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The cavitation characteristic of atmospheric pressure plasma sprayed 80Ni20Cr / Al₂O₃-TiO₂ powder for Cu-Al alloys

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Ceramics are frequently used in special mechanical parts due to high wear resistance and corrosion resistance. In particular, deposition with plasma heat source produces particularly excellent wear resistance, corrosion resistance, and thermal stability. For plasma coating materials, Al_2O_3 and TiO_2 are being researched, and it has been found that the addition of TiO_2 to Al_2O_3 base greatly improves fracture toughness and wear resistance. In this study, the atmospheric pressure plasma coating technology was applied to ALBC3 alloy which is often used in marine environment due to excellent corrosion resistance, and the cavitation characteristics of the $80Ni20Cr/Al_2O_3$ -TiO₂ double coating layers were evaluated. The result of experiment revealed that the application of coating technology for improvement of corrosion resistance and cavitation resistance in marine environment should be considered at the viewpoint of mechanical characteristics. Furthermore, the $80Ni20Cr/Al_2O_3$ -TiO₂ double coating layers used in this study presented excellent characteristics.

Key words: 80Ni20Cr/Al₂O₃-TiO₂, Atmospheric pressure plasma coating, Cavitation, Sea water, Thermal spray.

Introduction

With recent advanced technical developments, an increasing number of parts are being exposed to extreme conditions. Materials used for these applications require much higher levels of surface performance including thermal stability, corrosion resistance, wear resistance, and erosion resistance [1-3]. Particularly in the marine environment, corrosion damages easily occur because passive films are destroyed by Cl⁻ ions and pitting is generated by the effect of cavitation resulting from high velocity flow [4-5]. To prevent these damages and achieve high surface performance, various techniques including painting, CVD, PVD, and thermal spray coating are being applied. In particular, thermal spray coating is one of the surface modification methods that satisfies the aforementioned conditions, which melts metal or ceramic materials which are collided against the substrate to form films through solidification and deposition. Its advantage is that coating layers of various materials can be fabricated regardless of the type, shape and size of substrate [6-7]. The atmospheric pressure plasma(APP) coating technique does not need expensive vacuum equipment and is applied to various fields because it enables rapid processes, cost savings, and the design of multi-layered structure. In this study, the APP technique was applied to aluminum-bronze

(ALBC3) alloy for the double coating of 80Ni20Cr and Al_2O_3 -TiO₂. Al_2O_3 -TiO₂, which was selected as coating material, has excellent erosion resistance and high hardness as ceramic material, and TiO₂ has the effect of improving mechanical properties and preventing the attachment of marine organisms [8-9]. Therefore, in this study, to improve the durable life of the equipment exposed to marine environment, APP coating technique was applied to ALBC3 alloy and its cavitation damage behavior was investigated.

Experiment Details

This research used ALBC3 alloy, which is often applied in marine environment due to excellent corrosion and cavitation resistance. Additionally, double layer of 80Ni20Cr bonding coating and Al₂O₃-TiO₂ top coating were fabricated on ALBC3 alloy using APP coating technology. The chemical composition of ALBC3 alloy and spraying condition of APP are shown in Table 1 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 [10]. 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 [11-15]. The hardness for cross-sectional area was measured by micro-Vickers hardness tester applying load of 100kgf for 5 seconds. The cavitation experiment

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Argon [ℓ/min]		Spray distance [mm]	Feed rate [g/min]	Hydrogen [ℓ/min]	Curren [A]	t	Powder gas [ℓ/min]	Traverse speed [mm/s]	
65		140	40	14	600		2.3	8	
38		120	50	14	600		3.2	8	
Table 2. Chemical compositions for ALBC3 and 80Ni20Cr/Al ₂ O ₃ -TiO ₂ powder (wt.%).									
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 ₂ O ₃			TiO ₂		SiO ₂		Fe ₂ O ₃		
95.4 - 98.0			≤ 0.60		≤ 0.60		2.0-3.5		
Ni					Cr				
Balance					≤ 20				
	Arg [ℓ/m 6: 33 ompositions f Cu Balance 4 95.	$\begin{array}{c} \text{Argon} \\ [\ell/\text{min}] \\ 65 \\ 38 \\ \hline \\ \text{ompositions for ALBC} \\ \hline \\ \text{Cu Al} \\ \hline \\ \text{Balance 9.30} \\ \hline \\ & \text{Al}_2\text{O}_3 \\ 95.4 - 98.0 \\ \hline \end{array}$	$\begin{tabular}{ c c c c c } \hline Argon & Spray \\ distance & [mm] \\ \hline 65 & 140 \\ \hline 38 & 120 \\ \hline \end{tabular}$	$\begin{array}{c c} Argon \\ [\ell/min] \\ \hline \\ [\ell/min] \\ \hline \\ 65 \\ 38 \\ \hline \\ 120 \\ \hline \\ 50 \\ \hline \\ $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	

