

# EFFECT OF HIGH TEMPERATURE OXIDATION ON THE CORROSION BEHAVIOR OF ALUMINIZED LOW CARBON STEEL IN MOLTEN ALUMINUM

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Received: March 2015

Accepted: May 2015

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**Abstract:** Hot dip aluminizing was carried out on the low carbon steel rod under optimized conditions. The aluminized samples were further oxidized at 1000°C in air atmosphere at two different times of 20 and 60 minutes. Microstructure study and phase analysis were studied by scanning electron microscopy and X-ray diffraction methods, respectively. The characterization of the coating showed that,  $\text{Fe}_2\text{Al}_5$  has been the major phase formed on the surface of specimen before heat treatment. Following the oxidation of the coating at high temperature,  $\text{Al}_2\text{O}_3$  was formed on the surface of coating while  $\text{Fe}_2\text{Al}_5$  transformed into  $\text{FeAl}$  and  $\text{Fe}_3\text{Al}$  which are favorable to the hot corrosion resistance of the coating. Corrosion resistance of aluminized samples before and after heat treatment was evaluated by rotating the samples in the molten aluminum at 700°C for various times and the dissolution rate was determined. The obtained results showed that by oxidizing the coating at high temperature, the corrosion resistance of the samples in molten aluminum improves significantly.

**Keywords:** low carbon steel, hot dip aluminizing, high temperature oxidation, corrosion

## 1. INTRODUCTION

Aluminizing is a viable method for improvement of high temperature corrosion resistance of steels [1-3]. Since aluminized steel has a high reflectivity and superior electrical and thermal conductivity; it is often used for specific applications such as automotive industries [4], bridges and pressure containers [5]. Among all techniques of coating, hot dip aluminizing is the most economical one which is widely used for aluminum coating [6]. During the aluminizing process  $\text{Fe}_2\text{Al}_5$  is the major compound to be formed [6-9] which contains 30% vacancies through which the rate of diffusion of atoms enhances significantly [6, 10]. Thus,  $\text{Fe}_2\text{Al}_5$  phase grows fast by increasing the temperature due to high concentration of vacancies [8, 11]. The hot corrosion resistance of aluminized steel is further improved by formation of dense  $\text{Al}_2\text{O}_3$  layer during oxidation at high temperatures [6, 12]. In addition  $\text{Fe}_2\text{Al}_5$  is converted to the phases with lower aluminum content like  $\text{FeAl}$  and  $\text{Fe}_3\text{Al}$  which improve the corrosion resistance of the coating [6, 13]. Numerous studies focused on the formation mechanism of intermetallic layer

during the coating process [6-9, 13, 14] while some other researches dealt with the growth rate of aluminum layer and intermetallic layer during the hot-dipping process [8, 11, 15-18]. According to the findings of these researches, the growth rate of pure aluminum layer formed on the surface of the steel substrate as well as the intermetallic layer increase as the melt temperature increases [11].

Despite the numerous studies focused on the corrosion of aluminized steel in different NaCl environments [2, 3], few research has been done on the hot corrosion of coating in molten aluminum. Thus we investigated the corrosion behavior of hot-dip aluminized mild steel which is followed by high temperature oxidation in aluminum melt.

## 2. MATERIALS AND EXPERIMENTAL

Low carbon steel rods of 8mm diameter were prepared and used as substrate for hot-dip aluminizing. The chemical composition of the mild steel used in this study is given in Table 1. High purity aluminum (>99.9%) was used for preparation of the molten bath.

**Table1.** Chemical compositions of the steel substrate

| elements            | C    | Si   | Mn   | P     | S     | Fe      |
|---------------------|------|------|------|-------|-------|---------|
| Composition (wt. %) | 0.12 | 0.17 | 0.68 | 0.112 | 0.033 | Balance |

### 2.1. Pre-Treatment of Samples

Prior to dipping the steel samples in molten aluminum, they were degreased in a 3wt%  $\text{Na}_2\text{CO}_3$  solution for 5 minutes and rinsed with distilled water. Afterwards, they were descaled by immersing in a 10wt% HCl solution for 5 minutes followed by rinsing in distilled water. Finally the samples were dipped in NaF- KCl- NaCl flux for 15 minutes.

