Electrodeposition of Titanium Aluminide (TiAl) Alloy from $AlCl_3$–BMIC Ionic Liquid at Low Temperature

Pravin S. Shinde, Yuxiang Peng and Ramana G. Reddy

Abstract Titanium and its intermetallic titanium aluminide (TiAl) alloys are technologically exciting materials due to their unique thermomechanical properties such as low density, excellent strength, and exceptional corrosion resistance. Herein, we demonstrate a low-cost route to electrodeposit TiAl alloy from liquid (IL) using a 2:1 molar ratio of aluminum chloride ($AlCl_3$) and 1-butyl-3-methylimidazolium chloride (BMIC). The cyclic voltammetry (CV) and chronoamperometry (CA) techniques were used to investigate the electrosynthesis parameters. The electrodeposition of phase-pure TiAl was accomplished on a copper cathode at a constant potential at 100 °C in a three-electrode configuration that involved Ti plate counter electrode (anode) as a sacrificial donor source of Ti ions in the IL and titanium or platinum wire as a reference electrode. The electrodeposited TiAl alloy electrodes were characterized using scanning electron microscopy, energy-dispersive X-ray spectroscopy, and X-ray diffraction methods. The electrodeposited TiAl alloy exhibited uniform, smooth, and compact morphology.

Keywords TiAl alloy · Electrodeposition · BMIC–$AlCl_3$ · Ionic liquid

Introduction

Titanium (Ti) metal has been playing a progressively vital role for several alloys including iron, aluminum, vanadium, and molybdenum to produce stronger lightweight alloys for aerospace, military, automotive, medical, and several industrial applications because of its corrosion-resistant property and highest strength-to-weight ratio. One of the simplest ways to synthesize Ti metal is through electrochemical manufacturing using domestic metal sources such as scraps in ionic liquid (IL) electrolytes at relatively low temperatures (~100 °C). Electrodeposition of metallic

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Ti using titanium scrap material at low temperatures is of particular interest. Unfortunately, the electrochemical mechanism for titanium deposition is more complicated than other metals such as aluminum because of its different oxidation states (II, III, and IV). Therefore, it is often electrodeposited in the form of alloys, such as titanium aluminide (TiAl). TiAl alloy, the intermetallic formed from Ti and aluminum (Al) metals, is receiving increasing attention as high-temperature structural materials due to their unique thermomechanical properties such as low density, excellent strength, high melting point, and good oxidation resistance and structural stability. Although Ti is highly corrosion-resistant, stronger, and 45% lighter than steel [1], it is expensive and difficult to extract and machine [2].

The electrodeposition of Ti and TiAl alloys has been performed via an energy-efficient and cost-effective extraction process (alternative to existing Kroll's process) using the molten chloride/fluoride salt electrolytes [3–12]. Stafford conducted the electrodeposition of $TiAl_3$ alloy on Cu substrate using chloroaluminate salt of $AlCl_3$–NaCl (2:1 molar ratio) at 150 °C [13]. The electrochemical studies of $TiCl_4$ in a strongly Lewis acidic room temperature molten salt showed that Ti^{4+} is reducible to Ti^{3+} and Ti^{2+} in two steps with one-electron charge transfer each, while Ti^{3+} was deposited at the electrode as a dark thin film, mostly as $TiCl_3$ organic salts [14]. However, the application of molten salts for the electrodeposition of TiAl alloys is mainly limited due to the high melting points, viscosities, and corrosivity of the salts. Stafford et al. [15] studied the electrochemistry of titanium using $2A1C1_3$–NaC1 electrolyte in which the oxidation of titanium yielded Ti(II), Ti(III), and Ti(IV) complexes. The divalent species Ti(II) led to electrodeposit TiAl alloys, while the trivalent species are sparingly soluble. The TiAl alloy is deposited on Cu rotating disk and wire electrode from an acidic $AlCl_3$–EMIC–$TiCl_2$ electrolyte at room temperature. TiAl alloy containing up to 19 at.% Ti is produced from a saturated solution of Ti(II) in the 2:1 molar ratio of $AlCl_3$ and EMIC at low current densities. They found a small amount of purple precipitate, identical to solid $TiCl_3$ in the 1.5:1 molar ratio melt electrolyte after the dissolution of $TiCl_2$ but was not evident for the 2:1 molar ratio melt. Legrand et al. [9] investigated the stability of Ti(II) species in $AlCl_3$–$DMSO_2$ (dimethyl sulfone) electrolyte at 130 °C using voltammetry and chronopotentiometry. The reduction in Ti(III) to Ti(II) involves an electrochemical–chemical mechanism, i.e., reversible electron transfer followed by a homogeneous oxidation reaction of Ti(II) to Ti(III) with $DMSO_2$ acting as oxidizing species. Despite several attempts to deposit phase-pure Ti, it only resulted in the co-deposition of Al and Ti. Nevertheless, the low-temperature electrochemical synthesis of TiAl alloys using IL is not only energy efficient but also eliminates high-temperature melting and consolidation processes. It is always a challenging task to electrodeposit phase-pure titanium due to the complex electrochemistry of titanium in chloroaluminate IL electrolyte and passivation of electrode surface with $TiCl_3$.

