Investigating the Corrosion Resistance of Ti-Al Coating on Structural Steel Components

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Abstract

Carbon steel is widely used in infrastructure, manufacturing, and structures due to its cost-effectiveness and robust mechanical properties. However, the susceptibility of steel structures to corrosion in various working environments has been a longstanding concern. In this study, we explored the potential of titanium-aluminum (Ti-Al) coating as a surface treatment to enhance the corrosion resistance of low-carbon steel. The coating was applied using the arc spraying technique, where two materials were melted by an arc and then distributed onto the substrate using compressed air. To evaluate the corrosion resistance of the coated samples, we conducted immersion tests following the ASTM G31 standard for durations of 625 and 1000 hours. Additionally, electrochemical technique was employed to assess the anti-corrosion performance of both the Ti-Al coating and the substrate. Surface characterization was carried out using scanning electron microscopy equipped with energy-dispersive X-ray spectroscopy (SEM-EDX), as well as measurements of hardness and roughness. The SEM-EDX analysis revealed uniform distribution of titanium and aluminum across the surface and within the coating. Moreover, the coating significantly altered the surface roughness. Electrochemical corrosion testing indicated that the Ti-Al coating exhibited lower corrosion current and corrosion potential, suggesting its potential to enhance the corrosion resistance of the substrate. The SEM-EDX revealed cracks on the coating surface and the oxidation level of the coating surface varied with immersion time. The hardness of the coating was found to be relatively lower than that of the substrate, while the surface roughness was higher. Overall, the findings suggest that Ti-Al coating holds promise for enhancing the corrosion resistance of steel structures, as evidenced by its low corrosion current density and corrosion potential in corrosive environments.

Introduction

Steel, one of the most commonly construction materials utilized in various industries, is chosen for its outstanding mechanical properties, high strength, welding properties, as well as cost-effectiveness. However, the corrosion of steel equipment and structures in corrosive environments presents a critical challenge, leading to a notable degradation in their performance and lifespan, necessitating prompt resolution [1]. The application of coatings represents a promising avenue for mitigating corrosion and extending the operation lifespan of steel components. The thermal spray technique demonstrates efficacy as a surface protection method, capable of fabricating protective coatings [2-4]. Arc spraying constitutes a thermal technique wherein an electric arc is generated between two consumable electrodes while compressed gas serves to atomize and propel the molten electrode materials onto the substrate. The arc spraying method is extensively employed owing to several benefits, including energy efficiency and cost-effectiveness [5-8]. This technique offers an economically viable means to generate protective coatings on steel surfaces.

Protective coatings, such as aluminum alloy coating or zinc alloy coatings, are considered to be the most useful approach for protecting steel structures against corrosive environments[9]. Generally, sacrificial metallic coatings provide three mechanisms to protect steel substrates: the isolation effect of the coating itself, the sacrificial anode function of cathodic protection, and the isolation effect of corrosion products of the coating [10, 11]. Various corrosion tests have been conducted to examine the corrosion resistance of thermally sprayed aluminum. Han et.al [12] explored the corrosion performance and effect of the thickness of an aluminum coating using the thermally sprayed method. They found that the scarification of the aluminum coating occurred during the corrosion and found that thicker coatings represented better corrosion behavior during the test. Other researchers [1, 9, 12] showed that thermally sprayed aluminum coatings could protect low-carbon steel from corrosion in chloride-containing atmospheres through salt spray tests and field tests.

The distinctive properties of titanium, including its high strength-to-weight ratio and good corrosion resistance, have made this material a favorable option for several applications. Zhao et.al [13] investigated the effects of arc spray process parameters on the corrosion behavior of titanium coatings. They found that the corrosion resistance of the coating is sensitive to the spray process, and corrosion current density decreased due to the optimization of process parameters. The reaction with oxidation during the spraying process results in the formation of oxides, which subsequently diminish the cohesive strength and corrosion resistance of the coatings.

While the corrosion resistance of aluminum coating has been extensively investigated in published literature, few studies have examined the surface characteristics and corrosion resistance of titanium-aluminum alloy coatings. In this study, a 3%Ti-Al coating was sprayed using the wire arc spraying technique. The surface characteristics, microstructure, chemical composition, microhardness, and corrosion resistance of the 3%Ti-Al coating were studied in detail and compared with carbon steel.

