ELECTRODEPOSITION OF TITANIUM-ALUMINUM ALLOYS IN THE LEWIS ACIDIC ALUMINUM CHLORIDE-1-ETHYL-3-METHYLIMIDAZOLIUM CHLORIDE MOLTEN SALT

Tetsuya Tsuda and Charles L. Hussey, and Gery R. Stafford

Department of Chemistry and Biochemistry
The University of Mississippi, P.O. Box 1848
University, Mississippi 38677

Materials Science and Engineering Laboratory
National Institutes of Standards and Technology
Gaithersburg, Maryland 20899

ABSTRACT

The chemical and electrochemical behavior of titanium was examined in the Lewis acidic aluminum chloride-1-ethyl-3-methylimidazolium chloride (AlCl_3-EtMehnCl) molten salt at 353.2 K. Dissolved Ti(II), as TiCl_2, is stable in the 66.7-33.3 m/o composition of this melt, but shows a slight tendency to disproportionate in the 60.0-40.0 m/o melt. At low current densities, the anodic oxidation of Ti(0) does not lead to dissolved Ti(II), but to an insoluble passivating film of TiCl_3. At high current densities or very positive potentials, Ti(0) is oxidized to Ti(IV); however, the electro-generated Ti(IV) vaporizes from the melt as TiCl_4(g). The electrodeposition of Ti-Al alloys was investigated at Cu rotating wire electrodes. Ti-Al alloys containing up to ~ 19 a/o titanium could be electrodeposited from saturated solutions of Ti(II) in the 66.7-33.3 m/o melt at low current densities, but the titanium content of these alloys decreased as the reduction current density was increased. The pitting potentials of these electrodeposited Ti-Al alloys exhibited a positive shift with increasing titanium content comparable to that observed for alloys prepared by sputter deposition.

INTRODUCTION

It is has been demonstrated that the resistance of aluminum to chloride-induced pitting corrosion can be improved significantly by alloying with transition metals such as Cr, Cu, Mo, Mn, Nb, Ta, Ti, V, and Zr and rare earths such as Er. However, improved corrosion resistance is not observed unless these solutes are present at concentrations greatly exceeding their normal equilibrium solubilities, which in most cases is less than 1 % atomic fraction (a/o). This is because the pitting potential of aluminum is often related directly to the solute concentration, with greater concentrations leading to increased corrosion resistance.(1, 2) However, if the solute metal forms a precipitate, then the corrosion resistance of the aluminum is reduced because the precipitated solute forms microgalvanic corrosion cells.(3) Thus, nonequilibrium alloying methods such as rapid solidification or melt spinning ion implantation, reactive plasma spraying, sputter deposition, and thermal evaporation are needed in order to prepare single phase materials. However, a more
advantageous method for producing these alloy films is electrodeposition because this approach can lead to alloy coatings of uniform composition and structure.

Titanium is one of several transition elements that have been found to improve the corrosion resistance of aluminum. The electrochemistry of titanium has been studied extensively in Lewis acidic chloroaluminate melts and it has been determined that Ti-Al alloys can be electrodeposited from solutions of Ti(II) in these melts. In 66.7-33.3 percent mole fraction (m/o) AlCl₃-NaCl melt at 423 K, Ti-Al alloys containing up to 28 a/o Ti could be obtained by varying the Ti(II) concentration and/or the applied current density. However, when the Ti(II) concentration was raised above 150 mM in this melt at this temperature, the Ti content of the alloy became virtually independent of the current density, and TiAl₃, with an ordered L1₂ crystal structure was produced under these conditions.

In this article, we report the electrochemistry of titanium in the Lewis acidic AlCl₃-1-ethyl-3-methylimidazolium chloride (AlCl₃-EtMeImCl) molten salt at 353.2 K as it pertains to the electrodeposition of Ti-Al alloys. The aim of this study is to clarify the effects of the melt composition, Ti(II) concentration, and hydrodynamic transport rate on the Ti-Al alloy composition and to determine the best route for introducing Ti(II) into the electroplating bath.

