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Chapter 18

Electrochemical Preparation of Titanium and its Alloy in Ionic Liquid

Cunying Xu and Yixin Hua

Additional information is available at the end of the chapter

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1. Introduction

Titanium and its alloys are widely used in aerospace, medical and structural applications because of their unique specific strength that is maintained at elevated temperature, high corrosion resistance and excellent biocompatibility. However, the use of them has been highly selective due to high cost resulting from their high energy consumption and complicated procedure. Therefore, researchers around the world attempt to find a cheap and simple process for production of titanium and its alloys. Electrochemical preparation is a promising method for fabrication of titanium and its alloys, because it is simple, manufacturable, inexpensive, and its ability to control crystal structure and morphology of them by adjusting electrochemical parameters. Since the deposition potential of titanium is more negative than that of hydrogen, the deposition of titanium or its alloys from aqueous solution is impossible. As a result, aprotic solvents such as molten salts, in which the evolution of hydrogen is precluded, may be good alternatives to aqueous solution for the electrochemical preparation of titanium and its alloys. The electrochemical preparation of titanium and its alloys has been widely studied in conventional inorganic molten salts, but the results are disappointed because these fused salts have many disadvantages, such as high melting point, high viscosity, and high corrosivity.

In recent three decades, ionic liquids as environmentally benign solvents have drawn much attention and have been found wide applications in the organic synthesis, catalyst, electrochemistry, and extraction separation. For electrochemical application ionic liquids combine the advantages of both aqueous solution and high temperature molten salt: they display wide electrochemical window, excellent electrical conductivity, negligible vapor pressure, low melting point (100°C), wide temperature range for the liquid phase, and free from hydrogen evolution. Thus, Ionic liquids are good solvents for the electrochemical preparation of metals and alloys, especially for active elements. The electrochemical preparation of titanium and its

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alloys from ionic liquids has been investigated by several researchers. Based on our previous work and those reported by others, we will show the electrochemical preparation of titanium and its alloys such as Al-Ti, Zn-Ti and Al-Mn-Ti in ionic liquid.

2. Electrochemical preparation of titanium from ionic liquid

2.1. Electrodeposition of titanium from ionic liquid

Titanium is an industrially important metal used in many applications, because of its unique properties such as excellent corrosion resistance and high specific strength. Since the electrodeposition of titanium is impossible from aqueous solution, the high temperature molten salt as a promising electrolyte for the production of titanium has been investigated by many researchers. The electrodeposition of titanium from high temperature molten salt had been developed and scaled up until a pilot plant by Italian Ginatta Titanium Turin and America New-Jersey Company. The obtained titanium had low impurity contents, depending on the purity of the $TiCl_4$. However, this process was eventually abandoned due to some technology and economic problems, including incontrollable back reaction of between $TiCl_2$ and chlorine to $TiCl_4$, difficulties to change the cathodes and high corrosion caused by the hot chlorine gas. Recently, there were some attempts to electrodeposit titanium at room temperature in the air and water-stable ionic liquid using $TiCl_4$ as a source of titanium [1-4]. Freyland et al. reported for the first time electrodeposition of titanium in l-methyl-3-butyl-imidazolium bis(trifluoromethylsulfone)imide ([Bmim]BTA) and 1-butyl-3-methylimidazolium bis((trifluoro- methyl)sulfonyl)amide ([Bmim]Tf_2N) containing $TiCl_4$ as a source of titanium at room temperature [1, 2]. The cyclic voltammograms showed that Ti(IV) was reduced to Ti(II) and subsequently reduced to Ti(0) in [Bmim]Tf_2N ionic liquid. In situs canning tunneling microscopy (STM) measurements showed that titanium may be electrodeposited at the step edge of highly oriented pyrolytic graphite (HOPG) in nanowires [1] and on Au(111) substrate in ultrathin layers [2].

