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Resistance of Thermal-Sprayed Duplex Coating Composed of Aluminum and 80Ni-20Cr Alloy against Aqueous Corrosion

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The development of corrosion-resistant sprayed coatings without sealing is required to increase the reliability of the thermal spray coating method and to expand the field of application for wet corrosion environments. The conventional wire flame-sprayed aluminum coating on steel without sealing has poor resistance against aqueous corrosion and has restricted practical use. A duplex coating composed of sprayed aluminum on an 80Ni-20Cr alloy undercoat exhibited sufficient resistance in a hot, near-neutral aqueous environment through a trial use in a vegetable oil process. In this paper, the mechanism of corrosion resistance of the duplex coating is investigated by electrochemical polarization measurements and electron probe microchemical analysis (EPMA) to examine the individual role of each layer and the change of the microstructure with time.

Keywords 80Ni-20Cr alloy, aluminum, aqueous corrosion, duplex coating, polarization, wire flame spraying

1. Introduction

Thermal spray coating materials to prevent aqueous corrosion, which can be produced by conventional on-site thermal spraying, have been developed by using stainless alloys[1] and titanium[2] combined with resin sealing. Such a barrier-type coating containing organic resins, however, is limited to use at ambient temperature and is not adopted under high-temperature conditions.

On the other hand, sprayed coatings, which do not act as barrier films, consist of sacrificial anode metals, such as aluminum, zinc, or Al-Zn alloy. The mechanism of protection is attributed to the electrochemical cathodic protection, and superior performance is obtained under an atmospheric corrosion environment, especially with post-treatment of sealing or painting.[3,4] Such a coating without any post-treatment, however, does not always show superior resistance in aqueous corrosion environments with chlorides,[4,5] and/or at an elevated temperature,[3] or under cavitation conditions,[6] especially for long exposure times experienced in practice.

The protective effect of aluminum sprayed over a sprayed 80Ni-20Cr alloy continued for a period of over 10 years in a near-neutral aqueous environment at an elevated temperature <120 °C in the vegetable oil extraction process has been reported.[7] The protection effect of the sprayed aluminum on the duplex coating was estimated to be due to both the electrochemical effect and the sealing effect against pores of the sprayed 80Ni-20Cr alloy layer, but details of the mechanism are not clear.

In this paper, the individual behavior of the components of the duplex coating composed of sprayed aluminum and 80Ni-20Cr alloy were measured electrochemically, and the protection mechanism was determined in detail, focusing on the function of each layer and the change of its microstructure with time.

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2. Experimental Procedure

The coating used in the electrochemical investigations was prepared by wire flame spraying using METCO 12E equipment (Sulzer Metco, Tokyo, Japan) on a blasted carbon steel substrate, $100 \times 50 \times 3$ mm, with wires of 80Ni-20Cr alloy, and aluminum, 3.1 mm in diameter. The chemical composition of the wires and the spraying parameters are shown in Table 1 and 2, respectively. The thickness of the sprayed layers was controlled from 100 to 150 μm for 80Ni-20Cr alloy and 200 to 250 μm for aluminum. The test electrodes were cut to a rectangle geometry, soldered to a lead wire, and mounted with an epoxy resin, except for an exposed area of 10×20 mm.

Some measurements were conducted by using the detached films after spraying onto an un-grit-blasted steel surface. Solid metals of the related materials were also tested to enable a comparison with the sprayed specimens.

Electrochemical measurements were conducted in a model solution simulated to the process liquor in the vegetable oil extractor.[7] Analytical results of the process liquor and composition of the modeled solution are listed in Table 3. Based on the analytical data, the model solution was prepared with potassium acetate, magnesium hydrogen-phosphate, calcium hydrogen-phosphate, potassium lactate, potassium sulphate, and hydrochloric acid.