Experimental

Preparation. HA350 structural steel plates (Size: 40mm × 40mm ×8mm) were selected as the substrate. HA350 is a Hot Rolled (H) Aluminium Killed (A) structural steel with a guaranteed minimum upper yield stress of 350 MPa [14]. The chemical composition of the substrate is shown in Table 1 [15]. Before spraying, the samples were blasted to the cleanliness of SA3. Using titanium-aluminum wire with 3% titanium, the coating was applied by Metallisation arc 150/S500 equipment with a nozzle air pressure of 5 bar using 2 mm wire and 450 amps.

Table 1 Chemical composition of HA350 structural steel

Chemical Analysis	Mn	Si	C	Fe
HA 350 (weight %)	1.10	0.02	0.18	98.59

Surface characterizations. The specimen’s cross-section was ground and polished using metallographic sandpaper (5-20 µm), followed by a final polishing step using a 1 µm diamond solution. The microstructure and chemical composition of coatings were examined using scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDX).

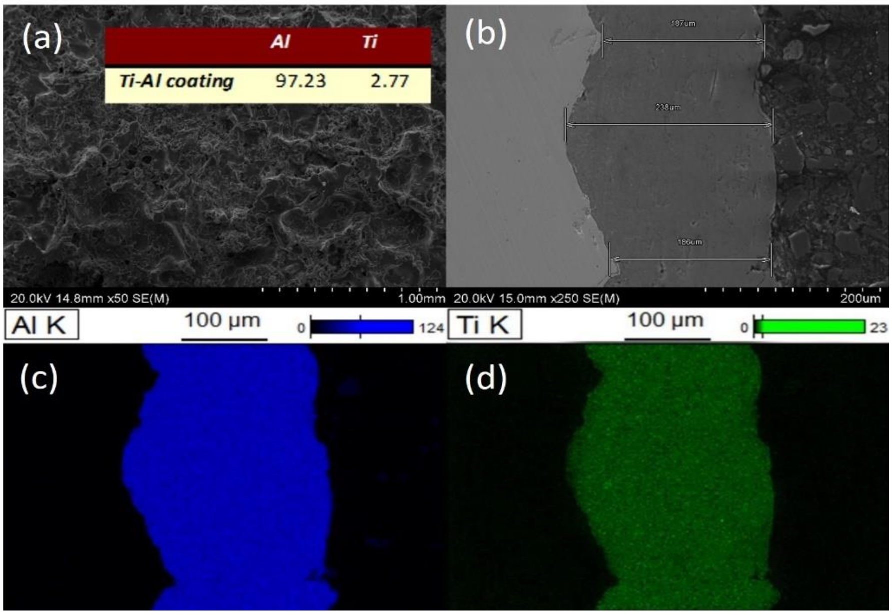
Immersion corrosion test. According to the SNZ TS 3404 [16], the highest corrosion rate in New Zealand is around 80µm/year. Accordingly, this investigation adopts 3.5 wt% NaCl solution as the most common corrosive agent having a pH range of 6.8 to 7.2. It was used to for immersion test for duration of 625h and 1000h according to ASTM G-31 standard and ASTM G-44 [17, 18]. The evolution and comparison of the Ti-Al coating were recorded by digital camera, and corrosion products were analyzed by SEM and EDX.

Microhardness. The microhardness of the coating was assessed using a Vickers hardness tester (LM – 800AT, LECO, Michigan, USA) under a load of 100N and a holding time of 10s. Ten indentations averaged the final value. The coatings after immersion corrosion were also subjected to microhardness test to investigate the effects of corrosion.

Electrochemical corrosion test. An electrochemical workstation (CHI660E, Chenhua, Shanghai, CN) was used to explore corrosion resistance details. The flat test cell (K0235, Lastek, Australia) was employed, leaving a geometrical surface area of 1cm² exposed to a 3.5 wt% NaCl solution. There was a three-electrode system including a saturated potassium chloride electrode as a reference electrode, platinum as the counter electrode, and the sample as the working electrode. The measurement range of the Tafel polarization curve was -0.5V to +0.5V based on the open circuit potential (OCP), and the scan rate was 0.33mV/s.