In the present work, a novel low-temperature synthesis route for electrodeposition of titanium aluminide (TiAl) alloy is demonstrated using titanium as sacrificial anode in ionic liquid (IL) electrolyte containing aluminum chloride ($AlCl_3$) and 1-butyl-3-methylimidazolium chloride (BMIC). Although several literature data are available to understand the electrochemical phenomenon of titanium and aluminum ions in ionic liquid electrolytes, the bulk electrodeposition of TiAl alloys using ionic liquid at low temperature has not been explored. This work involves developing a process for bulk electrodeposition of Ti or TiAl alloys using BMIC at low temperature and studying the deposited material by structural, morphological, and compositional characterizations.

Experimental Details

The aluminum chloride ($AlCl_3$) and 1-butyl-3-methylimidazolium chloride (BMIC) were used as received. A standard three-electrode electrodeposition set-up was used. The cell was air-free with an arrangement for continuous purging of ultra-high pure (UHP) Ar gas at a streamlined low flow rate. The temperature was controlled using a hot plate and monitored accurately using a thermometer inserted in a cell. TiAl alloy was deposited electrochemically on a copper plate as well as on platinum wire using $AlCl_3$–BMIC (molar ratio = 2:1) IL electrolyte at fixed applied potentials (−1 to −1.3 V vs. Ti) and the electrolyte temperatures (110 °C). The approach to incorporate Ti into the TiAl alloy involved the use of Ti counter electrode as a sacrificial anode as a source of Ti ions in the IL electrolyte. Ti metal sheet and copper plate served as anode and cathode, respectively. Ti or Pt served as reference electrodes in a three-electrode system. The cyclic voltammetry (CV) and chronoamperometry (CA) techniques were used to study the oxidation–reduction reactions and also to electrochemical deposition of TiAl alloy. The electrodeposited TiAl alloy electrodes were characterized using scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), and X-ray diffraction (XRD) techniques.

Results and Discussion

Here, we outline some of the fundamental studies on low-temperature electrochemical production of dendrite-free smooth TiAl alloys which can open a new route in aluminum and titanium process metallurgy. Figure 1 shows an experimental set-up of a typical electrochemical cell. The electrochemical cell for CV study consisted of Pt wire as a working electrode (WE), Ti or Pt wire as a reference electrode (RE), and Ti plate as a sacrificial anode working electrode (WE), which are immersed in an ionic liquid of $AlCl_3$–BMIC (molar ratio 2:1) at 100 °C. A slow and steady UHP argon gas flow is maintained throughout the experiment. The IL electrolyte is also stirred continuously at a constant speed (~60 rpm). The weights of CE and WE are measured on a microbalance before starting the electrochemical deposition. The weight gain on WE or weight loss from CE can be considered as one of the first steps toward confirmation of the electrodeposits.

