ALUMINIDE COATING CHARACTERIZATION ON 304 SS USING SLURRY ALUMINIZING PROCESS

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Abstract. The application of aluminide coatings using the slurry aluminizing process has attracted significant attention in industry to enhance the corrosion resistance of structural materials exposed to severe environmental conditions. Nevertheless, several challenges have emerged, including the migration of aluminium from the coating into the substrate and mismatched in the coefficient of thermal expansion (CTE). To address these issues, 304 SS was chosen as the substrate due to its superior compatibility with the coating in terms of CTE. The objective of this project is to investigate the influence of various temperatures and durations on the formation of aluminide coatings containing alumina. The aluminide coating was created through a slurry aluminizing procedure, which involved mixing a slurry composed of 70% Al and 30% Al_2O_3 with polyvinyl alcohol (PVA). This coating was uniformly applied to the substrate. Subsequently, the coated samples underwent different heat treatment conditions, specifically at temperatures of 650 °C, 680 °C, and 700 °C, for durations ranging from 4 to 10 hrs. Detailed characterization of aluminide coating morphology, energy-dispersive X-ray (EDX), phases, porosity, and corrosion behaviour were evaluated using scanning electron microscope (SEM), X-ray diffraction (XRD), optical microscope (OM) and linear polarization (NOVA 1.7 software). Analysis using energy-dispersive X-ray (EDX) and X-ray diffraction (XRD) techniques revealed the presence of $FeAl_3$ formation at the outermost layer and the development of the FeAl phase within the interdiffusion zone (IDZ). Remarkably, the samples that underwent heat treatment at 700 °C for 10 hours displayed significantly enhanced corrosion resistance. Consequently, the aluminide coating developed on 304 SS, characterized by the presence of the FeAl phase, demonstrates substantial potential for use as an effective protective coating.

Keywords: Slurry aluminizing, stainless steel 304, Fe-Al intermetallic compounds

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Introduction

Austenitic stainless steels are susceptible to corrosion when exposed to aggressive corrosive conditions, such as aqueous environments, high temperatures, stress, and various service conditions. To address this issue, there is a focus on altering the surface properties of these steels by creating corrosion-resistant coatings. Surface modification of stainless steel with aluminide layers has gained significant importance due to its industrial feasibility and cost-effectiveness in enhancing corrosion resistance [1-2]. The penetration of aluminium into the substrates can form dense and stable protective alumina in a high-temperature environment, which improves corrosion resistance properties [3]. Aluminide coatings exhibit exceptional oxidation resistance because they can develop protective scales [4-5]. Slurry aluminizing has garnered increasing interest for coating large components due to its ease of manufacturing, environmental friendliness, and cost-effectiveness [6]. Among aluminide coatings, iron aluminide coatings created through slurry aluminizing on austenitic stainless steel are particularly favoured. This preference is attributed to their superior mechanical properties and low coefficient of thermal expansion (CTE) when combined with aluminide coatings.

Consequently, the likelihood of crack formation in the coating is reduced on austenitic steels because of the closer match in CTE between the austenitic stainless steel and the coating [6]. Furthermore, the depletion of aluminium in these coatings poses a challenge to the long-term performance of aluminide coatings. This depletion occurs due to the inward diffusion of aluminium into the substrate, leading to the precipitation of segregation phases at high temperatures instead of the growth of an alumina scale on the outer layer. To address this issue, Javan et al. [7] introduced alumina particles as inert fillers to reduce the local melting and sintering of aluminium particles. The ratios of Al, Si, and Al_2O_3 affect the microstructure of the coating [8]. While some research has explored the use of alumina along with other variables like temperature and duration, that could potentially impact the process and growth kinetics of aluminide coating development. This project aimed to examine the development of aluminide coatings enriched with Al_2O_3 on 304 stainless steel surfaces. This investigation involved subjecting the steel to various temperatures and times via slurry aluminizing. The analysis encompassed an assessment of the coating's surface morphology, chemical composition, the identification of compound phases formed, and an evaluation of the coating's corrosion resistance.

