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Corrosion characteristic of coated specimen with 80Ni20Cr / Al_2O_3-TiO_2 powder for ALBC3

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In recent years, surface treatment techniques that give thermal stability, corrosion resistance and erosion resistance to the surface without damaging the characteristics of substrate are in the spotlight. Among them, plasma spray is being used in a wide variety of applications including aerospace, automobiles, and offshore plants because it offers high deposition efficiency and high quality coating layers. In particular, the atmospheric pressure plasma coating gives benefits in cost savings because it does not need expensive vacuum equipment. Therefore, in this study, Al_2O_3-TiO_2 atmospheric pressure plasma coating, which has excellent corrosion resistance and economic efficiency was applied to aluminum-bronze alloy and its electrochemical behavior in seawater was evaluated. As a result, it showed excellent corrosion resistance thanks to the insulation characteristics of the ceramic materials and the effects of sealers.

Key words: Corrosion, Atmospheric pressure plasma, Coating, Ceramic, 80Ni20Cr, Al_2O_3-TiO_2.

Introduction

Due to the rapid industrialization and dramatic increase in the demand for fossil fuels, next-generation energy sources are urgently needed. Among them, the ocean that occupies 71% of the earth is emerging as the vital energy source. However, environmentally friendly energies are difficult to commercialize with economic efficiency due to enormous installation costs. Thus, tidal current power generation systems are getting the limelight because of low construction costs and almost no effects on the ecosystem. Despite these advantages, however, damages by the severe ocean environment are inevitable. The blades in particular, which are core components, suffer a combination of corrosion and erosion which decreases service life and increases maintenance costs. To prevent these damages, many efforts are being made to improve characteristics through various alloys and microstructure controls. Among them, the thermal spray technique was first developed by M. U. Schoop in Switzerland in 1910s as melting thermal spray method to supply molten lead into compressed air jet that was heated with a combustion heat source [1]. In late 1950's, the U.S-Thermal Dynamics corp. further developed by a plasma thermal spray device for national aeronautics and space administration (NASA) aircraft. It's simple progress and widely applied to material variety so, these researches are being carried out [2-3]. Especially, plasma thermal spray method would have enabled film forming of oxides, carbides, and fluorides with have high melting point that cannot be reached with conventional combustible gas heat sources. Among them, the Al_2O_3-TiO_2 coating layer is widely used thanks to its excellent resistance to wear, corrosion, and erosion [4-5]. In related studies, Yýlmaz compared the mechanical characteristics of Al_2O_3-TiO_2 at different contents with austenite 304L stainless steel [5]. As a result, it was found that the greater the content of TiO_2, the greater the fracture toughness and the lower the micro hardness of the coating layer became. Furthermore, Yusoff studied on the effects of powder size and bond coating layer on the electrochemical behavior of the Al_2O_3-TiO_2 plasma coating layer in seawater [6]. This reduced pores in the bond coating layer while increasing surface roughness and corrosion rate. Furthermore, the nanoparticle coating layer showed lower corrosion rate than the micro particle coating layer. In this study, Al_2O_3-TiO_2 atmospheric pressure plasma coating was applied to aluminum-bronze alloy that is widely used offshore plants due to excellent corrosion resistance, toughness and impact resistance and its corrosion resistance was evaluated by electrochemical behavior in marine environment.

Experiment Details

This research used ALBC3 alloy, which is often applied in marine environment due to excellent corrosion. Additionally, double layer of 80Ni20Cr bonding coating and Al_2O_3-TiO_2 top coating were fabricated on ALBC3 alloy using atmospheric pressure plasma spray (APS) coating technology. The chemical composition of ALBC3 alloy and spraying condition of APS are shown in Table 1

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Table 1. Spray condition for atmospheric pressure plasma coating process.