To decide the deposition potentials of Al and Ti, the cyclic voltammogram is recorded by scanning the cathode electrode potential in the negative direction from

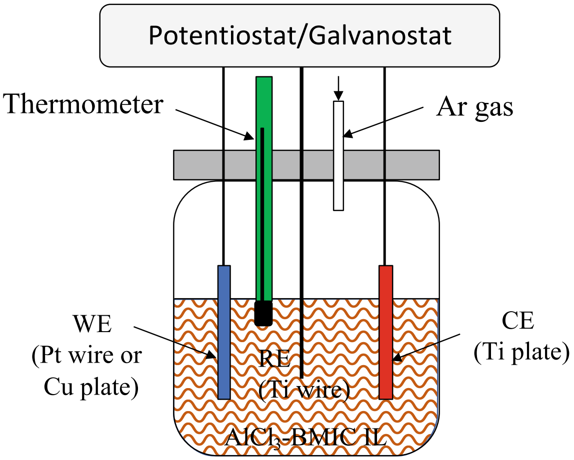


Fig. 1 Schematic experimental set-up for electrochemical deposition of TiAl alloy from ionic liquid

+1 V to −1.6 V vs. Ti at 110 °C. Figure 1a shows the cyclic voltammogram of $AlCl_3$–BMIC IL recorded on Pt wire electrode at the scan rate of 300 mV s^{-1}. The area of WE immersed inside the electrolyte is 0.118 cm^2. It is known that highly acidic $AlCl_3$–BMIC has a higher content of $AlCl_3$ (e.g., the molar ratio of 2:1); $AlCl_3$ reacts with tetra-chloroaluminate ions ($AlCl_4^-$) ions to produce hepta-chloroaluminate ions ($Al_2Cl_7^-$) in $AlCl_3$–BMIC ionic liquid (Reaction 1). Dent et al. [16] and Abdur-Saha et al. [17] have studied the structure of various divalent metal chlorides dissolved in acidic $AlCl_3$–BMIC ionic liquid electrolyte. The metal ions form a complex with $Al_2Cl_7^-$ ions in the ionic liquid. Hussey et al. [18] showed that divalent Ti (II), which allows the process control and optimum deposition, is present in the form of Ti-hepta-chloroaluminate complex $[Ti(Al_2Cl_7)_4]^{2-}$ according to Reaction (2).

Figure 2 shows the cyclic voltammogram of $AlCl_3$–BMIC on polished titanium wire recorded at the scan rate of 300 mV s^{-1}. When the CV is swept from 1 V or open-circuit potential towards a negative direction, a tiny reduction peak at 0.187 V vs. Ti appears. This peak is due to a two-electron reduction in Ti-hepta-chloroaluminate complex ions from ionic liquid according to Reaction (3) to deposit metallic Ti on a copper substrate. As the potential sweeps further toward more negative potentials, the cathodic current becomes steady until −1.0 V vs. Ti and increases rapidly giving rise to a reduction peak at −1.4 V vs. Ti, which signifies the deposition of Al according to the Reaction (4). During the reverse sweep, a broad oxidation peak at −0.06 V vs. Ti followed by a tiny peak at 0.475 V vs. Ti appears, which dictates the anodic stripping of Al and Ti complex species, respectively. The ratio of cathodic peak current (E_{pc}) and anodic peak current (E_{pc}) measured for reduction/oxidation reactions for Ti during forward and reverse sweeps is close to unity ($E_{pc}/E_{pa} \sim 1$). Moreover, the interpeak distance (ΔE_p) is 0.288 V. That is, $(\Delta E_p) = |E_{pc} - E_{pa}| = 28.8$ mV. For an entirely reversible reaction, the $\Delta E_p = 2.303RT/nF = 59.2$ mV/n, where n represents the number of electrons exchanged during the reduction or oxidation reaction. The

