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Co-deposition of Al-Cr-Ni Alloys Using Constant Potential and
Potential Pulse Techniques in $\text{AlCl}_3\text{-NaCl-KCl}$ Molten Salt

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Abstract

To improve the oxidation resistance of TiAl intermetallic compound under high temperature condition, cathodic co-deposition of Al-Cr and Al-Ni alloy was carried out by constant potential control or potential pulse control in $\text{AlCl}_3\text{-NaCl-KCl}$ molten salt containing CrCl_2 and/ or NiCl_2 at 423 K. Cathodic reduction of Ni and Cr starts at potential of 0.8 and 0.15 V vs. Al/Al^{3+} in the molten salt, respectively. The co-deposition of Al, Cr, and Ni occurred at potentials more negative than -0.1 V to form a mixture of intermetallic compounds of Cr_2Al , Ni_3Al , and Al_3Ni . Concentration of Cr in the deposit was enhanced to 43 at% at -0.1 V; however, concentration of Ni in the deposit was 6 at% at the same potential. The concentration of Ni further decreased with more negative potential to 1 at% at -0.4 V. The potential pulse technique enhanced the Ni concentration in the deposit to about 30 at%, due to anodic dissolution of Al content from the deposit at the higher side of potential on the potential pulse electrolysis.

Keywords: Molten salt, Co-deposition, Aluminum alloy, Electroplating, Pulse electrolysis

1. Introduction

TiAl intermetallic compound may be one of the candidates for next turbine blade materials of internal combustion engine. However, the corrosion resistance of TiAl intermetallic compound is not sufficient for use at temperature higher than 900 °C (1173 K). To improve the oxidation resistance under the high temperature condition, we have proposed a resistive coating of Al-Cr or Al-Cr-Ni alloy layer which was produced by electroplating on the TiAl intermetallic compound from molten salt.[1,2] For keeping adhesion of the coating to the substrate TiAl and lowering production cost, we have applied electrolysis in a low-temperature molten salt to the coating formation. There have been several papers on electrodeposits of Al, Cr, and Ni from the low-temperature molten salt [3-7]; however, there are few reports on the deposits of alloys consisting of Al, Cr, and Ni. In this paper, we present co-deposition of Al, Cr, and Ni or these alloys from $\text{AlCl}_3\text{-NaCl-KCl}$ molten salt containing CrCl_2 and NiCl_2 at 423 K. A relation between the alloy composition and potential under potential control electrolysis was reported. Further, the potential pulse electrolysis was applied for enhancement of Ni content in the alloy deposit.

2. Experimental

Anhydrous chromium chloride (CrCl_2 , Aldrich, 99.99% pure), and anhydrous nickel chloride (NiCl_2 , Aldrich, 99.99% pure) were used as received. Aluminum chloride (Aldrich, 99.9% pure) was sublimated and condensed for purification before use. A schematic illustration of the electrochemical cell used for the electroplating is shown in Fig. 1. The cell was made of Pyrex glass cylinder and equipped with a heater around the outside. A mixture of 61 mol% AlCl_3 - 26 mol% NaCl - 13 mol% KCl of 300 g was melted in the cell at 423 K. A glassy carbon (GC, Tokai carbon, GC-20) plate with surface area of 3 cm² and a pure aluminum plate (Niraco, 99.99%, 12 cm²) were used as the working electrode and as the

counter electrode, respectively. Pure aluminum rod (Niraco, 99.99%) placed in a small Pyrex glass tube filled with the AlCl_3 - NaCl - KCl melt was used as the reference electrode. To maintain electrical contact between the electrolyte melt and the reference electrode, a small hole was made by insertion of asbestos at the bottom of the tube. Electrolysis was carried out with a Hokuto-Denko HAG-5010 potentiostat.