### 2.2. Aluminizing and High Temperature Oxidation

The prepared samples were aluminized in molten aluminium for 4 minutes and then were taken out from the melt and cooled in air to room temperature. By increment of aluminizing time, thickness of brittle  $\text{Fe}_2\text{Al}_5$  increases and at lower times aluminum layer will be peeled off [16]. At the end, the dipped samples were held in a muffle furnace under air atmosphere at 1000 °C for 20 and 60 minutes.

### 2.3. Corrosion Test in Aluminum Melt

The corrosion behaviour of the heat treated samples was evaluated at 700 °C temperature for different times by rotating the samples in molten aluminum. These samples were stirred by mechanical stirrer which was made by Shimi Fan Co.

### 2.4. Analysis of Samples

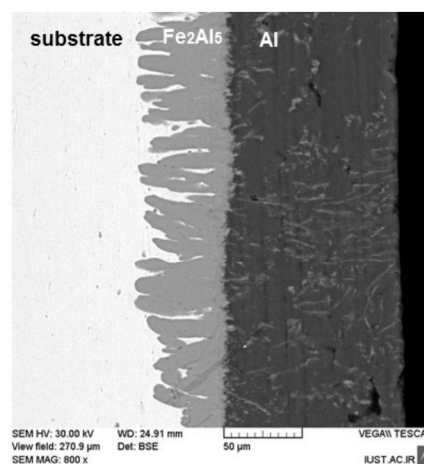
Before microstructural investigations of samples by scanning electron microscopy (Philips XL30 Model), coated specimens passed metallographic operations and then etched in 2% Nital solution. In addition, X-ray diffractometry (Philips PW1800 Model) analysis was used to determine phase structures. Corrosion of the samples in aluminum melt was evaluated by measuring the amount of iron dissolved in the melt. The iron content of the

melt was measured by using atomic absorption spectroscopy (Avanta  $\Sigma$ ).

## 3. RESULTS AND DISCUSSION

### 3.1. Microstructure Investigations

The micrograph of aluminized steel is shown in Fig.1. As can be clearly seen in the figure, an intermetallic layer between steel substrate and aluminum layer has been formed. The intermetallic layer is grown towards the substrate and therefore an un-evenly interface is formed between these layers which is finger-like as reported by other researchers as well [6-8, 19, 20]. X-ray diffraction and EDS analysis show that, the dominant phase in intermetallic layer is  $\text{Fe}_2\text{Al}_5$ . Because of Large lattice interstice of  $\text{Fe}_2\text{Al}_5$ , aluminum atoms can diffuse easily in the growing front of  $\text{Fe}_2\text{Al}_5$  crystals at high temperature [6].

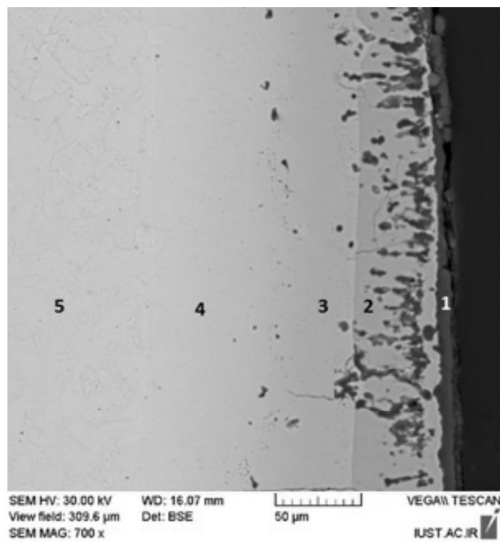


**Fig. 1.** SEM micrograph of aluminized specimen at 750 °C for 4 minutes.

### 3.2. Heat Treatment

Fig. 2 illustrates cross section micrographs of specimen which aluminized at 750 °C for 4 minutes and heat treated in air atmosphere at





**Fig. 2.** Back scatter electron image of aluminized mild steel for 4 minutes at 750°C and oxidized for 20 minutes at 1000 °C.