Material and Methods

The substrate material used in this study was 304 stainless steels. Initially, the specimens underwent manual grinding and degreasing through immersion in an ultrasonic bath, followed by rinsing with distilled water. Subsequently, the samples were dried using a hot air dryer after the cleaning process. The slurry used in this process consisted of a mixture of powder and binder. A beaker containing distilled water was placed on a hot plate stirrer and heated to a temperature of 85 °C, that is close to the glass transition temperature of PVA. PVA powder was then added to the water, and the stirring process continued to ensure complete dissolution of the PVA. Following this, aluminium (Al) and aluminium oxide (Al_2O_3) were gradually introduced to the binder mixture and homogenized using a magnetic stirrer. The prepared slurry was subsequently poured into a gravity-fed, air-pressurized spray gun. The slurry was uniformly sprayed onto the substrate, and this spraying process was repeated twice. The first and second coated samples were weighed to ensure that a total mass/area ratio fell

within the range of 15 to 30 mg cm^{-2}. Following the completion of two cycles of the coating process, the samples were left to dry in ambient air for one hour before undergoing a heat treatment process. The samples were then subjected to thermal treatment in an argon gas atmosphere with a heating rate of 10 °C per minute. The thermal treatment consisted of two steps:1) the specimens were heated in a furnace at 400 °C for one hour to cure the binder and 2) the specimens were heated at various temperatures of 650 °C, 680 °C, and 700 °C, for durations of 4, 6, 8, and 10 hours. The cross-section morphology of aluminide coating was observed using scanning electron microscope (SEM) while the elemental composition was measured using energy dispersive X-ray spectroscopy (EDX). The phases present in the aluminide coating then was determined using X-ray Diffraction (XRD). Potentiostat/galvanostat was utilized to determine the corrosion rate. In addition, ImageJ software was used to examine the porosity of the aluminide coating from image captured using optical microscope (OM).

Results and Discussion

SEM Morphology and EDX Analysis

Figures 1, 2 and 3 show the SEM cross-section image of aluminide coating after heat treated. The image shows the aluminide layer developed at 4 hours was discontinuous and non-uniform. However, at 10 hours, a continuous and uniform aluminide coating was formed. The results are influenced by the presence of aluminium atoms diffusing into the substrate's surface. However, ensuring a consistent concentration of aluminium atoms on the surface is a bit challenging. To address this, allowing sufficient time for the atoms to diffuse leads to a gradual increase in the thickness of the coating [1] SEM cross-section image for aluminide coated sample heat treated 680 ºC for 4, 6, 8 and 10 hours are presented in Figure 4. The image shows the aluminide phases such as Fe_2Al_5, Fe_3Al and FeAl layer was developed in the coating of which increases in thickness in prolonged heat treatment and time. Similar results are shown in [9]. The aluminide coating was continuous and uniform with increasing time from 4 to 10 hours. EDX analysis was carried out for sample heat treated for 10 hours and it was found that the outer and inner layers were enriched with aluminium concentration, implying that Al-rich intermetallic compounds, $FeAl_3$, were formed. The phase transformation of aluminide coating commences with the formation of $FeAl_3$, which, upon prolonged soaking, evolves into Fe_2Al_5, then followed by FeAl [10]. Additionally, findings from [10] revealed a substantial decrease in the concentration of $FeAl_3$ after 8 hours of heating, whereas in this project, the presence of $FeAl_3$ was still detectable even after 10 hours of heating. Thus, indicating a suppression of Fe_2Al_5 growth. Furthermore, a thin light grey layer in the interdiffusion zone (IDZ) separated the coating and the substrate was confirmed as FeAl phase (Figure 5 and Table 1). The result was further supported by XRD analysis (Figure 6).

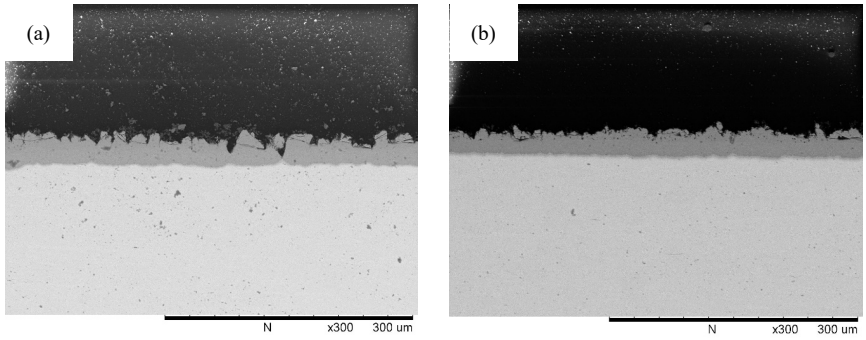

Figure 1: SEM cross-section image of aluminide coating heat-treated at 650 ºC for (a) 4 hours and (b) 10 hours