Results and Discussion

Characterization. Figure 1(a) depicts SEM images and the chemical composition of the Ti-Al coating. The coating surface exhibited roughness, with the presence of pinholes and pores. The content of Ti in the coating was approximately 3wt%, which corresponds to the composition of the coating wire. Figure 1(b) indicates that the thickness of the coating is around 200 µm, and the coating bonds well with the substrate, showing no pores or cracks. It can be observed from Figures 1(c) and 1(d) that the Ti and Al elements were evenly distributed throughout the coating.



	Al	*Ti*
Ti-Al coating	97.23	2.77

Fig. 1 SEM images of the (a) coated surface, and (b) cross-section; (c) Al and (d) Ti elements.

Figure 2 presents SEM images and the chemical composition of the sample's surface after sandblasting treatment. The surface, blasted to cleanliness of SA3, exhibited lower roughness compared to the untreated surface. Fe and Mn elements were observed to be distributed in the substrate. The results of Energy Dispersive X-ray Spectroscopy (EDX) indicated that the content of Fe and Mn was consistent with the information provided by the manufacturer.

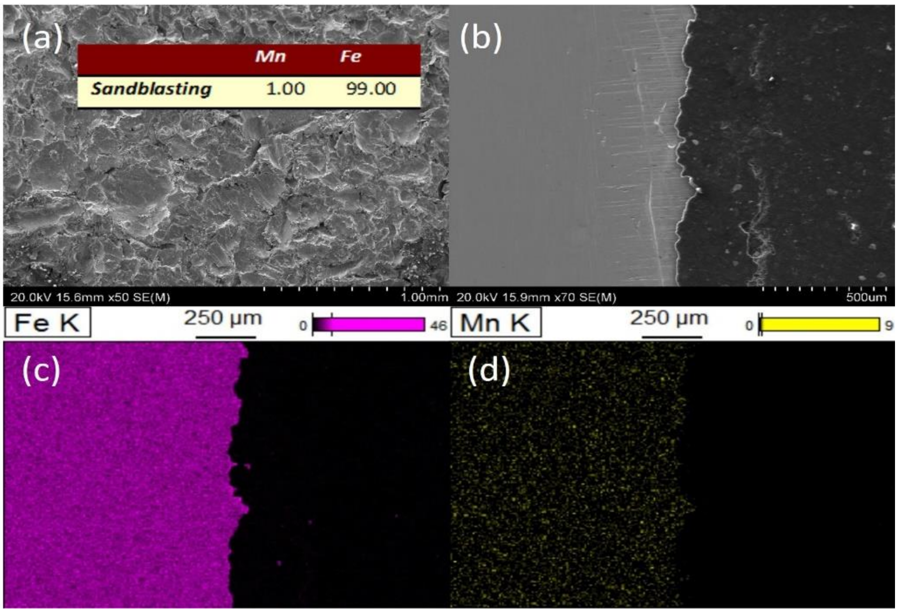


Fig. 2 SEM images of (a) sandblasting surface, and (b) cross-section, (c) Fe and (d) Mn elements.