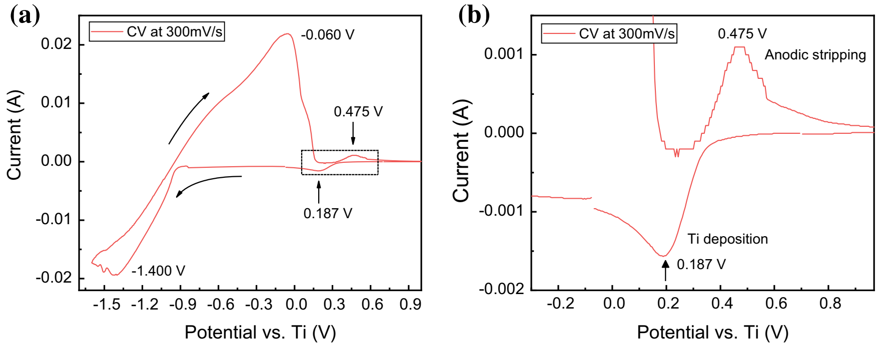


Fig. 2 **a** Cyclic voltammogram of $AlCl_3$–BMIC on polished titanium wire vs. Ti at the scan rate of 300 mV s^{-1} at 100 °C, and the corresponding, **b** magnified view of the same showing cathodic deposition of Ti and subsequent anodic stripping during reverse direction

number of electrons involved in the reduction or oxidation reaction according to Reaction (3) is 2. For two-electron reduction or oxidation reaction, the value of ΔE_p should be 29.6 mV, which is close to the observed value of 28.8 mV. This suggests that the charge transfer processes involving deposition/stripping of Ti is reversible.

Anodic reactions:

$$AlCl_3 + 7(AlCl_4)^- \rightarrow 4(Al_2Cl_7)^- + 1.5Cl_2 + 2e^- \tag{1}$$

$$Ti(anode) + 4(Al_2Cl_7)^- \rightarrow \left[Ti(Al_2Cl_7)_4\right]^{2-} + 2e^- \tag{2}$$

Cathodic reactions:

$$\left[Ti(Al_2Cl_7)_4\right]^{2-} + 2e^- \rightleftharpoons Ti(cathode) + 4(Al_2Cl_7)^- \tag{3}$$

$$4(Al_2Cl_7)^- + 3e^- \rightleftharpoons Al(cathode) + 7(AlCl_4)^- \tag{4}$$

The reduction peak at −1.4 V vs. Ti and anodic stripping peak at −0.06 V vs. Ti in Fig. 2a is separated by $\Delta E_p = {\sim}1.34$ V. Higher value of ΔE_p (>59.2 mV/n, considering a three-electron reduction reaction, $n = 3$) for Al deposition indicates that the electrochemical process is quasi-reversible. To further confirm on the electrochemical deposition of Ti, CV of $AlCl_3$–BMIC (molar ratio 2:1) electrolyte is re-recorded on titanium wire using platinum reference electrode as shown in Fig. 3a. The reduction peak at −0.6 V vs. Pt confirms the deposition of Ti, which is in line with the reduction peak observed for Ti from [EMIm]Tf_2N containing 0.25 M $TiCl_4$ electrolyte as shown in Fig. 3b [19].

The electrochemical deposition of TiAl alloy is performed with the help of potentiostat with different applied potentials and the deposition times. The cathodic electrodeposition of TiAl is initially performed using CA technique at −1.3 V vs. Ti