Anodic polarization characteristics were measured in the model solution under boiling conditions. Potentiodynamic polarization with a sweep rate of 20 mV/min was adopted. Prior

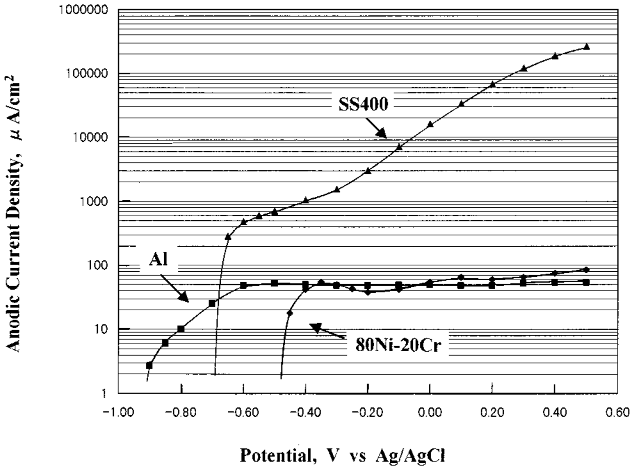

Fig. 1 Anodic polarization curves of the solid aluminum, 80Ni-20Cr alloy, and the steel substrate in the boiling model solution

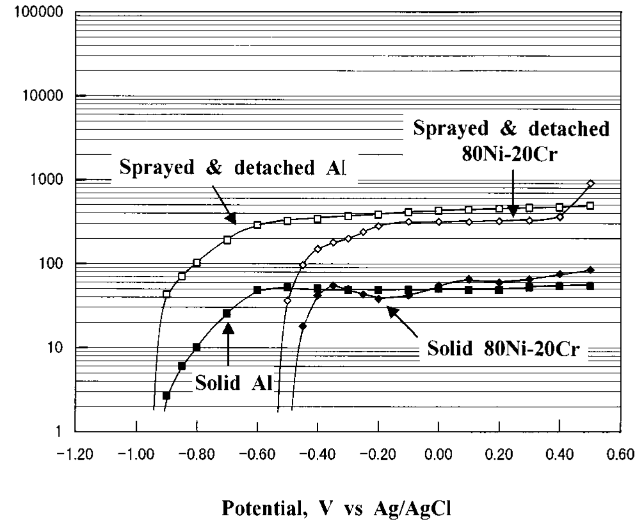

Fig. 2 Influence of thermal spraying on the anodic polarization curve of aluminum and 80Ni-20Cr alloy compared with the original solid material

Table 1 Chemical composition of the spraying materials (mass%)

Material	Ni	Cr	Al	Fe	C	Si	Mn
Ni-Cr alloy	77.75	19.55	…	0.83	0.035	1.16	0.30
Al	…	…	99.80	0.10	…	0.08	…

Table 2 Spraying parameters

	Fuel gas pressure (MPa)			Flow rate (m³/h)			Stand-off distance (mm)
	O_2	C_2H_2	Air	O_2	C_2H_2	Air	
Al	0.25	0.10	0.45	1.79	1.06	0.73	120–150
80Ni-20Cr	0.23	0.11	0.42	1.85	1.06	0.70	120–150

Table 3 Composition of the process liquor and the model solution (ppm)

Composition	Process liquor	Model solution
PH	6.1	7.4
P	90	148
Fe^{2+}	40	…
Mg^{2+}	60	60
Ca^{2+}	30	30
K^+	500	1200
Cl^-	8	14
SO_4^{2-}	130	132
Lactate	1740	1740
Acetate	530	530
Succinate	60	…
Formate	40	…

to the polarization, the spontaneous corrosion potential was meas-ured for 1 to 2 h, until it reached a steady-state rest potential.

Changes in the electrochemical characteristics, the surface property, and the microstructure of the exposed duplex coating were also determined in comparison to the as-sprayed film, by measuring anodic polarization, surface roughness, and EPMA elemental mapping. The surface roughness was measured by the stylus tester SE-2300 (Kosaka Kenkyusho Co., Tokyo, Japan).

3. Results and Discussion

3.1 Basic Corrosion System

In order to understand the basic corrosion system of the materials and the environment, anodic polarization curves of each solid metal, that is, carbon steel (SS400), 80Ni-20Cr alloy, and aluminum, were measured (Fig. 1).