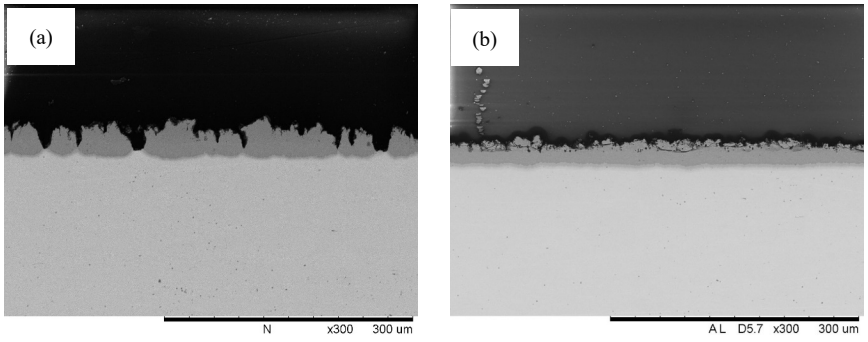

Figure 2: SEM cross-section image of aluminide coating heat-treated at 680 ºC for (a) 4 hours and (b) 10 hours

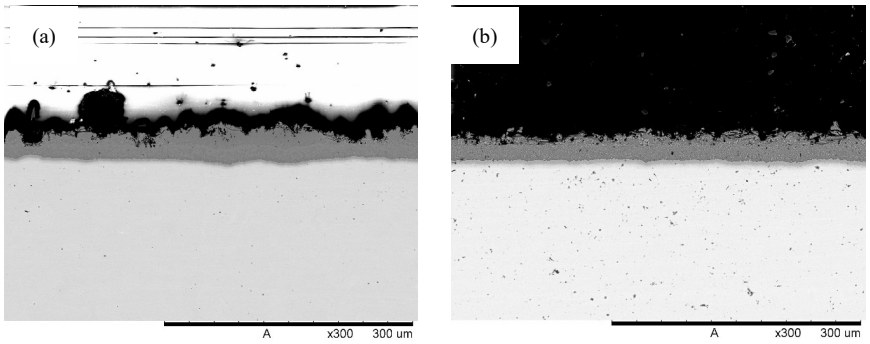

Figure 3: SEM cross-section image of aluminide coating heat-treated at 700 ºC for (a) 4 hours and (b) 10 hours

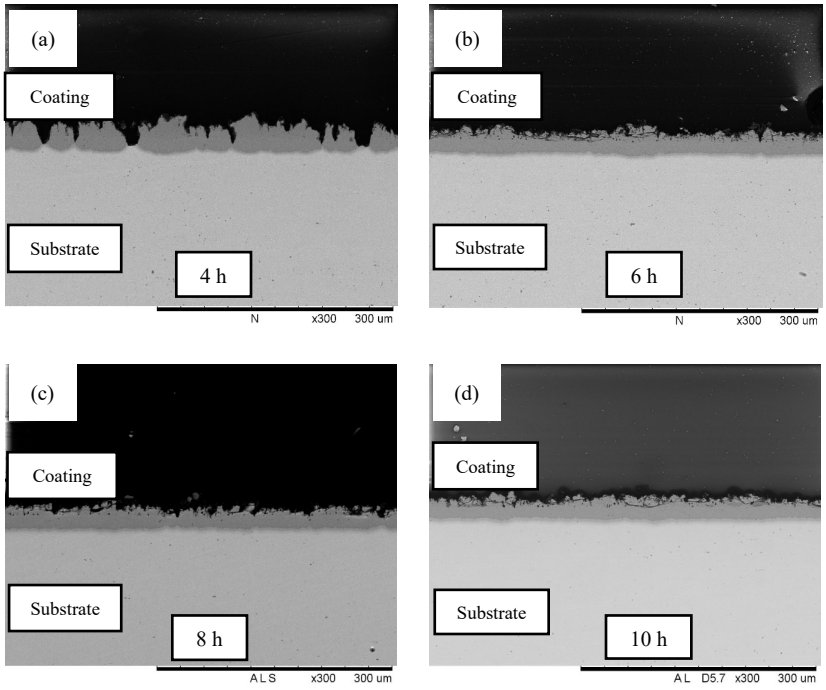

Figure 4: SEM cross-section image of aluminide coating heat-treated at 680 °C for (a) 4 hours, (b) 6 hours, (c) 8 hours and (d) 10 hours

