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Estimation of the lifetime of Al/Ni-plated material for wet-seal area in molten carbonate fuel cells

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Abstract

Al/Ni-plated material, which is produced by electroplating of Ni and Al on a stainless-steel substrate followed by heat-treating at 750°C, has been investigated for the wet-seal material. In order to estimate the lifetime of the material, Type A and Type B were prepared, and immersion test in molten carbonate and heating test in air at various temperatures were carried out. Results of this study are summarized as follows. Two types of Al/Ni-plated material showed a good corrosion resistance against the molten carbonate at 650°C in 70% air/30% CO_2 for 14 500 h. In the accelerated heating test, Al concentration in the Al–Ni layer kept nearly constant after 10 000 h, but voids were observed at the Al–Ni layer/the substrate interface. It was found that the growth rate of void, which was calculated from the area fraction of voids observed at each temperature, was proportional to temperature. The log k decreased linearly with $1/T$, where k was a constant of the growth rate of voids. It was suggested that the lifetime of the Al/Ni-plated material is expected to be more than 40 000 h at 650°C in molten carbonate. © 1998 Elsevier Science S.A.

Keywords: Molten salt; Corrosion; Intermetallic compound; Plating

1. Introduction

Since a molten carbonate fuel cell (MCFC) separator is exposed to the highly corrosive environment of the wet-seal area, a high-corrosion resistant material is required for the wet-seal material. It is well known that surface-treated materials, such as Al diffusion treatment or Al spraying on stainless steel, are used [1,2] for the wet-seal material. However, even these surface-treated materials do not have sufficient corrosion resistance as a wet-seal material.

We have investigated Al/Ni-plated material, which is produced by electroplating of Ni and Al on stainless steel followed by heat treatment. The $LiAlO_2$ layer, which has a high corrosion resistance against molten carbonate, is established on an Al–Ni intermetallic compound formed on the surface of this material by the heat treatment [3].

In this study, emphasis was placed on an estimation of the lifetime of the Al/Ni-plated material as the separator, calculated from results of an immersion test and a heating test.

2. Experimental procedures

2.1. Specimens

Details of specimens are shown in Table 1, and chemical composition of the substrate is shown in Table 2. Two types of specimens were prepared in order to investigate the effect of thickness of electroplated Al on the surface structure. The process of making Al/Ni-plated material is shown in Fig. 1. Al/Ni-plated materials were produced by electroplating of Ni and Al on the stainless-steel substrate followed by heat treatment at 750°C.

Fig. 2 shows schematic illustrations for the microstructure of the diffused layer formed on Al/Ni-plated materials. Two specimens are clearly different in terms of microstructure of the diffused layer formed by heat treatment. In this paper, a definition of 'diffused layer' is

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Table 1

Al/Ni-plated materials used in immersion test and heating test

	Substrate	Plating thickness		Condition of heat treatment
		Ni (μm)	Al (μm)	
Type A	Type 310S	5	15	750°C, 1 h
Type B	Type 310S	5	10	750°C, 1 h

as follows: region of substrate where electroplated Al and Ni diffuse and also where the Al–Ni intermetallic compound layer (Al–Ni layer) formed on the surface of the material.

2.2. Immersion test

Test pieces were 20 mm wide and 50 mm long. They were put in an alumina crucible filled by 62 mol% Li_2CO_3/38 mol% K_2CO_3, then kept in 70% air/30% CO_2 at 650°C for the decided time. This environment simulates that of a cathode of MCFC.

2.3. Heating test

The dimension of the test pieces were 20 mm wide and 30 mm long. These specimens were oxidized in air at 650°C, 700°C, and 750°C.

2.4. Analysis of the surface of the tested pieces

The tested pieces of the immersion test and the heating test were analyzed in cross-section of the surface by scanning electron microscopy (SEM), electron probe microanalizer (EPMA), and X-ray diffraction.

Table 2

Chemical composition of the substrate (mass%)

	C	Si	Mn	P	S	Ni	Cr
Type 310S	0.06	0.80	1.03	0.015	0.003	19.68	25.67

3. Results and discussion

3.1. Immersion test

SEM images of the cross-section of the surface layer formed on Al/Ni-plated materials before and after immersion tests at 650°C are shown in Fig. 3. Al/Ni-plated materials showed good adhesion of the coated layer, and corrosion did not take place in the diffused layer and the substrate.

The schematic illustrations of the diffused layer before and after the immersion test are shown in Fig. 4. As a result of X-ray diffraction and X-ray photoelectron spectroscopy, it was found that an $LiAlO_2$ layer was formed on the surface of both Type A and Type B. It is considered that $LiAlO_2$ was formed by reaction of CO_3^{2-} ion, O^{2-} ion, and Li^+ ion in molten carbonate with Al contained in the material. The Al–Ni layer was formed under the $LiAlO_2$ layer; it was found that Al was concentrated at the surface after immersion test for 14 500 h.

