Electrodeposition of Al-Ti alloys from aluminum chloride-N-(n-butyl)pyridinium chloride room temperature molten salt

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Received 22 May 2001; revised received 30 August 2002; accepted 12 September 2002

Electrodeposition of aluminum-titanium alloys has been carried out onto platinum and mild steel cathodes from 6.14:3.07:0.09 (mole ratio) AlCl₃-BPC-TiCl₄ molten bath by controlled-potential and pulse potential methods. High concentration of TiCl₄ (>0.1 mol dm⁻³) interferes with the deposition processes of Al and Al-Ti alloys. The deposition of pure titanium from this electrolyte is difficult, but titanium is co-deposited with aluminum in the form of alloys. The morphologies of the electrodeposited layers have been investigated by X-ray diffractometer and scanning electron microscope. The cathodic current efficiency for the deposition of alloys is about 97%.

The excellent high oxidation temperature resistance as well as creep resistance of aluminum-titanium alloys have led to the consideration of these order alloys for structural applications. Titanium and alloys have been used in aeronautics because of high temperature oxidation resistance, high strength and lightness. Various processing methods have been used to fabricate these materials. The present study demonstrates that electrodeposition may be useful in producing Al-Ti alloys from room temperature molten salt. Electrodeposition is an attractive method for fabricating alloys/intermetallic compounds since high temperature consolidation is unnecessary, undesirable compositional inhomogeneties are very limited in scale, and grain sizes are typically very small. Although the electrodeposition of titanium from high temperature alkali-chloride melts has been extensively investigated, the direct electrodeposition of Al-Ti alloys has only recently been reported.

Recently Robinson et al.¹¹ and Gale et al.¹² have reported a system which appears to be a viable alternative to the inorganic chloroaluminates because they can be employed almost at room temperature. These system form an organic chloroaluminates melts, which are obtained by mixing certain anhydrous organic chloride salts such as N-(n-butyl)pyridinium chloride (BPC) or 1-methyl-3-ethylimidazolium chloride (MEIC) with AlCl₃. Recently, considerable interest on the electroplating of aluminum and its alloys from room temperature melts, e.g. AlCl₃-MEIC¹³, AlCl₃-BPC¹⁴-¹⁸ has developed.

Robinson et al.¹¹ has reported that the major aluminum containing species in the basic or neutral (1:1 mole ratio) AlCl₃-BPC melt is AlCl₄⁻ anion. However, when the molar ratio of AlCl₃-BPC increases from 1:1 to 1.86:1, the main species in the melt is Al₂Cl₇⁻ anion. In the 2:1 AlCl₃-BPC melt, only Al₂Cl₇⁻ anion has been detected by the Raman spectroscopy.¹¹ It is clear from the structure of the melt that only Al₂Cl₇⁻ anion can deposit aluminum on the cathode because of the very negative reduction potential of AlCl₄⁻ compared with that of BP⁺ cations.

The aim of this work is the feasibility study to obtain Al-Ti alloys from 2:1 AlCl₃-BPC melt containing TiCl₄.

Experimental Procedure

Chemicals
Aluminum chloride (AlCl₃), 99.99%. N-(n-butyl)pyridinium chloride (BPC), 99.9%, and titanium tetrachloride (TiCl₄), 99.99%, in a sealed glass tubes were supplied by Sowekawa Chemicals Co., Tokyo, Japan.

Melt preparation
AlCl₃-BPC melt (mole ratio, 2:1) were prepared and purified, as described elsewhere.¹⁶,¹⁸ All operations with the chemicals were carried out in dry glove box under an argon atmosphere containing less than 1 ppm H₂O and O₂. TiCl₄ was introduced into the melt by a syringe. The density of TiCl₄ was 1.726 g
Electrochemical cell and electrodes

The electrolysis cell, made of Pyrex glass with a fitted Pyrex glass cap was used in this study. About 10 cm³ of 2:1 (mole ratio) AlCl₃-BPC melt containing TiCl₄ and 1 cm³ of 2:1 AlCl₃-BPC melt were introduced into the bulk and reference electrode compartments respectively in all experiments.

Platinum (50x5x0.1 mm³) or mild steel (50x10x0.4 mm³) and pure titanium (50x10x0.2 mm³) plates were used as working and counter electrodes respectively, which were immersed in the bulk electrolyte. Pure aluminum plate (50x2x0.5 mm³) was used as a reference electrode and immersed in 2:1 AlCl₃-BPC melt of the reference electrode compartment. The melt level in the reference compartment was kept slightly higher than that in the bulk melt compartment. Throughout the work, all potentials were quoted with respect to this Al/2:1 AlCl₃-BPC reference electrode that would be written as Al/Al⁺⁺ electrode in this paper.