However, Endres et al. reported that their attempts to deposit micrometer thick titanium deposits with the recipe in Ref. [2] failed. Instead of titanium metal, polymeric subvalent titanium halide species are obtained. Moreover, they extensively investigated whether titanium could be electrodeposited from its halides ($TiCl_4$, TiF_4, TiI_4) in different ionic liquids, namely 1-ethyl-3-methylimidazolium bis(tri- fluoromethylsulfonyl)amide ([Emim]Tf_2N), 1-butyl-1-methyl-pyrrolidinium bis(trifluoromethylsul- fonyl)amide ([BMP]Tf_2N), and trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)amide ([$P_{14,6,6,6}$]Tf_2N). The cyclic voltammetry and electrochemical quartz crystal microbalance (EQCM) measurements show that, instead of elemental Ti, only non-stoichiometric halides are formed, for example with average stoichiometries of $TiCl_{0.2}$, $TiCl_{0.5}$ and $TiCl_{1.1}$ [3]. Wallace et al. used pyrrole and polypyrrole as a nucleating agent to induce titanium depositionin in [Emim]Tf_2N [4]. Titanium containing polypyrrole codeposits have been achieved, but bulk metallic titanium is not observed. The measurement results from in situ EQCM indicate that the viscosity of ionic liquid electrolyte increases significantly in the process of electroreducing $TiCl_4$, furthermore

titanium deposition might change with breakdown of Tf_2N [5]. Abbott has explained that the obvious increase in electrolyte viscosity results from the change of double layer interface structure during electrolysis [6]. In addition, we also tried to electrodeposit titanium in the ionic liquids 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF_4) and 1-butyl-3-methylimidazolium hexafluorophosphate([Bmim]PF_6) containing $TiCl_4$. There is again no evidence for the titanium electrodeposited from both ionic liquids except $TiCl_x$ deposited on the surface of cathode. The formation of insoluble titanium chloride complex usually involves the solvent, which was proved by the experimental results obtained from electrochemical and chemical reduction of $TiCl_4$ in ionic liquids. Thermodynamically, the electrodeposition of Ti should be possible in ionic liquids, as its electrode potential is -1.64 V vs. NHE. Aluminum has practically the same electrode potential for reduction (about -1.67 V vs. NHE), which can be electrodeposited quite easily in different ionic liquids. Nevertheless, more effort is required to find a suitable ionic liquid and especially the right titanium precursors for a technically relevant process.

2.2. Direct electrochemical reduction of titanium oxide to titanium

At present, titanium is industrially produced by the Kroll process in which titanium tetrachloride is reduced to titanium sponge by magnesium. This is a complicated and time-consuming batch process, which makes titanium an expensive metal [7]. Although titanium has many very useful properties such as high strength, low density and very good corrosion resistance, its application is restricted by the high processing cost. With this background, much effort has been directed towards the development of alternative low-cost processes to produce titanium. Various new methods have been developed, including FFC [8], OS [9], EMR [10] and PRP [11]. The FFC method is considered as the most promising alternative method for production of titanium, but it is potentially limited by high reaction temperature.

Recently, we reported for the first time that the direct electrochemical reduction of titanium dioxide to metallic titanium at room temperature in in Lewis basic $AlCl_3$-1-butyl-3-methylimidizolium ($AlCl_3$-BMIC) ionic liquid [12, 13]. The TiO_2 film obtained by oxidizing titanium foil in a furnace at 823 K in air for 144 h was used as the working electrode and a silver wire as the reference electrode. The typical cyclic voltammograms of oxidized titanium electrode in $AlCl_3$-BMIC melt at 343 K was shown in Figure 1. The initial sweep toward more negative potentials exhibits two clearly-defined reduction waves A and B at -0.33 and -0.60 V (vs. Ag), which may be owing to reduction of the TiO_2 film. Furthermore, the anodic peak observed in the solid curve at -0.18 V (vs. Ag) is indicative of metal dissolution, which has been formed in the original cathodic sweep. After 5 minute electrolysis, the oxidation peak at the cathode potential of -1.6 V (dash line) becomes greater, which indicates that a substantial amount of fresh titanium metal was available for the oxidation.

For more extensive reduction, the oxidized Ti strip was held at a potential of -1.6V for 8 h. The reduction waves and their corresponding anodic waves were absent, and the appearance of cyclic voltammogram was very similar to that of the bare Ti foil. The result indicates that titanium oxide can be electroreduced to Ti metal.

