

Corrosion Behavior of Plasma Sprayed Al₂O₃/ Ti-Al Coating on Steel Substrate

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Abstract

Corrosion behavior of double-layered Al₂O₃/ Ti-Al coating on a steel substrate formed by a plasma spraying, as an alternative to a Cr plating was investigated in several solutions; 3.5 mass% NaCl, 1N HCl, 1N H₂SO₄ and 1N HNO₃ solution. Potentiodynamic polarization measurements and salt spraying test were carried out to clarify a protection mechanism of the coating on the substrate in comparing with the Cr plating. The coating could afford cathodic protection to the steel substrate in the NaCl, the HCl and the HNO₃ solution by dissolving the Al phase of the Ti-Al layer. Besides, the barrier protection due to the dense structure of the Ti-Al coating was recognized in the H₂SO₄ solution. The corrosion protection performance of the Al₂O₃/ Ti-Al coating on steel was superior to that of the Cr plating except in the HNO₃ solution.

Keywords: Plasma spraying, Al₂O₃ coating, Ti-Al undercoating, Corrosion protection, Cr plating alternative.

1. Introduction

Cr plating from a chromic acid bath is required to replace alternatives from the viewpoint of environmental regulation. An Al₂O₃ coating by thermal plasma spraying should be one of the substitutions for the plating. We have developed the Ti-Al coating as the undercoating for the Al₂O₃ coating on steel substrate to achieve high adhesiveness. (S.Adachi, et al, 2007) For industrial utilization, the corrosion protection performance of the undercoating is also important, because the Al₂O₃ coating itself is inactive against corrosion reaction but a substrate often corrodes due to the presence of interconnected pores in the coating. (E.Celik, et al, 1997) The aim of this study is to examine the corrosion behavior of the double-layered Al₂O₃/ Ti-Al coating on steel substrate in comparing with the Cr plating, and the possible application of the Al₂O₃/ Ti-Al coating in various solution environment as an alternative to the Cr plating is discussed.

2. Experimental Procedure

2.1 Fabrication of sprayed Al₂O₃/ Ti-Al coating

Ti powder with powder size distributions of 60 – 80 μm, and Al powder with powder size distributions

of 40 – 60 μm were used as starting materials. The Ti powder was blended uniformly with the 50 mass% Al powder in advance, and the blended powder applied for the spraying. The plasma spraying was performed in the air atmosphere using plasma torch of Aeroplasma Limited Company APS7050 system. The Ti-Al coating with thickness of 100-150 μm was deposited on the steel substrate (JIS SS400, corresponding to ISO E275A). In addition, a sprayed Ti coating or a sprayed Al coating was also fabricated. And then the Al₂O₃ coating with thickness of about 300 μm was deposited on the undercoating by the plasma spraying.

The single Al₂O₃ coating on the steel was deposited with no undercoating.

Cr plating with about thickness of 40 μm on the steel substrate by using a sargent bath was also prepared for comparison.

The porosity of the coating was obtained by calculating the rate of the area of the pores by image analysis of the cross-section.

2.2 Corrosion test

Electrochemical polarization measurement was carried out by using a potentiostat of the HZ-3000 (Hokuto denko corporation), and it's conditions were reference electrode of an Ag/ AgCl, counter electrode

of a platinum plate, scan rate of 0.8 mV/sec, and temperature of 303 K. The experiments were conducted in 3.5 mass% NaCl solution, 1N HCl solution, 1N H₂SO₄ solution and 1N HNO₃ solution. The NaCl solution was degassed by N₂ gas for more than 1800 s before the measurement to eliminate the influence of dissolved oxygen. Rest potential was first measured after immersion of the sample for 300 s, and then polarization curve was measured. After the measurement, quantitative analysis of metals in the test solutions was performed by ICP-AES (SHIMAZU IPS-2000).

The salt spray test was also performed with both the Al₂O₃/Ti-Al coating and the Cr plating.

3. Results and Discussion

3.1 Neutral NaCl environment

Figure 1 shows SEM image of cross section of the sprayed Al₂O₃/Ti-Al coating on the steel substrate. The undercoating of Ti-Al coating is observed to have a dense laminated structure, in which bright area is Ti compounds phase (mainly consisted of TiN_{0.3} and TiNO) and dark area is Al phase.