Electrochemical instrumentation

All cyclic voltammetry, chronoamperometry and chronopotentiometry for the electrolytes were performed using a Hokuto Denko HAB-151 potentiogalvanostat, Tokyo, Japan, equipped with potential sweeper. Cyclic voltammograms were recorded on an X-Y recorder (Type-3077, Yokogawa, Japan). Chronoamperograms and chronopotentiograms were recorded on an X-Y recorder (SP-HSP, Riken Denshi Co., Ltd., Japan). All electrochemical measurements were carried out at room temperature. The resistance of the electrolyte (6.14:3.07:0.09 AlCl₃-BPC-TiCl₄ melt) in the three electrode systems was measured by the impedance method with a frequency response analyzer (FRA) coupled to a GPIB and an IBM computer. A more detailed description of the instruments on impedance measurement techniques has been reported earlier. Impedance measurements were carried out between the frequency range of 10 kHz and 10 mHz. The resistance of the electrolyte was obtained from the measured impedance in the high frequency range. The measured solution resistance of the electrolyte is 137 Ω cm.

Results and Discussion

Voltammetry on titanium electrode in 2:1 AlCl₃-BPC melt

In order to probe the electrodeposition of Al-Ti alloys, cyclic voltammetric experiments have been carried out on titanium electrode (50x5x0.1 mm³) in pure 2:1 AlCl₃-BPC melt. Fig. 1 shows the cyclic voltammogram on the polished titanium electrode in 2:1 AlCl₃-BPC melt without and with titanium ion present at 25°C. The rest potential is 0.85 V versus Al/Al⁺⁺ reference electrode. In the first cycle (without titanium ion), as the potential sweep is decreased from 0.85 V versus Al/Al⁺⁺ towards the aluminum deposition potential, a cathodic wave is observed at −0.08 V. If the potential is reversed prior to aluminum deposition, an anodic peak is observed at 0.08 V. It is likely that this is due to the underpotential deposition (UPD) of aluminum onto titanium. As the reverse potential sweep is increased from the dissolution potential of the deposited aluminum, a rapid increase of the anodic current is observed at 1.05 V. The rapid increase of this anodic current corresponds to the dissolution of titanium from the working electrode (Ti). The colour of the electrolyte becomes light yellow which may be due to the presence of Ti(IV) in aluminum-titanium alloys were electrodeposited onto platinum and steel cathodes by controlled-potential and pulse potential methods at 25°C from 2:1 AlCl₃-BPC melt containing 0.09 mol dm⁻³ TiCl₄.

Deposit characterization

The surface morphology of the electrodeposited layer was noticed by scanning electron microscope (SEM) (ABT-5, TOPCON, Tokyo, Japan) equipped with an Olympus camera. The crystallinity and structure of the electrodeposited Al-Ti alloy samples were studied by X-ray diffractometer (XD-3A, Shimadzu, Japan) using Ni-filtered CuKα radiation (30 kV, 10 mA) with a measuring speed of 1° min⁻¹ and time constant 2s. X-ray diffraction patterns were recorded on a chart recorder. The aluminum and titanium contents of the electrodeposited film were quantitatively analyzed by electron probe microanalyzer (EPMA) (EPMA-8705, Shimadzu, Japan) against the standard samples of pure aluminum (99.99%) and pure titanium (99.9%). The chemical analysis of the electrodeposited Al-Ti alloy was carried out by inductively coupled plasma emission atomic spectrometer (ICP) (STS 1500 VR, Seiko Instruments, Japan).

Aluminum-titanium alloys were electrodeposited onto platinum and steel cathodes by controlled-potential and pulse potential methods at 25°C from 2:1 AlCl₃-BPC melt containing 0.09 mol dm⁻³ TiCl₄.
the melt. Kage et al.\textsuperscript{19} have reported that during the coulometric dissolution, titanium in 2:1 AlCl\textsubscript{3}-BPC melt exists in the tetravalent state, possibly [Ti(Al\textsubscript{2}Cl\textsubscript{7})\textsubscript{2}]\textsuperscript{2-}. However, in the second cathodic scan, a first reduction wave (C\textsubscript{1}) with a peak potential at 0.91 V, a second wave (C\textsubscript{2}) with a peak potential at 0.29 V, a third wave (C\textsubscript{3}) with a peak potential of 0.03 V, and the fourth wave (C\textsubscript{4}) with the start of the current increase at -0.01 V were observed. The second reverse scan consisted of a first oxidation peak (P\textsubscript{41}) at 0.08 V, a second peak (P\textsubscript{42}) at 0.5 V, and the dissolution current wave of titanium at 1.05 V. The intensity of the first, second, third reduction peaks and the second oxidation peak increases with the increase of the concentration (amount) of the dissolved titanium ion in the melt. It is likely that the third reduction wave (C\textsubscript{3}) is very close to the fourth reduction wave (C\textsubscript{4}) which is the deposition current of aluminum. Pure titanium deposition could not be obtained from this electrolyte by controlled-potential or controlled-current methods. However, titanium is co-deposited with aluminum in the form of an alloy from this electrolyte by controlled-potential and controlled-current methods. The deposit obtained at a deposition potential of -0.2 V contains Al-6 at % Ti alloy.