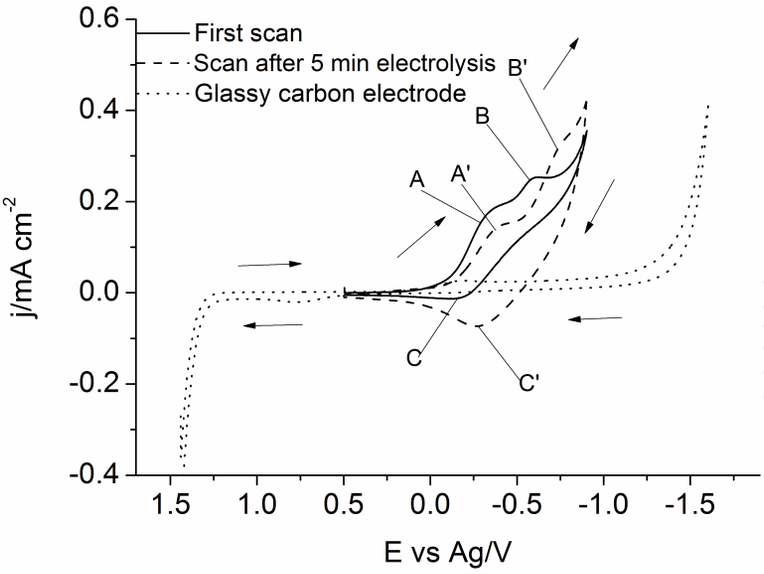


Figure 1. Cyclic voltammograms of oxidized Ti foil and glassy carbon electrode in Lewis basic $AlCl_3$-BMIC obtained at 50m V s^{-1} and 343 K. [Ref.12]

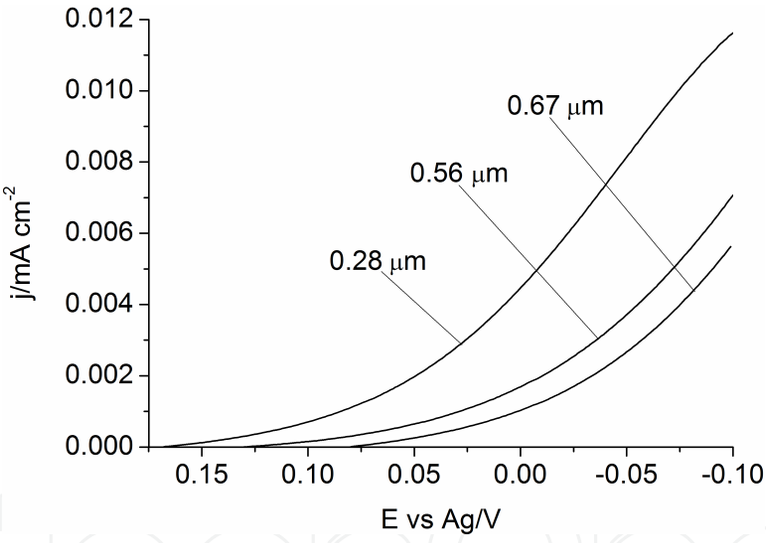


Figure 2. Cathode polarization curves for oxidized Ti foils with different thickness of titanium oxide film in Lewis basic $AlCl_3$-BMIC at 343K and 5mVs^{-1}. [Ref.12]

The cyclic voltammetry experiments demonstrated a dependence of the reduction potential on the thickness of TiO_2 film formed on the Ti foil, as shown in Figure 2. The initial reduction potentials shift to more negative potential with increasing the thickness of oxide film. An increase in thickness of oxide film (resistance) might enhance the cathode polarization, which was resulted from the cathode inhibition effect of the oxide film on the reduction process. Thus the direct electrochemical reduction of bulk TiO_2 should need a greater overpotential.

Tafel curves recorded at oxidized Ti foil with different thickness of TiO_2 film indicated that equilibrium potential negatively shifted, and the exchange current density as well as cathode

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Tafel slope decreased along with an increasing linear polarization resistance when TiO_2 film became thicker. Obviously, direct electrochemical reduction of bulk TiO_2 should need a greater driving force. This conclusion was in agreement with the cyclic voltammetry measurement.

