reactions fronts, where sulfur and oxygen were detected by EDS analysis, were also prevalent at the internal coating/substrate interface. Intergranular corrosion towards the matrix could also be detected, but in lower degree than those detected in the reactor-corroded samples. Dispersed oxides were also noticed in the matrix region immediately under the coating/matrix interface, revealing the beginning of internal oxidation.

4. Discussion

Aluminum sprayed coatings may be expected to offer good protection for aggressive environments containing oxygen and sulfur, due to its ability to form a dense and homogeneous layer of aluminum oxide, avoiding the diffusion of external corrodents elements to the interior of the material [12].

The presence of S, C and O in the samples corroded in the FCCU, showed that those elements were able to diffuse to the interior of the coatings, via short-circuit paths, reaching the steel substrate and initiating internal corrosion there.

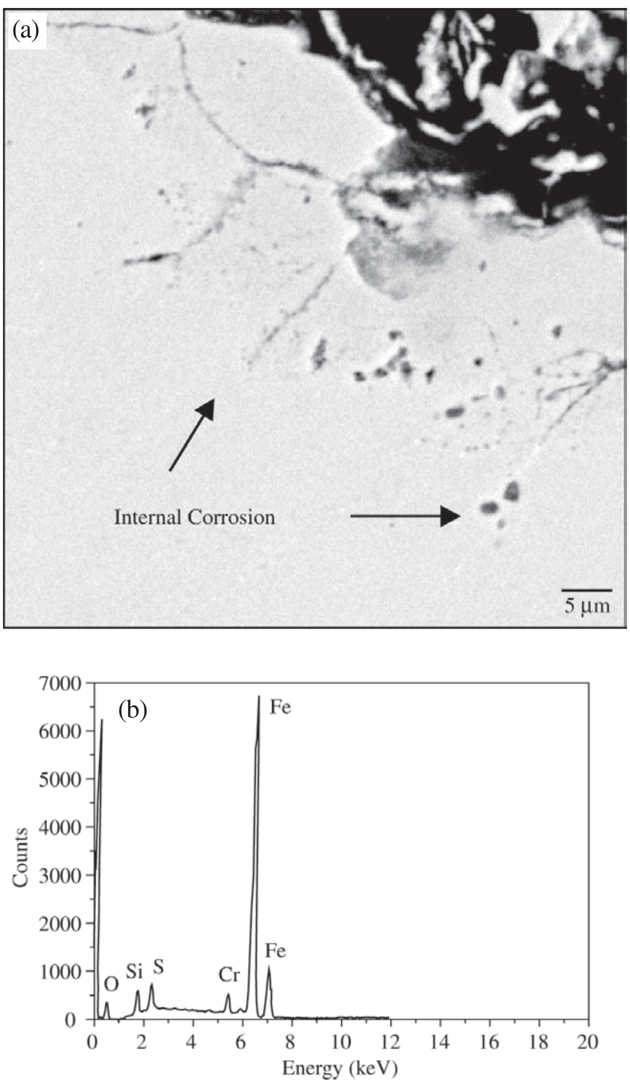

Figure 2. a) Cross-section of aluminum coated steel. The image shows the region immediately under the Al-Fe-Cr coating; b) EDS spectrum of one point inside the grain boundaries, revealing the presence of O and S.

It is believed that the porosity in the coating provided short-circuit paths for corrodants to penetrate through the coating and that this effect was enhanced by the fact that