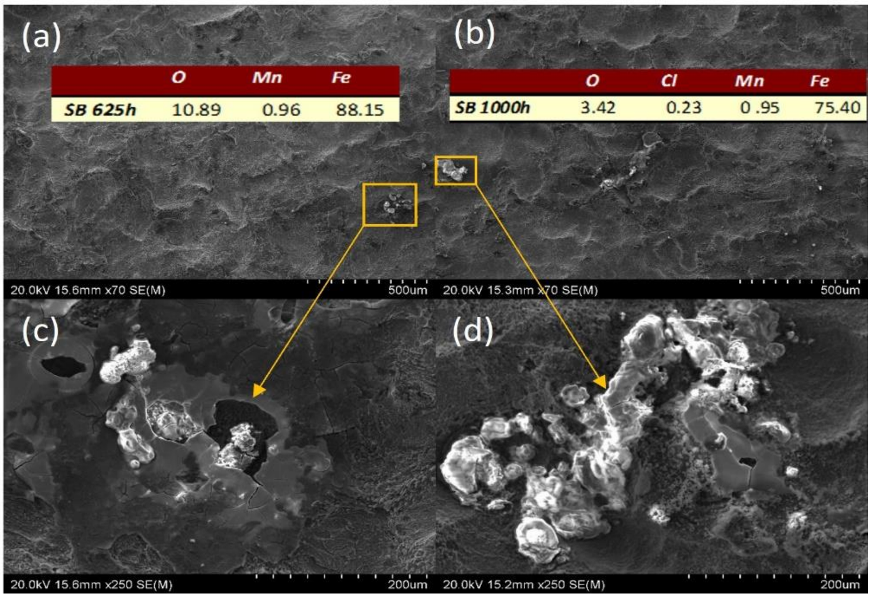
Immersion corrosion test. Figures 3 and 4 depict the photographs before and after immersing the uncoated and sandblasted, and Ti-Al coated samples in a 3.5 wt% NaCl solution for 625 hours and 1000 hours. Brown corrosion products are visible on the surface of the sandblasted samples. Comparing the 625-hour and 1000-hour immersion test durations, it is evident that the samples exposed for 1000 hours have darker brown corrosion products and sandblasted samples had high mass loss. Upon observation of the substrate after immersion in the saltwater solution, significant adherence of corrosion products to the surface is noted. During the ultrasonic cleaning process, part of the brown layer formed on the surface of sandblasting samples was easily removed, whereas some brown spots were retained on the surfaces as shown in Figure 3.

The Ti-Al coatings showed that white corrosion products developed on the coating surface following immersion in salt water for 625 hours. Despite cleaning, these corrosion products remained. Compared with the 625-hour sample, the specimen immersed for 1000 hours exhibited a brighter surface, with maintained surface roughness, indicating that the surface will not be etched due to corrosion. The weight of the Ti-Al coating increased after corrosion, attributed to the deposition of white corrosion products on the surface of the coating, which cannot be easily removed.

Fig. 3 Photographs of the uncoated and sandblasted sample as blasted and after 3.5 wt% NaCl for 625 hours and 1000 hours

Fig. 4 Photographs of Ti-Al coated sample as coated and after 3.5 wt% NaCl for 625 hours and 1000 hours

SEM and EDX analyses revealed the microstructures and chemical composition of the samples on their surfaces. Figure 5 provides details of the sandblasted layer after the immersion test. Compared with the uncorroded sample, there are few spark spots on the surface of the sandblasted sample, and with longer immersion times, the number of spark points also increased. High-magnification images show the details of spark spots, with some fragments adhering to the surface. EDX results indicate that the main components of these fragments are Fe, O, Cl, and Mn. The sandblasted sample after 1000 hours showed a higher oxidation level than that of after 625 hours. Localized corrosion initiation by the breakdown of the passive film and metastable growth of small pits on the verge of stability is the main corrosion category observed in sandblasted samples. Subsequently, pitting on a boldly exposed surface grew significantly after this stage [19, 20].



	O	Mn	Fe
SB 625h	10.89	0.96	88.15

	O	Cl	Mn	Fe
SB 1000h	3.42	0.23	0 .95	75.40

Fig. 5 SEM images of sandblasted surface and corrosion for 625 hours (a, c) and 1000 hours (b,d).

Figure 6 illustrates the morphologies of corrosion products of immersed samples after 625 hours and 1000 hours. After corrosion of the Ti-Al coating, partial cracks appeared on the surface of the coating, which filled the surface after 1000 hours of corrosion, forming loose corrosion products. Figures 6 (b) and (d) show island-shaped fragments formed by the rupture of the oxide layer. EDX results indicate that the oxidation of the coating increased as the immersion time extended, with a relatively decreased aluminum content. Compared to the original coating images before the immersion tests, aluminum was heavily corroded after these tests. The Cl- ions in the solution are the main factor causing corrosion [21]. These ions hinder the possible formation of the oxide film on the coating surface and, in turn, damage the formed passive layers [22], resulting in local corrosion. The layer contains 2.08% of Ti, 40.14% of Al, and 57.16% of O atoms, respectively, indicating the porous area after corroding aluminum, with oxygen atoms penetrating to form corrosion products with high oxygen content [23]. EDX analysis on the surface of the Ti-Al coating showed no Fe element present, indicating that the coating inhibited substrate corrosion, which is corroborated by the subsequent electrochemical corrosion section.