In quantitative analysis of Cr and Ni content, small part of clear melt was collected from molten salt containing CrCl_2 and NiCl_2 and weighed. The collected melt was dissolved in 0.1 mol dm^{-3} hydrochloric acid and analyzed by ICP-AES(Seiko instrument SPS-3000). Voltammograms were measured at a potential range from 1.4 to -0.4 V vs. Al/Al^{3+} with a scan rate of $5.0 \times 10^{-3} \text{ V s}^{-1}$ in the molten salt containing CrCl_2 and NiCl_2 . Electrodeposition films of Al-Cr-Ni alloys were prepared on the GC electrode at constant potential in the range from -0.1 to -0.4 V in the molten salt with a constant charge density of 40 C cm^{-2} . Electrodeposition by potential control pulse technique was also carried out. Electrodeposits formed were analyzed by X-ray diffraction (XRD, JEOL JDX-3500, $\text{Cu-K}\alpha$ radiation) and fluorescence X-ray spectroscopy (JEOL JSX-3220Z, Rh target).

3. Results and Discussion

3.1 Saturated concentration of chromium chloride and nickel chloride

The dissolution of CrCl_2 and NiCl_2 was first examined in the AlCl_3 - NaCl - KCl molten salt. Figure 2 shows change in the concentration of chromium ion and nickel ion in the AlCl_3 - NaCl - KCl molten salt with time after addition of CrCl_2 and NiCl_2 into the melt. From Fig. 2, the dissolution almost reaches saturation in 1 h for both salts. The saturated concentration of CrCl_2 and NiCl_2 dissolved in the molten salt was found to be about $8 \times 10^{-2} \text{ mol dm}^{-3}$ and $5 \times 10^{-2} \text{ mol dm}^{-3}$ at 423 K, respectively. The concentrations are in agreement with the results reported by Moffat. [3] The molten salt saturated by CrCl_2 and NiCl_2 was

used for the following electrolysis.

3.2 Cyclic voltammogram measurement

A voltammogram is shown in Fig. 3, in which the potential is scanned from 1.4 V to -0.4 V at a sweep rate of 5×10^{-3} V s⁻¹ on the glassy carbon electrode in the electrolyte of the AlCl₃-NaCl-KCl melt containing CrCl₂ and NiCl₂, and then reversely scanned. The current density (CD)-potential relation between 0.5 and 0.8 V vs. Al/Al³⁺ is inserted into Fig. 3 with an enlarged scale of CD. The rest potential of the glassy carbon in the melt was about 0.8 V. A small cathodic current peak was observed at 0.72 V (P1) on the voltammogram. Since the voltammogram in the AlCl₃-NaCl-KCl melt without NiCl₂ did not have any cathodic current in this region, the current at P1 may be attributed to electrodeposition of Ni. The cathodic peak position is in agreement with the reported by Moffat for Ni deposition. [4] Cathodic CD starts to increase at 0.18 V (P2) and reveals a shoulder at about 0.10 V. After the shoulder, CD linearly increases in the potentials more negative than 0.0 V (P3). The cathodic CD for the shoulder from 0.18 to 0.10 V and the linear increase from 0 V are electrodeposition of Cr-Al alloy and metallic Al, respectively, as having shown in our previous paper. [1]

When the potential is reversed at -0.4 V, anodic CD appears from 0.0 V to 0.7 V. The anodic CD corresponds to anodic dissolution of the electrodeposits formed by the previous cathodic scan. The anodic reactions corresponding to the anodic peaks are not clear, however, it is conceivable that P4 corresponds to dissolution of metallic Al, P5 to dissolution of Cr-Al alloy and P6 to Ni-Al alloy. The small peak (P7) which may be a reverse reaction of P1, i.e., dissolution of metallic Ni.

3.3 Relation between potential and composition in constant potential control electrolysis

Electrodeposition with a constant charge density at 40 C cm⁻² was carried out on glassy

carbon at various potentials of -0.1 , -0.2 , -0.3 , and -0.4 V in the melt containing CrCl_2 and NiCl_2 in order to examine the influence of the potential on the composition of the deposits. Transients of CD are shown in Fig. 4 during constant potential electrolysis at -0.1 , -0.2 , -0.3 , and -0.4 V. Cathodic CD increases with decreases of potential. Time period more than 2000 s is required at potentials of -0.1 and -0.2 V for reaching charge density of 40 C cm^{-2} ; however, electrolysis to 40 C cm^{-2} is reached in 300 s at -0.4 V.

