Electrodeposition of Titanium-Aluminum Alloys from Lewis Acidic $AlCl_3$-1-Ethyl-3-methylimidazolium Chloride Melts

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The resistance of aluminum to chloride-induced pitting corrosion is enhanced considerably when it is alloyed with transition metals, provided that these elements are present in solid solution with the aluminum at concentrations greater than their usual equilibrium solubilities. In this article, we report the electrochemistry of titanium in the Lewis acidic $AlCl_3$–1-ethyl-3-methylimidazolium chloride ($AlCl_3$–EtMeImCl) molten salt at 353 K as it pertains to the electrodeposition of Ti-Al alloys. The aim of this study is to clarify the role of the melt composition, Ti(II) concentration, and hydrodynamic transport rate on the alloy composition.

The dissolution of $TiCl_2$ was investigated as a method to introduce Ti(II) into the $AlCl_3$–EtMeImCl melt. However, dissolved Ti(II) is unstable and converts to sparingly soluble $TiCl_3$ by reaction with adventitious O_2 in the glove box, even when the O_2 concentration is very small (< 5 ppm). The stabilization of dissolved Ti(II) was achieved by taking advantage of the thermodynamically favored reaction[1]

$$2\ \mathrm{Ti(III)} + \mathrm{Ti} \rightleftharpoons 3\ \mathrm{Ti(II)} \qquad [1]$$

The rate of $TiCl_2$ dissolution could be greatly enhanced by adding titanium metal to the electrochemical cell because any Ti(III) that is produced is immediately converted to Ti(II). The solubility of Ti(II) increases as the melt is made more acidic, i.e., as the $Al_2Cl_7^-$ concentration in the melt is increased. Thus, the $TiCl_2$ dissolution reaction must be

$$TiCl_2 + zAl_2Cl_7^- \rightleftharpoons Ti(AlCl_4)_p^{(p-z)-} + (2z\text{-}p)AlCl_4^- \qquad [2]$$

Figure 1 shows cyclic voltammograms recorded at stationary and rotating platinum disk electrodes in the $AlCl_3$–EtMeImCl melt with and without added Ti(II). It was reported that the overpotential for aluminum deposition increases and the Al stripping wave shifts to positive values in acidic $AlCl_3$–NaCl melt after the addition of Ti(II).[2] This same result was observed when Ti(II) was added to acidic $AlCl_3$–EtMeImCl melt (Fig. 1). Furthermore, the positive shift in the Al stripping wave was dependent on the Ti(II) concentration in the melt.

The electrodeposition of Ti-Al alloy on copper substrates was investigated in the $AlCl_3$–EtMeImCl (x_{Al} = 0.600) melt containing 59.5 mM Ti(II) at a current density of -10 mA cm^{-2} at 353 K. Compact, crystalline, chloride-free Ti-Al deposits were obtained during these experiments. The titanium content of these alloys depends on the rotation rate of the electrode as shown in Fig. 2, reaching a maximum value of 11 atomic percent (a/o) as the rotation rate is increased above 500 rpm. The electrodeposited Ti-Al alloys were not intermetallic compounds, but solid solutions. Furthermore, the Ti content of the alloy increased as the melt was made more acidic, and it was possible to prepare alloys containing 19 a/o Ti in x_{Al} = 0.667 melt. Preliminary experiments indicate that these electrodeposited Ti-Al alloys are significantly more resistant to chloride-induced pitting corrosion than pure Al.

1. L. Legrand, A. Chausse, and R. Messina, *Electrochim. Acta*, **46**, 2407 (2001).
2. G. R. Stafford, *J. Electrochem. Soc.*, **141**, 945 (1994).

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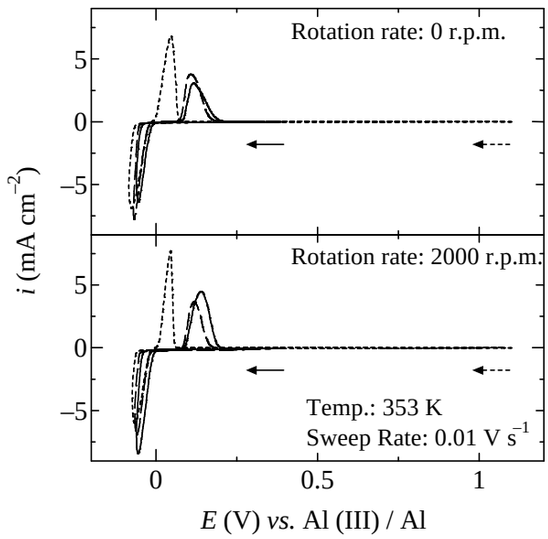

Fig. 1 Cyclic voltammograms recorded at stationary (top) and rotating (bottom) disk electrodes in $AlCl_3$–EtMeImCl (x_{Al} = 0.600) melt; (•••) pure melt, (- -) 40.4 mM Ti(II), and (—) 59.5 mM Ti(II).

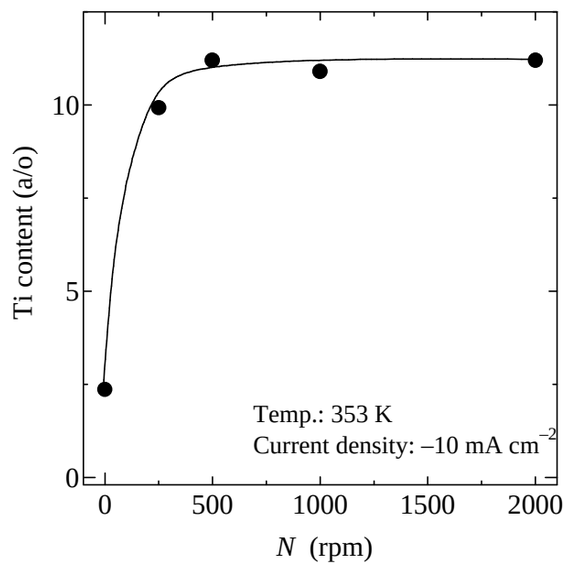

Fig. 2 Dependence of the Ti content (a/o) on the electrode rotation rate, N, for Ti-Al alloys electrodeposited from the $AlCl_3$–EtMeImCl (x_{Al} = 0.600) melt containing 59.5 mM Ti(II).