

# Long-term corrosion resistance of Al–Ni-plated material and Al-plated material in molten carbonate environment

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## Abstract

Al–Ni-plated material, which was produced by Ni and Al electroplating on a Type 310S stainless steel substrate followed by heat-treating at 1023 K, has been developed for the wet-seal material of MCFC. In order to compare the corrosion resistance of Al–Ni-plated material with that of Al-plated material, which simulated the Al-sprayed material presently used as wet-seal material, an immersion test was carried out in molten carbonate in 70% air–30% CO<sub>2</sub> gas at 923 K for 14,500 h. Both Al–Ni-plated material and Al-plated material showed good corrosion resistance during this test period. From the analyses of the surface, in cross-section, of these materials after the test, however, it was confirmed that a large amount of Al in Al–Ni-plated material was retained as an Al–Ni intermetallic compound under the LiAlO<sub>2</sub> layer, while the Al in Al-plated material tended to diffuse from the surface into the substrate during the test. It is suggested that the lifetime of the Al–Ni-plated material is longer than that of the Al-plated material, since Al–Ni intermetallic compounds in the Al–Ni-plated material provide a supply of Al to the LiAlO<sub>2</sub> layer, the stability of which leads to prolonged corrosion resistance of the wet-seal material to molten the carbonate. Therefore, it is expected that the Al–Ni-plated material maintains a higher corrosion resistance, compared with the present material used for the wet-seal area of MCFC. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** Molten salt; Corrosion; Intermetallic compound; Plating

## 1. Introduction

Since the wet-seal area of the Molten Carbonate Fuel Cell (MCFC) separator is exposed to a highly corrosive environment, a high-corrosion resistance is required for the wet-seal material. It is well-established that surface-treated materials, prepared by Al diffusion treatment or Al spray-

ing on stainless steel, are used [1,2] for the wet-seal material. Even these surface-treated materials, however, do not have sufficient corrosion resistance as a wet-seal material.

We have investigated Al–Ni-plated material, which was produced by electroplating of Ni and Al on stainless steel followed by heat treatment. It was clear that a LiAlO<sub>2</sub> layer, which has a high-corrosion resistance against molten carbonate, was formed on the Al–Ni intermetallic compound in this material during the immersion test [3,4].

In this study, emphasis was placed on a comparison of the long-term corrosion resistance of Al–Ni-plated material with that of Al-plated material which simulated the

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Table 1  
Al–Ni-plated materials and Al-plated materials used in immersion test

	Substrate	Plating thickness ( $\mu$ -mm)		Condition of heat treatment	
		Ni	Al		
Al–Ni-plated material	Type A	Type 310S	5	15	1023 K, 1 h, in Ar gas
	Type B	Type 310S	5	10	
Al-plated material	Type E	Type 310S	–	15	1023 K 1 h, in Ar gas
	Type F	Type 316	–	15	

Table 2  
Chemical compositions of the substrate (mass%)

	C	Si	Mn	P	S	Ni	Cr	Mo
Type 310S	0.03	0.46	0.39	0.016	0.001	20.36	24.77	–
Type 316	0.06	0.70	1.75	0.030	0.001	12.86	16.55	2.35

Al-sprayed material used for wet-seal material in molten carbonate environments.

## 2. Experimental procedure

### 2.1. Specimens

Four types of specimens were prepared in order to examine the effect of thickness of electroplated Al and substrate on the surface structure. Details of specimens are shown in Table 1, and chemical compositions of the substrate are shown in Table 2. Both Type A and Type B are Al–Ni-plated materials, which were produced by electroplating Ni and Al on the stainless steel substrate followed by heat treatment at 1023 K. Both Type E and Type F are Al-plated materials, which were produced by electroplating Al on the stainless steel substrate followed by heat treatment at 1023 K. The fabrication of Al–Ni-plated material and Al-plated material is shown in Fig. 1.