The composition of electrodeposits formed under the constant potential control was analyzed by fluorescence X-ray spectroscopy. Relation between the deposition potential and the composition is listed in Table 1. From Table 1, the concentration of Al is seen to be relatively high, and the concentration of Cr strongly depends on the deposition potential. The concentration of Ni in the electrodeposits is very small, decreasing with more negative potential. Surface morphology of the almost deposits is flat, however when Ni content in the deposit increases, roughness increases and adherence for GC electrode decreases. Figure 5 shows the XRD pattern of the electrodeposits formed at potentials from -0.1 to -0.4 V. Metallic Al and intermetallic compounds of Cr_2Al and Al_3Ni were detected for the deposits formed at potential of -0.4 V. For the deposits formed at -0.3 , -0.2 and -0.1 V, the intermetallic compounds are found. From the results, it is seen that the deposits formed at potentials between -0.1 and -0.3 V consist of almost same compounds of Cr_2Al , Ni_3Al and Al_3Ni . From a thermodynamic point of view, formation of NiAl may easily occur, however Ali et al. reported electrodeposition of only Ni_3Al in $\text{AlCl}_3\text{-BPC}$ molten salt. In this study, formation of Cr_2Al may contribute to the balance of Ni_3Al and Al_3Ni phases. Broad peaks were observed in XRD patterns, and this may be due to fine grain size or big lattice strain. Considering the above, these electrodeposits formed on the electrode may be meta-stable alloy film.

3.4 Potential pulse electrolysis

The concentration of Cr in the deposit can be enhanced by electrolysis of relatively more negative potential however, there is a limit for enhancement of Ni concentration by constant potential electrolysis. For enhancement of both Ni and Cr in the deposit, potential pulse electrolysis was examined. For the pulse, we controlled the following parameters, as illustrated in Fig. 6; the positive potential (E_p), the negative potential (E_n), frequency (f), and duty ratio (τ_p/τ_n). In the potential pulse, the intermetallic compounds and metallic Al are deposited during the period at the negative potential, E_n , and Al content is preferentially dissolved from the deposit during the period at the positive potential, E_p . The preferential dissolution of Al content may be expected to enhance the Ni and Cr contents in the deposit alloy. The relations between composition of electrodeposits and potential pulse parameters are shown in Fig. 7.

As shown in Fig. 7(a), the more positive E_p induces the lower concentration of Cr. This result shows dissolution of Cr at potential of 0.5 V occurs easily than that of at 0.1 V. In Fig. 7 (b), the more positive E_n results in the higher concentration of Cr. This can be due to increase of reduction current of Al ion at potential of -0.2 V. When the duty ratio, τ_p/τ_n , is made smaller, the concentration of Cr and Ni increases (Fig. 7(c)). When the frequency, f , is made higher, the Ni concentration increases and the Cr concentration decreases (Fig. 7(d)). The effects of frequency and duty ratio on alloy concentration are not strong, however, these parameters may have a strong effect on the concentration in other combinations with E_p and E_n . Relatively flat electrodeposit is formed at frequency of 0.5 Hz, on the other hand, powdery electrodeposit is formed at 5 Hz. The effect of frequency may be reflected for morphology change of electrodeposit rather than the concentration. In these pulse deposition, the Ni concentration of the deposit is enhanced to 32 at% under the pulse condition of $E_p = 0.5$ V, $E_n = -0.1$ V, $f = 1$ Hz, and $\tau_p/\tau_n = 2 / 3$ under which the Cr concentration is 11 at%.

From the result, it is found that the pulse electrolysis is effective for enrichment of Ni content. For more improvement of oxidation resistance of TiAl at high temperatures, the coating of Al-Cr-Ni alloy with the Ni concentration higher than 50 at% is required. [9] We further examine the pulse potential condition to obtain higher concentration of Ni content in the deposit.

Conclusions

For preparation of an oxidation resistance layer under high temperature condition, co-deposition of intermetallic compounds of Cr_2Al , Ni_3Al , and Al_3Ni as well as metallic Al was done by potentiostatic electrolysis in 61 mol% AlCl_3 - 26 mol% NaCl - 13 mol% KCl containing of CrCl_2 and NiCl_2 at 423 K.