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



Fig. 1. Schematic diagram of cavitation experiment.

was performed with cavitation erosion tester (Fig. 1) that utilizes the piezoelectric effect. For the oscillation, alternating current was applied to the conical horn so as to generate axial oscillations. The power source of 220 V/60 Hz is converted and amplified to 20 KHz rated ocilliation through an electronic circuit. The amplitude was maintained constant at 30 µm by the constant amplitude automatic controller. The bath for cavitation was made of acryl to avoid effect of electrochemicasl corrosion, and natural seawater of 15 °C was used as solution. The specimen was placed to the holder, facing the horn of the oscillator and maintaining 1mm of distance to the specimen. To measure weight loss, the specimen was cleaned before and after the experiment with ultrasonic washing machine and dried in vacuum dryer for 72 hours, and then surface degradation was evaluated by weight loss

and cavitation rate. Further to measuring weight loss, the damaged surface after the cavitation experiment was analyzed by scanning electron microscope (SEM) and 3D microscope to evaluate the amount of damage with time.

Results and Discussion

Fig. 2 compares the micro-Vickers hardness measurements of the cross-section of the 80Ni20Cr/Al₂O₃-TiO₂ APP coating layer. The substrate ALBC3 showed the average hardness of 155 Hv, and the 80Ni20Cr coating layer showed the average hardness of 225 Hv, which was higher by about 70 Hv than that of the aluminum-bronze substrate which was manufactured by sand casting. The top coating layer Al₂O₃-TiO₂ showed the highest hardness at 454 Hv. These differences in hardness are associated with the chemical composition and porosity of each coating layer. As a ceramic material that corresponds to a stabilized oxide matter, Al₂O₃ has very high hardness and excellent corrosion resistance. The sealant showed the lowest hardness and no improvement of cavitation resistance can be expected, but electrochemical characteristics can be



Fig. 2. Comparison of micro-Vickers hardness for atmospheric pressure plasma coating layer.



Fig. 3. Cross-section and surface observation for 80Ni20Cr / Al2O3-TiO2 atmospheric pressure plasma coating.



Fig. 4. Comparison of damage behavior for 80Ni20Cr / Al₂O₃-TiO₂ atmospheric pressure plasma coating with cavitation time.

improved by preventing the voids and defects in the coating layer from contacting with external corrosive environment. This hardness measurement can predict the resistance of materials against external physical forces [16-17]. Typically, hardness is proportional to cavitation resistance. Therefore, it is expected that cavitation resistance would improve because the bond coating layer which enhances the adhesion strength of the substrate and the top coating layer, and the top coating layer that directly prevents damages from external environment showed higher hardness values than those of the substrate. In general, the formation of a robust coating layer with no voids or cracks has been known to greatly improve the hardness, resistance to high-temperature corrosion, and corrosion resistance [11].

Fig. 3 shows surface observation and cross-sectional view of $80Ni20Cr/Al_2O_3$ -TiO₂ coating deposited by APP. The thickness of 80Ni20Cr bonding coating and Al_2O_3 -TiO₂ top coating was found to be approximately 100 µm and 300 µm, respectively. It is common in the APP coating method that gases and impurities in atmosphere are mixed to produce voids in coating [18].

The same was true for the Al_2O_3 -TiO₂ coating having many voids. One possible reason for the formation of voids is that the plasma jet sprayed from the nozzle layered together with molten particles and restrained gas, and the gas trapped during cooling is released to form the voids [19].

Fig. 4 observes the surface damage behavior after cavitation experiment on the 80Ni20Cr/Al₂O₃-TiO₂ APP coating layer. No damages observable by naked eye occurred until 20 minutes into the experiment. Damages started from the horn contours at 40 minutes, and a generally rough surface was observed at 90 minutes. After 120 minutes, cavitation and corrosion damages were generated at the interface between the substrate and coating layer, which decreased adhesion strength and increased the delamination of the coating layer [20]. The cavitation resistance of coatingsubstrate system is generally affected by adhesion strength, as well as by cooling rate, generation of oxide and compounds, the compactness and porosity of the coating layer [17]. In particular, the fused particles during the plasma spray have compressive residual stress inside the coating due to contraction and



Fig. 5. Weightloss and cavitation rate for $80Ni20Cr / Al_2O_3$ -TiO₂ atmospheric pressure plasma coating with cavitation time.

solidification at room temperature or due to forced cooling, and this residual stress causes the delamination of the coating layer. Afterwards, the delamination of coating layer accelerated over time and the exposed area of the substrate increased. With the increasing cavities formed by the ultrasonic waves with the increasing experiment time, the energy applied to the specimens accumulated and this increased the amount of damages. Furthermore, the greatest damage appeared at the center of the specimen. It was also reported in the studies of other researchers that the velocity at the center of the specimen is the fastest and the damages at the center of specimen are closely associated with such high flow rate [21].