Immersion-tested pieces were intentionally fractured for the purpose of observation of the surface layers. SEM images of the fractured surface are shown in Fig. 5. It is observed that all of the oxide layers were about 3 to 4 μm in thickness, which means that the thickness of the oxide

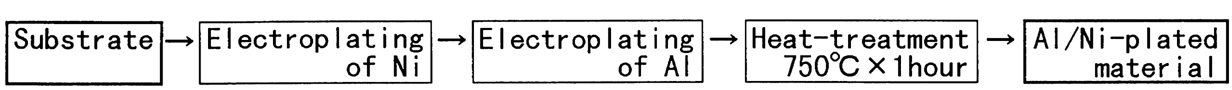

Fig. 1. Process of making Al/Ni-plated material.

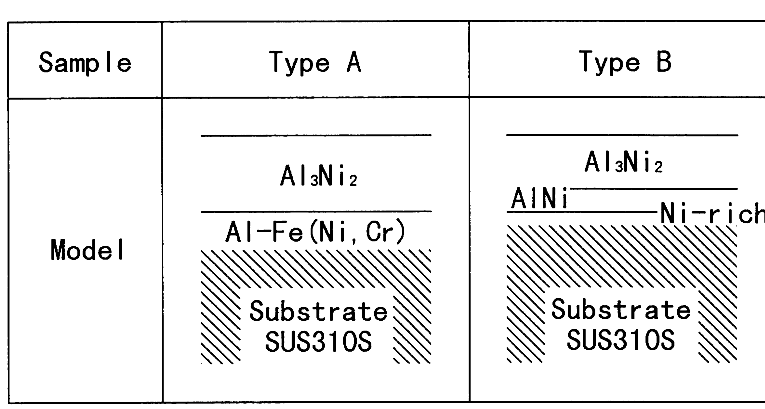

Fig. 2. Schematic illustration of cross-sectional structure of Al/Ni-plated materials.

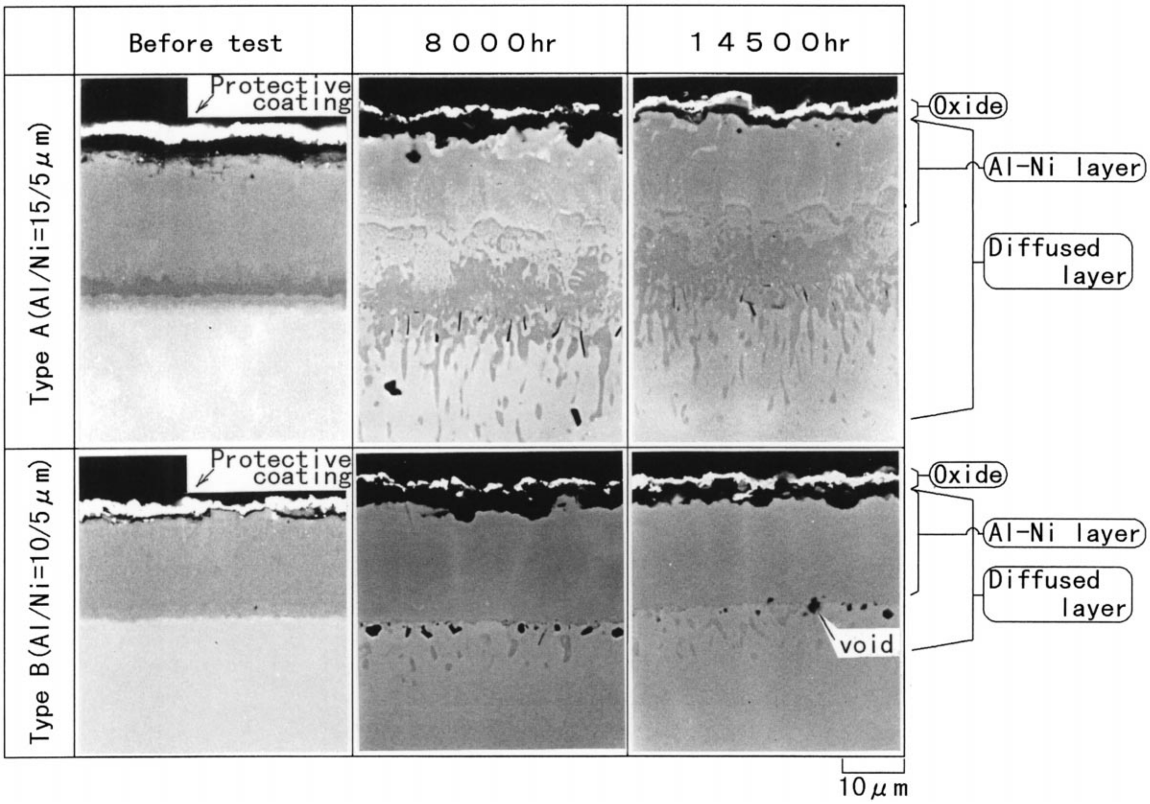

Fig. 3. SEM images of cross-section of the surface layer of Al/Ni-plated materials before and after immersion test at 650°C.