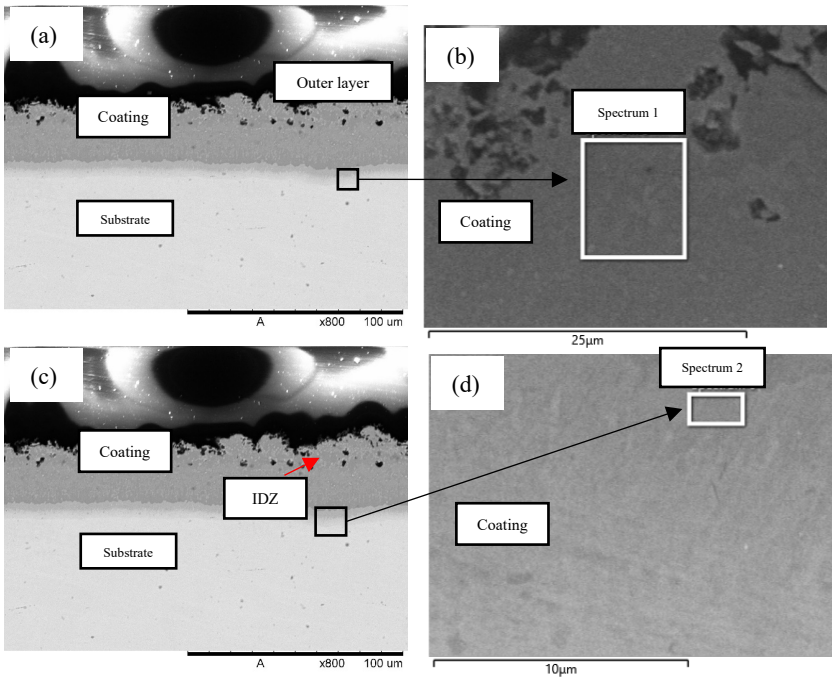

Figure 5: (a, c) SEM cross-section images and (b, d) EDX of substrate heat-treated at 680 ºC for 10 hours

Table 1: EDX chemical composition of spectrum 1, and 2 for sample heat-treated at 680 °C for 10 hours

Element	Spectrum 1		Spectrum 2	
	wt.%	at.%	wt.%	at.%
C	17.44	38.60	15.25	37.73
Al	42.89	42.26	30.14	33.19
Cr	7.26	3.71	7.70	4.40
Fe	31.97	15.22	35.86	19.08
Ni	0.45	0.20	11.05	5.59
Total	100.00	100.00	100.00	100.00