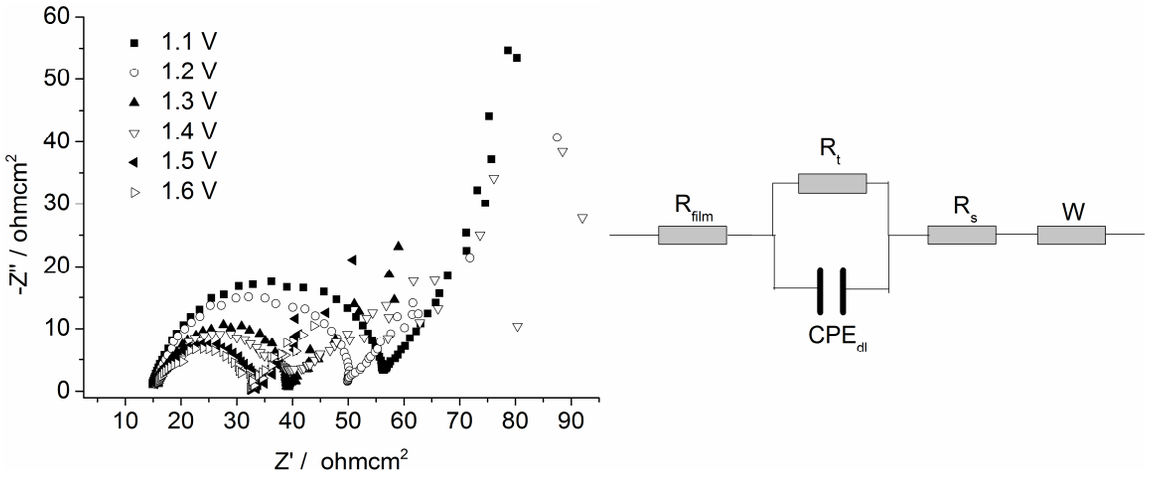


Figure 3. Alternating current impedance spectra of oxidized Ti foil in Lewis basic $AlCl_3$-BMIC at 343 K and corresponding equivalent circuit. [Ref.13]

Alternating current impedance spectra of oxidized Ti foil clearly showed that an increase in cathodic overpotential led to a decrease in reduction charge resistance (see Figure 3). One semicircle was observed in the higher frequency region of all Nyquist plots obtained at different cathodic potential, suggesting that the interface charge transfer process between the TiO_2 film and ionic liquid could be the rate-determining step for the reduction of TiO_2 film. On the contrary, a nearly linear increasing of −Z with Z at the low frequency region may be attributed to the mass transfer in the ionic liquid. The equivalent circuit has been used to simulate the Ti/TiO_2 film/IL (ionic liquid) system, which fitted the experimental data best (Figure 3). In this system, R_{film} and CPE_{film} represent the resistance and capacity of oxide film respectively; R_t refers to the charge transfer resistance process occurring on the oxide film surface; CPE_{dl} delegates the double capacity at the interface between the oxide film and tested IL; R_s can be explained to be the resistance of the tested IL; W can describe the diffusion control process at low frequency. Fitted results from Alternating current impedance spectra of oxidized Ti foil with different TiO_2 thickness showed that the R_{film} increased with increasing of thickness of TiO_2 film.

For increasing the reduction rate of this process, the dependence of electrochemical behavior of TiO_2 film on the reaction temperature was investigated. The cathode polarization curves of oxidized titanium foil in $AlCl_3$-BMIC at different temperatures showed that cathode overpotential decreased with an increase in reaction temperature. Accordingly, it is concluded that increasing reaction temperature can weaken the cathode inhibition of this reduction process. Alternating current impedance experiments of TiO_2 films at different temperatures showed that the resistance of the electrochemical reduction decreased with the reaction temperature increasing. The parameters fitted from experimental data by the equivalent circuit mentioned

above showed increasing temperature made the charge transfer resistance R_t and tested IL resistance R_s decline.

Metallographic microscopic image showed the reduced TiO_2 film obviously has metallic luster, implying that TiO_2 film was reduced to metal. It was found that a lot of bubbles were generated at the bottom of cathode and less at anode during the electrochemical reduction process of TiO_2 film. It could be predicted that the reduction of TiO_2 film in basic $AlCl_3$-BMIC was possibly occurred at the edges of the foil, mostly due to the different potential distribution at the edges of the electrode.

From the above results, it is evident that TiO_2 film can be electroreduced in $AlCl_3$-BMIC ionic liquid. As further proof of this conclusion, the electrochemical reduction of titanium dioxide pellet in ionic liquid was investigated. After electrochemical reduction for 48 h, the TiO_2 pellet visually turned to bright black. The X-ray photoelectron spectroscopy indicated the electroreducted TiO_2 pellet contains a small amount of titanium metal, suggesting that TiO_2 may be reduced to metallic Ti in this experiment, but the reaction rate is very low.