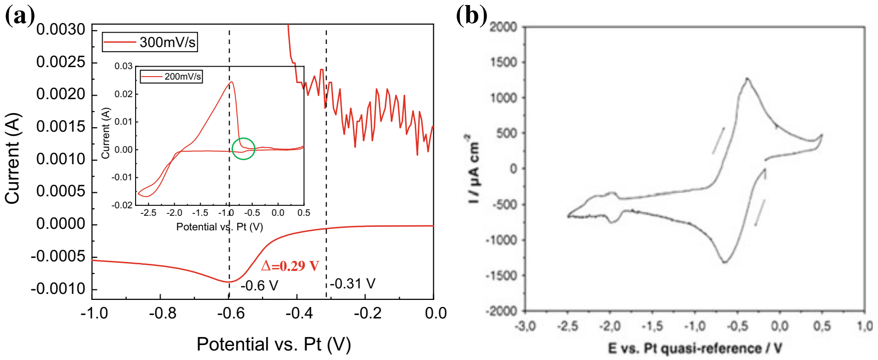


Fig. 3 **a** Cyclic voltammogram (magnified view) of $AlCl_3$–BMIC on polished titanium wire vs. Pt at the scan rate of 300 mV s^{-1} at 100 °C (Inset shows the full CV). **b** Cyclic voltammogram of $[EMIm]Tf_2N$ containing 0.25 M $TiCl_4$ on Au(111) substrate vs. Pt at a scan rate of 10 mV s^{-1} at room temperature [19]

(which is slightly lower than the cathodic peak potential) for 1 h at 110 °C using a three-electrode configuration with the copper plate as WE, sacrificial Ti anode as a CE, and Ti as a RE. Then, TiAl is also deposited on the copper plate by decreasing the cathodic reduction potential to −1.0 V vs. Ti while increasing the deposition time to 2 h.

The deposited TiAl material is characterized using X-ray diffraction (XRD) and SEM-EDS techniques. Figure 4a, b shows the XRD patterns of TiAl alloy deposited on copper at −1.3 V and −1.0 V vs. Ti, respectively. The insets in the respective XRD patterns shows the digital photographs of TiAl alloy deposited on the copper cathode for different deposition potentials. The deposits appear to be very smooth with dendrite-free growth, unlike previous reports. The XRD patterns of TiAl sample deposited for 1 and 2 h show that the peaks correspond to TiAl according to the standard diffraction data (ICDD#01-084-3906). XRD detected neither Ti nor TiAl intermetallic compounds. However, the diffraction peaks got shifted slightly in the XRD pattern. Tsuda et al. [18] observed the occurrence of Al peaks in the XRD besides TiAl peaks. In our case, no peaks of metallic Al in the diffraction pattern are observed. This confirms that the electrodeposit exists in the alloy form.

Then, to examine the morphology and confirm the chemical composition of the deposits, the SEM and EDS analyses are performed, as shown in Fig. 5a, b. SEM image at low magnification shows uniform coverage of larger grains with cracks. However, the deposits are dense despite some cracks at high magnification. The EDS spectrum recorded over a large selected area reveals ~3 at.% Ti and 97 at.% Al in the deposit. No other impurity peaks are observed apart from Ti and Al. After deposition of TiAl, the mass of Cu substrate is increased by 4.6 mg, and that of Ti plate is decreased by 17 mg. Only 3 at.% (5 wt%) Ti is noticed in TiAl alloy from EDS. Based on the weight loss of Ti plate, the initial concentration of dissolved Ti in the ionic liquid is calculated as 1.1986×10^{-5} mol L^{-1}. More work is underway to improve the amount of Ti deposited in TiAl alloy.