EXPERIMENTAL

NOTE: Certain trade names are mentioned for experimental information only; in no case does it imply a recommendation or endorsement by NIST.

The procedures used for the synthesis of EtMeImCl, the purification of AlCl₃ by sublimation, and the preparation and purification of the AlCl₃-EtMeImCl molten salt were identical to those described in previous articles. Anhydrous titanium (II) chloride (Aldrich, 99.98 %) and anhydrous titanium (III) chloride (Aldrich, 99.999 %) were used as received. Titanium (IV) chloride (Matheson Coleman & Bell, 99.5 %) was used after dehydration. All molten salt experiments were carried out in a nitrogen gas-filled glove box (VAC Atmospheres NEXUS system) with O₂ and H₂O < 5 ppm. All electrochemical experiments were conducted in three-electrode cells. For experiments in the molten salt, the working electrode was either a Pine Instruments Teflon-sheathed platinum rotating disk electrode (geometrical area = 0.099 cm²), a length of 0.5 mm diameter titanium wire (Alfa Aesar, 99.98 %), or a small disk electrode prepared by sealing a length of the aforementioned titanium wire in a Pyrex glass tube and cutting off the end of the sealed tube so as to expose the cross section of the Ti wire. Coils of 1.0 mm diameter aluminum wire (Alfa Aesar, 99.999 %) were used for the counter and reference electrodes. These electrodes were immersed in melt with the same composition as the bulk melt, but were separated from the bulk melt by a porosity E glass frit (Ace Glass). The aluminum electrodes were cleaned with a mixture of concentrated H₂SO₄, HNO₃, and H₃PO₄, rinsed with distilled H₂O, and dried under vacuum before use.

Alloy samples of approximately 10 μm thickness were electroplated from solutions of Ti(II) in the AlCl₃-EtMeImCl molten salt onto a length of 1.25 mm diameter copper wire. The composition of each sample was determined by EDX spectroscopy. Potentiodynamic
pitting corrosion measurements were carried out on these alloy samples at room temperature
in a 0.1 mol L\(^{-1}\) solution of NaCl in distilled H\(_2\)O. This solution was deaerated with nitrogen
gas before each experiment. The reference electrode for these measurements was a sodium-
saturated calomel electrode (SSCE), and the counter electrode was a large surface area
platinum wire coil. A known length of the plated Cu wire was exposed to the NaCl solution
by using a heat-shrink Teflon tubing mask, and the sample was scanned at 0.5 mV s\(^{-1}\) by
using cyclic staircase voltammetry.

RESULTS AND DISCUSSION

Dissolution of TiCl\(_2\)

The dissolution of solid TiCl\(_2\) was investigated as a method to supply Ti(II) in Lewis
acidic AlCl\(_3\)-EtMeImCl melts for the electrodeposition of Ti-Al alloys. TiCl\(_2\) dissolved
slowly in these melts at 353 K; dilute solutions of Ti(II) appeared pale-green. The solubility
of TiCl\(_2\) in the two melt compositions used for this investigation, 60.0-40.0 and 66.7-33.3
percent mole fraction AlCl\(_3\)-EtMeImCl, designated hereafter as the 60.0 and 66.7 m/o melts,
respectively, was estimated by preparing saturated solutions of TiCl\(_2\) in both melts at 353.2
K, dissolving a weighed portion of the supernatant liquid from these saturated solutions in
distilled water, and determining the Ti(II) concentration with atomic absorption
spectroscopy using standard methods. The results of these experiments are given in Table I.
Because the solubility of TiCl\(_2\) increases with increasing melt acidity, i.e., with increasing
Al\(_2\)Cl\(_7\) concentration, the TiCl\(_2\) dissolution reaction must be:

\[
2 \text{Al}_2\text{Cl}_7^- + \text{TiCl}_2 \rightleftharpoons \text{Ti(II)(solv)} + 4 \text{AlCl}_4^- \quad [1]
\]

However, as will be shown later in this article, the solvated Ti(II) species is likely to be
polymeric or aggregated, especially when the Ti(II) is present at high concentrations. By
contrast to TiCl\(_2\), TiCl\(_3\) was found to be virtually insoluble in all compositions of the acidic
AlCl\(_3\)-EtMeImCl melt.