The rest potentials of the coatings in the 3.5 mass% NaCl solution are shown in **Table 1**. The rest potential of the Al₂O₃/Ti coating was -0.39 V, which was almost the same as the one of single Al₂O₃ coating. So, the Ti coating would exhibit no effect on corrosion protection. The rest potentials of the Al₂O₃/Ti-Al coating and Al₂O₃/Al coating were much more negative of about -1 V than those of the single Al₂O₃ coating and the Al₂O₃/Ti coating, and considered to be reflecting the dissolution of Al phase in the undercoating.

By the salt spray test of 600 h the Al₂O₃/Ti-Al coating showed no rust on the surface. At 1248 h, only the white rust of aluminum hydroxide was observed. These results indicate that the Al phase of

the Ti-Al coating could afford galvanic protection to the substrate at the beginning of the corrosion test, and then the interconnected pores in the Al₂O₃ coating would be sealed with the aluminum hydroxide to prevent penetrating the salt mist. In this way, the Ti-Al undercoating would provide long-term protection of the substrate from corrosion.

As for the Cr plating on the steel substrate, the red rust was observed at 24 h by the salt spray test, and the rest potential of the plating was -0.46 V electropositive compared to the substrate potential. These results show the Cr plating itself is inactive in the corrosion environment, however the corrosion protection ability of the plating is much lower than those of the Al₂O₃/Ti-Al coating owing to the presence of interconnected pores in the plating.

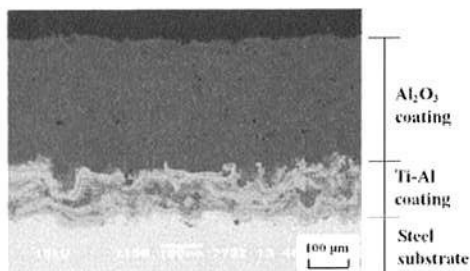


Fig.1 SEM image of the cross section of sprayed Al₂O₃/Ti-Al coating on steel substrate.

3.2 Non-oxidizing acid HCl and H₂SO₄ solutions

The rest potentials of the Al₂O₃ coatings in non-oxidizing acid HCl solution are shown in **Table 1**. The rest potentials of the Al₂O₃/Ti-Al coating and the Al₂O₃/Al coating were about -0.75 V, a little lower than those of the Al₂O₃/Ti coating and the single Al₂O₃ coating. The polarization behaviors with the

Table 1 Rest potentials of Al₂O₃ coatings and Cr plating on steel substrate in various solutions; Al₂O₃/Ti-Al coating, Al₂O₃/Ti coating, Al₂O₃/Al coating, Al₂O₃ coating, Cr plating.

Solution	Rest potential, E / V					
	Substrate	Al ₂ O ₃	Al ₂ O ₃ /Ti-Al	Al ₂ O ₃ /Ti	Al ₂ O ₃ /Al	Cr plating
NaCl	-0.61	-0.34	-1.0	-0.39	-1.1	-0.46
HCl	-0.43	-0.57	-0.74	-0.58	-0.76	-0.75
H ₂ SO ₄	-0.46	-0.57	-0.53	-0.55	-0.53	-0.42
HNO ₃	-0.27	-0.39	-0.41	-0.35	-0.46	-0.33

Al₂O₃ coatings and the Cr plating are shown in **Figure 2**. The corrosion potentials of Al₂O₃/ Ti-Al coating and Al₂O₃/ Al coating were more negative in comparison with the single Al₂O₃ coating and the Al₂O₃/ Ti coating. By the quantitative analysis of metals in the HCl solution after the polarization measurement, the concentrations were found to be Al 5.4 ppm, Ti 0.04 ppm and Fe 0.33 ppm. These results show that the Al phase in the Ti-Al coating could afford cathodic protection to the substrate in the HCl solution as same as in the NaCl solution, and the Ti compound phase exhibited no improvement in corrosion protection ability of the coating.

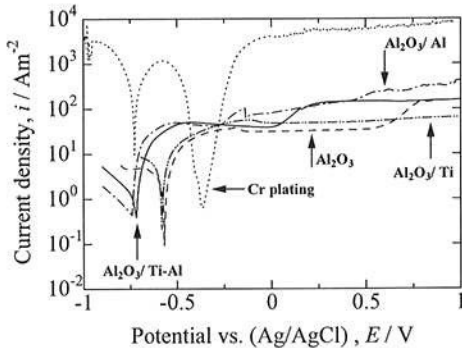


Fig.2 Polarization curves of Al₂O₃ coatings and Cr plating on steel substrate in 1 N HCl solution; Al₂O₃/ Ti-Al coating, Al₂O₃/ Ti coating, Al₂O₃/ Al coating, Al₂O₃ coating, Cr plating.