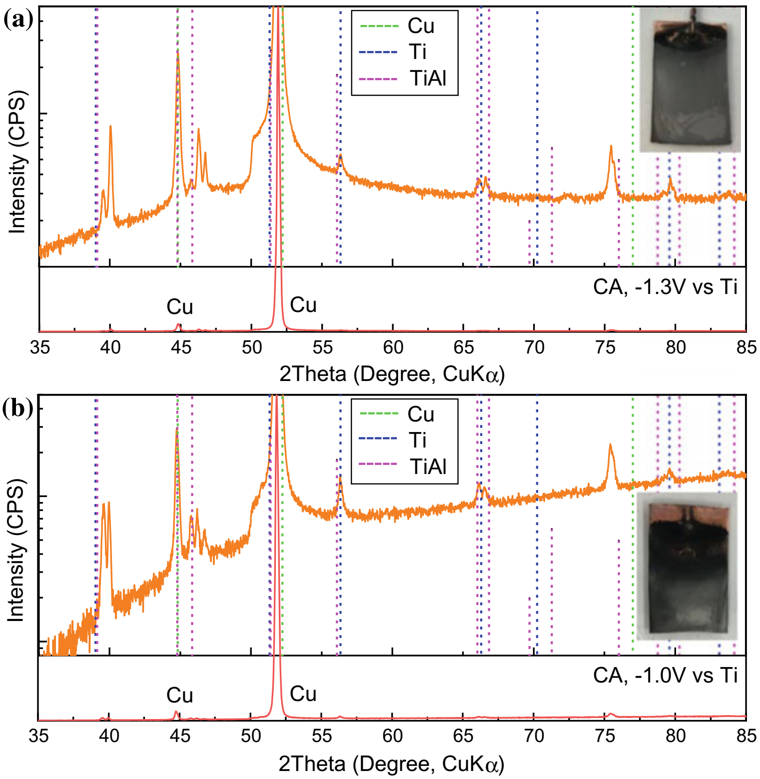
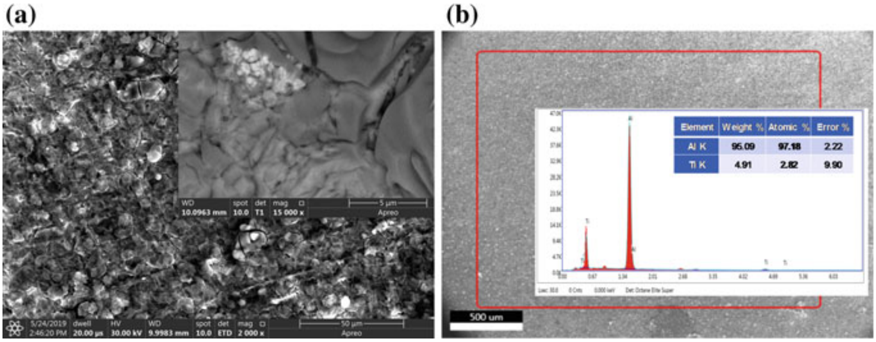


Fig. 4 XRD patterns of the electrodeposited TiAl alloy on the copper substrate at **a** −1.3 V vs. Ti for 1 h and **b** −1.0 V vs. Ti for 2 h (Insets show the respective photographs of TiAl alloy deposited on Cu electrodes)



Element	Weight %	Atomic %	Error %
Al K	95.09	97.18	2.22
Ti K	4.91	2.82	9.90

Fig. 5 **a** Surface morphology of TiAl alloy on copper at 2000× (Inset shows magnified image at 15,000×); **b** EDS analysis on a selected area, revealing the chemical composition of Ti and Al in TiAl deposit on copper deposited at −1.3 vs. Ti for 1 h

Thus, through this work, we demonstrated that it is feasible to synthesize TiAl alloy by dissolving Ti scraps in ionic liquid. This electrochemical process has the potential to be employed for large scale production. Our future work is based on electrodepositing Ti-rich TiAl alloys using different ionic liquids at different bath temperatures. The efforts will also be made to investigate the effect of the addition of Ti species ($TiCl_4$) into the electrolyte in addition to the use of Ti scrap as a sacrificial anode.

Conclusions

This study demonstrated electrosynthesis of titanium–aluminum (TiAl) alloy from $AlCl_3$–BMIC ionic liquid at relatively low temperature. Constant potential production of TiAl alloys is performed on Pt and Cu cathodes from $AlCl_3$–BMIC ionic liquid with a molar ratio of 2:1 at the applied potentials ranging from -1.0 to -1.3 V at 100 °C ± 2 °C. TiAl alloys produced at a relatively lower applied voltage (-1.0, -1.3 V) are dark, uniform, dendrite-free, and compact in nature. The amount of Ti in the TiAl is still 3% for 1 h deposition at -1.3 V vs. Ti, which could be improved further by controlling the number of Ti species and their concentration in the electrolyte.

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