- (1) Cathodic reduction of Ni and electrodeposition of Al-Cr alloy start at potential of 0.8 V and 0.18 V vs. Al/Al^{3+} in the molten salt, respectively.
- (2) Co-deposition of the intermetallic compounds takes place by electrolysis at potentials more negative than -0.1 V.
- (3) Cr concentration in deposit is enhanced to about 40 at% at -0.1 V. under constant potential control; however, Ni concentration remains less than 6 at% at the same potential.
- (4) Ni concentration in the deposit is enhanced to 32 at% when the potential pulse condition is optimized.

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Caption

Fig. 1 Schematic illustration of electrochemical cell.

Fig. 2 Change in concentration of Cr and Ni ions with time during dissolution of CrCl_2 and NiCl_2 in AlCl_3 - NaCl - KCl molten salt.

Fig. 3 Cyclic voltammogram on GC electrode in AlCl_3 - NaCl - KCl melt containing CrCl_2 and NiCl_2 . The enlarged voltammogram was inserted at the potentials between 0.5 and 0.8 V.(inset)

Fig. 4 Change of CD with time on GC electrode during constant potential electrolysis at potentials of -0.1 , -0.2 , -0.3 , and -0.4 V.

Fig. 5 XRD pattern of electrodeposits formed at potentials of -0.1 , -0.2 , -0.3 , and -0.4 V.

Fig. 6 Illustration of parameters for potential pulse electrolysis.

Fig. 7 Relation between pulse electrolysis parameters and concentration of Al, Cr and Ni in the deposits. The parameters changed during potential electrolysis are (a)positive potential, E_p , (b)negative potential, E_n , (c)duty ratio, τ_p/τ_n , and (d)frequency, f .

Table 1 Concentration of Al, Cr and Ni in deposits as a function of deposition potential.