layer was kept constant up to 14 500 h in molten carbonate. Therefore, it can be clearly stated that Al/Ni-plated materials have an excellent corrosion resistance to molten carbonate for as long as 14 500 h because of the formation of the protective layer, $LiAlO_2$, on the surface of the materials.

3.2. Heating test

SEM images of the cross-section of the surface layer formed on Al/Ni-plated materials before and after heating tests are shown in Fig. 6. The surface layer and the diffused layer showed a good adhesion at each temperature for

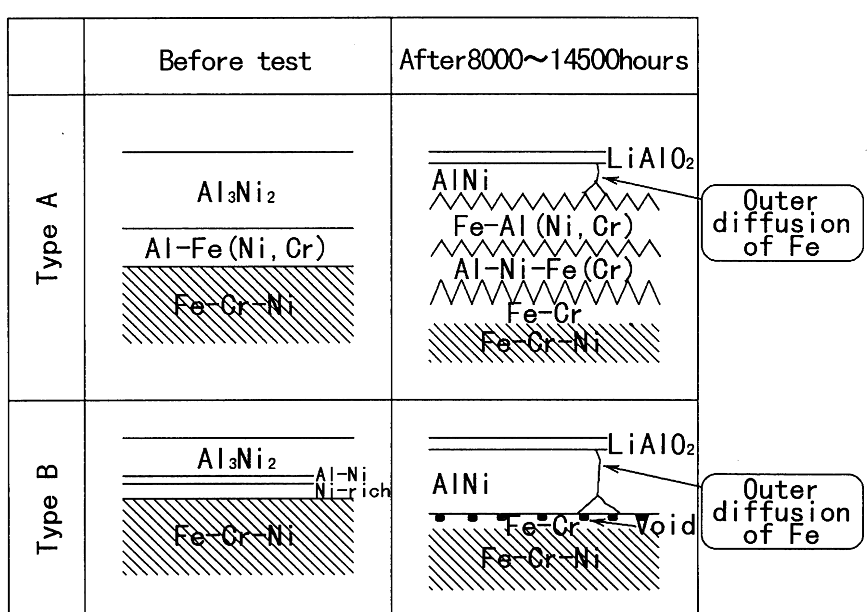

Fig. 4. Transition of surface structures of Al/Ni-plated materials before and after immersion test at 650°C.

