Structure and Oxidation Resistance of Flamesprayed Fe–Ni–Al Coating

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Abstract. Two types of Fe–Ni–Al coatings as Fe75Ni15Al10 and Fe56Ni14Al30 were successfully deposited on the surface of low carbon steel using the flamespray technique. Coated samples were then annealed in a vacuum furnace at 800°C for two hours and evaluated for high temperature oxidation resistance at 800°C for up to 8 cycles. The phases and structure of Fe-Ni–Al coatings before and after the oxidation test were studied using X-ray diffraction (XRD) and scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectrometer (EDX). According to the oxidation kinetic curve, both of the coating compositions had lower mass gains compared to the low carbon steel. After 8 cycles of exposure, however, the coatings tend to spall off due to the difference in thermal expansion coefficient between the substrate and coating.

1. Introduction

The use of carbon steels in structural applications for instance in advanced power plants seems reasonable for its good mechanical properties, ease in fabrication, and low production cost [1]. Power plants’ strive to achieve high efficiency production with the least carbon emissions is demanding on the operational temperature and pressure of the working fluid, which sparks the question ‘What can be done to achieve this?’ By referring to a basic principle, the thermal efficiency equation \( \eta = \frac{T_H - T_C}{T_H} \) states that by increasing the operational temperature can help raise the maximum efficiency. Nonetheless, the fact that working at elevated temperature conditions effects materials in a way that makes them easily degraded through oxidation, corrosion, or erosion, resulting in a shortened material life-time.

Coating comes to mind in terms of protecting materials from environmental degradation and the chosen method for this research was by flamespray. Flamespray was chosen for its versatility, portability, and has low capital cost [2]. Thick layers can be fashioned as well as its relative ease when training the operators [3]. When selecting the compound; nickel has resistance towards high temperature corrosions and provides strength and ductility [2,4] and aluminum as the main contributor in providing strength and oxidation resistance [2]. Aluminum creates a thin Al2O3 protective layer [5] that prevents the materials below it to defuse upwards making it a great barrier to prevent oxidation.

For applicational purposes, coated substrates were annealed in a vacuum furnace to obtain a uniform coating structure and enhance the bonding between coating and surface [6] and tested at 800°C.
in the hopes of obtaining better results at lower temperatures for high temperature structural applications. Two compound variations were considered being Fe$_{75}$Ni$_{15}$Al$_{10}$ and Fe$_{56}$Ni$_{14}$Al$_{30}$.

2. Experimental Procedure

In this work, low carbon steel plate was chosen as the substrate. It was cut to 10 mm $\times$ 10 mm $\times$ 3 mm then polished using silicon carbide abrasive papers from #100 to #1200 which was then cleaned with ethanol in an ultrasonic cleaner bath for 10 minutes. Powders of Fe, Ni, and Al were mixed in a simple mixer with the amount of 11.769 grams of Fe, 2.474 grams of Ni, and 0.757 grams of Al for Fe$_{75}$Ni$_{15}$Al$_{10}$ as well as 9.858 grams of Fe, 2.591 grams of Ni, and 2.551 grams of Al for Fe$_{56}$Ni$_{14}$Al$_{30}$ making the total mixture 15 grams per side of the substrate.

The flamespray was done using Metallisation MK74 Flamespray System with oxygen and acetylene gasses. Prior to powder spraying, the substrates were given surface treatment by milling them for 30 minutes in a shaker mill to make the substrate surface more malleable. Substrates were then hung on the stand and sprayed from an approximately 17 cm distance with 15 grams of mixture powder. After spraying, the coated samples were allowed to cool down before given annealing.

Sample annealing was done in a vacuum furnace that was earlier flushed with argon gas. The samples were put in the furnace chamber at room temperature and then the furnace was evacuated. Temperature was then raised slowly up to 800°C and held for two hours before letting the temperature lower to room temperature to take out the samples. The purpose of sample annealing was to improve the coating structure and reduce the residual stress.

To test its oxidation resistance, the samples were put inside a muffle furnace at 800°C. After 20 hours of exposure, the samples were taken out to let cooldown in open air for 4 hours. The cycle was repeated eight times to obtain the kinetic oxidation rate. The kinetic curve was obtained by dividing the mass gain of the samples with its respective surface area [7]. The sample masses were weighed once the samples have obtained room temperature during the cooldown time within each cycle.