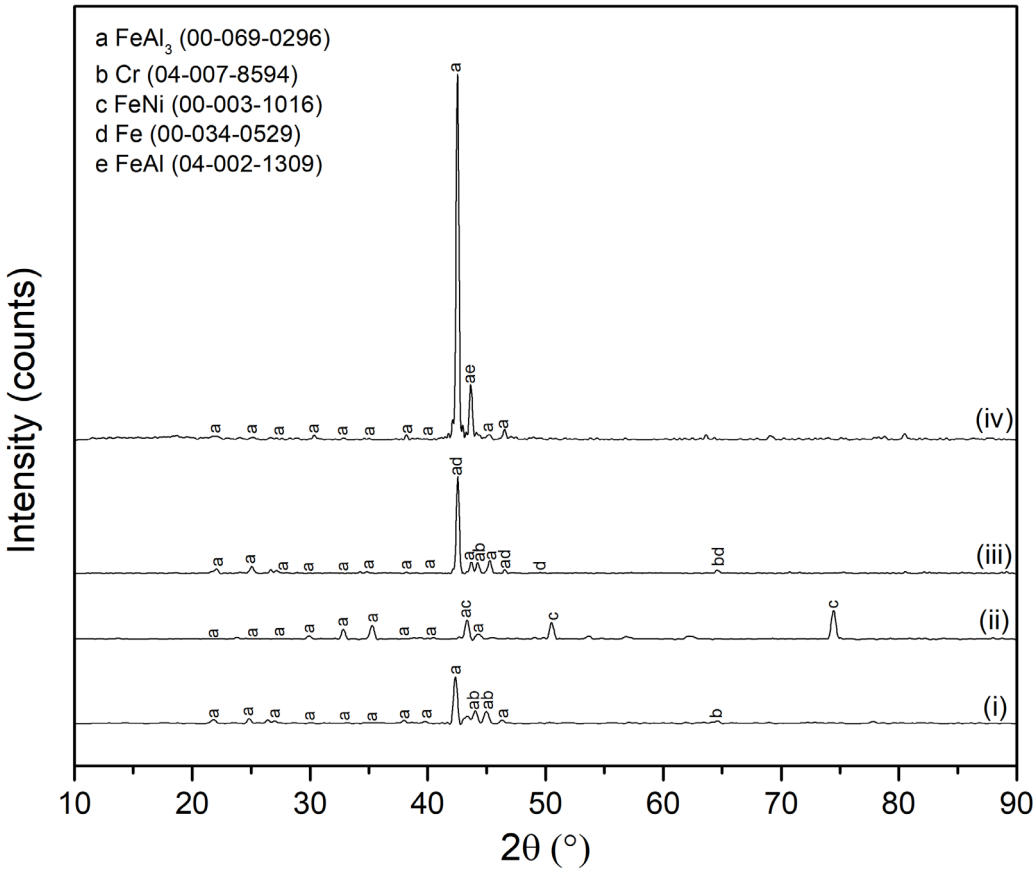

Figure 6: XRD analysis of sample heat-treated at 680 °C for (i) 4 hours, (ii) 6 hours, (iii) 8 hours, and (iv) 10 hours

Porosity Measurement

Porosity measurements were conducted on specimens subjected to heat treatment (650 °C, 680 °C, and 700 °C) for durations of 8 and 10 hours, respectively. Surface morphology of the coating was acquired using an optical microscope, as depicted in Figure 7. Subsequently, ImageJ software was employed to analyse the porosity measurement by calculating the percentage of the porous area.

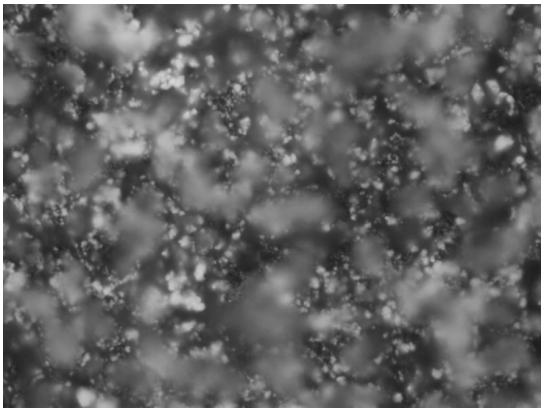

Figure 7: Surface morphology of the sample after heat-treated

Figure 8 shows the average area of porosity, which was calculated based on twenty measurements. Interestingly, there is no substantial difference in the average area of porosity among all the samples. However, there is an increasing trend in porosity as both the heat treatment temperature and duration were raised. The sample that underwent heat treatment at 700 °C for 10 hours exhibited the highest area percentage of porosity, reaching a value of 69.1%. In contrast, the sample subjected to heat treatment at 650 °C for 8 hours displayed the lowest area percentage of porosity, with a value of 60.27%.