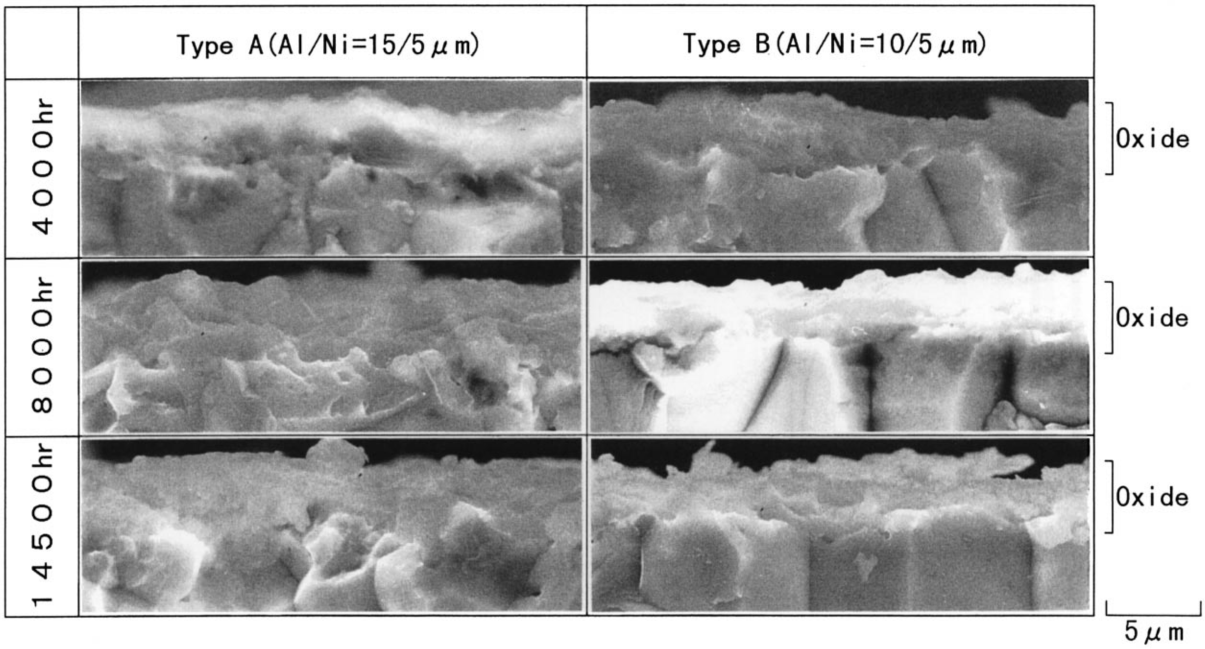

Fig. 5. SEM images of cross-section of the oxide of Al/Ni-plated materials after immersion test.

10 000 h. Voids were apparent in both Type A and Type B. While voids condensed just beneath the Al–Ni layer in Type B, voids were dispersed in substrate in Type A. As the voids formed in line at the Al–Ni layer/substrate interface in Type B, there is a possibility that the surface layer spalled after the longer heating period.

Characteristic X-ray images of elements in cross-section of the surface layer formed on the Al/Ni-plated materials after the heating test at 750°C for 10 000 h are shown in Fig. 7. The structure of the diffused layer after the heating test seemed very close to that of the immersion-tested piece. Taking results of X-ray diffraction and EPMA into consid-

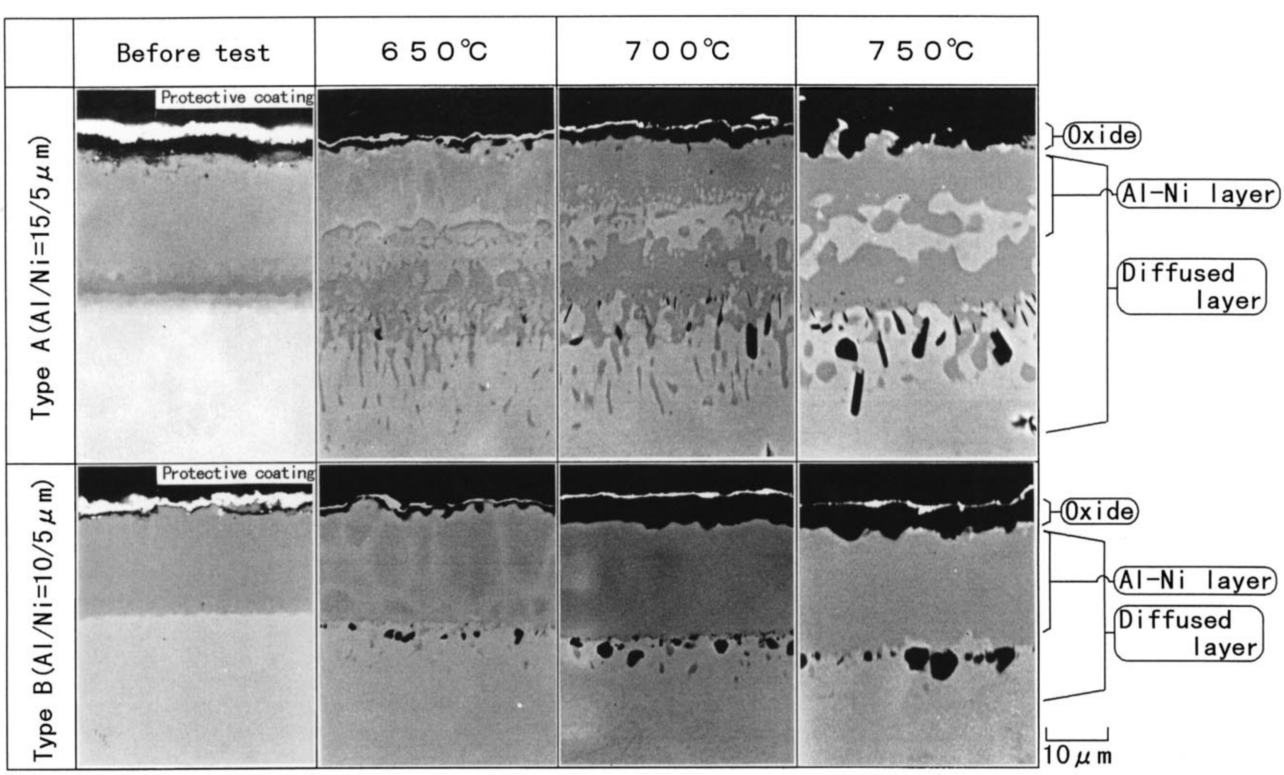

Fig. 6. SEM images of cross-section of the surface of Al/Ni-plated materials before and after heating test for 10 000 h.

eration, the surface layer was identified as Al_2O_3. The results of the heating test and the immersion test were close in terms of establishing Al-oxide, although the respective structure of Al-oxide was different.