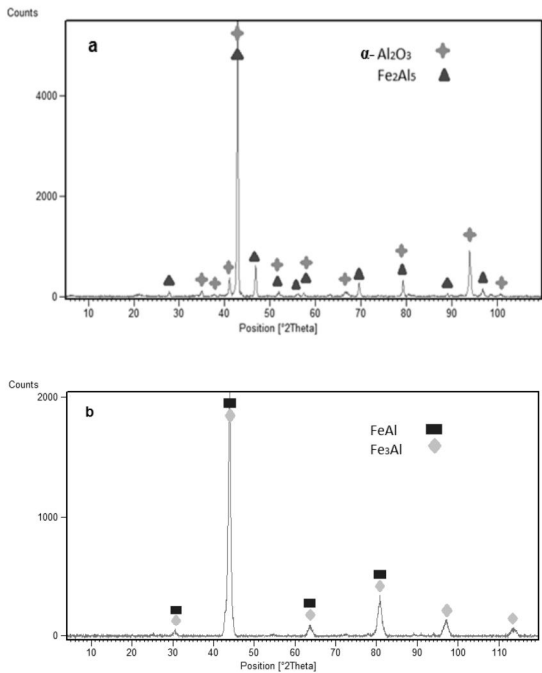
1000 °C for 20 minutes. EDS compositional analyses of marked points in this figure is listed in Table 2. It can be seen the newly formed phase just on the substrate has no cracks (Fig. 2). In the oxidation treatments of the coated samples, the  $\text{Fe}_2\text{Al}_5$  phase in inner layer is transformed into phases with less aluminum. The aluminum consumption mainly occurs in two ways which are outward diffusion of aluminum to form  $\text{Al}_2\text{O}_3$  scale and aluminum inward diffusion toward the steel substrate [7]. Oxygen diffuses into  $\text{Fe}_2\text{Al}_5$  phase because of large lattice interstice. It is realized from EDS results that aluminum oxidation occurs and aluminum content becomes less appreciated by other researchers [6, 13].

Fig.3 shows XRD analysis for specimen aluminized at 750 °C for 4 minutes and heat treated in air atmosphere at 1000 °C for 20 minutes. It can be found that, Fe-Al intermetallic layer formed is transformed from layer with a higher iron composition into layers with a lower iron composition. In other words  $\text{FeAl}_3$  and  $\text{Fe}_2\text{Al}_5$  with a serrated interface with the substrate converted to  $\text{FeAl}$  and  $\text{Fe}_3\text{Al}$  with a continuous interface [21].

It can be distinguished by XRD analysis of the

**Table 2.** EDS analysis of the marked points in Fig.2

| Elements<br>(wt. %)<br>Marked<br>points in Fig.2 | O    | Al   | Fe   | Au<br>(coated<br>for SEM) |
|--------------------------------------------------|------|------|------|---------------------------|
| 1                                                | 33.3 | 60.4 | 5.1  | Bal.                      |
| 2                                                | 3.2  | 49.5 | 46.1 | Bal.                      |
| 3                                                | 0    | 33.6 | 65.2 | Bal.                      |
| 4                                                | 0    | 12.5 | 85.7 | Bal.                      |
| 5                                                | 0    | 0    | 97.8 | Bal.                      |



**Fig. 3.** XRD pattern of specimen aluminized at 750 °C for 4 minutes and heat treated at 1000 °C for 20 minutes. a) Sample surface, b) surface of the sample after removal a 100 μm layer from the surface by machining.

surface that  $\alpha\text{-Al}_2\text{O}_3$  is formed on the surface of coating.

Fig.4 shows SEM image of specimen which aluminized at 750°C for 4 minutes, then heat treated in air atmosphere at 1000°C for 60 minutes. EDS analyses of marked points in this figure is given in Table 3.