Fig. 2 shows schematic illustrations of the diffused layer formed on Al–Ni-plated materials and Al-plated materials before the immersion test. There is a definite difference between the diffused layer of the Al–Ni-plated materials and that of the Al-plated materials. In this work,

“diffused layer” is defined as the sum total of the Al–Ni intermetallic compound layer (Al–Ni layer) and the diffusion layer of Fe–Cr or Fe–Ni containing Al.

### 2.2. Immersion test

Test pieces were 25-mm wide and 35-mm long. They were placed in an alumina-crucible filled with 62 mol%  $\text{Li}_2\text{CO}_3$ –38 mol%  $\text{K}_2\text{CO}_3$  then, kept in 70% air–30%  $\text{CO}_2$  gas at 923 K for a predetermined time. This condition simulated the cathodic environment of the MCFC.

### 2.3. Analysis of the surface

The test pieces, after the immersion test, were analyzed in surface cross-section by SEM, EPMA, and X-ray diffraction.

## 3. Results and discussion

SEM images of the cross-section of the surface layer formed on Al–Ni-plated materials before and after immersion tests at 923 K are shown in Fig. 3, and those of Al-plated materials are shown in Fig. 4. Each material showed good adhesion with no corrosion in the diffused layer or the substrate. There were voids in the interface of the diffused layer and substrate of each material after the test.

Fig. 5 shows EPMA line analyses for the cross-sections of the surfaces of the Al–Ni-plated materials and the Al-plated materials after immersion testing for 14,500 h. In this figure, the observed area of O peaks were indicated as

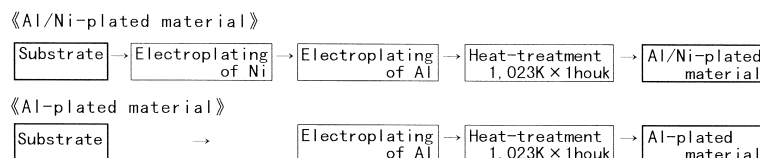


Fig. 1. Fabrication of Al–Ni-plated material and Al-plated material.

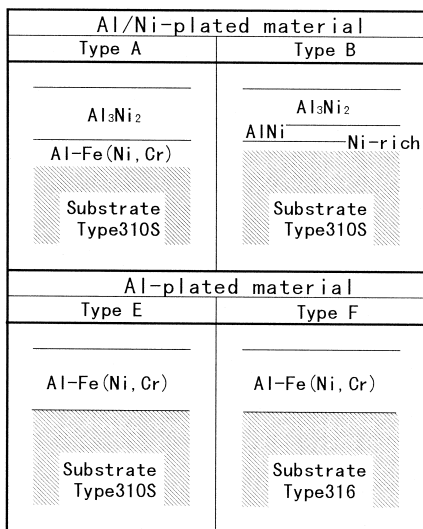


Fig. 2. Schematic illustration of cross-sectional structure of Al–Ni-plated materials before and after immersion test at 923 K for 14,500 h.

“Oxide”. An Al-oxide layer was formed on the surface of each material. A large amount of Al was retained in the Al–Ni layer, as observed for Al–Ni-plated materials, even after immersion testing for 14,500 h. On the other hand, a large amount of Al tended to diffuse from the surface into the substrate in the Al-plated materials.

The change in the thickness of the diffused layer for each material is shown in Fig. 6. In the Al–Ni-plated materials, both Type A and Type B, the thickness of the diffused layer remained constant from 4000 to 14,500 h. The value of Type A is thicker than that of Type B.

In the Al-plated materials, both Type E and Type F, the thickness of the diffused layer gradually increased with immersion time. The value of Type E is thinner than that of Type F throughout the test.