A small amount of purple precipitate identical to solid TiCl\(_3\) was present in the
60.0 m/o melt after the dissolution of TiCl\(_2\), but was not obvious in the 66.7 m/o melt.
The presence of TiCl\(_3\) in solutions of TiCl\(_2\) could arise through routes, disproportionation
of the dissolved Ti(II) as shown in Eq. 2

\[
3\text{Ti(II)} \rightleftharpoons 2\text{Ti(III)} + \text{Ti} \quad [2]
\]

or by oxidation of the Ti(II) through reaction with adventitious impurities in the melt or
with oxygen in the glove box atmosphere. Sørlie and Øye (13) reported that Ti(II) has a
slight tendency toward disproportionation in AlCl\(_3\)-KCl melts containing less than 60.0 m/o
AlCl\(_3\) but is stable in strongly Lewis acidic melts. On the other hand, Legrand et al.(14)
concluded that the disproportionation of Ti(II) to Ti and Ti(III) is unlikely because it is a
three-centered reaction. They proposed that the conversion of Ti(II) to TiCl\(_3\) in AlCl\(_3\)-
dimethylsulfone solutions results from the reaction of Ti(II) with trace amounts of oxidizing
impurities in the melt or with adventitious O\(_2\) in the glove box. Because the moisture and
oxygen content of our glove box system is less than 5 ppm, and the AlCl\(_3\)-EtMeImCl
molten salts used in this investigation are purified extensively by electrolysis before use, the oxidative pathway proposed by Legrand et al. (14) seems unlikely.

In order to examine the stability of dissolved TiCl₂, the room-temperature UV-visible absorption spectra of Ti(II) in both 60.0 and 66.7 m/o AlCl₃-EtMelmCl were recorded as a function of concentration (Figure 1). In the 60.0 m/o melt, Ti(II) exhibits bands at 344 and 444 nm, whereas the spectra of Ti(II) in 66.7 m/o melt show bands at 339 and 433 nm and a shoulder at 407 nm. In addition, the Ti(II) spectra in these two melts differ considerably at wavelengths greater than 500 nm. Figure 2 shows the relationship between the Ti(II) concentration and the absorbance at 444 nm in the 60.0 m/o melt and 433 nm in the 66.7 m/o melt. The plot constructed with absorbance data in the 66.7 m/o melt shows good adherence to Beer’s law over the composition range that was examined. However, the absorbance of the 444 nm band in 60.0 m/o melt was generally smaller than that for the corresponding band in the 66.7 m/o melt, and most significantly, it did not obey Beer’s law. Although there was no obvious evidence of TiCl₃ or Ti metal in the dilute solutions employed for this spectroscopic investigation, we conclude from the nonlinearity of the Beer’s law plot that Ti(II) has a slight tendency toward disproportionation in the 60.0 m/o melt. Thus, in view of the uncertainty about the Ti(II) concentration, we report herein only qualitative data for experiments carried out in the 60.0 m/o composition of the AlCl₃-EtMelmCl melt.