In aluminized sample which heat treated for 60

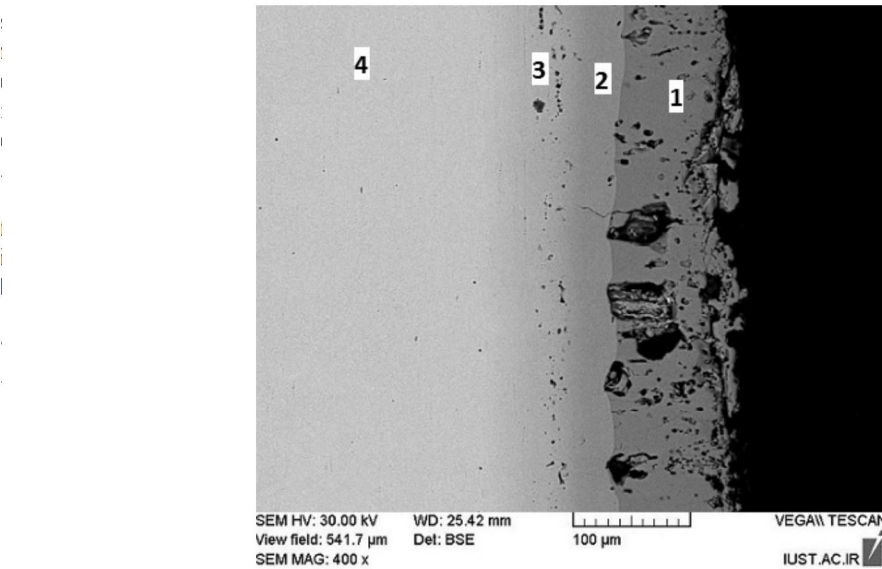


Fig. 4. Back scatter electron image of aluminized mild steel for 4 minutes at 750 °C and oxidized for 60 minutes at 1000 °C.

minutes at 1000 °C, aluminum amount is reduced from surface to center of sample. XRD pattern of the sample is the same as aluminized sample which oxidized for 20 minutes, but new peaks can be seen at higher intensities. Table 4

Table 3. EDS analysis of the marked points in Fig.4

| Marked points in Fig.2 \ Elements (wt. %) | O   | Al   | Fe   | Au (coated for SEM) |
|-------------------------------------------|-----|------|------|---------------------|
| 1                                         | 2.3 | 52.9 | 43.0 | Bal.                |
| 2                                         | 3   | 39.1 | 56.2 | Bal.                |
| 3                                         | 2.2 | 19.1 | 77.0 | Bal.                |
| 4                                         | 0   | 0    | 98.4 | Bal.                |

Table 4. Comparison of intermetallic layers thickness after heat treatment.

| Condition \ Phase               | Oxidation for 20 minutes | Oxidation for 60 minutes |
|---------------------------------|--------------------------|--------------------------|
| Fe <sub>2</sub> Al <sub>5</sub> | 61.81±8.40               | 92.08±4.62               |
| FeAl                            | 35.5±6.54                | 48.47±2.75               |
| Fe <sub>3</sub> Al              | 63.89±2.41               | 77.36±5.55               |

compared thickness of intermetallic layers for oxidized samples in different times.

Aluminum atoms from surface penetrate into substrate during oxidation. By increment of oxidation time, aluminum atoms which belong to Fe<sub>2</sub>Al<sub>5</sub> phase reach to substrate [6, 13] and for this, not only thickness of intermetallic phases increases but also formation of vacancies causes to change the shape voids in Fe<sub>2</sub>Al<sub>5</sub> phase.

Intermetallic phases and Al<sub>2</sub>O<sub>3</sub> layer have quite different thermal expansion coefficient and this result in the formation of cracks in Al<sub>2</sub>O<sub>3</sub> layer [10, 22, 23] and as oxidation time goes on, crack formation in Al<sub>2</sub>O<sub>3</sub> layer get more frequent. As a consequence of having free path in the form of cracks, oxygen can penetrate into inner layers. The voids which are seen between FeAl and Fe<sub>3</sub>Al are detectable by considering kirkendall effect [7, 19, 23].

### 3. 3. Corrosion in Molten Aluminum

Fig. 5 shows quantity of iron dissolved in molten aluminum. Corrosion resistance was improved in coated sample as shown in this figure. Increment of oxidation time causes more iron enters in molten aluminum. Because by



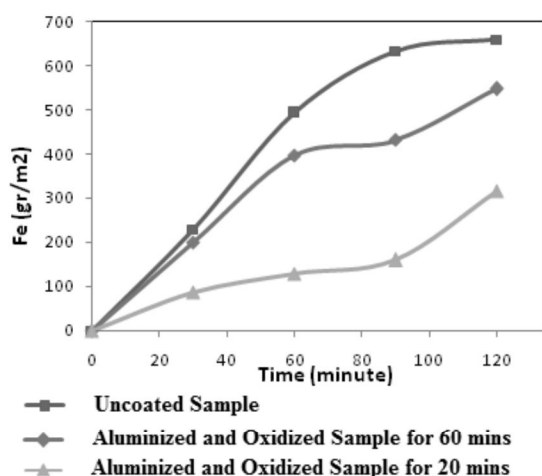


Fig. 5. Corrosion rate curves of coated and uncoated samples in aluminum melt at 700 °C.

increasing of oxidation time, more aluminum atoms reach to the intermetallic layers. So thickness of intermetallic layers increases and effect of thermal expansion coefficient improves. Also by increasing of oxidation time, more oxygen atoms can penetrate into inner layers. So cracks formation in all of layers will be increased [23]. More cracks can be seen in beneath layers of sample which oxidized for 60 minutes in Fig. 6. Then iron can penetrate from substrate into molten aluminum.