Powder	Argon [ℓ / min]	Spray distance [mm]	Feed rate [g/min]	Hydrogen [ℓ / min]	Current [A]	Powder gas [ℓ / min]	Traverse speed [mm/s]
80Ni20Cr	65	140	40	14	600	2.3	8
Al_2O_3-TiO_2	38	120	50	14	600	3.2	8

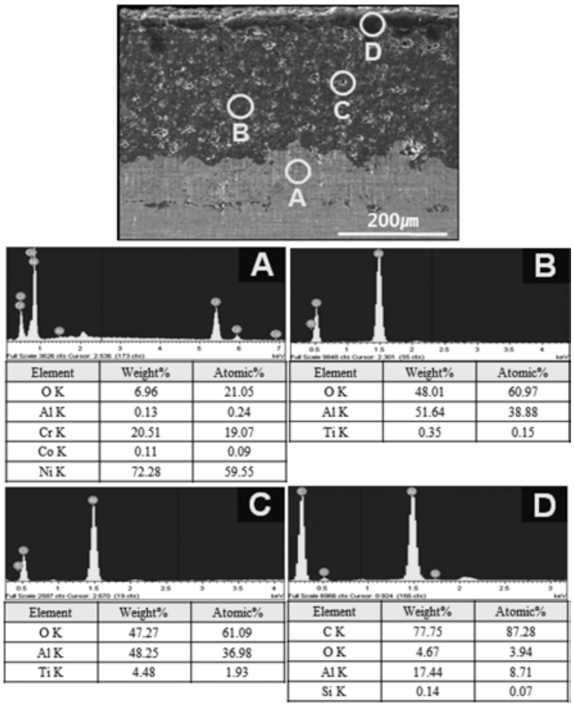
Table 2. Chemical compositions for ALBC3 and Al_2O_3-TiO_2 (wt.%).

ALBC3	Cu	Al	Fe	Ni	Zn	Sn	Pb	Si	Mn
	Balance	9.30	3.66	4.39	0.34	0.01	0.013	0.17	0.55
Al_2O_3-TiO_2	Al_2O_3 95.4-98.0		TiO_2 ≤ 0.60			SiO_2 ≤ 0.60		Fe_2O_3 2.0-3.5	
80Ni20Cr	Ni Balance					Cr ≤ 20			

and Table 2, respectively. Generally, owing to the nature of the process, the plasma coating contains voids or defects inside where Cl^- ion can be permeated, lowering corrosion resistance Therefore, the sealer coating was applied over the coating in order to prevent cracks and creation of voids inside of the coating. Generally, various processes such as irradiation after spraying and sealing treatment after laser hybrid spraying are being introduced to improve such porosity [7-8]. The spot energy-dispersive x-ray spectroscopy (EDS) analysis was conducted for cross-section of the specimen. The polarization system consisted of a Pt coil, which acted as a counter electrode, and an Ag/AgCl saturated KCl reference electrode. The natural potential measurement test was performed for 86,400 seconds to measure the potential behavior over time. The anodic and cathodic polarization experiments from the open circuit potential to +3.0 and −2.5 V (SSCE) were carried out at a scan rate of 2 mV/sec at room temperature after immersion for 3,600 seconds. Tafel analysis took effect from the open circuit potential +0.25 V and −0.25 V (SSCE) for the Ag/AgCl electrode, respectively and were carried out at a scan rate of 2 mV/sec at room temperature.

Results and Discussion

Fig. 1 represents the result of spot EDS analysis for the cross-sections of 80Ni20Cr / Al_2O_3-TiO_2 APS coating layer. The spectrum A corresponds to the bond coating 80Ni20Cr, most of which consisted of Ni and Cr at 72.28 wt.% and 20.51 wt.%, respectively, and Al and O were detected. Spectrum B is a fine microstructure in the top coating layer consisting of Al and O at 51.64 wt.% and 48.01 wt.%, respectively, and almost no Ti was detected. Spectrum C is in the same coating layer as spectrum B, but it corresponds to voids, and a relatively large quantity of Ti was detected. Spectrum D corresponds to sealer mainly consisting of C, and Al and O were detected due to the effect of the top coating



Element	Weight%	Atomic%
O K	6.96	21.05
Al K	0.13	0.24
Cr K	20.51	19.07
Co K	0.11	0.09
Ni K	72.28	59.55

Element	Weight%	Atomic%
O K	48.01	60.97
Al K	51.64	38.88
Ti K	0.35	0.15

Element	Weight%	Atomic%
O K	47.27	61.09
Al K	48.25	36.98
Ti K	4.48	1.93

Element	Weight%	Atomic%
C K	77.75	87.28
O K	4.67	3.94
Al K	17.44	8.71
Si K	0.14	0.07

Fig. 1. Spot EDS analysis for 80Ni20Cr / Al_2O_3-TiO_2 atmospheric pressure plasma coating.

layer and the atmospheric oxygen.