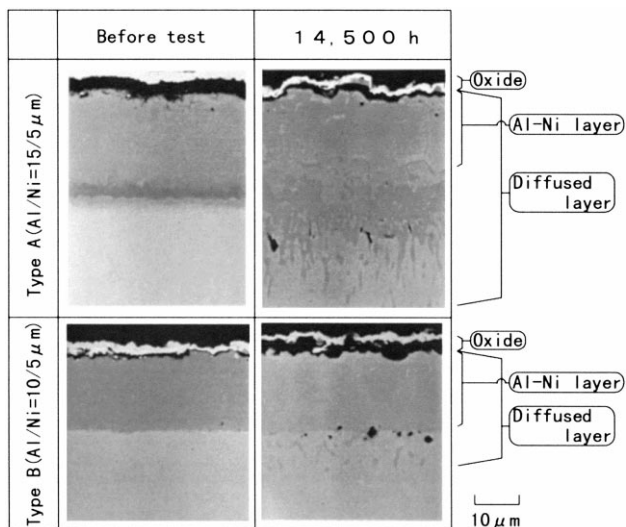


Fig. 3. SEM images of cross-sections of the surface layer of Al–Ni-plated materials before and after immersion test at 923 K at 14,500 h.

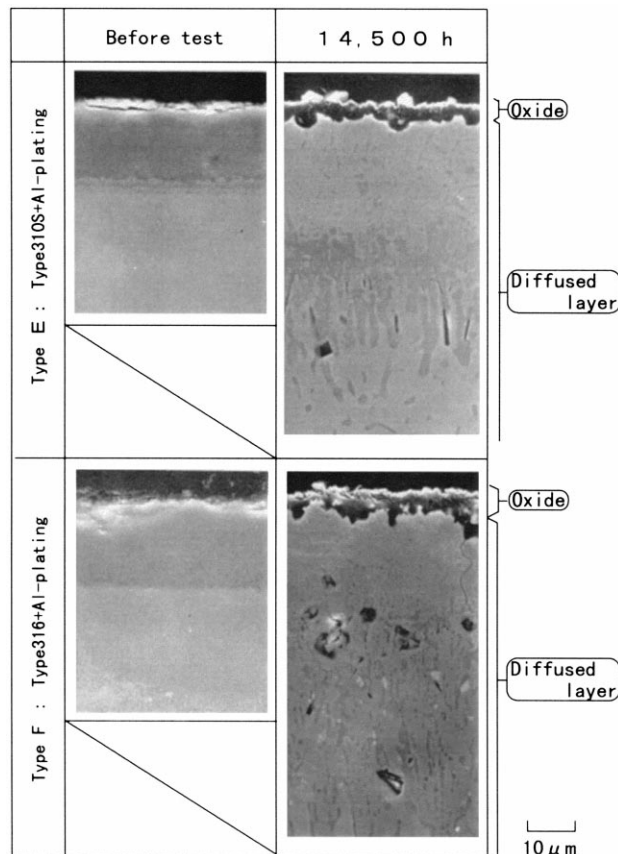


Fig. 4. SEM images of cross-sections of the surface layer of Al-plated materials before and after immersion test at 923 K for 14,500 h.

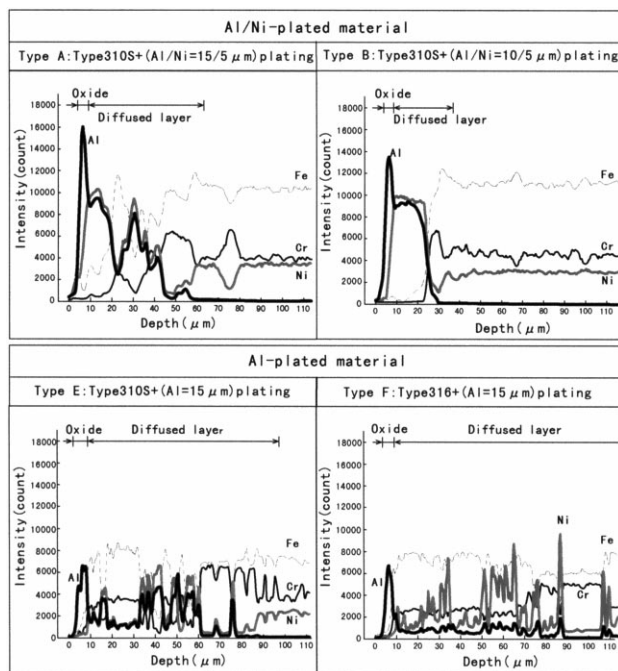


Fig. 5. EPMA line analyses for the cross-sections of the surface of Al–Ni-plated materials and Al-plated materials after immersion test at 923 K for 14,500 h.