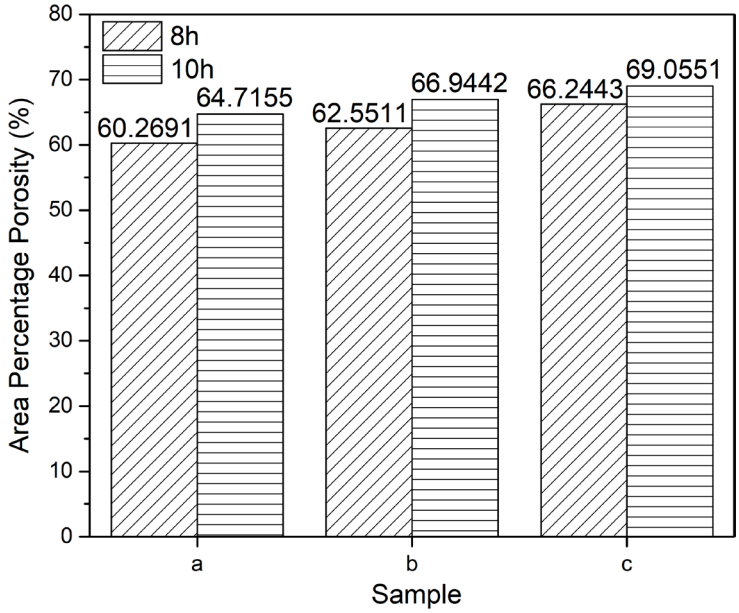

Figure 8: Percentage porosity area of sample after heat-treated at (a) 650 ºC (b) 680 ºC and (c) 700 ºC

The inward diffusion of Al particles in the coating is responsible for the formation of pores. The amount of pores was affected by the rate of Al diffusion during the heat treatment process [10-11]. According to the Arrhenius equation, the diffusion rate is generally temperature dependent. Because the diffusion rate of Al is faster at higher temperatures, the area percentage porosity of the sample that was heat treated from 650 °C to 700 °C increased.

Furthermore, Kepa et al. [12] and Yener et al. [13] reported that heat treatment time increased the amount of porosity. According to Yener et al. [14], the porosities observed thickened and penetrated deeper with longer durations. The obtained results are consistent with previous studies.

Corrosion Behaviour of Aluminide Coating

Corrosion assessments were carried out on selected samples after heat treatment as shown in Figure 9. Meanwhile, Table 2 presents the corrosion data for the samples treated for 8 and 10 hours at 650 °C, 680 °C, and 700 °C. Based on Table 2, it is evident that the corrosion rate displays a decreasing trend as the temperature and time of heat treatment increases. Specifically, the sample treated at 700 °C for 10 hours exhibited the lowest corrosion rate of 0.0280 mm/year. Conversely, the highest corrosion rate was recorded for the sample subjected to heat treatment at 650 °C for 8 hours, which reached 0.218 mm/year. This observation indicates that a lower corrosion rate corresponds to a higher resistance of the aluminide-coated sample against corrosion.

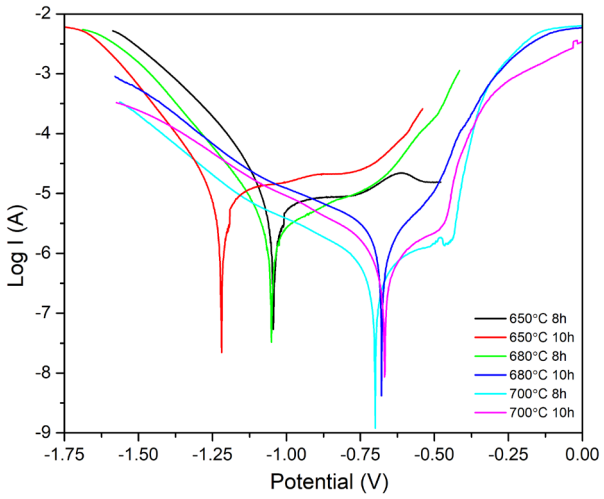

Figure 9: Tafel plot for sample heat-treated at 650 ºC, 680 ºC and 700 ºC for 8 hours and 10 hours

Table 2: Corrosion data for sample heat-treated at 650 ºC, 680 ºC and 700 ºC for 8 hours and 10 hours

Sample		E_{corr} (V)	I_{corr} (µA)	Corrosion rate (mm/year)
Temperature (°C)	**Time (hours)**			
650	8	-1.0284	21.2610	0.2184
	10	-1.2146	14.9140	0.1532
680	8	-1.0522	9.1196	0.0937
	10	-0.6688	7.8516	0.0806
700	8	-0.7023	2.7247	0.0464
	10	-0.6709	1.6438	0.0280

Conclusions

The aluminide coatings were successfully developed on samples that underwent heat treatment at various temperatures and times. These coatings exhibited a consistent composition, with both the outer and inner layers predominantly composed of $FeAl_3$, while a thin layer of FeAl phase formed in the interdiffusion zone (IDZ) of the coating. Notably, the aluminide coating thickness increased with higher aluminizing temperatures and longer treatment times. The incorporation of Al_2O_3 effectively mitigated the inward diffusion of aluminium and facilitated the growth of the FeAl layer. Furthermore, the sample subjected to 700 °C for 10 hours displayed remarkable corrosion resistance, as evidenced by its lower corrosion rate compared to the other specimens.