During previous investigations conducted in AlCl₃-NaCl-KCl, Ti(II) was introduced into the melt by the direct reduction of TiCl₃ or TiCl₄ with Ti or Al metal. (9) This method was investigated in 66.7 m/o AlCl₃-EtMelmCl melt by using TiCl₃ and Al. No UV-vis spectrum was observed for Ti(III) in the supernatant liquid of melts containing solid TiCl₃, attesting further to its insolubility in this melt. However, if sufficient powdered TiCl₃ was added to a known volume of melt to produce a 4.86 mM solution and this suspension of TiCl₃ is stirred with a small piece of Al metal at 353.2 K, then the solution becomes green and exhibits a spectrum identical to that for Ti(II) (Figure 1). Furthermore, the absorbance of the 433 nm band in this spectrum is in excellent agreement with the data for Ti(II) solutions shown in Figure 1, indicating complete conversion of the TiCl₃ to Ti(II). This may be an important result because Ti and TiCl₃ are much less expensive than TiCl₄. Thus, the in-situ reduction of TiCl₃ to soluble Ti(II) by Ti or Al metal may be a useful route for introducing Ti(II) into a plating bath.

**Anodic dissolution of titanium metal**

Anodic linear sweep voltammograms that were recorded at a stationary titanium disk electrode in the 66.7 m/o melt as a function of temperature are shown in Figure 3. At room temperature, the Ti electrode must be scanned to approximately 0.60 V before dissolution commences. As the temperature of the melt is raised to 353.2 K and higher, the potential for the onset of Ti dissolution decreases. At all of the temperatures that were investigated, oxidation of the Ti electrode proceeds until the electrode is covered with a passive film of precipitated TiCl₃, which then blocks the electrode. At elevated temperatures, this film breaks down when the potential is scanned above about 1.0 V as signaled by a sharp rise in the anodic current and the production of Ti(IV). Although a small current continues to flow at room temperature as the potential of the Ti electrode is scanned above 1.0 V, no appreciable breakdown of the TiCl₃ passive film occurs and so there is no sharp rise in current signaling the generation of Ti(IV). Because Ti(II) is stable in this melt (vide supra),
it is unlikely that the first wave in the voltammograms shown in Figure 3 arises from the direct oxidation of Ti(0) to TiCl₃. Instead, the first wave must arise from the successive reactions shown below

\[ \text{Ti}(0) \rightleftharpoons \text{Ti}(\text{II}) + 2 \text{e}^- \quad [3] \]

\[ \text{Ti}(\text{II}) + 6\text{AlCl}_4^- \rightleftharpoons \text{TiCl}_3(s) + 3\text{Al}_2\text{Cl}_7^- + \text{e}^- \quad [4] \]

This could only be possible if the potential for the reaction in Eq. 3 is very close to that for the reaction in Eq. 4. In aqueous solutions, the standard potentials of the Ti(II)/Ti and Al(III)/Al couples are virtually identical. (15) If this is also the case in acidic chloroaluminate melts, then the fact that the reactions in Eq. 3 and 4 are observed at essentially the same potential suggests that a considerable overpotential is required to initiate the oxidation of Ti metal (Figure 3). This supposition is also consistent with the observed temperature dependence of the potential at which the onset of Ti oxidation is observed. However, these results indicate that it is not possible to introduce Ti(II) into the AlCl₃-EtMeImCl melt by anodic oxidation of Ti metal.

**Electrodeposition of Ti-Al alloys**

It is well established that the electrodeposition of Al from acidic inorganic chloroaluminate melts containing Ti(II) results in the formation of Ti-Al alloys. Figure 4 shows cyclic voltammograms for stationary and rotating Pt disk electrodes in the 60.0 m/o melt with and without added Ti(II). It was demonstrated during a previous investigation that the potential of the Al stripping wave shifts positively in acidic AlCl₃-NaCl melt after the addition of Ti(II). (8) This behavior occurs because Ti co-deposits with Al to form Ti-Al alloy, which is more difficult to oxidize than pure Al. Similar behavior is observed in AlCl₃-EtMeImCl containing Ti(II). Furthermore, the magnitude of this shift increases with increasing Ti(II) concentration. Virtually identical results were observed in the 66.7 m/o AlCl₃-EtMeImCl melt. However, the addition of Ti(II) to acidic AlCl₃-EtMeImCl melt did not increase the overpotential for Al deposition as found for Ti(II) solutions in AlCl₃-NaCl. In fact, a small positive shift is evident.