Characterization tests were conducted using X-ray diffraction (XRD), optical microscopy (OM), and scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectrometer (EDX) to identify the phase composition and microstructure of the coating before and after the high temperature oxidation test.

3. Results and Discussion

3.1. Coating Observation

The cross-sectional micrographs of Fe–Ni–Al coatings using optical microscope are shown in Fig. 1.

**Figure 1.** Optical microscope images of [A] Fe$_{75}$Ni$_{15}$Al$_{10}$ coating and [B] Fe$_{56}$Ni$_{14}$Al$_{30}$ coatings at 10× magnification.

Observations show that powder coatings adhered to the substrate successfully and have developed a fairly thick coating layer for each of the samples where Fe$_{75}$Ni$_{15}$Al$_{10}$ obtained a 0.17 mm and Fe$_{56}$Ni$_{14}$Al$_{30}$ obtained a 0.22 mm.
Based on XRD results, peak reflections show that five phases as Fe–Ni, AlNi, Al, NiO, and (Fe0.87O)10 were formed. The oxide compounds were obtained due to the oxidation of the powder coating elements during the coating process. The same phenomenon occurred after the deposition of Fe40Al coating using HVOF spray technique [8] which can happen with other thermal spray processes as well [9]. Ideally oxide scales are to be developed on the external layer during the cyclic oxidation test and not earlier, for it will compromise the oxidation resistance of the coatings.

The Cross-sectional microstructures of the coatings after annealing are shown in Fig. 3. It can be seen that even though the coating thickness stayed the same for both samples, a gap appeared between the coating and the substrate of sample Fe75Ni15Al10. This occurrence might be caused by the difference of the coating and the substrates thermal expansion coefficient. X-ray diffraction patterns as shown in Fig. 5 also reveals that a new phase was acquired namely NiFe2O4. Even if the heat treatment was done in anevacuated environment, the existing oxide phases still can react to each other thus creating a new oxide phase.
3.2. Kinetic Oxidation of Fe$_{75}$Ni$_{15}$Al$_{10}$ and Fe$_{56}$Ni$_{14}$Al$_{30}$ coatings at 800 °C

The kinetic oxidation rate of Fe$_{75}$Ni$_{15}$Al$_{10}$ and Fe$_{56}$Ni$_{14}$Al$_{30}$ coatings is shown in Fig. 6.

The curve proves that the presence of Fe–Ni–Al coatings improves the oxidation resistance of low carbon steel. The carbon steel stands at the top of the curve for it has the most mass gain showing that it has the least oxidation resistance. As for the Fe$_{56}$Ni$_{14}$Al$_{30}$ coating which contains the highest Al concentration, it exhibits the lowest mass gain among the three samples. This suggests that it has a better oxidation resistance compared to the low carbon steel and Fe$_{75}$Ni$_{15}$Al$_{10}$ coating.
Figure 7 shows the X-ray diffraction patterns of the coatings after the cyclic oxidation test at 800°C for 8 cycles. It appears that various oxide phases were found in both samples. In the Fe₅₆Ni₁₄Al₃₀ coating, however, iron–nickel and aluminum–nickel phases can still be observed.

![Figure 7. X-ray diffraction patterns of [A] Fe₇₅Ni₁₅Al₁₀ and [B] Fe₅₆Ni₁₄Al₃₀ coatings after cyclic oxidation test.](image)

Structurally, the cyclic oxidation test rendered the samples to develop a thick oxide layer. With a total layer thickness—consisting of a layer of coating and a layer of oxide of 1.81 mm for Fe₇₅Ni₁₅Al₁₀ and 0.70 mm for Fe₅₆Ni₁₄Al₃₀, further proves that Fe₅₆Ni₁₄Al₃₀ has the better oxidation rate (Fig. 6). Furthermore, through elemental mapping in Fig. 9 and Fig. 10, it can be seen that the elemental distribution shows that the coating were both lifted away from the substrate. A clear difference in how the coatings were lifted lies between the coating and the substrate. For Fe₇₅Ni₁₅Al₁₀, between the coating is a thick oxide layer and for Fe₅₆Ni₁₄Al₃₀ there is a gap.