3.3. Al-oxide layer of the surface of Al/Ni-plated material

It is important for the material to contain sufficient amounts of Al in the diffused layer for the purpose of keeping an excellent corrosion resistance to molten carbonate. As mentioned above, the structure of the layer after the heating test is similar to that after the immersion test in molten carbonate. Therefore, it is considered possible to predict the lifetime of the Al/Ni-plated material in molten carbonate from the results of the heating test, i.e. this test can be taken as an accelerated test of the immersion test at 650°C.

SEM images of cross-section of the surface layer of the Al/Ni-plated materials after the heating test are shown in Fig. 8. It appears that the thickness of the Al-oxide layer after the heating test at 650°C for 10 000 h (Fig. 8) and the one after the immersion test at 650°C for 8000 h (Fig. 5) were nearly equal, which means that the growth rates of the Al-oxide layer in the immersion test and the heating test were nearly equal.

Changes in concentration of elements in the Al–Ni layer as a function of time are shown in Fig. 9. The vertical axis indicates ratios of the peak intensities of Fe, Cr, Ni, and Al

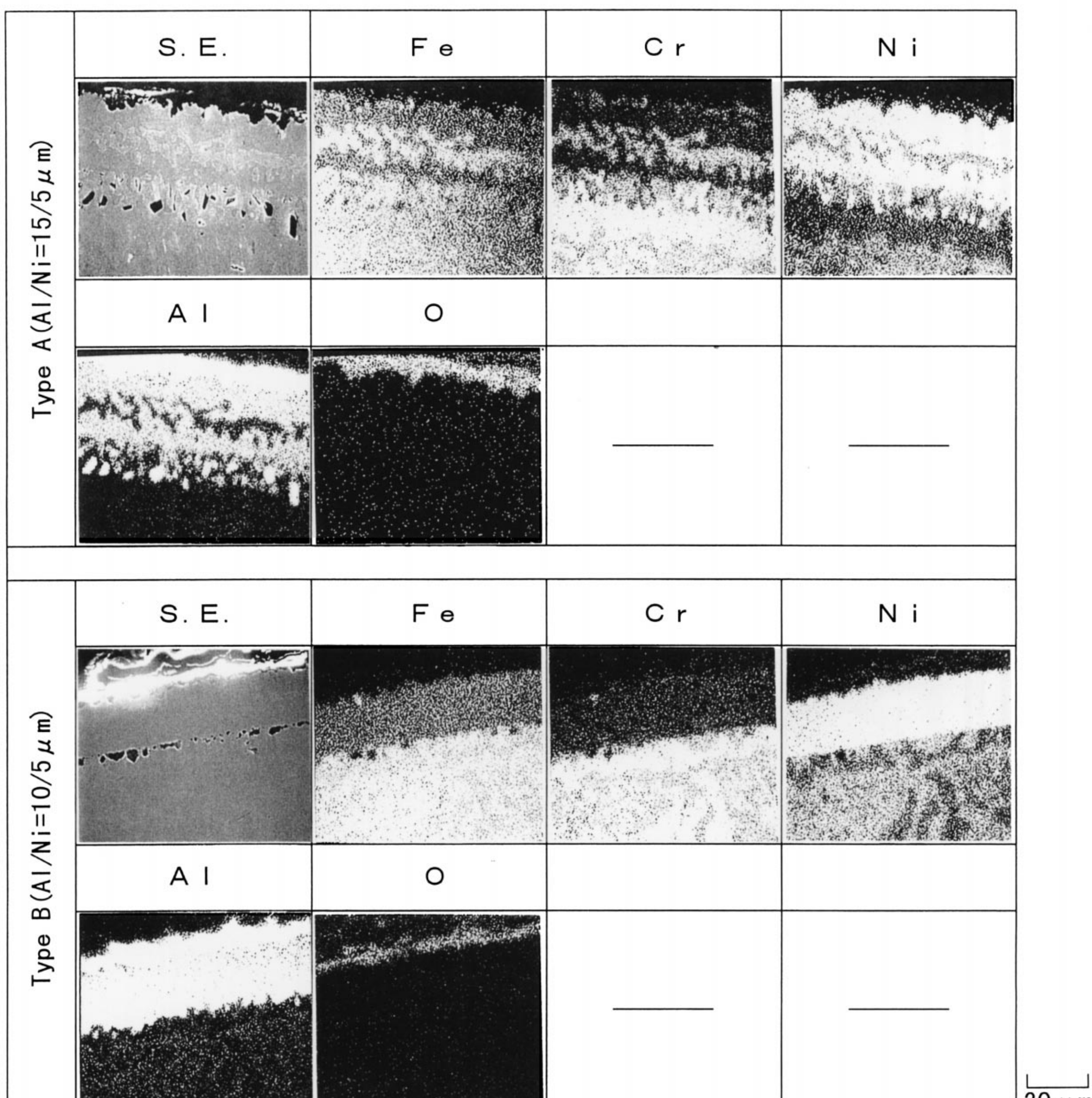

Fig. 7. Characteristic X-ray images of cross-section of the surface layer of Al/Ni-plated materials after heating test at 750°C for 10 000 h.

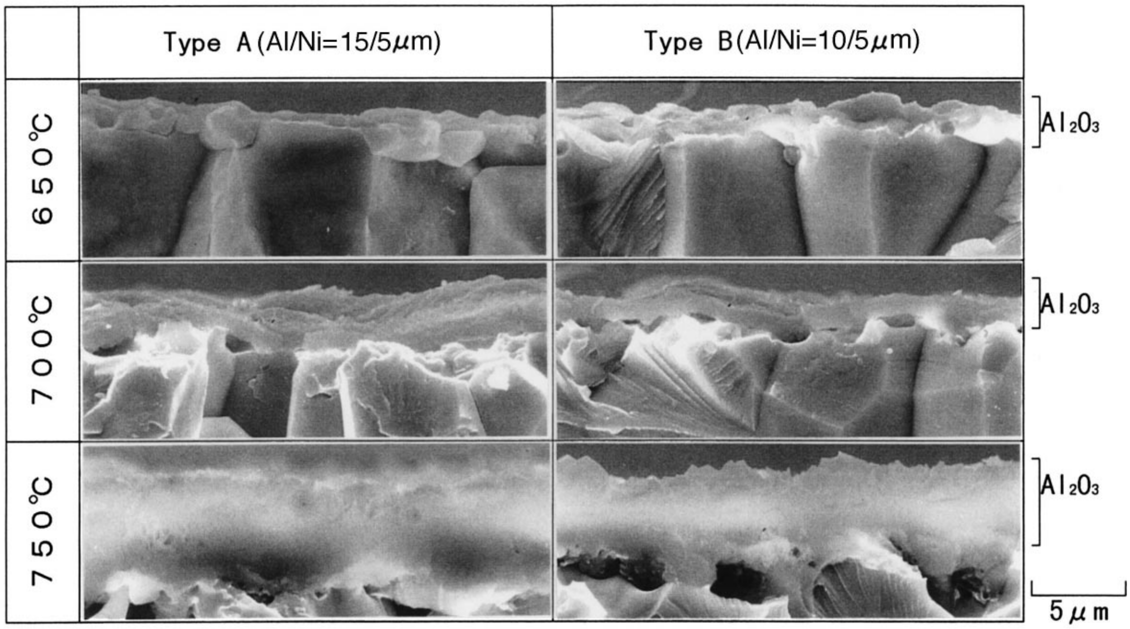

Fig. 8. SEM images of cross-section of the surface oxide of Al/Ni-plated materials after heating test for 10 000 h.