The spontaneous potential of SS400 is at −0.65 V (versus Ag/AgCl), which is similar to its reversible potential. Anodic polarization from the spontaneous potential causes active dissolution, and the corrosion current estimated by the Tafel extrapolation method is about 300 μA/cm^2.

The spontaneous potential of aluminum is −0.9 V, which is sufficiently less noble than that of SS400 and for cathodic protection. On the other hand, 80Ni-20Cr alloy may also be protective because of its stable passive behavior if the sprayed film is a barrier type of coating.

The anodic polarization behavior of aluminum shows also a passive dissolution, which is almost the same as that of 80Ni-20Cr alloy.

3.2 Deterioration of Materials by Flame Spraying

The effect of the flame spraying process on the deterioration of sprayed materials of 80Ni-20Cr alloy and aluminum was assessed by polarization measurements. Polarization curves of the detached film after spraying, which was chosen to eliminate the effect of the steel substrate, are shown in Fig. 2 and compared to the corresponding solid metals.

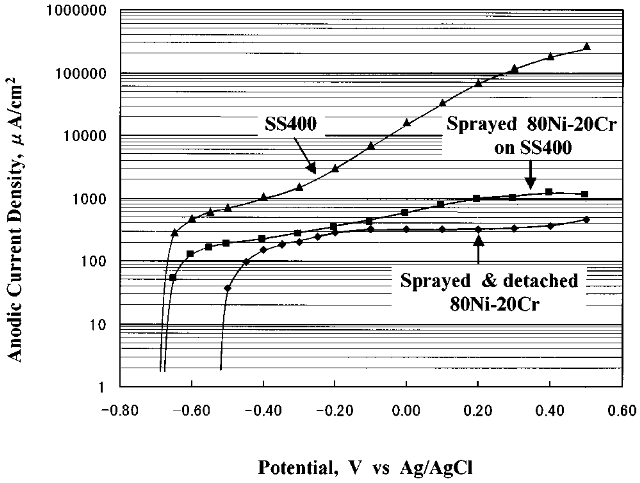

Fig. 3 Anodic polarization curve of the sprayed 80Ni-20Cr alloy on the steel substrate, compared with those of the detached film and of the steel

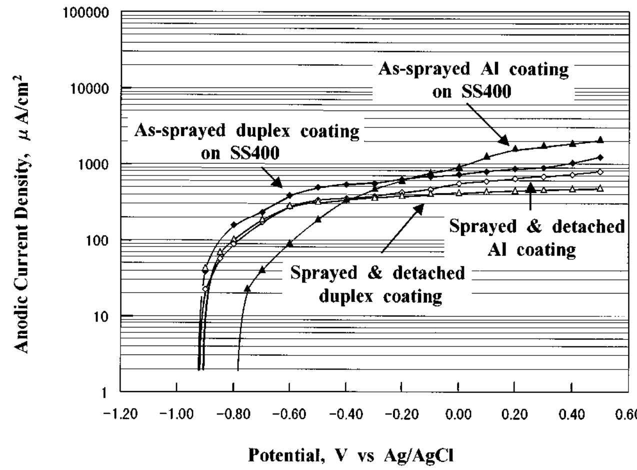

Fig. 5 Comparison in anodic polarization curves of the duplex coating and the aluminum single layer coating between those with substrate (as-sprayed) and without substrate (detached)

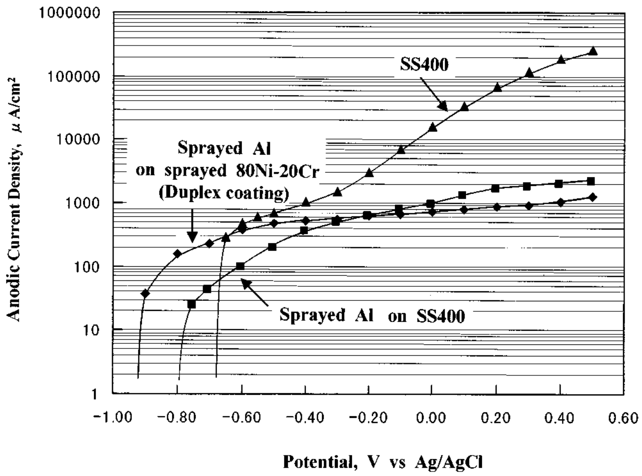

Fig. 4 Comparison in the anodic polarization curve of aluminum spraying between those sprayed on the steel substrate directly and on the undercoat layer of the sprayed 80Ni-20Cr alloy (duplex coating)