Fig. 1

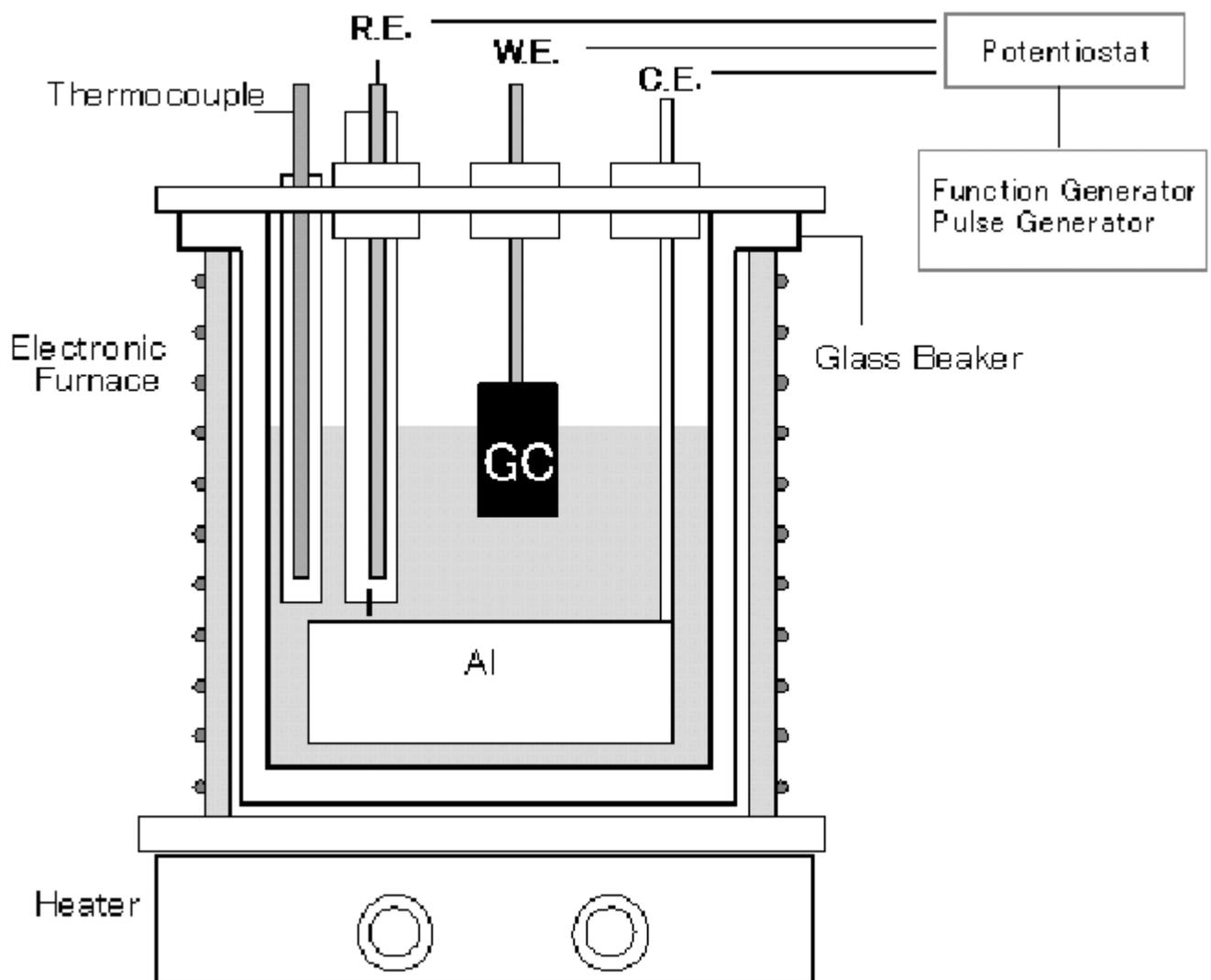


Fig. 2

