

Corrosion Protection on High-temperature Sulfidation of Fe-Base Alloys

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Abstract: Fe-20%Ni-25%Cr alloys were aluminized through the pack-cementation technique by immersing them in the pack that consisted of the source metal, an activator, an inert filler. After aluminized Fe-20%Ni-25%Cr alloys were corroded at 800 °C for 10-100 hr in (0.9448 atm N₂ + 0.031 atm H₂O + 0.0242 atm H₂S)-mixed gas condition. Pack-cementation is a good surface treatment technique for development of corrosion resistance coating to be utilized at high temperature corrosive condition. The corroded test coupons were characterized by a scanning electron microscope (SEM), Energy Dispersive X-Ray Spectrometer (EDS), an electron probe micro-analyzer (EPMA), an X-ray diffractometer (XRD) with Cu-K α radiation. The aim of this study is to study the microstructural transformation of the pack-cementation aluminized coating before and after corrosion. Pack-cementation aluminized in the formation of Fe₃Al intermetallic compound layer on the matrix. The Fe₃Al intermetallics have reasonable corrosion and oxidation-resistance, because of the aluminized coating corroded mainly to α -Al₂O₃ through the selective oxidation of Al in the outer Fe₃Al coating.

Key words: Sulfidation, aluminizing, pack-cementation, corrosion.

1. Introduction

High-temperature coal-fired power gas turbines, petrochemical units, combustion gases, direct fired furnaces have a big problem caused by fine dust. In particular, coal-fired power generation, it is considered to be the main culprit of the emission of acid gas and fine dust, and there is a continuous demand for the development of a system that can operate coal in an environmentally friendly manner. Integrated Gasification Combined Cycle (IGCC) is an environmentally friendly power generation technology that uses coal to react with oxygen and water vapor to convert it into synthetic gas (CO + H₂) and convert it into fuel gas turbines and steam turbines. Integrated Gasification Combined Cycle (IGCC) is high efficiency power generation, recovery of hydrogen and sulfur are possible, emissions of pollutants are lower compared with existing coal-fired power generation. However, IGCC operating condition is more severe high temperature/high pressure than general coal-fired power generation and the content of N₂, H₂O, CO₂ and H₂S element gases are high [1], [2]. Especially corrosion is more serious in sulfur-containing atmospheres. SO₂, H₂S corrosion rate is 10 to 100 times faster than O₂ and air condition [3]. Sulfur atom generates void and form crack, thereby causing on the spallation of the scale. Pack-cementation is one of the surface treatment methods to protect the base metal from corrosion and improving corrosion resistance, and widely used in power generation equipment, various industrial and aircraft engine parts manufacturing

processes [4], [5]. Aluminizing is the process of pack-cementation method, it can provide high aluminum concentration on the alloy surface. Due to that is formed the thermodynamically stable Al_2O_3 protective scales of practical metallic materials. G Hu, F Wang, R Drevet [6], [7] have discussed in detail the high temperature oxidation and corrosion behavior by pack-cementation on (Fe, Ni)-base alloys. However, there have few studies on the corrosion characteristics of aluminized diffusion-coatings on (Fe, Ni)-base alloys in $\text{N}_2/\text{H}_2\text{O}/\text{H}_2\text{S}$ gases. Therefore, this study aims to investigate the Fe-base alloys(20%Ni-25%Cr) was aluminized via pack cementation, and corroded at 800 °C in $\text{N}_2/\text{H}_2\text{O}/\text{H}_2\text{S}$ -mixed gases similar to the IGCC operating atmosphere. The objective of this research is to corrosion resistance and characteristics of the coated samples. The corrosion protection and coatings research must demonstrate an understanding of theories and concepts that are relevant to the coating parameters, substrate compositions, temperature and time to reveal the factors affecting the corrosion characteristic of metals.

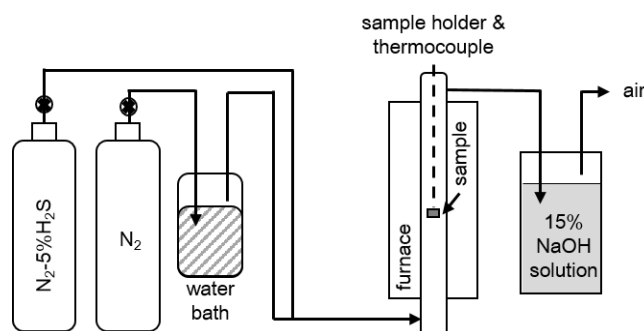


Fig. 1. Corrosion testing apparatus.