The mechanism for electroreduction of TiO_2 in high temperature molten salt has been extensively studied. It is generally known that oxygen ions are formed at cathode and oxygen evolves at the surface of the anode [7]. However, a lot of bubbles are generated in cathode region during the electrochemical reduction of TiO_2 and only a few of bubbles are observed in anode region, indicating that the reduction process of TiO_2 in ionic liquid is different from that in high temperature molten salt and may be attributed to interfacial electrochemical reaction mechanism. TiO_2 is an n-type semiconductor that has a wide band gap ($E_g \approx 3.2$ eV) [14-16], which makes charge transfer more difficult than other narrow ones. The increase in cathodic polarization may cause the electronic bands bending downward at the interface between TiO_2 and ionic liquid, resulting in a decrease of the space- charge region of TiO_2 with formation of electron-accumulation layer at the surface of TiO_2, where oxygen ions are formed, and as a consequence, the TiO_2 is reduced [17]. Correspondingly, it is considered that TiO_2 film is reduced in $AlCl_3$-BMIC melt according to these steps below (Figure 4).

(1) With negative shift of cathode potential, the electronic bands at the interface between TiO_2 and ionic liquid bent downward, where charge transfer occurred. In other words, oxygen ions are generated as a result of TiO_2 molecules reacting with electrons at the interface of TiO_2 /ionic liquid ($TiO_2 + 4e \rightarrow Ti + 2O^{2-}$). (2) The space formed among these reduced Ti would be filled with ionic liquid at once. (3) The oxygen ions dissolved in ionic liquid would diffuse through the porous layer of reduced titanium. (4) Oxygen ions diffused from cathode region to the surface of the anode and anodically discharged to form O_2 ($2O^{2-} \rightarrow O_2 \uparrow + 4e$). (5) When new generated titanium film formed which then served as anode, O_2 was generated at the interface of new generated titanium, TiO_2 and ionic liquid. At this moment, the anode just acted as a conductor.

In short, TiO_2 film on titanium foil can be electroreduced to metallic Ti in $AlCl_3$-BMIC melt at room temperature. However, reduction of bulk TiO_2 needs greater overpotential, so the electrochemical reduction of TiO_2 to metal is very difficult. More effort is required to find a

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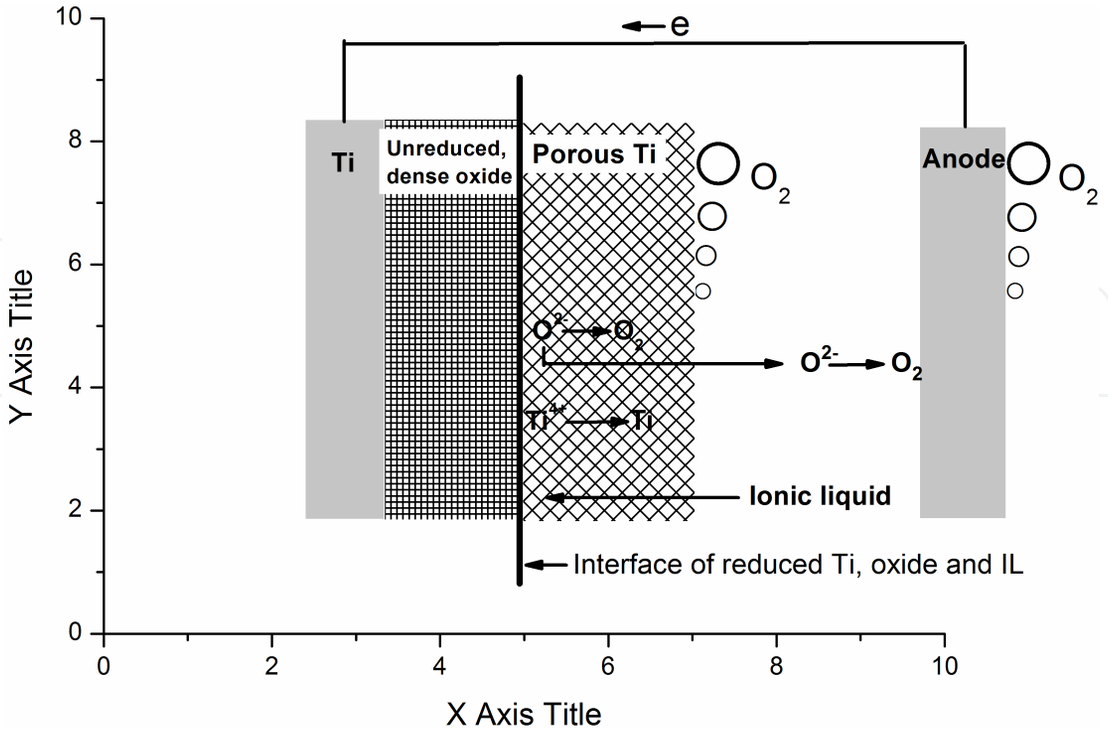