In order to investigate the formation of bulk Ti-Al alloys, electrodeposition was performed by using dc galvanostatic methods at a current density of -10 mA cm⁻² in a Ti(II)-saturated melt. The substrate for these experiments was a copper rotating disk electrode (Cu-RDE). In the 66.7 m/o AlCl₃-NaCl melt at 423.2 K at Ti(II) concentrations greater than 150 mM, the Ti content of the Ti-Al alloy becomes virtually independent of the current density, and TiAl₃ is the predominant alloy produced under these conditions. (8, 16) However, different results were obtained in the 66.7 m/o AlCl₃-EtMeImCl melt at 353 K. Although solutions containing more than 150 mM Ti(II) can be prepared in this melt without difficulty (Table I), the Ti content of bulk Ti-Al alloys prepared in these solutions was found to increase as the applied current density is decreased. This result is expected if the potential of the Ti(II)/Ti reaction is about the same as that for the Al(III)/Al couple because at low reduction current densities and correspondingly less negative potentials, the partial current density for Ti would be a larger fraction of the total current. At larger reduction current densities or more negative potentials, the partial current for Ti probably reaches its mass transport-limited value whereas the partial current density for Al continues to increase relative to the Ti current density, becoming a larger fraction of the total current and resulting
in alloy deposits with a smaller fraction of Ti. The minimum current density that we used in these investigations was -2.5 mA cm⁻²; electrodeposits that were produced at this current density contained ~ 19 a/o Ti (Table II). The results of this investigation indicate that the titanium content of Ti-Al alloys electrodeposited from the AlCl₃-EtMeImCl melt is limited by the solubility of TiCl₂ and the minimum practical current density that can be used for the timely preparation of such deposit.

Pitting potential measurements

Potentiodynamic anodic polarization curves recorded in deaerated aqueous NaCl for Ti-Al alloys electrodeposited on copper wire electrodes are shown in Figure 5. As noted for Mn-Al alloys examined under similar conditions, (17) Ti-Al alloys display a stable passive region characterized by a very small potential-independent current followed by a sudden rise in current at the pitting potential. The variation of the pitting potential with alloy composition is shown in Figure 6. The addition of ~ 5 a/o Ti increases the pitting potential of the alloy by about 0.3 V; however, alloys containing 15 a/o Ti show only a 0.45 V increase in pitting potential relative to pure Al. Thus, the greatest benefit is realized by the addition of a relatively modest amount of Ti. This same result was noted for electrodeposited Mn-Al alloys, except that the formation of a two-phase f.c.c. + glass structure for alloys containing more than 5 a/o Mn led to a decrease in the pitting potential. (17) The increase in the pitting potential observed for electrodeposited Ti-Al alloys is comparable to that found for Ti-Al alloys prepared by sputter deposition. (4)

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REFERENCES

1. G. S. Frankel, R. C. Newman, C. V. Jahnes, and M. A. Russak, *J. Electrochem. Soc.*, 140, 2192 (1993).
2. J. R. Davis, "Corrosion of Aluminum and Aluminum Alloys", ASM International, Materials Park, OH, 1999.
3. W. C. Moshier, G. D. Davis, and G. O. Cote, *J. Electrochem. Soc.*, 136, 356 (1989).
4. G. S. Frankel, M. A. Russak, C. V. Jahnes, M. Mirzamaani, and V. A. Brusic, *J. Electrochem. Soc.*, 136, 1243 (1989).
5. K. W. Fung and G. Mamantov, *J. Electroanal. Chem.*, 35, 27 (1972).
6. R. T. Carlin, R. A. Osteryoung, J. S. Wilkes, and J. Rovang, *Inorg. Chem.*, 29, 3003 (1990).
7. G. M. Janowski and G. R. Stafford, *Metall. Trans. A*, 23A, 2715 (1992).
8. G. R. Stafford, *J. Electrochem. Soc.*, 141, 245 (1994).
9. J. Uchida, H. Seto, and A. Shibuya, *J. Surf. Finishing Soc. of Japan*, 46, 1167 (1995).
10. H.-Y. Hsu, D.-L. Chen, H.-W. Tsaur, and C.-C. Yang, in "Twelfth International Symposium on Molten Salts" (P. C. Trulove, H. C. De Long, G. R. Stafford, and S. Deki, eds.), Vol. PV 99-41, p. 585. The Electrochemical Society, Inc., Honolulu, HI, 1999.
Table I. Solubility of Ti(II) in acidic AlCl$_3$-EtMeImCl