The figure indicates that the spray procedure does not change the spontaneous corrosion potential and increases the anodic passive current density by an order of magnitude. The increase of the anodic current may be explained by increasing the actual surface area with increasing surface roughness and open pores in the sprayed layer.

The polarization characteristics suggest that flame spraying has caused little deterioration, in at least the electrochemical aspects, for both the sprayed aluminum and 80Ni-20Cr alloy.

3.3 Preventive Effect of Sprayed 80Ni-20Cr Alloy

The effect of single layer spraying of 80Ni-20Cr alloy on the substrate was evaluated by comparing its polarization behavior with those of the detached film and the steel substrate, the results of which are shown in Fig. 3. The sprayed 80Ni-20Cr alloy on the steel causes no change on the spontaneous corrosion potential compared with the bare steel, and it decreases the dissolution current to a level between the bare substrate and the detached film. These facts suggest that the anodic behavior of the 80Ni-20Cr alloy sprayed steel is almost equivalent to that of the bare steel, except that dissolution is restricted only to the defects and pores in the sprayed 80Ni-20Cr alloy layer. Single layer spraying of the 80Ni-20Cr alloy, therefore, has little effect for preventing the corrosion of the steel substrate, unless its defects and pores are sealed by a post-treatment.

3.4 Effect of Aluminum on Single Layer Spraying and on Duplex Coating

The effects of the sprayed aluminum on the carbon steel and on the sprayed 80Ni-20Cr alloy are shown in Fig. 4. Each spontaneous potential of the duplex spraying, ca. −0.9 V, and the single layer aluminum spraying, ca. −0.8 V, is less noble than that of the steel, ca. −0.65 V, which demonstrates a potential difference in the cathodic protection in both cases. The potential of the duplex coating, however, is less noble (at about 100 mV) than that of the single layer spraying and is almost the same as that of solid aluminum and of the detached aluminum film.

The results suggest that the effect of cathodic protection on the duplex coating is more complete for steel corrosion, and less consumptive for the sacrificial aluminum, than that for direct aluminum spraying.

3.5 Role of the 80Ni-20Cr Alloy Undercoat Layer in Duplex Coating

In order to clarify the change of the sacrificial load for the sprayed aluminum by the existence of the 80Ni-20Cr alloy undercoat layer, anodic polarization behaviors of both coatings are compared with those with the substrate (as-sprayed) and without the substrate (detached film) (Fig. 5).

The electrochemical behavior of the as-sprayed duplex coating is almost duplicated by the detached film. This behavior con-