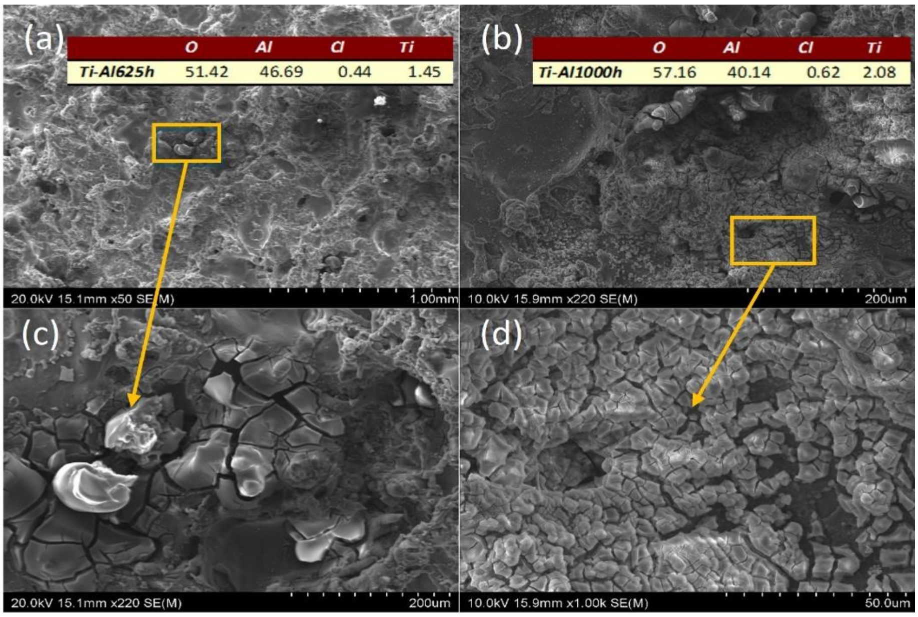


Fig. 6 SEM images of Ti-Al coating and corrosion details for 625 hours (a, c) and 1000 hours (b, d)

Microhardness. The cross-sectional hardness of the Ti-Al coating and sandblasted surfaces was measured immediately after coating and blasting, yielding averages of 90 HV100 and 183 HV100, respectively. Previous studies have assessed the cross-sectional hardness of Ti-Al arc-sprayed coatings. For instance, Hansol [19] reported a hardness of 138 HV0.025 for twin wire arc-sprayed Ti-Al coatings. Hardness values can vary depending on the coating composition and applied conditions, influenced by different microstructures. Nonetheless, the hardness values measured in this study are considered reasonable.

Following immersion in salt water for 625 hours, the average cross-sectional hardness of the Ti-Al coating increased to 104 HV100, further rising to 112 HV100 after extending the immersion time to 1000 hours. This increase in hardness is attributed to the solid strengthening phenomenon resulting from the presence of Ti [19], as supported by EDX results. Additionally, prolonged immersion in salt water promotes the development of an Al-Ti system within the coating, causing Ti dissolution within the Al matrix in a supersaturated state [19]. This phenomenon contributes to increasing the hardness of the coating. In contrast, the cross-sectional hardness of the sandblasted surface remained unchanged after the immersion test. This stability can be attributed to the removal of corrosion products during cleaning procedures.

Electrochemical behavior of Ti-Al coating. Tafel polarization curves of Ti-Al coating and sandblasting in 3.5wt% NaCl solution are shown in Figure 7. Table 2 lists the electrochemical behavior of the coating, including the corrosion potential ($E_{corrosion}$), corrosion current density ($I_{corrosion}$) and corrosion rate. The corrosion potential values of sandblasted and Ti-Al coated samples were -0.6V and -1.1V respectively. In general, the coatings have a more negative corrosion potential, i.e. the corrosion of the coating will occur before the substrate to protect the substrate as a sacrificial anode. Further, the corrosion current of Ti-Al coated samples ($4.7\mu A/cm^2$) is much lower than that of sandblasted surface ($17.2\mu A/cm^2$). The term '$I_{corrosion}$' indicates the rate at which corrosion progresses during the corrosion process, with higher values suggesting a faster rate of corrosion progression [23]. As a protective coating of steel, arc-sprayed Ti-Al coating not only exhibits good cathodic protection through the sacrificial anode effect, but also has a low corrosion rate, which is beneficial for long-term corrosion protection.