Figure 4. Model for the reduction process of oxides film on titanium foil in Lewis basic $AlCl_3$-BMIC ionic liquid. [Ref. 13]

suitable ionic liquid and especially the right methods of making TiO_2 electrode to improve conductivity of TiO_2 with a technically relevant process.

3. Electrodeposition of titanium alloys in ionic liquid

3.1. Electrodeposition of Al-Ti alloy

Al-Ti alloys are widely used in aerospace industry because of their excellent corrosion resistance, high temperature oxidation resistance and mechanical properties [18, 19]. As Al and Ti are reactive metal ($E^{\circ}_{Al(III)/Al}$ = –1.67 V vs. NHE, $E^{\circ}_{Ti(II)/Al}$ = –1.64 V vs. NHE), Al-Ti alloy can not be obtained from an aqueous electrolyte. The electrolytes for Al, Ti and Al-Ti alloy electrodeposition must be aprotic, such as high temperature molten salt or ionic liquid. The electrodeposition of Al-Ti alloys from high temperature molten salt has been extensively investigated [20], but many disadvantages such as high melting point, high viscosity, and high corrosivity limit its practical application. In recent years, the development of room-temperature ionic liquid has resulted in another potential approach for Al-Ti alloy electrodeposition. Tsuda et al. firstly investigated the electrochemical preparation of Al-Ti alloys from Lewis acidic $AlCl_3$-EMIC (aluminum chloride-1-ethyl-3-methylimidazolium chloride) melts with various concentration of Ti(II) at 353K [21, 22]. The Ti(II) ions used here can be obtained by the addition of $TiCl_2$ or by chemical reduction of $TiCl_3$ dissolved into ionic liquid by Al metal. In additions, our investigations conducted in $AlCl_3$-BMIC indicate that Ti(II) can also be obtained

in ionic liquid by the direct reduction of $TiCl_4$ with Al metal. Since $TiCl_4$ and $TiCl_3$, as well as aluminum, are much less expensive than $TiCl_2$, the in situ reduction of $TiCl_4$ or $TiCl_3$ to Ti(II) by aluminum metal may be a useful method for introducing Ti(II) into chloroaluminate ionic liquid.

It was proposed that $TiCl_2$ dissolves in the liquid by forming $[Ti(AlCl_4)_3]^-$ and its solubility increases with increasing ionic liquid acidity, i.e., with increasing $Al_2Cl_7^-$ concentration.

$$TiCl_2(s) + 2Al_2Cl_7^- \rightarrow \left[Ti\left(AlCl_4\right)_3\right]^- + AlCl_4^- \quad (1)$$

The liquid acidity is decreased by changing the molar ratio of $AlCl_3$ to BMIC from 2:1 to 3:2, leading to the disproportionation reaction of the $[Ti(AlCl_4)_3]^-$ for the production of $TiCl_3$ precipitates and metal Ti [21, 22].

$$3\left[Ti\left(AlCl_4\right)_3\right]^- + 3AlCl_4^- \text{ € } \quad 2TiCl_3(s) + Ti + 6Al_2Cl_7 \quad (2)$$