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Author Contributions

All authors contributed towards data analysis, drafting and critically revsing the paper and agree to be accountable for all aspects of the work.

Disclosure of Conflict of Interest

The authors have no conflict of interest.

Compliance with Ethical Standards

The work is compliant with ethical standards

References

[1] Troysi, F. D., & Brito, P. P. (2020). Development and Characterization of an Iron Aluminide Coating on Mild Steel Substrate Obtained by Friction Surfacing and Heat Treatment. *International Journal of Advanced Manufacturing Technology*. 111(9–10), 2569–2576.

[2] Triani, R. M., Gomes, L. F. D. A., Aureliano, R. J. T., Neto, A. L., Totten, G. E. & Casteletti, L. C. (2020). Production of Aluminide Layers on AISI 304 Stainless Steel at Low Temperatures Using the Slurry Process. *Journal of Materials Engineering and Performance.* 29(6), 3568–3574.

[3] Wu, D., Zheng, J., Liu, S., Wu, H., Wei, X. & Zhang, C. (2022). Effect of Water Vapor

Content on Corrosion Performance of Aluminide Coatings on TP347H in a Simulated Biomass Combustion Environment. *Journal of Materials Research and Technology*. 20, 1755-1769.

[4] Aguero, A., Gutierrez, M., Muelas, R. & Spiradek-Hahn, K. (2018). Overview of Steam Oxidation Behaviour of Al Protective Oxide Precursor Coatings on P92. *Surface Engineering.* 34, 30–39.

[5] Lu, J., Dang, Y., Huang, J., Zhou, Y., Yang, Z., Yan, J. & Gu, Y. (2019). Preparation and Characterization of Slurry Aluminide Coating on Super304H Boiler Tube in Combination With Heat-Treatment Process. *Surface and Coatings Technology*. 370, 97–105.

[6] Kobayashi, S. & Yakou, T. (2002). Control of Intermetallic Compound Layers at Interface between Steel and Aluminum by Diffusion-Treatment. *Materials Science and Engineering A.* 338(1–2), 44–53.

[7] Javan, M. K., Moghaddam, A. A., Farvizi, M., Abbasian, A. R., Shirvani, K., Hadavi, S. M. M. & Rahimipour, M.R. (2019). Effect of Aluminum to Alumina Particles Size Ratio on the Microstructural Aspects of Aluminide Coatings by LTHA Pack Cementation. *Materials Research Express.* 6(9), 096437.

[8] Yu, H., Fan, Q., Li, J., Ma, D., Gong, J. & Sun, C. (2023). Effect of Si Addition to Improve The Performance of Type II and Type I Hot Corrosion Resistance of Aluminide Coating. *Corrosion Science.* 212, 110937.

[9] Ndumia, J. N., Kang, M., Lin, J., Liu, J. & Li, H. (2022). Influence of Heat Treatment on the Microstructure and Wear Properties of Arc-Sprayed FeCrAl/Al Coating. *Coatings*. 12(3), 374.

[10] Sun, Y., Dong, J., Zhao, P. & Dou, B. (2017). Formation and Phase Transformation of Aluminide Coating Prepared by Low-Temperature Aluminizing Process. *Surface Coating Technology*. 330, 234–240.

[11] Dorcheh, A. S. & Galetz, M. C. (2016). Slurry Aluminizing: A Solution for Molten Nitrate Salt Corrosion in Concentrated Solar Power Plants. *Solar Energy Materials and Solar Cells.* 146, 8-15.

[12] Kepa, T., Pedraza, F. & Rouillard, F. (2020). Intermetallic Formation of Al-Fe and Al-Ni Phases by Ultrafast Slurry Aluminization (Flash Aluminizing). *Surface and Coatings Technology.* 397, 126011

[13] Yener, T. (2019). Low Temperature Aluminising of Fe-Cr-Ni Super Alloy by Pack Cementation. *Vacuum.* 162, 114-120.

[14] Yener, T., Erdogan, A., Gök, M. S. & Zeytin, S. (2021). Formation, Characterization, and Wear Behavior of Aluminide Coating on Mirrax® ESR Steel by Low-Temperature Aluminizing Process . *Journal of Tribology.* 143(1), 011703.