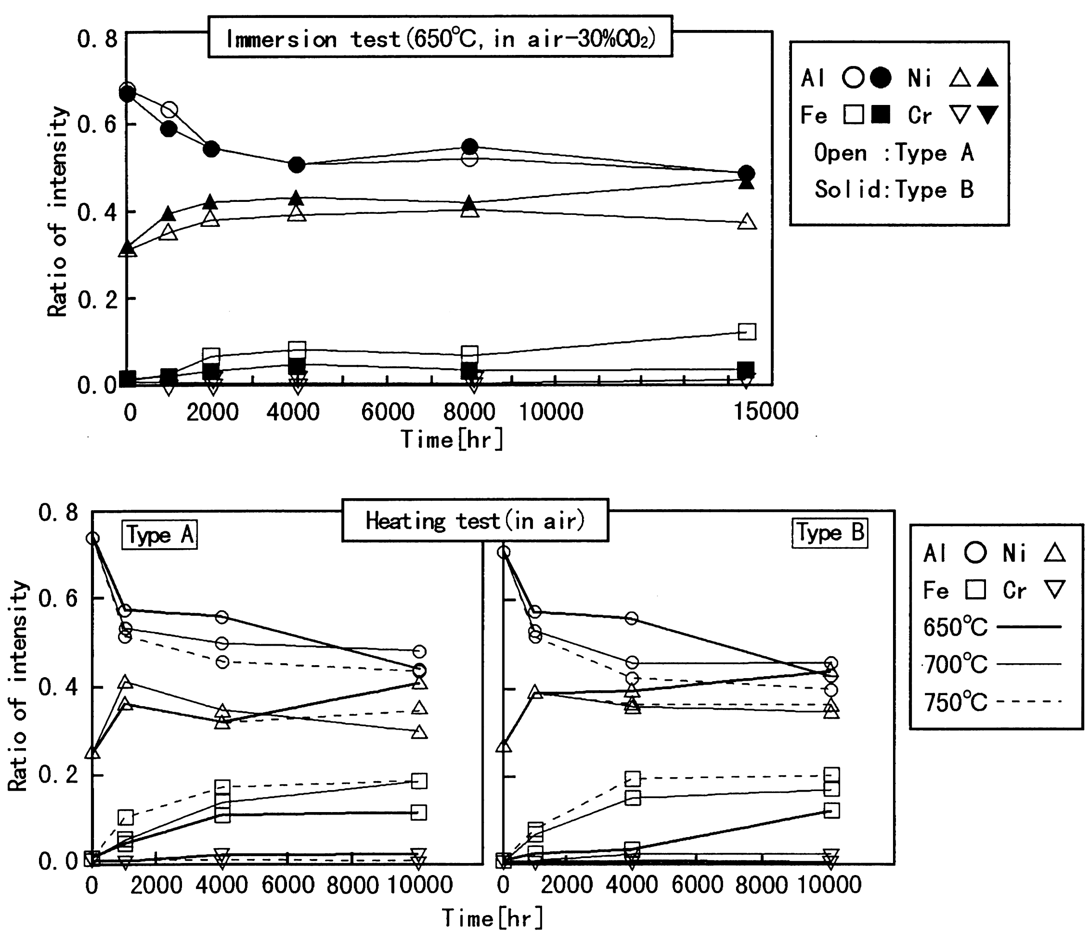

Fig. 9. Changes of composition of Al–Ni layer after immersion test.

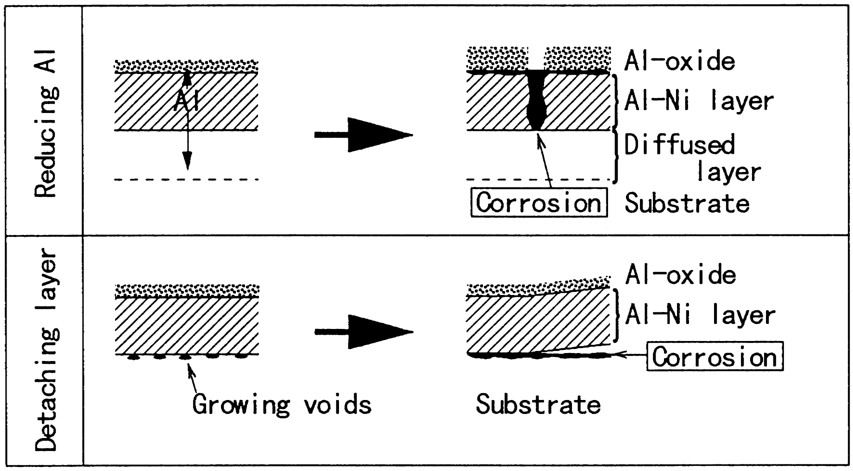

Fig. 10. Schematic illustration of reducing corrosion resistance of Al/Ni-plated material.

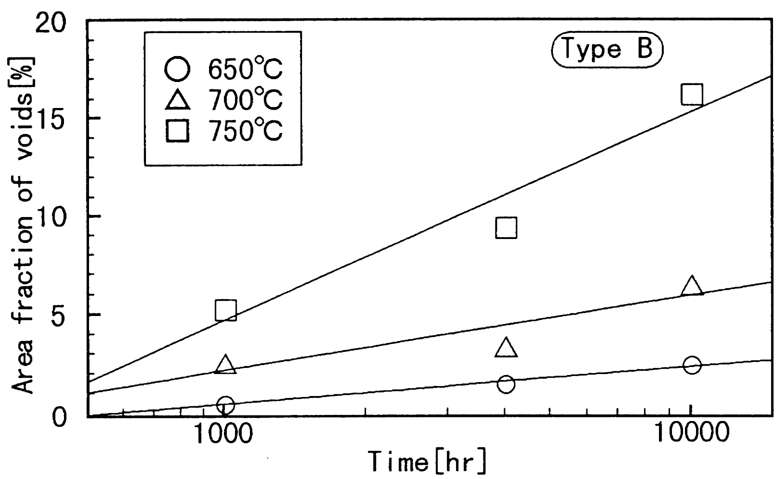

Fig. 11. Effect of heating time on area fraction of voids at various temperature.

to the total X-ray intensity obtained at 5 μm under the surface in 100-μm length scanning in the Al–Ni layer. In both the immersion test and the heating test, while Al concentration decreased, Fe concentration increased with time. However, there is a tendency that each alloying element concentration finally came to be constant in each test and temperature. It was found that Al concentrations in the Al–Ni layer after the immersion test and the heating test were close at 650°C for about 10 000 h. It is assumed that the consumption of Al in the Al–Ni layer at 650°C for about 10 000 h in the immersion test and the heating test were almost equal.