Based on these results, it is clear that the deposition of Al-Ti alloys from 2:1 AlCl\textsubscript{3}-BPC melt containing Ti(IV), supplied from chemicals, seems possible.

**Voltammetry of TiCl\textsubscript{4} in 2:1 AlCl\textsubscript{3}-BPC melt**

Figure 2 shows the cyclic voltamogram of 2:1 AlCl\textsubscript{3}-BPC melt containing various concentrations of TiCl\textsubscript{4} at 25°C onto platinum electrode. The concentration of TiCl\textsubscript{4} in Figs 2a, b and c were 1.00, 0.50 and 0.09 mol dm\textsuperscript{-3} respectively. The rest potential is 1.10 V versus Al/Al\textsuperscript{3+} reference electrode. In Figs 2a and b, the cathodic potential sweep was decreased from 1.10 V to -0.5 V and then the reverse potential sweep was increased from -0.5 V to 2.0 V. Aluminum reduction and oxidation waves, which are at or close to 0 V, were not observed. In the 2:1 AlCl\textsubscript{3}-BPC melt (acidic melt), the main aluminum containing species is Al\textsubscript{3}Cl\textsubscript{2} whose reduction occurs at or close to 0 V versus Al/Al\textsuperscript{3+} reference electrode\textsuperscript{18}. On the other hand, the main aluminum containing species in the 1:1 AlCl\textsubscript{3}-BPC melt (neutral melt) is AlCl\textsubscript{1} whose reduction potential is less than -1.0 V versus Al/Al\textsuperscript{3+}. As the acidity of the AlCl\textsubscript{3}-BPC melt is decreased, the activity of the AlCl\textsubscript{1} ion is also decreased whereas the activity of the AlCl\textsubscript{3} ion is increased. The reduction potential of the AlCl\textsubscript{1} species to Al is also decreased with the decrease in the concentration of AlCl\textsubscript{1} ion in the melt\textsuperscript{18}. Sorlie et al.\textsuperscript{20} have reported that titanium ion exists as octahedrally coordinated to chlorine in the 2:1 AlCl\textsubscript{3}-NaCl melt, and the species has generally been expressed as [Ti(AlCl\textsubscript{2})\textsubscript{3}]\textsuperscript{+}. More recently, Dent et al.\textsuperscript{21} and Abdul-sada et al.\textsuperscript{22} have reported that the
divalent metal chlorides exist in the acidic AICl-ImCl (Im = imidazolium) molten salt as [M(AICl4)]+.

Since the purpose of this study is not to resolve the structure of Ti(IV) in solution, it will be referred to as [Ti(AICl4)]+. Assuming Ti(IV) existing as [Ti(AICl4)]+, the activity of Al2Cl7 species in the bulk electrolyte (6.14:3.07:1.0 AICl3-BPC-TiCl4 melt) is much lower than that in the reference electrolyte (6.14:3.07 AICl3-BPC melt) owing to the formation of AICl4 species which can be represented by the following solvation reaction:

$$\begin{align*}
\text{TiCl}_4 &\rightarrow \text{Ti}^{4+} + 4\text{Cl}^- \\
4\text{Cl}^- + 4\text{AlCl}_3 &\rightarrow 8\text{AlCl}_4^- \\
8\text{AlCl}_4^- + \text{Ti}^{4+} &\rightarrow [\text{Ti}(\text{AlCl}_4)_x]^{4+} + (8-x)\text{AlCl}_4^- \\
\text{TiCl}_4 + 4\text{AlCl}_3 &\rightarrow [\text{Ti}(\text{AlCl}_4)_x]^{4+} + (8-x)\text{AlCl}_4^- \text{total reaction} \ldots (1)
\end{align*}$$

A change in the ratio of Al2Cl7 to AICl4 leads to the shift in the deposition potential of Al to more negative potential than that in the mixture of pure 2:1 AICl3-BPC melt in which no AlCl4 exists.