2. Experimental Procedure

Fe-base alloys having a nominal composition of Fe-20%Ni-25%Cr (wt.%) were cut to $2 \times 10 \times 10 \text{ mm}^3$ sized coupons, ground on 1200 grit paper, and ultrasonically cleaned in acetone and alcohol, and aluminized via pack cementation. Aluminizing is a thermo-chemical process consisting of saturating, by way of diffusion, of ferrous alloys, predominantly of steel, with aluminium. Pack-cementation aluminizing was performed by heating a pack that consisted of powders of (25%FeAl as the source metal + 5%NaF as an activator + 70% Al_2O_3 as an inert filler) at 1000 °C for 5 h in an H_2 atmosphere. The coated samples were charged into a quartz reaction tube at room temperature, heated to 800 °C in an N_2 atmosphere within 24 h, and corroded at 800 °C for 10~100 h under 1 atm of flowing $\text{N}_2/\text{H}_2\text{O}/\text{H}_2\text{S}$ -mixed gas. The composition of the corrosion gas was 0.9448 atm of N_2 + 0.031 atm of H_2O + 0.0242 atm of H_2S , and furnace-cooled to room temperature. Also drilled a $\Phi 0.3$ size hole before corrosion, which connected by a Pt wire and then placed into a uniform zone within the quartz reaction tube as shown in Fig. 1. The employed gas composition was attained by bubbling ($\text{N}_2+\text{H}_2\text{S}$)-mixed gases through a water bath kept at 25 °C, and by introducing this mixed gas into a quartz reaction tube that was vertically positioned at the center of an electrical furnace. After corrosion testing in (0.9448 atm N_2 + 0.031 atm H_2O + 0.0242 atm H_2S)-mixed gases, the weight gain of each sample was measured using a microbalance. The (0.9448 atm N_2 + 0.031 atm H_2O + 0.0242 atm H_2S)-mixed gases were discharged after neutralization with NaOH solution. The morphology and composition of the coated layer and scales were characterized by a scanning electron microscope (SEM) equipped with an energy dispersive spectroscope (EDS), an electron probe micro-analyzer (EPMA), and an X-ray diffractometer (XRD) with Cu-K α radiation at 40 kV and 150 mA in $\theta/2\theta$ configuration.

3. Results and Discussion

Fig. 2 shows the weight gain versus time plots for uncoated and aluminized Fe-20%Ni-25%Cr alloys

during corrosion in (0.031 atm H₂O + 0.0242 atm H₂S + 0.9448 atm N₂)-mixed gas at 800°C for 10 to 100 hours. The weight gain of each sample was measured using a microbalance at room temperature before and after each corrosion test. Weight gain of uncoated Fe-20%Ni-25%Cr alloy samples were 5~10 times higher than that of aluminized Fe-20%Ni-25%Cr alloy samples. The uncoated Fe-20%Ni-25%Cr alloy corroded fast with massive weight gains and suffered serious scale cracking and spallation. On the other hand aluminized Fe-20%Ni-25%Cr alloy samples were protected by the high Al contents coated layer. The Al coated layer for Fe-Cr-Ni alloys promotes the early formation and retention of the thermodynamically more stable α -Al₂O₃ oxide scale. Therefore aluminized Fe-20%Ni-25%Cr alloy samples showed a low weight gain, which was an effective surface modification treatment to protect the corrosion of Fe-base alloys.