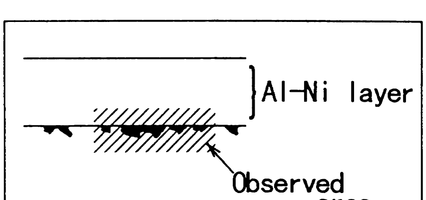

Fig. 12. Schematic illustration for the observed area for measuring the area fraction of voids.

3.4. Estimation of the lifetime of Al/Ni-plated material

The schematic illustration showing two kinds of possible mechanisms of loss of corrosion resistance for the Al/Ni-plated material is exhibited in Fig. 10. As the corrosion resistance of Al/Ni-plated material is dependent on the Al-oxide layer formed on the surface of the material, the corrosion resistance can be reduced when Al concentration in the Al–Ni layer decrease. The lifetime of Al/Ni-plated material could not be estimated, since Al concentration was nearly constant over the longer period, as shown in Fig. 9.

Since the corrosion resistance can be reduced if the Al–Ni layer comes off the substrate due to voids, an estimation of the lifetime of the Al/Ni-plated material was made by calculating a growth rate of voids for Type B. The quantities of voids are plotted as a function of the heating time in Fig. 11. The vertical axis indicates the area fraction of voids in a unit area. The area fraction of voids, shown in Fig. 12, was determined by measuring the total area of voids observed in a 30 × 100-μm square at 10 positions in each specimen.

The slopes of linear plots in Fig. 11 indicate the growth rate of voids at each temperature. Log k were plotted against

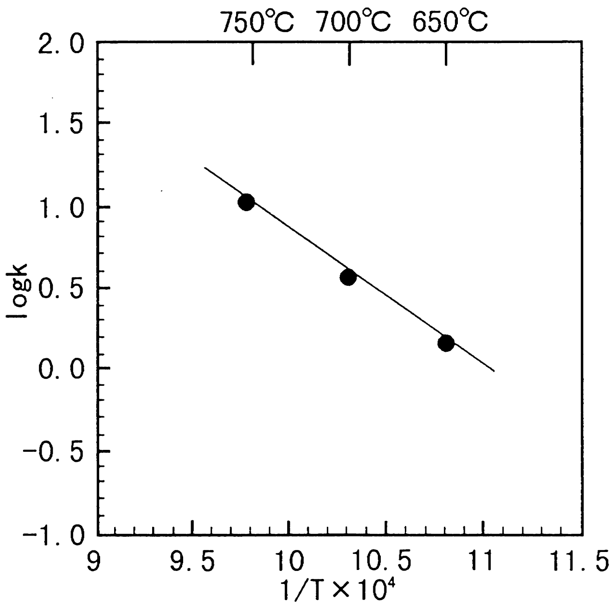

Fig. 13. Arrhenius plots of the growth of voids after heating test for 10 000 h.

$1/T$ as shown in Fig. 13. Where k is the growth rate of voids calculated from the slopes of linear plots in Fig. 11, and T is absolute temperature of the heating test. In Fig. 13, the same linear plot as in Fig. 11 can be seen. Log k decreases linearly, then the activation energy of forming voids, Q, calculated from the slope was 41 kcal/mol. This activation energy nearly coincides with that of formation of voids in heating aluminized steel, that is, $Q = 43.5$ kcal/mol [4]. From Fig. 13,

$$\log k(750°\text{C}) / \log k(650°\text{C}) = 1.03/0.18 = 5.7$$

so it is estimated that the condition of the heating test at 750°C for 10 000 h corresponded to that of the immersion test at 650°C for 60 000 h.

4. Conclusions

Supposing that the $LiAlO_2$ layer, which forms on the surface of the Al–Ni layer, has sufficient protectiveness against molten carbonate, it is considered that the lifetime of the Al/Ni-plated material depends on the detachment of the Al–Ni layer due to voids.

Considering results of the estimation of the lifetime for the Al/Ni-plated material in the heating test, it can be said that the lifetime of the Al/Ni-plated material is expected to be more than 40 000 h, which is the required lifetime for MCFC, at 650°C in molten carbonate.

Acknowledgements

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