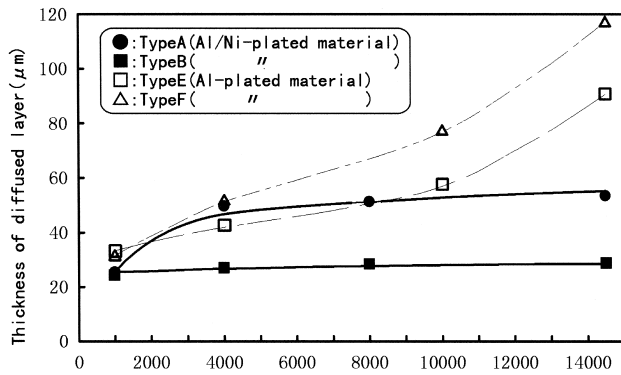


Fig. 6. Change of thickness of the diffused layer in Al–Ni-plated materials and Al-plated materials during immersion test.

X-ray diffraction patterns of the surface of each material after immersion testing for 14,500 h are shown in Fig. 7.  $\text{LiAlO}_2$  and Al–Ni diffraction peaks were observed on the surface of Al–Ni-plated materials.  $\text{LiAlO}_2$  and Fe–Cr diffraction peaks were observed on the surface of Al-plated materials.

The schematic illustration of the diffused layer after immersion testing for 14,500 h are shown in Fig. 8. From the results of SEM, EPMA, and X-ray diffraction, in the

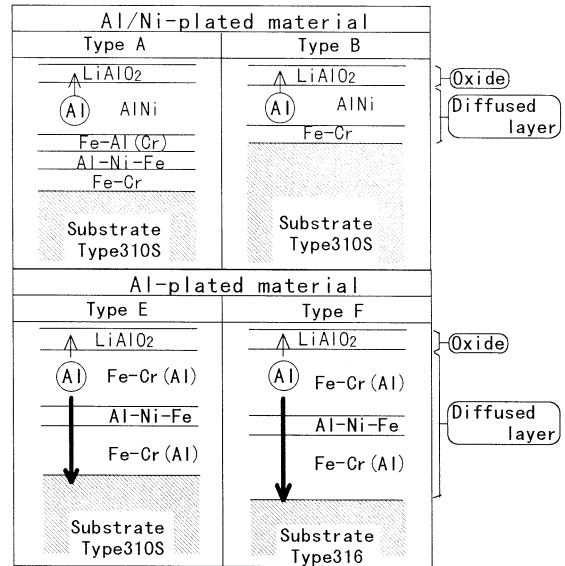


Fig. 8. Schematic illustration of the diffused layer after immersion test at 923 K for 14,500 h.

Al–Ni-plated materials, an Al–Ni intermetallic compound layer was retained in the diffused layer during immersion testing and diffusion of Al into the substrate was suppressed. Since the diffusion layer of Type A is thicker than