Furthermore, it is clear from Fig. 1 (dashed curve) that the reduction of the tetravalent titanium ion occurs in three consecutive steps. The first step may be the reduction of Ti(IV) to Ti(III), second step may be the Ti(III) to Ti(II) and the third step may be the Ti(II) to Ti(0). It is found that TiCl4 is only sparingly soluble in this melt. As the concentration of Ti(III) ion (produced by the reduction of Ti(IV) ion) exceeds the solubility limit then Ti(III) may be passivated on the electrode surface. This passive film blocks the electrode and prevents the reduction and oxidation reactions. At more oxidizing potentials (about 1.5 V) the protective nature of the film breaks down with the generation of Ti(IV) ion. This type of problem is observed in the electrolyte containing high concentration of TiCl4. It is concluded that the deposition of Al is suppressed owing to the decrease in the concentration of Al2Cl7 ion and the formation of passive film on the electrode surface in the 2:1 AICl3-BPC melt containing 1.0 and 0.5 mol dm⁻³ TiCl4.

On the other hand, deposition and dissolution current waves of aluminum are observed in Fig. 2c. It is clear from Fig. 2c that the low concentration of TiCl4 does not interfere on the reduction and the oxidation of aluminum in this melt. The cathodic and the anodic i-E curves in Fig. 2c are identical to that of in Fig. 1 (dashed curve). However, the magnitude of the peak current density ip is not equal, which depends on the concentration of Ti(IV) ion in the electrolyte. The first, second and third reduction waves (C1, C2 and C3) and the second and third oxidation peaks (P1 and P2) in the forward and reverse scans respectively are due to the presence of TiCl4 in the melt respectively. The deposit obtained from the fourth reduction wave (C4) at a deposition potential of -0.3 V contains Al-5 at % Ti alloy.

Figure 3 shows the effect of reversing the potential on the cyclic voltammogram of 2:1 AICl3-BPC melt at 25°C. Concentration of TiCl4, 0.09 mol dm⁻³; switching potential (a), 0.82; (b), 0.21; (c), 0.02 and (d), -0.12 V; sweep rate, 0.01 V s⁻¹; working electrode, Pt.

Figures 4 and 5 show the IR drop-compensated Tafel plot for the reduction of Ti(IV) on a platinum electrode in 6.14:3.07:0.09 AICl3-BPC-TiCl4 melt in the potential range of onset C1 and C2 respectively. The experimental Tafel slopes for the first (C1) and the second (C2) reduction wave of titanium are 115 and 120 mV dec⁻¹ respectively, which is equal to 60/nα², where n is the number of electron taking part into the reaction and α is the transfer coefficient (α = 0.5). The value of n for the first and the second reduction wave is 1 (one). Therefore, it is concluded...
that the first reduction wave is the reduction of Ti(IV) to Ti(III) and the second reduction wave is the reduction of Ti(III) to Ti(II). From the above results it is clear that Ti(IV) is first reduced to Ti(III). Ti(III) is then reduced to Ti(II) and Ti(II) is then reduced to Ti(0) in the third reduction wave \( (C_3) \). Similar types of result have been reported for the deposition of Al-Ti alloys from chloroaluminate electrolytes\(^2\). However, pure titanium could not be obtained in the deposits at a deposition potential range of onset \( C_3 \) (from the third reduction wave) by controlled-potential method. Moreover, co-deposition of aluminum and titanium is obtained from this electrolyte at a deposition potential of less than 0 V versus Al/Al\(^{3+}\). It is apparent that the reduction of Ti(II) to Ti(0) does not occur at potentials more positive than the deposition potential of aluminum. It should be noted that the deposition of pure titanium from this electrolyte is unlikely.

In the reverse scan, it is clear that the second oxidation peak \( P_{22} \) (which corresponds to \( C_2 \) and \( C_1 \)) is attributed to the dissolution of the deposited titanium from Al-Ti alloy or Ti to Ti(II) or Ti(III) and also to the oxidation of Ti(II) to Ti(III), and the third oxidation peak \( P_{23} \) (which corresponds to \( C_3 \)) is attributed to the oxidation of Ti(III) to Ti(IV).