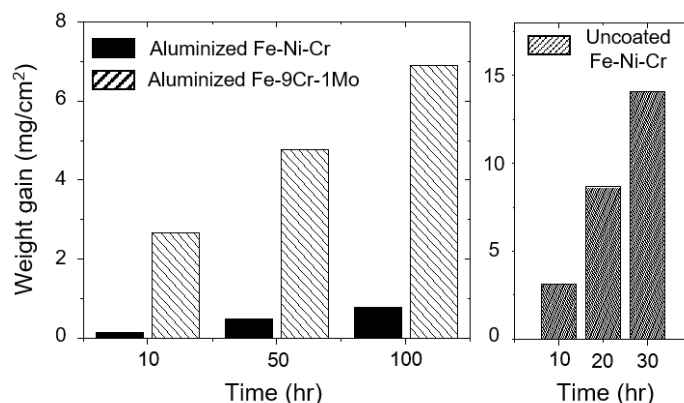


Fig. 2. Weight gain versus corrosion time curves of the uncoated and aluminized Fe-Cr-Ni alloy at 800 °C for 10-100 h in (0.031 atm H₂O+0.0242 atm H₂S+0.9448atm N₂)-mixed gas.

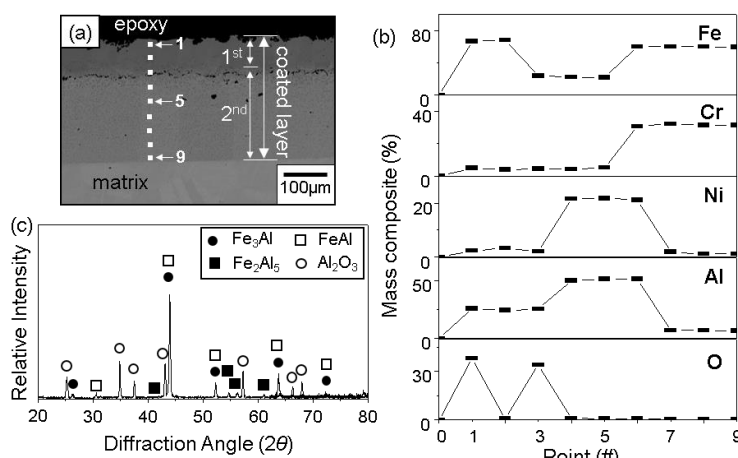


Fig. 3. Aluminized Fe-Cr-Ni alloy before corrosion. (a) SEM cross-sectional BSE image, (b) Spot analysis along 1-9, (c) XRD pattern.

Fig. 3 shows the SEM/EDS/XRD results of the aluminized Fe-20%Ni-25%Cr alloy. A continuous, uniform coating with a thickness of about 250 μ m was obtained. Coating layer can be divided into layers 1st and 2nd (Fig. 3a). The outer 1st layer was the 77 μ m-thick, inner 2nd layer was the 170~180 μ m-thick aluminized coating. During aluminizing, the counter diffusion of Al and substrate elements occurs, according to the diffusivity and solubility of the particular elements [8]. Sufficient amounts of Al were included into the Fe-Cr-Ni alloys to produce Fe₃Al, top α -Al₂O₃ oxide. Small dark spots in the boundary between the outer 1st layer and inner 2nd layer were principally Kirkendall voids that formed due to the outward diffusion of substrate elements [8], [9]. And also some small dots on the surface, which were alumina particles that were added in the pack as an inert filler. The EDS-analyzed compositions at the upper and lower part of the

coating were shown in Fig. 3(b). Intensity of the diffraction pattern was reduced Fe_3Al , FeAl , $\alpha\text{-Al}_2\text{O}_3$, Fe_2Al_5 in Fig. 3c. The aluminized coating layer mainly consisted of Fe_3Al , top $\alpha\text{-Al}_2\text{O}_3$ oxide layer which has oxidation and corrosion resistance[10].

Fig. 4 shows the SEM/EDS results of the uncoated Fe-20%Ni-25%Cr alloy after corrosion at 700 °C for 20 h in (0.031 atm H_2O +0.0242 atm H_2S +0.9448atm N_2)-mixed gas. Uncoated Fe-Cr-Ni alloys had a large weight gains, forming non-adherent, fragile, unstable sulfide scales as thick as 100 μm . Also the scale was prone to cracking and spallation (Fig. 4a). The fact that the outer scale was thicker than the inner scale indicates that the outward diffusion of Fe, Cr and Ni occurred more than the inward diffusion of sulfur and oxygen. The corrosion behaviour of various materials including the H_2S has had a quite serious and complex corrosion compared to other gas condition types such as oxygen. Therefore sulfur formed a non-protective (Fe,Cr,Ni)-S sulfides. The composition of the outer scale, middle scale and inner scale was 33Fe-10Ni-4Cr-52S, 10Fe-1Ni-36Cr-53S, and 11Fe-5Ni-36Cr-48S, in at.%, respectively, according to the EDS analysis(Fig. 4b).