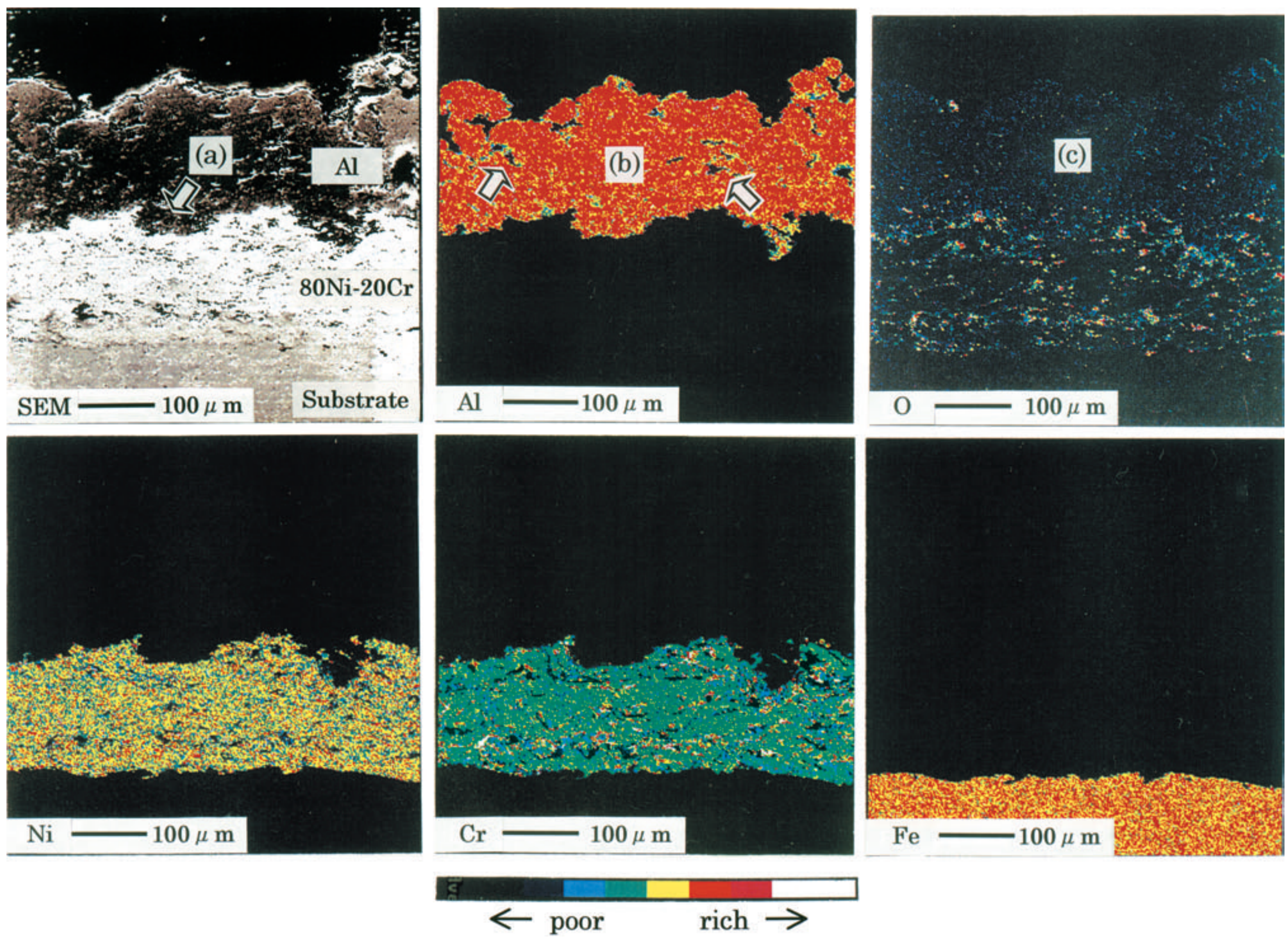

Fig. 6 SEM image and EPMA elemental mapping for Al, O, Ni, Cr, and Fe on the as-sprayed duplex coating

Table 4 Surface roughness change of the aluminum top coat on the duplex coating after long-term exposure in the field (μm) (Ry: maximum peak-to-valley height, and Rz: average peak-to-valley height)

Condition	Ry Measured	Ry Average	Rz Measured	Rz Average
As-sprayed	113.2	…	90.4	…
	127.3	…	106.1	…
	113.6	…	91.8	…
	138.1	126.3	100.9	100.4
	124.9	…	91.7	…
	150.0	…	125.3	…
	117.3	…	96.3	…
After 10 years of exposure	100.2	…	71.2	…
	106.3	…	68.3	…
	76.8	96.5	62.9	61.2
	83.6			
	94.7	…	44.2	…
	112.9	…	69.6	…
	100.9	…	63.2	…

trasts with the anodically shifted potential and an increased anodic dissolution current, which is observed for the as-sprayed aluminum coating compared to that of the detached aluminum film. These facts confirm that the 80Ni-20Cr alloy layer inhibits the polarization effects by the substrate and decreases the excess consumption of aluminum, thereby prolonging the lifetime of the duplex coating.