## CONCLUSIONS

Based on the results obtained in this work, the following conclusions can be drawn:

1. After aluminizing, an intermetallic layer with an un-evenly interface is formed at the interface of steel substrate and aluminum layer. XRD and EDS analysis proved that this phase was  $\text{Fe}_2\text{Al}_5$ .
2. The oxidation treatment of aluminized steel sample at high temperature in air resulted in the formation of  $\alpha\text{-Al}_2\text{O}_3$  thin layer on the surface of the sample.
3. The oxidation of aluminized sample at high temperature makes  $\text{Fe}_2\text{Al}_5$  phase be converted into intermetallic phases with less aluminum content including  $\text{FeAl}$  and

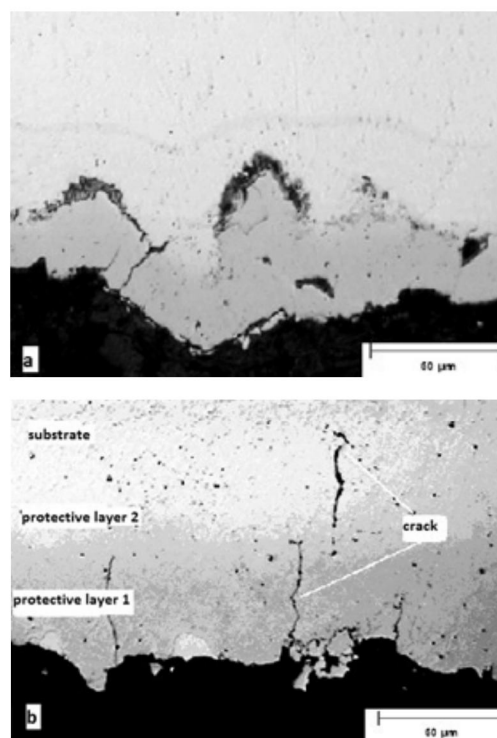


Fig. 6. Aluminized and oxidized sample for a) 20, b) 60 minutes after corrosion in aluminum melt at 700 °C for 2 hours.

$\text{Fe}_3\text{Al}$ .

4. Aluminizing and consequent oxidation treatment improves the corrosion resistance of mild steel in molten aluminum at 700 °C.
5. Increment of oxidation time reduces resistance of intermetallic and oxide layers.

## ACKNOWLEDGMENTS

The authors would like to express their gratitude to Mr. H. Mehrjou and Mrs. Rahimi for their assistances in carrying out the experiments.

## REFERENCES

1. Wang, C. J., Lee, J. W. and Twu, T. H., "Corrosion Behavior of Low Carbon Steel, SUS310 and Fe-Mn-Al Alloy with Hot-Dipped Aluminum Coatings in NaCl-induced Hot Corrosion". J. Surface and Coatings Technology, 2003, 163, 37-43.