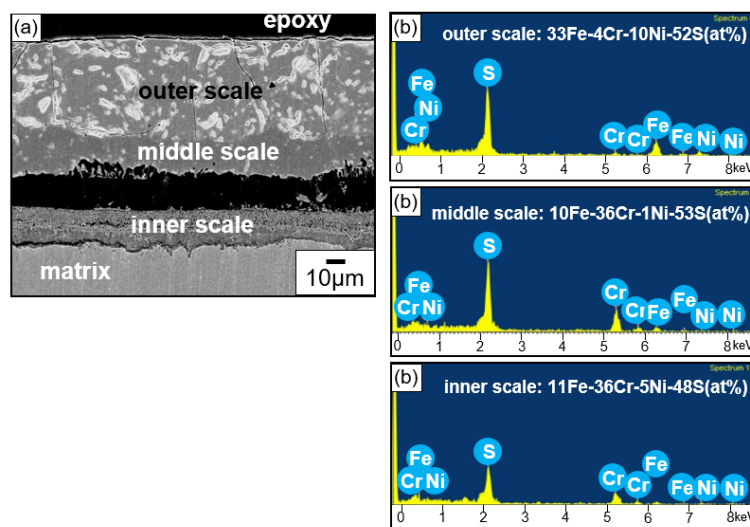


Fig. 4. Uncoated Fe-Ni-Cr alloy after corrosion at 700 °C for 20 h in (0.031 atm H_2O +0.0242 atm H_2S +0.9448atm N_2)-mixed gas. (a) SEM cross-sectional image, (b) EDS spectrum of outer/middle/inner scale.

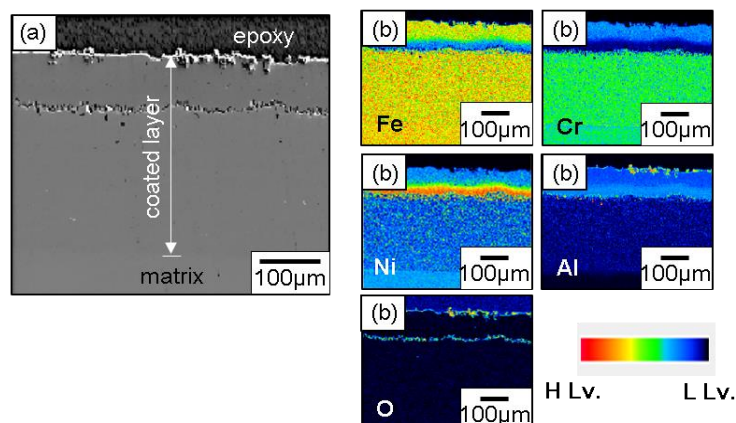


Fig. 5. Aluminized Fe-Ni-Cr alloy after corrosion at 800 °C for 50 h in (0.031 atm H_2O +0.0242 atm H_2S +0.9448atm N_2)-mixed gas. (a) SEM cross-sectional SE image, (b) EPMA mapping.

Fig. 5 shows the SEM/EPMA results of the aluminized Fe-20%Ni-25%Cr alloy after corrosion at 800 °C for 50 h in (0.031 atm H_2O +0.0242 atm H_2S +0.9448atm N_2)-mixed gas. The Fe_3Al intermetallic coated layer has extremely corrosion resistance and highly stable, whereby very slowly change occurred (Fig. 5a). Fig. 5b

shows the resulting Fe₃Al coated layer forms a protective α -Al₂O₃ scale during sulfidation exposure and provides excellent sulfidation resistance to the Fe-base alloys. Therefore sulfide was not formed. Because aluminized sample was able to form a protective α -Al₂O₃ oxide scale. The formation of a protective α -Al₂O₃ oxide scale resulting from high-temperature exposures in corrosion condition contributed to the enhanced corrosion resistance [8], [10]. During the corrosion, the coated layer was slightly widened owing to inter-diffusion. It was observed that Ni was enriched in 1st layer bottom part, while Cr was deficient in the same layer. Such an elemental distribution would depend on the inward diffusion of Al gradually decreased the concentration, amount, diffusivity, and solubility of substrate elements such as Fe and Cr.