While, in the H₂SO₄ solution, the differences among the rest potentials of the Al₂O₃ coatings are not admitted in Table 1. And also, there are no differences in either corrosion potentials observed in **Figure 3**, however the corrosion currents of them differs each other. The quantitative analysis of metals dissolved in the H₂SO₄ solution after the polarization measurement showed that the concentrations were Al 0.22 ppm, Ti 0 ppm and Fe 0.16 ppm respectively. The Al content was very small comparing with the one in the HCl solution. It is known that the Ti-Al coating surface was covered with the thin oxide layer formed during the plasma spraying by XPS analysis. This oxide layer would passivate to the Ti-Al coating to protect dissolving of the Ti-Al coating in the H₂SO₄ solution. The correlation between the porosity of the undercoating and the corrosion current calculated from Tafel extension method was shown in **Figure 4**. The current had a linear relationship with the porosity of the undercoating, and was not affected by the materials of the coating. This means that the mechanism of corrosion protection to the substrate

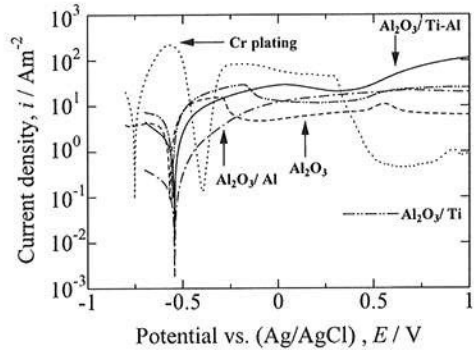


Fig.3 Polarization curves of Al₂O₃ coatings and Cr plating on steel substrate in H₂SO₄ solution; Al₂O₃/ Ti-Al coating, Al₂O₃/ Ti coating, Al₂O₃/ Al coating, Al₂O₃ coating, Cr plating.

would be a barrier effect to prevent the contact between the substrate and the solution environment. That is, the dense Ti-Al coating efficiently protects the substrate from corrosion by the barrier effect.

As for the polarization behaviors of the Cr plating in the HCl and the H₂SO₄ solutions, the corrosion potentials of about -0.75 V exhibited the corroding Cr plating itself, and those of about -0.4 V were derived from corroding the steel substrate. And also, the corrosion currents of the Cr plating were much higher than that of the Al₂O₃/ Ti-Al coating. These results indicate that the Cr plating is dissolved quickly in the non-oxidizing acid, and consequently would not contribute to the corrosion protection of the substrate.

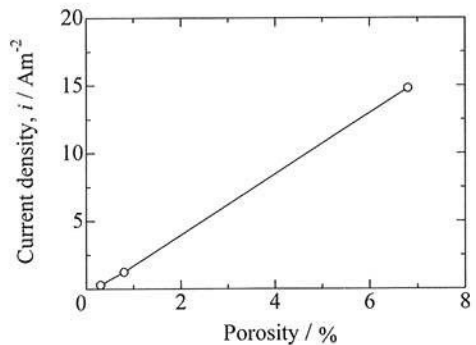


Fig.4 Effects of porosity in sprayed coatings on corrosion current in 1 N H₂SO₄ solution; Ti-Al coating, Ti coating, Al coating on steel substrate.

3.3 Oxidizing acid HNO_3

The rest potential of the Al_2O_3 / Ti-Al coating was slightly negative than that of the single Al_2O_3 coating in the HNO_3 solution (Table 1). And the quantitative analysis of metals in the HNO_3 solution after the polarization measurement showed that the concentrations were Al 0.51 ppm, Ti 0.01 ppm and Fe 0.04 ppm, consequently the Al phase in the coating dissolved to afford cathodic protection to the substrate. As for the Cr plating, the corrosion potential was electropositive of -0.3 V, and the corrosion current was much lower than that of the Al_2O_3 / Ti-Al coating. That is, the corrosion resistance of the Cr plating was superior to the Al_2O_3 / Ti-Al coating in the HNO_3 solution.

4. Conclusion

The protection mechanism of the Al_2O_3 / Ti-Al coating to the steel substrate from corrosion is identified to be the combination of the cathodic and barrier protection. This combination of protections

would perform to prevent the substrate from corrosion in the NaCl, the HCl, the H_2SO_4 and the HNO_3 solution.

Corrosion protection ability of the Al_2O_3 / Ti-Al coating was much superior to that of the Cr plating except in the HNO_3 solution. The Al_2O_3 / Ti-Al coating would be usable as a substitution for the Cr plating in various environment.

References

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