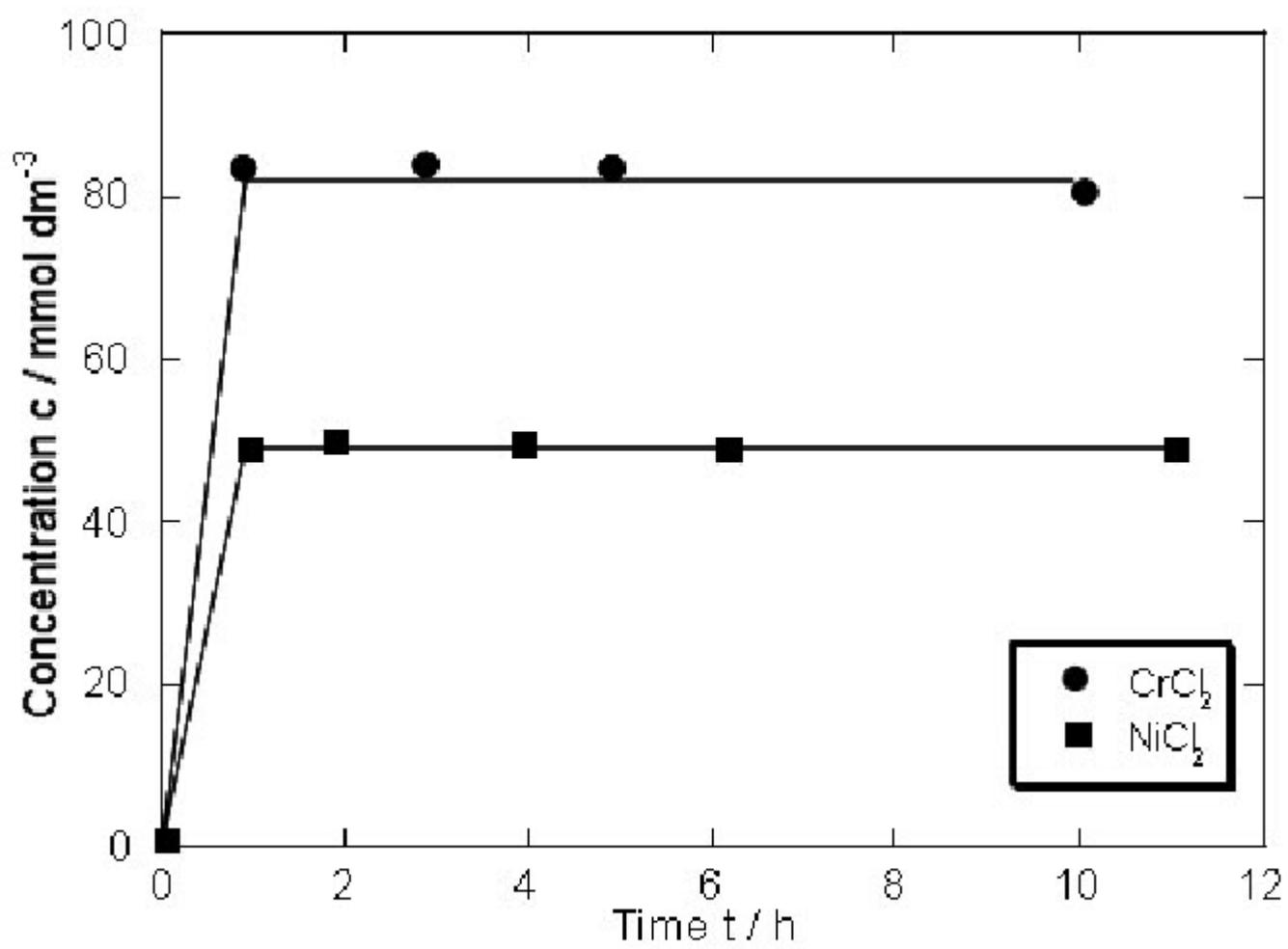


Fig. 3

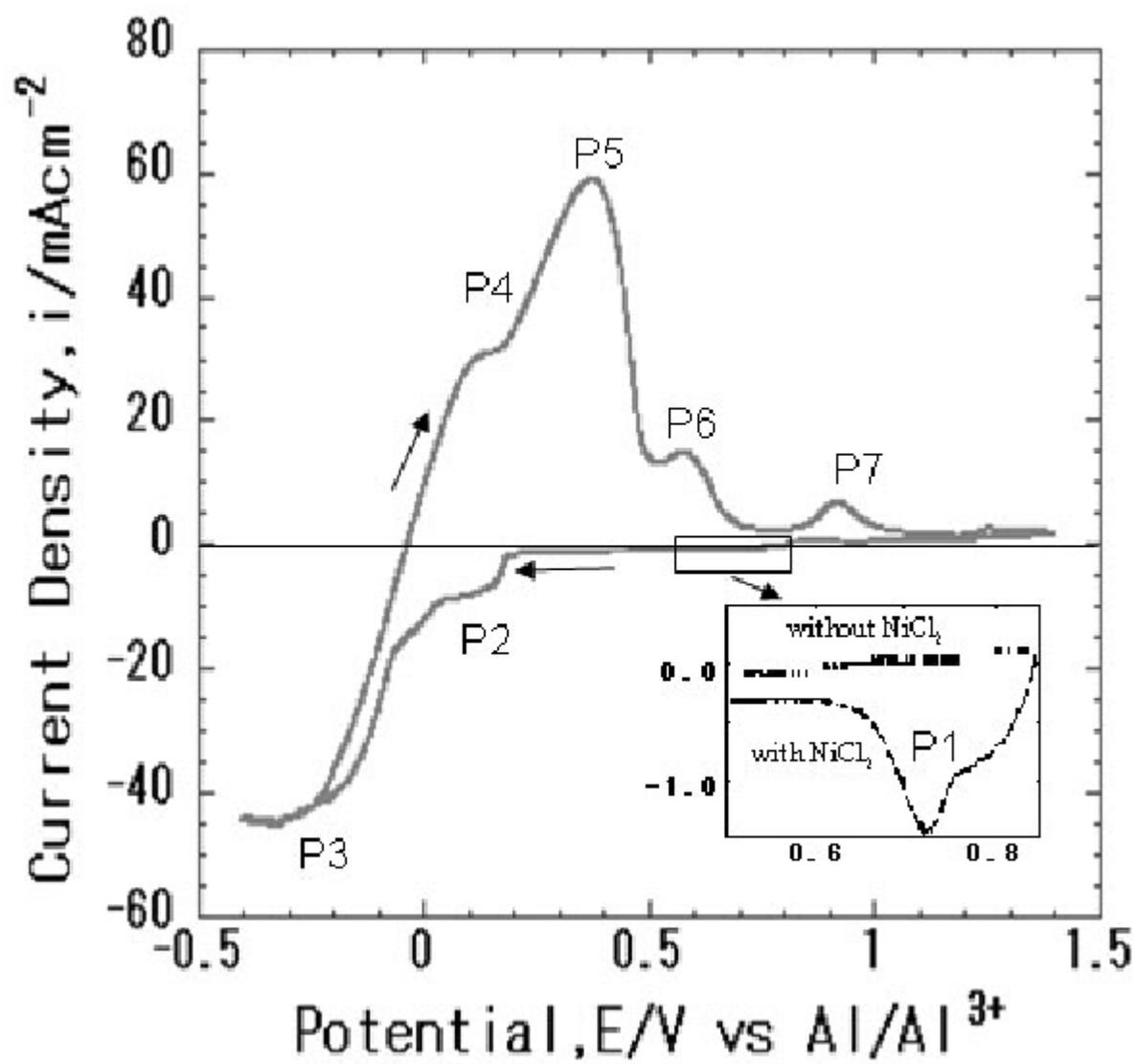