3.6 Change of Aluminum Layer of Duplex Coating after Long-Term Exposure

The surface roughness changes of the duplex coating before and after 10 years exposure in the practical field are shown in Table 4. The result shows that the surface of the sprayed aluminum of the duplex coating was changed to become smoother, and the porous structure of the sprayed aluminum became sealed with the dissolved aluminum after long exposure period.

Scanning electron microscope (SEM) images and the elemental mapping by EPMA of the as-sprayed and the exposed specimens are shown in Figs. 6 and 7, respectively. The results indicate the following.

- The interface between the sprayed aluminum and the sprayed 80Ni-20Cr alloy shows a clean structure, which would result in strong adhesion in the as-sprayed specimen shown as Fig. 6(a), and this is maintained for a long exposure time, as indicated in Fig. 7(d).
- Voids in the as-sprayed aluminum layer (arrows in Fig. 6b) are filled with aluminum oxide or hydroxide after exposure

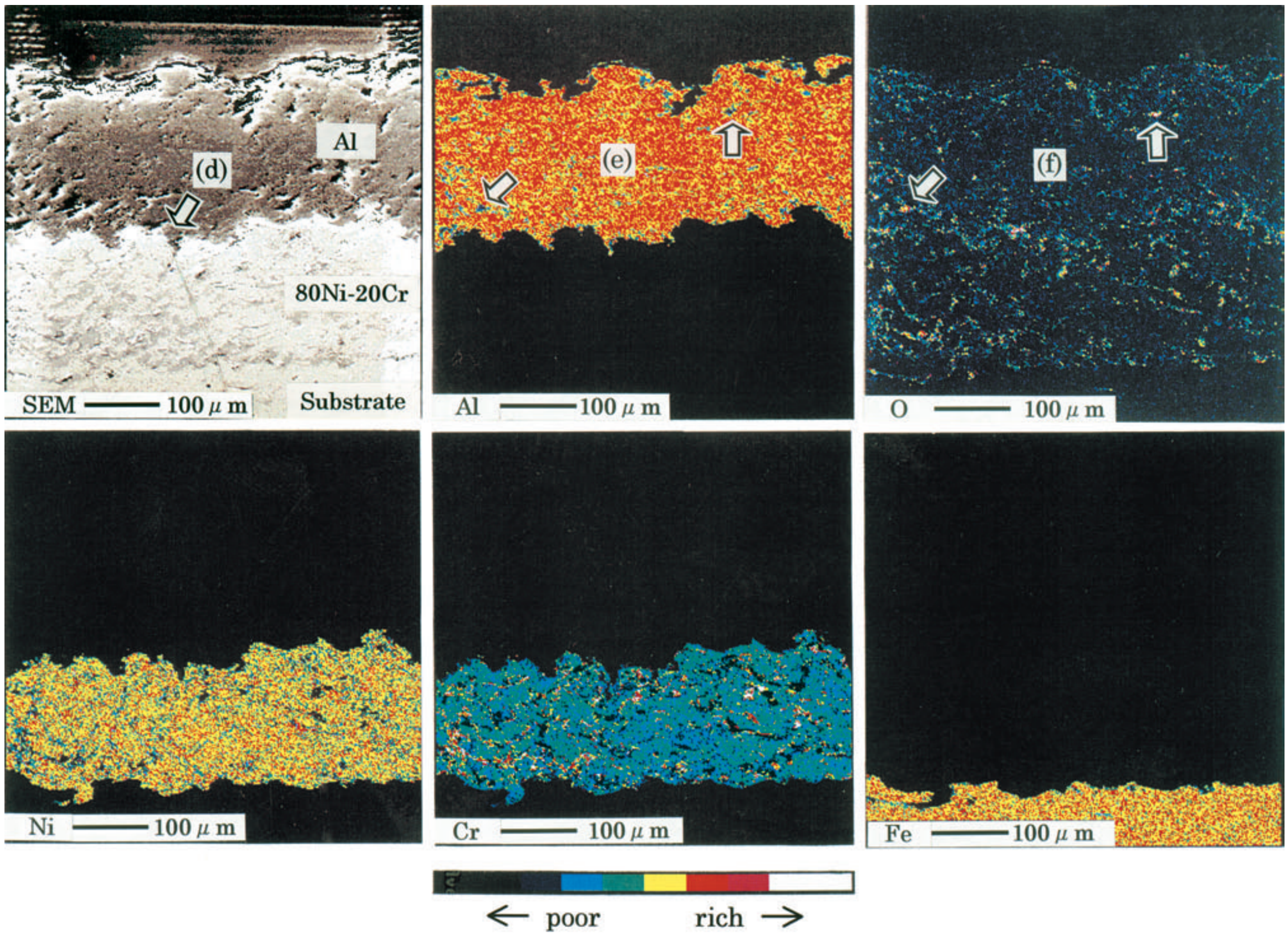

Fig. 7 SEM image and EPMA elemental mapping for Al, O, Ni, Cr, and Fe on the duplex coating after long-term exposure in field

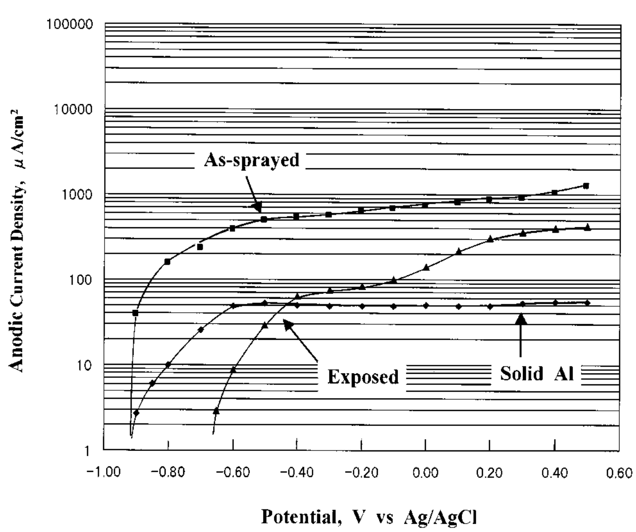

Fig. 8 Influence of long-term exposure in the field on the anodic polarization curves of the duplex coating, compared with the solid aluminum

(Fig. 7e). This is also indicated by an increase of oxygen in the sprayed aluminum by comparing Fig. 6(c) with Fig. 7(f). This phenomenon is similar to the sealing of anodized aluminum by steam or hot water.[8]

- No change is observed in the undercoat of the sprayed 80Ni-20Cr alloy layer. Penetration of aluminum to the undercoat layer is not detected.