2. Tsaur, C. C., Rock, J. C. and Chang, Y. Y., "The Effect of NaCl Deposit and Thermal Cycle on an Aluminide Layer Coated on 310 Stainless Steel". *J. Materials Chemistry and Physics*, 2005, 91, 330-337.
3. Liu, H. H., Cheng, W. J. and Wang, C. J., "The Mechanism of Oxide Whisker Growth and Hot Corrosion of Hot-Dipped Al-Si Coated 430 Stainless Steels in Air-NaCl(g) Atmosphere". *J. Applied Surface Science*, 2011, 257, 10645-10652.
4. De Cooman, B. C., Dillen, H., Storms, H., Bultinck, I. and Buyse, P., "An Industrial Application of High Frequency Internal Friction Measurements to Point Defect-Interface Interactions". *J. Alloys and Compounds*, 1994, 619-624.
5. Chen, C., Li, D. Y. and Shang, C. J., "Nanocrystallization of Aluminized Surface of Carbon Steel for Enhanced Resistances to Corrosion and Corrosive Wear". *J. Electrochimica Acta*, 2009, 55, 118-124.
6. Deqing, W., "Phase Evolution of Aluminized Steel by Oxidation Treatment". *J. Applied Surface Science*, 2008, 254, 3026-3032.
7. Wang, C. J. and Chen, S. M., "The High Temperature Oxidation Behavior of Hot-Dipping Al-Si Coating on Low Carbon Steel". *J. Surface and Coatings Technology*, 2006, 200, 6601-6605.
8. Cheng, W. J. and Wang, C. J., "Growth of Intermetallic Layer in the Aluminide Mild Steel during Hot-Dipping". *J. Surface and Coatings Technology*, 2009, 204, 824-828.
9. Palombarini, G., Casagrande, A., Carbucicchio, M. and Ciprian, R., "Protection Against Corrosion of Iron Alloys by Aluminized Coatings Produced Using Two Different Processes". *J. Hyperfine Interact*, 2008, 187, 125-130.
10. Cheng, W. J. and Wang, C. J., "Effect of Silicon on the Formation of Intermetallic Phases in Aluminide Coating on Mild Steel". *J. Intermetallics*, 2011, 1-6.
11. Deqing, W., Ziyuan, S. and Longjiang, Z., "A Liquid Aluminum Corrosion Resistance Surface on Steel Substrate". *J. Applied Surface Science*, 2003, 214, 304-311.
12. Cheng, W. J. and Wang, C. J., "EBSD Study of Crystallographic Identification of Fe-Al-Si Intermetallic Phases in Al-Si Coating on Cr-Mo Steel". *J. Applied Surface Science*, 2011, 257, 4637-4642.
13. Cheng, W. J. and Wang, C. J., "Microstructural evolution of intermetallic layer in hot-dipped aluminide mild steel with silicon addition". *J. Surface and Coatings Technology*, 2011, 205, 4726-4731.
14. Shahverdi, H. R., Ghomashchi, M. R., Shabestari, S. and Hejazi, J., "Microstructural Analysis of Interfacial Reaction between Molten Aluminum and Solid Iron". *J. Materials Processing Technology*, 2002, 124, pp 345-352.
15. Kobayashi, S. and Yakou, T., "Control of Intermetallic Compound Layers at Interface Between Steel and Aluminum by Diffusion-Treatment". *J. Materials Science and Engineering A*, 2002, 338, 44-53.
16. Rajendran, R., Venkataswamy, S., Jaikrishna, U., Gowrishankar, N. and Rajadurai, A., "Effect of Process Parameters in Hot Dip Aluminizing of Medium Carbon Steel", 2006.
17. Bouayad, A., Gerometta, Ch., Belkebir, A. and Ambari, A., "Kinetic Interactions between Solid Iron and Molten Aluminum". *J. Materials Science and Engineering A*, 2003, 363, 53-61.
18. Hwanga, S. H., Song, J. H. and Kim, Y. S., "Effects of carbon content of carbon steel on its dissolution into a molten aluminum alloy". *J. Materials Science and Engineering A*, 2005, 390, 437-443.
19. Cheng, W. J. and Wang, C. J., "Study of Microstructure and Phase Evolution of Hot-Dipped Aluminide Mild Steel during High-Temperature Diffusion Using Electron Backscatter Diffraction". *J. Applied Surface Science*, 2011, 257, 4663-4668.
20. Awan, G. H. and Hasan, F. U., "The Morphology of Coating/Substrate Interface in Hot-Dip-Aluminized Steels". *J. Materials Science and Engineering A*, 2008, 472, 157-165.
21. Abdolahi, B., Shahverdi, H. R., Torkamany, M. J. and Emami, M., "Improvement of the Corrosion Behavior of Low Carbon Steel by Laser Surface Alloying". *J. Applied Surface Science*, 2011, 257, 9921-9924.
22. Wang, C. J. and Badaruddin, M., "The

- Dependence of High Temperature Resistance of Aluminized Steel Exposed to Water-Vapor Oxidation". J. Surface and Coatings Technology, 2010, 205, pp 1200-1205.
23. Chang, Y. Y., Tsaur, C. C. and Rock, J. C., "Microstructure studies of an aluminide coating on 9Cr-1Mo steel during high temperature oxidation". J. Surface and Coatings Technology, 2006, 200, pp 6588-6593.