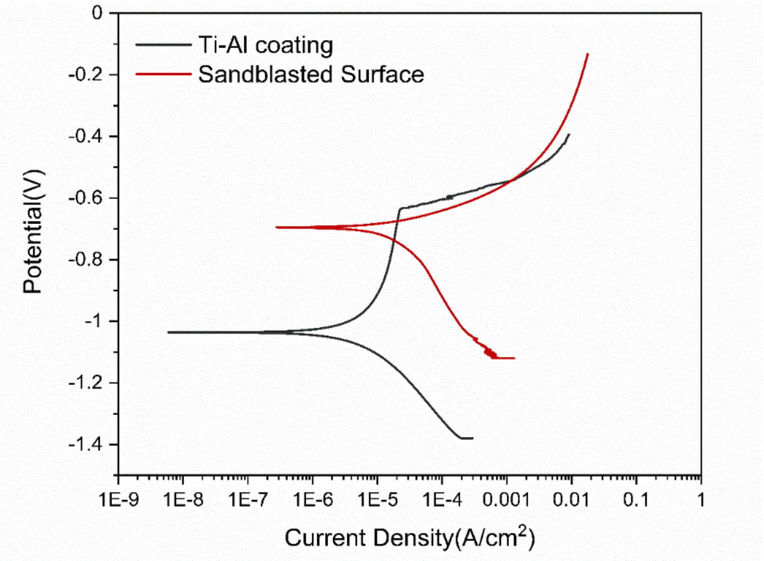


Fig. 7 Potentiodynamic polarization curve of Ti-Al coating and sandblasted surface

Table 2 Results of potentiodynamic polarization test in 3.5 wt% NaCl solution

	$E_{corrosion}$ (V)	$I_{corrosion}$ (μA/cm^2)	Corrosion Rate (mm/y)
Ti-Al coating	-1.1	4.7	0.08
Sandblasted surface	-0.6	17.2	0.22

Conclusion

This study prepared arc-sprayed Ti-Al coating and sandblasted surfaces (normal surface treatment to SA3), followed by microstructure analysis, basic mechanical performance evaluation and corrosion resistance assessment. To evaluate the corrosion resistance in saltwater environments, the coated and sandblasted samples were subjected to a 1000-hour immersion test in 3.5 wt% NaCl solution. The results indicated that the Ti-Al coating has an excellent corrosion resistance. Even after soaking in salt water for a long time, the coating still maintained its durability without peeling or substrate exposure, and the hardness of the coating increased after the immersion test. The electrochemical corrosion test results also provided that Ti-Al coating has lower corrosion rate (0.08mm/y) in corrosive environment, which can extend duration of protection for a given thickness. Hence, the Ti-Al coating may be considered as promising for applications in structural systems.

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References

[1] Y. Ding, F. Zhang, H. Zhou, S. Cheng, K. Xu, Z. Wang, S. Xie, J. Tian, Effect of Al Content on the Long-Term Corrosion Behavior of Arc-Sprayed ZnAl Alloy Coatings, Coatings 13(10) (2023)

[2] J. Kawakita, T. Fukushima, S. Kuroda, T. Kodama, Corrosion behaviour of HVOF sprayed SUS316L stainless steel in seawater, Corrosion science 44(11) (2002) 2561-2581.

[3] F. Ahnia, B. Demri, Evaluation of aluminum coatings in simulated marine environment, Surface and Coatings Technology 220 (2013) 232-236.

[4] Z. Kong, Y. Jin, G.M.S. Hossen, S. Hong, Y. Wang, Q.-V. Vu, V.-H. Truong, Q. Tao, S.-E. Kim, Experimental and theoretical study on mechanical properties of mild steel after corrosion, Ocean Engineering 246 (2022) 110652.

[5] M. Hauer, K.M. Henkel, S. Krebs, W. Kroemmer, Alternative gas mixtures in arc spraying: a chance to improve coating properties and residual stress states, Journal of Thermal Spray Technology 27 (2018) 106-118.