4. Conclusion

The aluminized diffusion-coating on Fe-20%Ni-25%Cr alloy was made by pack-cementation, and its corrosion behavior was studied by SEM/EPMA/EDS, and XRD, When corroded at 800 °C for 10-100 h in (0.031 atm H₂O+0.0242 atm H₂S+0.9448atm N₂)-mixed gas. The Fe₃Al intermetallics have reasonable corrosion and oxidation-resistance, because of the aluminized coating corroded mainly to α -Al₂O₃ through the selective oxidation of Al in the outer Fe₃Al coating. The α -Al₂O₃ oxide scale contributed to the enhanced corrosion resistance in high-temperature corrosion condition. The uncoated Fe-20%Ni-25%Cr alloy corroded rapidly, forming non-protective scales that consisted primarily of FeS, (Cr,Ni)-S.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

M.J. Kim wrote and edited the paper, and contributed in all activities. D.B. Lee substantial contribution to the production and analysis of the results.

Acknowledgment

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References

- [1] IEA Clean Coal Centre. (2013). Recent operating experience and improvement of commercial IGCC. UK.
- [2] Last, G, & Schmick, M. (2011). *Identification and Selection of Major Carbon Dioxide Stream Compositions* (pp. 15-22). Washington: Pacific Northwest National Laboratory.
- [3] Mrowec, S., Walec, T., & Werber, T. (1969). Inetics and mechanism of high-temperature sulfur corrosion of Fe-Cr-Al Alloys. *Oxidation of Metals*, 1(93), 481-504.
- [4] Wang, W., Zhang, Y., & Wilson, D. (2010). Formation of aluminide coatings on ferritic-martensitic steels by a low-temperature pack cementation process. *Surface and Coatings Technology*, 204(16-17), 2737–2744.
- [5] Mohammadi, K., & Haghi, A. (2008). A study on characterization of pack-cemented aluminide coating on metals. *Journal of Materials Processing Technology*, 201(1), 669–672.
- [6] Guoxin, H., Zhengxia, X., Jianju, L., & Yanhong, L., (2009). Microstructure and Corrosion Resistance of Simultaneous Al-Fe Coating on Copper by Pack Cementation, *Surface and Coatings Technology*, 203(22) 3392-3397.
- [7] Xu, C., Peng, Z., Zheng, L., & Wang, F. (2011). Erosion-corrosion in a laboratory scale coal-firing FBC of various aluminized coatings prepared by low-temperature pack cementation. *Surface and Coatings*

Technology, 205(19), 4540-4546.

- [8] Lee, J. C., Kim, M. J., & Lee, D. B. (2014). High-temperature corrosion of aluminized and chromized Fe–25.8 %Cr–19.5 %Ni Alloys in N₂/H₂S/H₂O-Mixed Gases. *Oxidation of Metals*, 87(5-6), 617–630.
- [9] Bateni, M., Shaw, S., Wei, P., & Petric, A. (2009). Deposition of Fe-Al intermetallic coatings on SOFC interconnects by pack cementation. *Materials and Manufacturing Processes*, 24(6), 626-632.
- [10] Young, D. J. (2008). *High Temperature Oxidation and Corrosion of Metals*, Elsevier, UK.

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Min Jung Kim wrote and edited the paper, and contributed in all activities. Dong Bok Lee also substantially contributed to the analysis of the results. Min Jung Kim graduated from Sungkyunkwan University in Korea. My major is advanced materials science & engineering and study field is metal corrosion mechanism. I published many papers on high-temperature corrosion of Fe-base alloy and coated sample. She is a visiting professor in the School of Advanced Materials Science & Engineering, Sungkyunkwan University, Suwon, Korea. she is very enthusiastic to study eco-friendly power generation technology materials and her commitment and passion extends far beyond academic pursuit to solving real environmental issue.