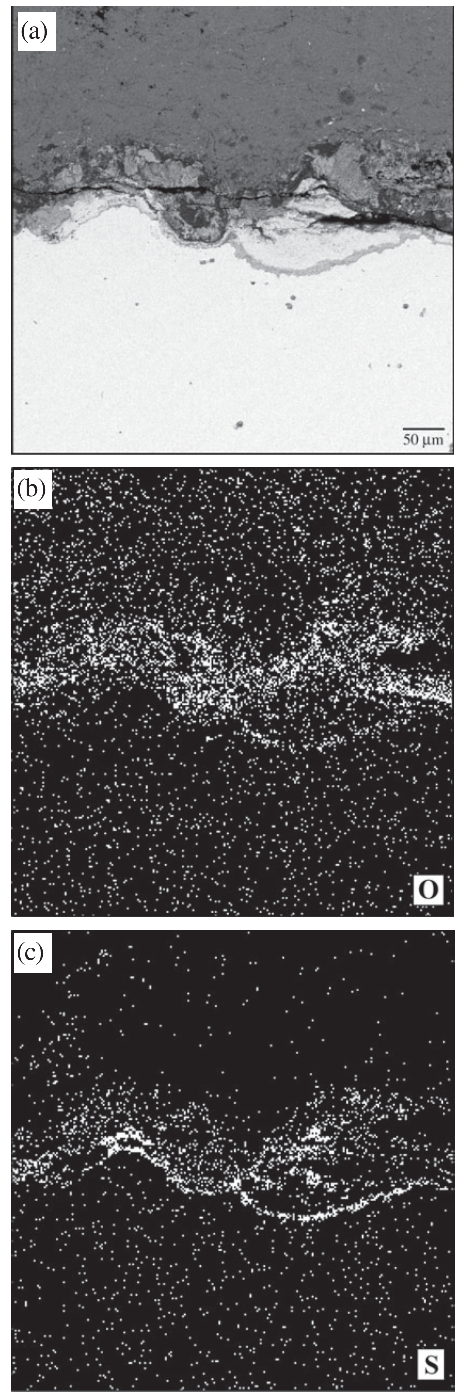

Figure 3. a) Cross-section of aluminum coated steel corroded in a vertical furnace, under simulated conditions, for 200h; b) and c) EDSmapping of oxygen and sulfur, respectively.

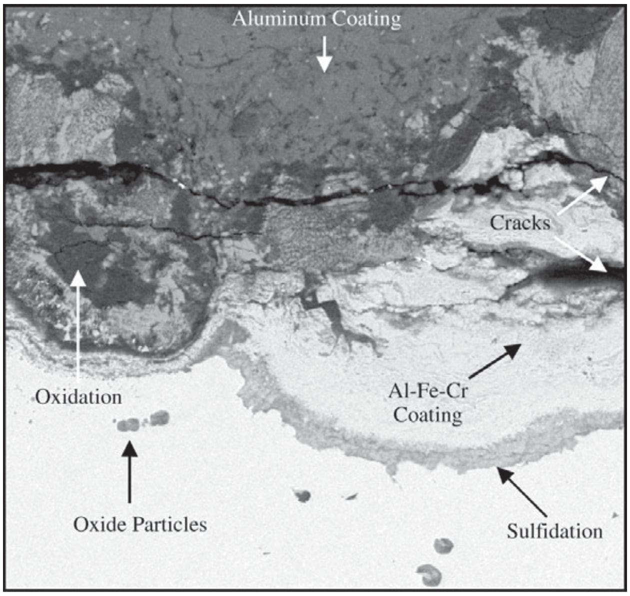

Figure 4. Cross-section of aluminum coated steel corroded at vertical furnace for 200h at a higher magnification.

most of the pores present in thermal spray coatings happen to be linked in an interlamellar interconnected manner[18]. After some time, cracks formed due to the corrosion process started also to show a high interconnection. Another point to be considered is the structure of sulfide scales. Sulfides are, by nature, porous and the presence of such structures within the material, can contribute even further for the short-path diffusion of the gaseous species into the metallic substrate[22].

All these phenomena promoted internal corrosion and coating spallation, decreasing the viability of using a thermal spray coating of the type used in this study in such aggressive atmosphere for long periods[19].

Pre-heating or sealing treatments were not performed in the material analyzed, which could have been a good method of preventing porosity and subsequent spallation in the Al coating[17]. Those pre-treatments were intentionally not performed, in order to test the inherent viability of the "as-received" coating in such an atmosphere, but it could be concluded that they were necessary in this situation. Also, the arc spray technique seemed not to be the most effective one to be used in this case, due to the results obtained. It is known that the HVOF technique has been the most useful process to reduce oxides and porosity, where those two parameters can be reduced to les than 2% and 1%, respectively[23].

5. Conclusions

- The thermal spray coating porosity provided paths for the easy access of the corrodent species from the external atmosphere to the second coating layer, initiating a process of degradation within it;
- The porous structure of the sulfides formed within the Al-Fe-Cr coating layer led to the creation of an interconnected lamellar structure and also to the formation of cracks, augmenting the corrosion process in the interface Al-Fe-Cr coating/matrix;
- Intergranular corrosion observed in the interface Al-Fe-Cr coating/matrix worked as a reaction front to the internal oxidation of the substrate;
- The presence of an Al-Fe-Cr under layer coating didn't prevent coating spallation;
- In this specific type of Al thermal spray coating, pre-treatments, such as porosity sealing and pre-heating treatment to increase adherence, are recommended as necessary for preventing steel corrosion;
- The arc spray technique was not effective for the protection of the steel in the mixed-gas atmosphere studied.

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