[6] K. Dejun, D. Xuequan, W. Jinchun, Effects of anodic oxidation on corrosion properties of Al coating by arc spraying in seawater, Surface and Interface Analysis 47(9) (2015) 911-918.

[7] J. Lin, Z. Wang, P. Lin, J. Cheng, X. Zhang, S. Hong, Microstructure and cavitation erosion behavior of FeNiCrBSiNbW coating prepared by twin wires arc spraying process, Surface and Coatings Technology 240 (2014) 432-436.

[8] V. Geamăn, M.A. Pop, I. Radomir, D.L. Motoc, Ni-5Al-cladding by thermal arc spraying, International Journal of Modern Manufacturing Technologies 6(1) (2014) 55-58.

[9] Z. Panossian, L. Mariaca, M. Morcillo, S. Flores, J. Rocha, J. Peña, F. Herrera, F. Corvo, M. Sanchez, O. Rincon, Steel cathodic protection afforded by zinc, aluminium and zinc/aluminium alloy coatings in the atmosphere, Surface and Coatings Technology 190(2-3) (2005) 244-248.

[10] S. Sugimura, J. Liao, Long-term corrosion protection of arc spray Zn-Al-Si coating system in dilute chloride solutions and sulfate solutions, Surface and Coatings Technology 302 (2016)

[11] W. Wu, G. Sun, Q. Wang, S. Lin, Preparation, Wear Resistance, and Corrosion Performance of Arc-Sprayed Zn, Al, and Zn-Al Coatings on Carbon Steel Substrates, Journal of Materials Engineering and Performance (2023) 1-14.

[12] H. Min Su, W. Yong Bin, K. Seok-Cheol, Y.-J. Jeong, J. Seok Ki, K. Seong-Jong, Effects of thickness of Al thermal spray coating for STS 304, Transactions of Nonferrous Metals Society of China 19(4) (2009) 925-929.

[13] W.M. Zhao, C. Liu, L.X. Dong, Y. Wang, Effects of Arc Spray Process Parameters on Corrosion Resistance of Ti Coatings, Journal of Thermal Spray Technology 18(4) (2009) 702-707.

[14] New Zealand. STANDARDS, AS/NZS 1594:2002 Hot-rolled steel flat products., 2002.

[15] New Zealand. STEEL, Data Sheet of HA350 (Hot-Rolled), 2012.

[16] New Zealand. STANDARDS, Durability requirements for steel structures and components, 2018.

[17] ASTM Committee, Standard Guide for Laboratory Immersion Corrosion Testing of Metals, ASTM G31, ASTM International, West Conshohocken, PA, USA, 2021.

[18] A. Committee, Standard Practice for Exposure of Metals and Alloys by Alternate Immersion in Neutral 3.5 % Sodium Chloride Solution, 2021.

[19] D.I. Seo, J.B. Lee, Localized corrosion and repassivation behaviors of additively manufactured titanium alloys in simulated biomedical solutions, npj Materials Degradation 7(1) (2023) 44.

[20] M. Barbosa, J. Bastos, J. García-Jareño, F. Vicente, Chloride role in the surface of nickel electrode, Electrochimica acta 44(6-7) (1998) 957-965.

[21] J. Huang, Y. Liu, J. Yuan, H. Li, Al/Al2O3 Composite Coating Deposited by Flame Spraying for Marine Applications: Alumina Skeleton Enhances Anti-Corrosion and Wear Performances, Journal of Thermal Spray Technology 23(4) (2014) 676-683.

[22] H. Kwon, Y. Park, U.H. Nam, E. Lee, E. Byon, Comparative Research on Corrosion Resistant Non-Skid Al and Al-3%Ti Coating Fabricated by Twin Wire arc Spraying, Korean J. Met. Mater. 61(4) (2023) 242-251.

[23] W. Wu, G. Sun, Q. Wang, S. Lin, Preparation, Wear Resistance, and Corrosion Performance of Arc-Sprayed Zn, Al, and Zn-Al Coatings on Carbon Steel Substrates, Journal of Materials Engineering and Performance 32(23) (2023) 10542-10555.