Ti(II) species tends to form polymers or aggregates upon increasing the Ti(II) concentration or the liquid acidity. The value of $D_{Ti(II)}$ decreases with the increase of the Ti(II) concentration, which is attributed to that the formation of a polymeric or aggregated species leads to a diffusing entity with a larger solvodynamic radius. Electrochemical, galvanostatic or potentiostatic, oxidation of Ti metal produces either insoluble passive $TiCl_3$ film or volatile $TiCl_4$ which can escape from the liquid. At higher potential, the $TiCl_3$ passive film breaks down and generates Ti(IV). The oxidation of metallic titanium to Ti(II) by direct anodization of Ti metal in this liquid has not been studied by Tsuda et al. Our observation indicates that the galvanostatic oxidation of titanium at the current density of 2-20 mA cm^2 produces Ti(IV). Furthermore, we can not obtain the Ti(II) in $AlCl_3$ based ionic liquid using either galvanostatic oxidation of titanium. These results suggest that anodic oxidation of metallic titanium is almost impossible for introducing Ti(II) because of the difficulty of controlling the oxidation potential.

From the cyclic voltammograms of stationary and rotating Pt disk electrodes in the acidic $AlCl_3$-EMIC melt containing Ti(II), it can be seen that the reduction potential of Ti(II) to Ti(0) is close to the deposition potential of Al [21, 22]. The potential of the stripping wave shifts positively due to the codeposition of Ti with Al to form Al-Ti alloy, which is more difficult to oxidize than pure Al. Furthermore, the value of negative shifts increases as the concentration of Ti(II) increases. The electrodeposition of bulk Al-Ti alloys is performed under constant current at a current density of 10 mA cm^{-2} in an ionic liquid with saturated Ti(II) [21]. The content of Ti in the Al-Ti alloys deposited in this way becomes higher with a decrease in applied current density, implying that the reduction of Ti(II) to Ti(0) occurs at a more positive potential than the deposition of Al. At low reduction current densities and correspondingly less negative potentials, the partial current density for the electrodeposition of Ti metal would be a larger fraction of the total current density. Increasing the total applied reduction current densities or making the applied potential more negative, the partial current for the electrodeposition of Ti

quickly increases to a mass transport limited value because Al (III) concentration is much more than Ti(II), while the partial current density for Al deposition will keep increasing, which causes an decrease in the Ti content of Al-Ti alloys deposited. The maximum content of titanium in Al-Ti alloys that are electrodeposited from this ionic liquid depends on the saturation concentration of $TiCl_2$ in the ionic liquid and the minimum current density that can be practically used. It can be seen from scanning electron images of the Al-Ti alloy electrodeposited that the deposits were compact, dense and composed of nodular crystals [21, 22]. The nodular crystals grow up as current density is increased or Ti content is decreased, indicating that the grain refinement is driven by the incorporation of Ti metal into the alloy rather than the deposition overpotential. This nicely demonstrates that the impurities and alloying additions have an impact on morphology of the deposit. The XRD (X-ray powder diffraction) analysis results indicate that electrodeposited Al-Ti alloys with the Ti content of 7.0-18.4 at.% are the disordered face-centered cubic (fcc) structure, as highly similar with the structure of Al. The lattice parameters of the alloys decrease, which is to be expected as the smaller Ti atoms substitute for Al atoms in the fcc lattice [22]. Furthermore, X-ray reflection peaks of the Al-Ti alloys broaden with increasing Ti content, suggesting a decrease in the grain size of the deposit. Recorded for Al-Ti alloys electrodeposited on copper electrodes in deaerated aqueous NaCl solution, the potentiodynamic anodic polarization curves show that the pitting potential of electrodeposited Al-Ti alloys significantly increases as compared to that of pure Al, which is in accord with that is observed for Al-Ti alloys obtained by sputter deposition [21].

Aliet al. examined the electrodeposition of Al-Ti alloys on platinum electrode in $AlCl_3$-BPC-$TiCl_4$ (molar ratio 6.14:3.07:0.09) ionic liquid using controlled-potential and pulse potential method at 298K [23]. Al-Ti alloys containing up to 27 % atomic fraction (a/o) titanium can be electrodeposited from this electrolyte at the deposition potential of -0.06 V vs. Al/Al(III), but the titanium content of these alloys decreases as the reduction current density is increased or the deposition potential is negatively shifted. The Al-Ti alloy deposits obtained either by controlled-potential or by pulse potential method are compact and smooth. The efficiency of the process is about 97%. The X-ray powder diffraction (XRD) patterns of the electrodeposits show that the electrodeposited alloy containing 27 at.% Ti is composed of Al, Ti and Al_3Ti, but a single phase of Al solid solution with Ti are obtained as the Ti content in electrodeposited alloy decreases to 15 at.%.