In the mapping analysis in Fig. 2 shows the EDS analysis results for a cross-section of the 80Ni20Cr / Al_2O_3-TiO_2 APS coating layer. The main component Cu was mostly detected in the substrate ALBC3. Furthermore, in the bond coating layer 80Ni20Cr, Ni and Cr were mostly detected, and O was partially detected, which seems to be an oxide matter layer resulting from combination with atmospheric oxygen during spray. Some oxygen was detected together with Al which escaped from the collision against the substrate during spraying at the interface between substrate and 80Ni20Cr. Because Al has high oxygen affinity, it will form oxides matter at the interface between the substrate and the bond coating layer, which is expected to affect the adhesion strength. In the top coating layer Al_2O_3-TiO_2, Al and O were mostly observed. As Ti was detected in the Al deficient area, it was found to consist of Al_2O_3 and TiO_2. It seems that other various oxides were not observed due to low oxygen affinity during spray flight because the material was powder-processed as stabilized, oxide matter [9]. It has been generally known that the plasma coating layer has high porosity because it is mixed with gases and impurities in atmosphere during

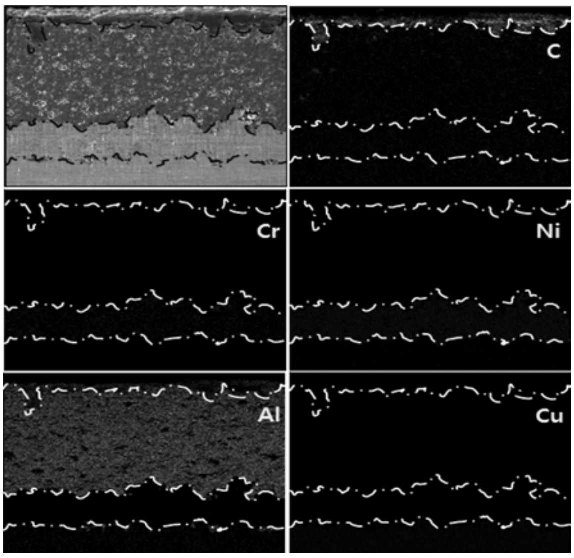


Fig. 2. EDS analysis of chemical elements for 80Ni20Cr / Al_2O_3-TiO_2 atmospheric pressure plasma coating.

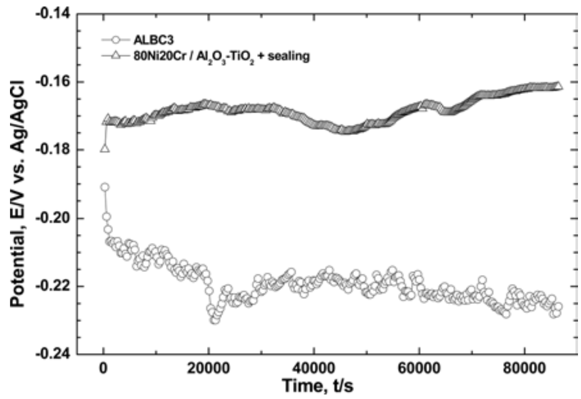


Fig. 3. Comparison of potential trend for ALBC3 and atmospheric pressure plasma coating layer.

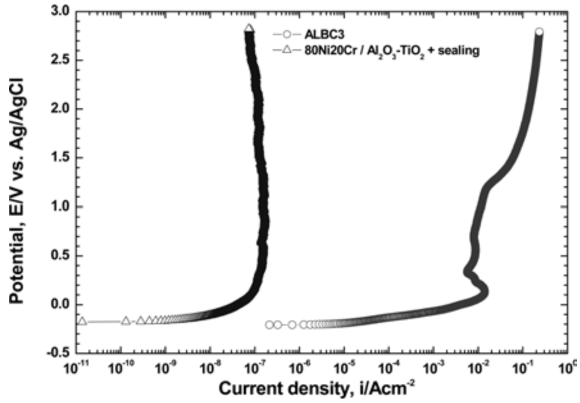


Fig. 4. Comparison of the anodic polarization trends for ALBC3 and atmospheric pressure plasma coating layer.

spray [10]. Many voids were also observed in the Al_2O_3-TiO_2 coating layer. A moderate porosity causes oxidation through the diffusion of oxygen into the gases, thereby creating a protective film [11]. An excessive porosity, however, accelerates the growth of oxides and increases the internal stress between coating layers, which can delaminate the coating layer due to decreased adhesion strength [12]. Therefore, an appropriate porosity must be maintained.