Fig. 4

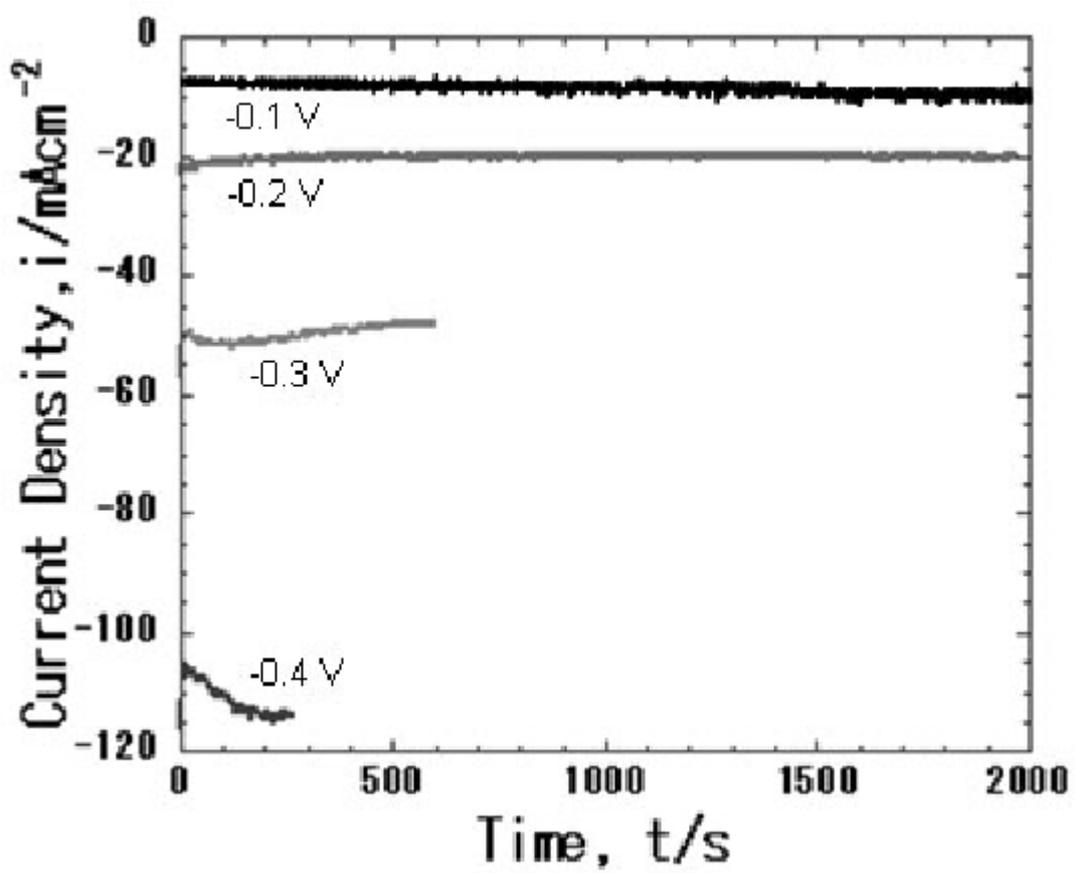