It seems that in the first incident where a gap formed after Fe₇₅Ni₁₅Al₁₀ annealing, that gap had given room for the substrate to oxidize heavily causing it to lift up the whole layer of coating that was supposed to protect the substrate. As for the gap formed after the oxidation process on Fe₅₆Ni₁₄Al₃₀, it is...
due to the vigorous heating and cooling of the sample during the cyclic oxidation test up to a point where the coating and the substrate can no longer hold on to each other caused by their thermal expansion coefficient difference.

Figure 9. Energy dispersive X-ray elemental images of Fe$_{75}$Ni$_{15}$Al$_{10}$ coating at [A] coating surface and [B] coating/substrate interface.

Figure 10. Energy dispersive X-ray elemental images of Fe$_{56}$Ni$_{14}$Al$_{30}$ coating.

4. Conclusions and Suggestions
The Fe–Ni–Al coatings held well enough after being deposited on the surface of the low carbon steel substrates using the flame spray technique and were able to be annealed, as well as to be put in the cyclic oxidation test. Kinetically, Fe$_{50}$Ni$_{14}$Al$_{30}$ having a higher amount of Al proved to have the better oxidation resistance out of the three as low carbon steel bore the least oxidation resistance.

Coating spall-off happened due to a mismatch in coefficient of thermal expansion between coating and substrate. However, structurally proven by the SEM–EDX images that had the coatings adhered better on the substrates, the coatings would have been a good enough protective layer for the substrate, as thinner oxide layers were produced above the coatings.

For further research it is advised to master the flame spray technique to prevent the occurrences of oxide phases, to lessen the pores created within the coating, and to perfectly obtain the ideal coating down to the coating thickness and density.

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References

[1] Sundawa RY, Aryanto D, Wismogroho AS, Sudiro T 2017 *Microstructure and phase composition of Fe–B–Al coatings on low carbon steel prepared by using mechanical alloying technique*. Journal of Physics: Conf. Series 817 012071.

[2] Bose S 2007 High temperature coatings (Oxford: Elsevier Ltd.) chapter 6 pg 72 and 103.

[3] Roberge PR 2008 Corrosion engineering principles and practice (Tronto: McGraw Hill) chapter 14 pg 633.

[4] Brady, James E. 2000 *Descriptive Chemistry of The Elements*. New York: John Wiley & Sons Inc.

[5] Birks N, Meier GH, Pettit FS 2006 Introduction to the high temperature oxidation of metals (Cambridge: Cambridge University Press) chapter 4 pg 82.

[6] Sudiro T, Sebayang P, Aryanto D, Hia AJ, Sebayang K 2015 *Structure and hardness characteristics of 50Cr-50Al coating prepared by mechanical alloying technique: effects of heat treatment temperature*. Teknologi Indonesia 38 (3) pg 156-162.

[7] Young D 2008 High temperature oxidation and corrosion of metals (Oxford: Elsevier Ltd.) chapter 1 pg 13.

[8] Guilemany JM, Cinca N, Dosta S, Cano IG 2008 *FeAl and NbAl\textsubscript{3} intermetallic–HVOF coatings: structure and properties*. Journal of Thermal Spray Technology vol.18(4) pg 536-545.

[9] Wang HT, Li CJ, Yang GJ, Li CX, Zhang Q, Li WY 2007 *Microstructural characterization of cold-sprayed nanostructured Fe–Al intermetallic compound coating and its ball-milled feedstock powders*. Journal of Thermal Spray Technology vol.16(5-6) pg 669-676.

[10] Halliday D, Resnick R 1988 Fundamentals of physics chapter 22 pg 516.

[11] Callister WD Jr., Rethwisch DG 2014 Materials science and engineering (New Jersey: John Wiley & Sons, Inc.).

[12] Totemeier TC, Wright RN, Swank WD *FeAl and Mo–Si–B intermetallic coatings prepared by thermal spraying*.

[13] Luer KR, DuPont JN, Marder AR 2000 *High-temperature sulfidation of Fe\textsubscript{3}Al thermal spray coatings at 600°C*. Lehigh University.

[14] Moyer TD, Dayananda MA 1976 *Diffusion in β\textsubscript{2} Fe–Ni–Al Alloys*. Metalurgical Transactions A pg 1035-1040.