Fig. 3 shows the natural potential measurements of the ALBC3 alloy and the 80Ni20Cr / Al_2O_3-TiO_2 APS coating layer. ALBC3 showed −0.19 V in the early stage of immersion and slowly shifted towards the active direction while repeatedly rising and falling in a narrow range. Oxides, chlorines, and hydroxides matter are formed on the surfaces of copper alloys exposed to seawater, and cuprous oxide (Cu_2O) has been known to maintain the most stable condition [13-14]. It seems that potential variations were observed when these protective coatings were destroyed by the Cl^- ions and then recreated. The 80Ni20Cr / Al_2O_3-TiO_2 coating layer, on the other hand, showed a nobler potential than the substrate and the potential difference between the substrate and the coating layer at the end was about 0.07 V. However, because the natural potential measurement found that the coating layer had nobler potential than the substrate, when galvanic corrosion occurs, the substrate will act as the anode and its interface with the coating layer will be corroded, resulting in delamination. Therefore, when a coating layer with a higher potential than the substrate is applied, a very compact coating should be formed. Because electrolyte penetration through such inner defects such as voids and macro or micro cracks aggravates corrosion and wear, resistance, special attention should be paid to sealing through sealing treatment.

Fig. 4 presents the anodic polarization behavior of ALBC3 alloy and 80Ni20Cr / Al_2O_3-TiO_2 APS coating layer. ALBC3 alloy showed a rapid increase in current density by the active dissolution reaction with the progress of anodic polarization. Furthermore, it showed passive characteristics with transient decrease of current density, but the application of corrosion protection is impossible for such high current density. Such passivity appears because the corrosion products by oxidation are formed solidly on the surface which interferes with charge transfer [13]. However, the oxidation products on the surface are removed together due to the oxygen and intergranular delamination caused by continuous active dissolution reaction. On the other hand, the 80Ni20Cr / Al_2O_3-TiO_2 coating layer showed a much lower current density than the substrate and excellent corrosion resistance is not appeared tendency of passivity. The reason for this seems to be anti-corrosive elements such as Ni, Cr, and Al. It exhibited considerably better characteristics than the substrate due to 80Ni20Cr / Al_2O_3-TiO_2 coating layer was found to have better corrosion resistance than ALBC3 due to its chemical composition with excellent corrosion resistance as well as through sealing treatment which prevents the penetration of electrolyte.

Fig. 5 depicts the cathodic polarization behavior of

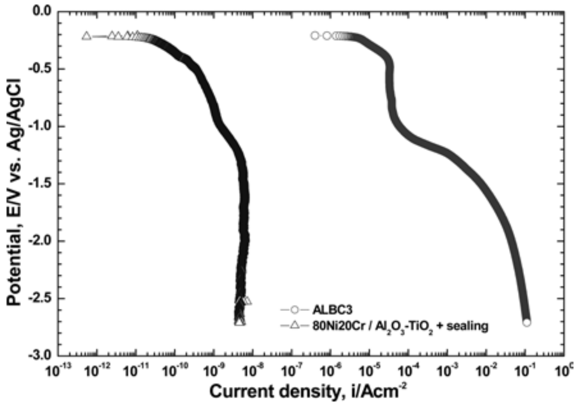


Fig. 5. Comparison of the cathodic polarization trends for ALBC3 and atmospheric pressure plasma coating layer.