The anodic polarization characteristic of the exposed duplex coating after 10 years of service is shown in Fig. 8, compared with the as-sprayed duplex coating and the solid aluminum. The long-term exposure decreased the anodic dissolution current toward the level of solid aluminum and shifted the corrosion potential to a more noble potential such as ca. −0.7 V. The change of the electrochemical behavior suggests that the surface activity of the sprayed aluminum on the duplex coating decreases to a more stable condition. Selective dissolution of the active sites and filling of the pores and voids with the dissolved aluminum oxide or hydroxide should be expected. The change of the structure resembles the sealing of micropores in anodized aluminum oxide.[8]

4. Conclusions

The excellent performance of the duplex coating composed of sprayed aluminum on sprayed 80Ni-20Cr alloy in a hot, near-neutral aqueous environment can be explained as follows.

- The fundamental mechanism of corrosion protection is due to cathodic protection by the sacrificial anode behavior of the aluminum sprayed as the top coat.
- The role of the undercoat layer of the sprayed 80Ni-20Cr alloy is to decrease the surface area of the steel substrate to be protected and reduce the sacrificing load for the aluminum, and also to increase the adhesion of the aluminum top coat by its roughness.
- The inhibited dissolution of the sprayed aluminum altered its surface to a smooth and stable character. This is similar to the sealing of micropores in anodized aluminum oxide and prolongs the lifetime of the duplex coating.

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