|                         | AlCl$_3$–EtMeImCl | AlCl$_3$–NaCl |
|-------------------------|-------------------|---------------|
| Temperature / K         | 353               | 423           |
| mol % AlCl$_3$          | 60.0              | 66.7          |
|                        | 66.7              |               |
| Solubility of Ti(II) / mM | 60 ± 1$^a$        | 170 ± 2$^b$   |
|                        | 325$^7$           |               |
| Color of the melts:     | $^a$ dark green   | $^b$ dark reddish-yellow |

Table II. Electrodeposited Ti-Al alloys

|                      | TiCl$_3$ | Electrodeposition current density / mA cm$^{-2}$ |
|----------------------|----------|-----------------------------------------------|
| Titanium content / a/o | 66.7     | -2.5  -5.0  -10.0  -15.0  -20.0 |
|                      | 19.1     | 17.5  15.1  12.8  12.4 |
Figure 1. UV-vis absorption spectra of Ti(II) in the AlCl$_3$-EtMeImCl melt: (top) 60.0 m/o melt, the Ti(II) concentrations were (a) 8.21, (b) 4.03 (c) 2.08, (d) 1.00 mM; (middle) 66.7 m/o melt, the Ti(II) concentrations were (e) 8.16, (f) 4.06, (g) 2.03, and (h) 1.01 mM; (bottom) 66.7 m/o melt, (i) after stirring with sufficient TiCl$_3$ to prepare a 4.86 mM solution, (j) after the addition of Al metal to the solution in (i) and stirring for several hours, (k) after the anodic oxidation of a Ti electrode at 0.60 V, and (l) after the addition of Al metal to the solution in (k) and stirring for several hours.

Figure 2. Beer's law plot for Ti(II) in the AlCl$_3$-EtMeImCl melt prepared from the data in Figure 1: (●) 444 nm, 60.0 m/o melt, (○) 433 nm, 66.7 m/o melt, and (▲) the solution in Figure 1j at 433 nm.
Figure 3. Linear sweep voltammograms recorded as a function of temperature in the 66.7 m/o AlCl₃-EtMelmCl melt at a Ti disk electrode (a) room temperature, (b) 353.2 K, and (c) 373.2 and a Pt disk electrode (d) room temperature. The potential sweep rate was 0.01 V s⁻¹.

Figure 4. Cyclic voltammograms recorded at a (top) stationary and (bottom) rotating Pt-RDE (2000 rpm) in the 60.0 m/o AlCl₃–EtMelmCl melt at 353 K: (-----) neat melt, (- - -) 40.4 mM Ti(II), and (— —) 59.5 mM Ti(II). The potential sweep rate was 0.01 V s⁻¹.
Figure 5. Potentiodynamic polarization curves for Al and Ti-Al alloys in deaerated 0.1 M aqueous NaCl: (a) Al (99.999 %), (b) Ti_{7.6}Al_{92.4}, (c) Ti_{11.4}Al_{88.6}, and (d) Ti_{15.7}Al_{84.3}. The scan rate was 0.5 mV s\(^{-1}\).

Figure 6. Pitting potentials as a function of the Ti content of the Ti-Al alloys in Figure 5: (a) Al (99.999 %), (b) Ti_{7.6}Al_{92.4}, (c) Ti_{11.4}Al_{88.6}, and (d) Ti_{15.7}Al_{84.3}.