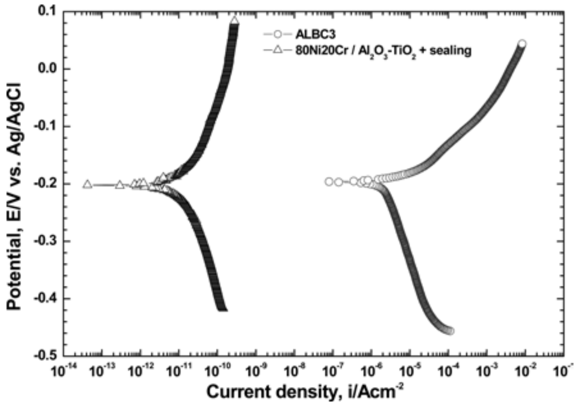


Fig. 6. Polarization trends for Tafel analysis of ALBC3 and atmospheric pressure plasma coating layer.

ALBC3 alloy and 80Ni20Cr / Al_2O_3-TiO_2 APS coating layer. 80Ni20Cr / Al_2O_3-TiO_2 did not show clear concentration polarization compared to ALBC3, but generally showed a very low current density than ALBC3. This concentration polarization is controlled by the diffusion rate of ions that move to the metal surface because of the limited concentration of oxygen ions in the solution. Therefore, the substrate is expected to have a faster diffusion rate of oxygen. Furthermore, ALBC3 underwent a rapid increase in current density as it progressed from concentration polarization to activation polarization by the reduction reaction of the dissolved oxygen, but the current density of 80Ni20Cr / Al_2O_3-TiO_2 did not increase despite the increase of polarization. This is because the charge transfer is restricted by Al_2O_3 which is a ceramic material corresponding to an insulator. As a result, 80Ni20Cr / Al_2O_3-TiO_2 coating for ALBC3 alloy is expected to exhibit better corrosion resistance in seawater environment than the substrate.

Fig. 6 shows the polarization behavior of the ALBC3 alloy and the 80Ni20Cr / Al_2O_3-TiO_2 APS coating layer for Tafel analysis. The anodic polarization behavior of ALBC3 alloy showed almost linear increase in current density with the increasing potential, but the 80Ni20Cr / Al_2O_3-TiO_2 coating layer showed a modest increase in current density. Measurements of the corrosion potential

Table 3. Results of Tafel analysis for ALBC3 and atmospheric pressure plasma coating layer.

Tafel analysis	ALBC3	80Ni20Cr / Al_2O_3-TiO_2 + sealing
Corrosion potential [V]	−0.2207	−0.2013
	−0.2155	−0.2384
	−0.2118	−0.2335
Average	−0.2187	−0.2244
Corrosion current density [A/cm^2]	1.0837×10^{-6}	1.3596×10^{-11}
	7.1634×10^{-7}	3.0272×10^{-11}
	7.3396×10^{-7}	9.4118×10^{-11}
Average	8.4467×10^{-7}	4.5995×10^{-11}

and corrosion current density of ALBC3 alloy through the Tafel extrapolation method showed −0.2187 V and 8.4467×10^{-7} A/cm^2, respectively. On the other hand, the 80Ni20Cr / Al_2O_3-TiO_2 coating layer showed the average corrosion potential of −0.2244 V which was similar to that of ALBC3, but its average corrosion current density was 4.5995×10^{-11} A/cm^2, which was 1.84×10^4 times lower. The reason that the 80Ni20Cr / Al_2O_3-TiO_2 coating layer showed better corrosion resistance than the substrate was that it not only contains highly corrosion-resistant elements, but also has insulation characteristics as ceramic material and the sealing effect. The polarization curves for 3 times experiments of the ALBC3 and 80Ni20Cr / Al_2O_3-TiO_2 coating layers were analyzed and the detailed measurements of the corrosion potential and corrosion current density are listed in Table 3.

Conclusions

The APS technology 80Ni20Cr / Al_2O_3-TiO_2 for ALBC3 alloy investigated corrosive resistance characteristic in order to improve equipment durability used in oceanic environment. Furthermore, the electrochemical experiment showed very excellent corrosion resistance due to the insulation characteristics of Al_2O_3 as ceramic material and the effect of sealer that sealed the fine voids and defects. In conclusion, the application of coating technology for improvement of corrosion resistance in marine environment should consider. The 80Ni20Cr / Al_2O_3-TiO_2 double coating layer indicated excellent electrochemical property.

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