Fig. 5

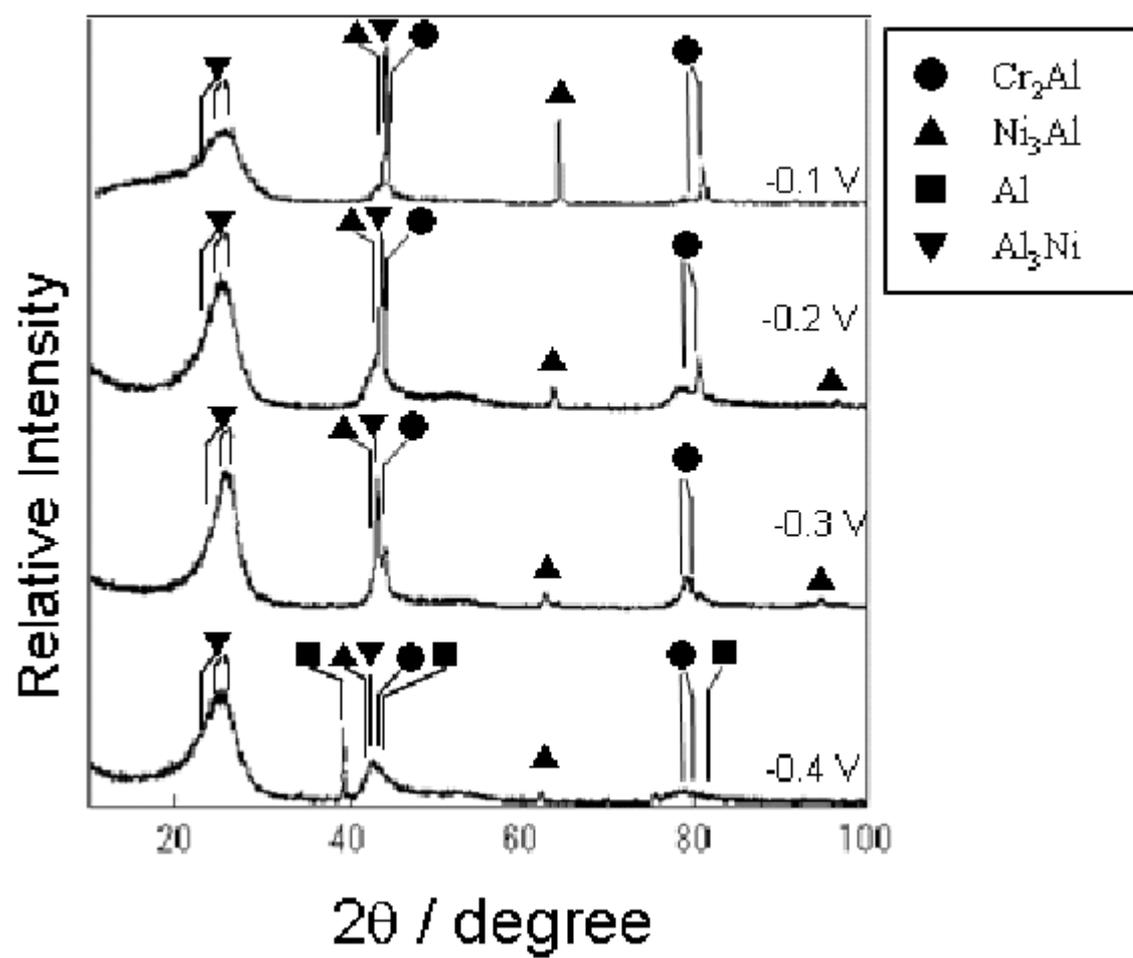


Fig. 6