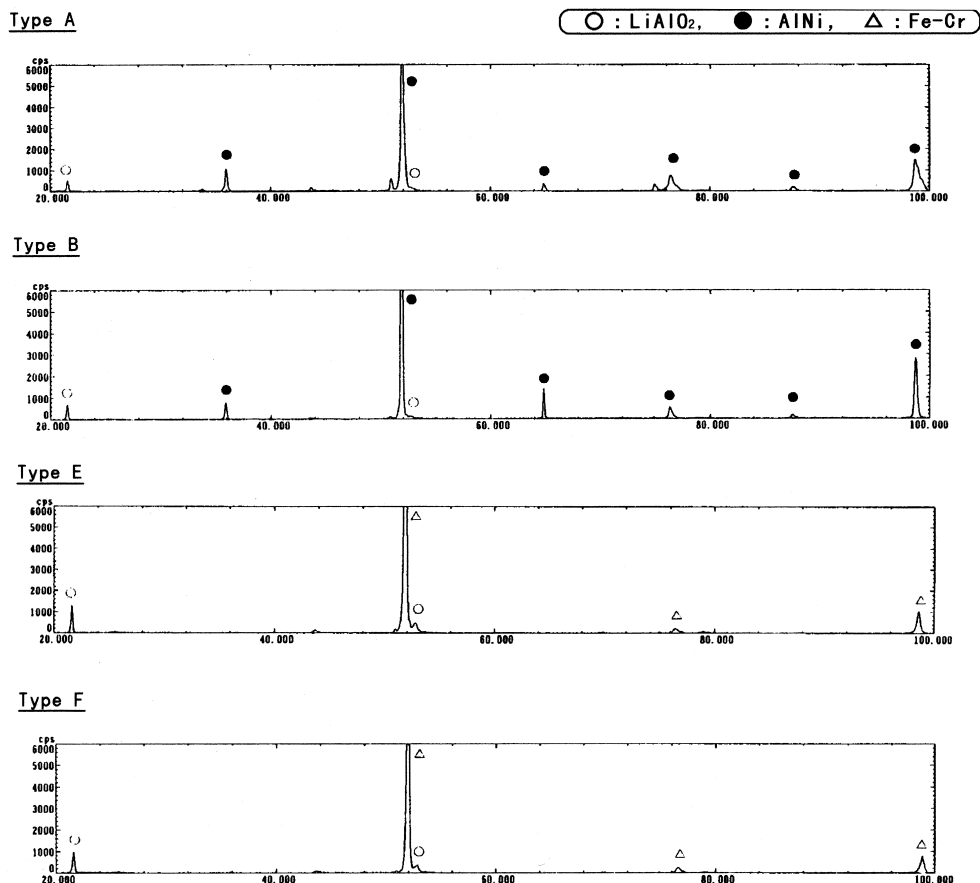


Fig. 7. X-ray diffraction patterns of the surface of Al–Ni-plated materials and Al-plated materials after immersion test at 923 K for 14,500 h.

that of Type B, the difference in the thickness of electroplated Al may be connected with the stability of the Al–Ni intermetallic compound layer. On the other hand, in Al-plated materials, Fe–Cr–Al or Fe–Ni–Al alloy layers were formed and Al diffused through the alloy layer into the substrate during the test. Since the diffused layer of Type E is thinner than that of Type F, the difference in the substrate may be connected with the diffusion rate of Al.

A  $\text{LiAlO}_2$  layer is necessary to maintain a high-corrosion resistance against molten carbonate. It is considered that since the Al–Ni intermetallic compound layer formed on the surface of the Al–Ni-plated material provides a supply of Al to the  $\text{LiAlO}_2$  layer, the corrosion resistance of the Al–Ni-plated material is maintained for a long time. It is also considered that since a large amount of Al diffused through the Fe alloy layers into the substrate in Al-plated material, the concentration of Al beneath the  $\text{LiAlO}_2$  is not sufficient to supply Al to the  $\text{LiAlO}_2$  layer. Therefore, it is suggested that the lifetime of the Al–Ni-plated material is longer than that of the Al-plated material which simulated the presently used material for the wet-seal area of the MCFC.

#### 4. Conclusions

From the results of comparisons of the long-term corrosion resistance of Al–Ni-plated material with that of Al-

plated material in immersion tests in molten carbonate at 923 K for 14,500 h, it can be affirmed that the lifetime of the Al–Ni-plated material is longer than that of the present material used for the wet-seal area of MCFCs.

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