Fig. 5 compares the weight loss and cavitations rates after cavitation experiment on the $80Ni20Cr/Al_2O_3$ -TiO₂ APP coating layer. Although the weight loss varied a little, it generally tended to continuously

increase with time. For such erosion damages, the impact erosion resulting from the direct collision of the liquid jets or drops against the solid surface, and the cavitation erosion due to the impact pressure and the bubble collapsing. Thus, damages increase with the accumulation of physical external forces with time, but the increase rates vary depending on the coating material or surface condition. The cavitation rate decreased between 20 and 40 minutes of experiment. In general, single materials have incubation period in which the weight loss is stagnant due to the formation of compressive residual stress caused by the water cavitation peening effect in the early stage [22-23]. In this experiment, the incubation period was from the point where the sealer layer with low hardness was damaged first until the full-scale damage of the exposed top coating layer at 60 minutes. Afterwards, the cavitation rate steadily increased with the damage of the top coating layer and reached the highest value at 120 minutes when part of the substrate began to be exposed. After that, the cavitation rate increased with the continuous damage of the top coating layer, but the delamination of the top coating layer was delayed by the anchor effect of the remaining bond coating layer and the cavitation rate decreased [24]. Furthermore, after 240 minutes, the substrate was completely exposed with the delamination of the bond coating layer, and the cavitation rate increased.

Fig. 6 exhibits the surface damages after cavitation experiment on the 80Ni20Cr/Al₂O₃-TiO₂ APP coating layer with a scanning electron microscope. Before damages, a sealer was observed together with spherical coating layer particles on the surface. Spray coating forms voids when the gases that had been absorbed



(a) As-received, 20min, 40min, 60min, and 90min (b) 120min, 180min, 240min, and 300min **Fig. 6.** Surface morphologies for 80Ni20Cr / Al₂O₃-TiO₂ atmospheric pressure plasma coating after cavitation test.



Fig. 7. 3D analysis (a) and damage depth (b) for 80Ni20Cr / Al₂O₃-TiO₂ atmospheric pressure plasma coating after cavitation test.

during melting are sprayed to the outside. In this experiment, the defects or voids on the surface were sealed by the sealer [19]. This application of sealer improves corrosion resistance and durability by blocking the diffusion of oxygen and hydrogen atoms, and the penetration routes of electrolyte. Between 20 minutes and 60 minutes of the experiment, no damages of the top coating layer were observed and the gloss disappeared as the sealer was delaminated from the surface. At 90 minutes, the sealer was fully removed and a large damage of a crater shape was observed. At 120 minutes, exposure of the substrate started and the coating layer was delaminated, and the exposed area of the substrate increased over time. After 180 minutes, damages of the substrate were observed as well. Consequently, the cavitation damages tended to start from the center and continuously increased in proportion to time.

Fig. 7 observes the surface damages after cavitation experiment on the 80Ni20Cr/Al₂O₃-TiO₂ APP coating layer with a 3D microscope. The depth of the substrate surface applied with sealer was 66 µm before the experiment. It seems that the thinly applied sealer penetrated into voids and defects. At 60 minutes, no large damages were observed and the maximum depth of damage was 130 µm. At 120 minutes, it rapidly increased to 325 µm. It seems that almost no damages were produced in the early stage due to a transient increase in cavitation resistance as the compressive residual stress resulting from the water cavitation peening effect was formed, but full-scale damages were generated later when a larger cumulative pressure was applied. After 120 minutes, the damages to the direction of depth were restricted by the compressive residual stress which was formed again as the substrate was exposed, and the exposed area of the substrate increased with the delamination of the remaining coating layer.

Conclusions

The cavitation resistance characteristics of ALBC3 alloy to which the 80Ni20Cr/Al₂O₃-TiO₂ APP coating technique was applied were evaluated to improve the durability of the equipment used in marine environment. The hardness measurement of the top coating layer Al₂O₃-TiO₂ showed 454 Hv which was more than twice as large as that of the substrate, which suggests improved cavitation resistance. In the cavitation experiment, damages started from the center with the highest flow rate and steadily increased over time. In conclusion, the application of coating technology for improvement of corrosion resistance and cavitation resistance in marine environment should be considered cavitation characteristics. The 80Ni20Cr/Al₂O₃-TiO₂ double coating layer used in this study exhibited excellent characteristics.

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