**Electrodeposition of Al-Ti alloys**

Bulk aluminum-titanium alloy deposition experiments were carried out by controlled-potential and pulse potential methods from 6.14:3.07:0.09 (mole ratio) AlCl\(_3\)-BPC-TiCl\(_4\) melt at 25\(^\circ\)C. The deposition conditions and the chemical analysis results of the electrodeposited layers are summarized in Table 1. The observed highest titanium content is 27 at\%. The thickness of the deposited layers is about 7 \( \mu \)m. The scanning electron micrographs of the deposited surfaces are shown in Fig. 6. The deposited surfaces were very smooth and bright metallic colour to look at. Figs 7 and 8 show the X-ray diffraction patterns of the deposited layer onto platinum. The atomic ratio of aluminum and titanium in Figs 7 and 8 are 73:27 and 90:10 respectively. In Fig. 7, the diffraction peaks at \( 2\theta = 44.7^\circ, 65.1^\circ \) and \( 78.2^\circ \) correspond to Al, the diffraction peaks at \( 2\theta = 35.1^\circ, 40.1^\circ \) and \( 53^\circ \) correspond to Ti and the diffraction peaks at \( 2\theta = 41.9^\circ \) and \( 47.4^\circ \) correspond to AlTi intermetallic compounds.

It is seen from Fig. 7 that Al, Ti and Al-Ti diffraction peaks are observed in the deposit obtained at a deposition potential of \(-0.06 \) V by controlled-potential method. On the other hand, Ti diffraction peaks are not observed in the deposit obtained by pulse potential method (Fig. 8). However, aluminum diffraction peaks have been shifted from their standard position to higher angle indicating the formation of Al solid solution with Ti. The diffraction peaks are very sharp and there is no broad peak in the diffraction patterns. The X-ray diffraction pattern indicates that the deposits have crystalline structure. The practical compositions of the deposited Al-Ti alloys are obtained from the chemical analysis by ICP. The cathodic current efficiency for alloy deposition is about 97\%.
Table 1—Deposition condition and the chemical analysis results of the electrodeposited Al-Ti alloys

<table>
<thead>
<tr>
<th>Run no.</th>
<th>Deposition potential $E$/V vs. Al/Al$^{3+}$</th>
<th>Deposition current density $i$/A m$^{-2}$</th>
<th>Pulse potential method</th>
<th>Atomic ratio of Al and Ti in the deposits.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.06 V</td>
<td></td>
<td></td>
<td>73:27</td>
</tr>
<tr>
<td>2</td>
<td>-0.20 V</td>
<td></td>
<td></td>
<td>91:9</td>
</tr>
<tr>
<td>3</td>
<td>-0.30 V</td>
<td></td>
<td></td>
<td>95:5</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>-4</td>
<td></td>
<td>91:9</td>
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<tr>
<td>5</td>
<td></td>
<td>-8</td>
<td></td>
<td>95:5</td>
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<tr>
<td>6</td>
<td></td>
<td>-12</td>
<td></td>
<td>98:2</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td></td>
<td>$E_1$ = -0.1 V, $E_2$ = -0.32 V</td>
<td>85:15</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td></td>
<td>$E_1$ = -0.18 V, $E_2$ = -0.3 V</td>
<td>90:10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$t_1$ = 1.04 s, $t_2$ = 0.5 s</td>
<td></td>
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<tr>
<td></td>
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<td></td>
<td>$t_1$ = 0.02 s, $t_2$ = 0.1 s</td>
<td></td>
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</tbody>
</table>

Fig. 6—Scanning electron micrographs of the electrodeposited surface. Atomic ratio of Al and Ti in (a), 73:27 and (b), 85:15; thickness of the deposit, 7 μm.

Fig. 7—X-ray diffraction pattern of the electrodeposited layer. Atomic ratio of Al and Ti in the deposit, 73:27; substrate, Pt.

Fig. 8—X-ray diffraction pattern of the electrodeposited layer. Atomic ratio of Al and Ti in the deposit, 90:10; substrate, Pt.
It is somewhat surprising that alloys having a higher titanium content (>27 at%) are not deposited. However, the present result is important as it indicates that titanium could be electrodeposited in the form of Al-Ti alloy from the room temperature molten salt other than the high temperature molten salt.

Conclusions
(i) The electrodepositions of aluminum-titanium alloys have been carried out onto platinum and mild steel cathodes from 6.14:3.07:0.09 (mole ratio) AlCl3-BPC-TiCl4 molten bath by controlled-potential and pulse potential methods.
(ii) The electrodeposited alloys containing 0 to 15 at% Ti is a single phase of Al solid solution with Ti. However, more than one phases are obtained in the alloys containing >15 at% Ti.
(iii) The deposited surfaces are very smooth and have bright metallic colour. The cathodic current efficiency for alloy deposition is about 97%.

References