The electrodeposition of Al-Ti alloys on Au(111) in an acidic aluminum chloride-1-butyl-3-methylimidazolium chloride($AlCl_3$-BMIC) containing 10 mmol $TiCl_4$ at 298 K was also reported by Freylandet al. [22, 24]. From cyclic voltammograms, it is found that Ti(IV) can be firstly electroreduced to Ti(III) and subsequently reduced to Ti(II), whereby Ti (III) is formed precipitates on the electrode as sparingly soluble $TiCl_3$. The reduction of Ti(III) to Ti(II) occurs at a potential where underpotential deposition (UPD) of Al on Au(111) also occurs. Furthermore, the codeposition of Al and Ti is followed by the deposition of bulk Al. A stripping peak is observed at more negative potential relative to the Al stripping during an anodic scan, which is assigned to oxidation of Al-Ti alloy. The electrochemical scanning tunneling microscopy (EC-STM) analysis for the underpotential deposits show that Al preferentially grow up along the step edges of Au substrate resulting in step edge decoration, whereas Al-Ti grow into

smaller clusters homogenously spread on the Au electrode. Furthermore, the Al-Ti clusters are clearly smaller in size than the Al clusters. The formation of an Al-Ti alloy phase in the electrodeposits is further confirmed by an X-ray photoelectron spectra (XPS) analysis.

Reddy et al. attempted electrochemical production of Al-Ti alloys from $AlCl_3$-BMIC-$TiCl_4$ (molar ratio 2:1: 0.019) and $AlCl_3$-BMIC (molar ratio 2:1) ionic liquids at temperature between 70-125°C and constant voltage between 1.5-3.0 V [25, 26]. The Al-Ti alloys containing about 15-27 at% Ti are produced with a current efficiency of about 25-38%. Ti content in Al-Ti alloy deposits decreases as the applied cell voltage increases or the temperature increases. Increasing the applied cell voltage probably leads to mass-transport-limited value for Ti deposition, while the total charge passed through the cell still increases, resulting in the Ti content in the alloy deposits decreasing. The scanning electron micrographs show that the deposits are nodular but not so dense or compact. As the applied voltage decreases, average particle size decreases and deposits becomes uniform and compact. In addition, the deposits particle size increases slightly with the temperature increasing from 70 to 100℃. But increasing temperature beyond 100°C, particles begin to grow quickly, which results in the formation of clusters rather than separated particles. At low voltage or low temperature, lower the migration rate of reducible ions and growth rate of crystal nuclei make the deposits become smoother and fine grained. Finally, the optimum conditions for production of smooth, compact, fine particle size and high Ti content Al-Ti alloys are 1.5-2.0 V voltage and 70-100°C temperature. The X-Ray diffraction (XRD) analysis of electrodeposited alloy confirms the formation of Ti-Al alloy. The cathodic current efficiency in $AlCl_3$-BMIC-$TiCl_4$ electrolyte is very low (25-38%) for all experiments. The lower current efficiency is due to the formation of $TiCl_3$ passive layer on electrode surfaces, which retards the kinetics of redox reaction, and reduces the cathode current efficiency. This obstacle of low current efficiency can be overcome by using $AlCl_3$-BMIC instead of $AlCl_3$-BMIC-$TiCl_4$. Titanium metal is used as the anode and its dissolution serves the source of Ti ion in the electrolyte. The cathodic current efficiency of the process in $AlCl_3$-BMIC as electrolyte is up to 78-87%. The absence of $TiCl_4$ in the electrolyte reduces the formation of $TiCl_3$ passive layer on the electrodes because $TiCl_4$ is easily reduced to $TiCl_3$. The energy consumption for the production of Ti-Al alloy using this ionic liquid is about 3.92-9.47 kWh/kg, which is far lower than that for the commercially production of Al-Ti in molten salt.

Although the Al-Ti alloy can be successfully produced using constant voltage in $AlCl_3$-BMIC-$TiCl_4$, (molar ratio 2:1:0.019) and $AlCl_3$-BMIC (molar ratio 2:1) electrolytes, the studies on process variables are limited to applied voltage and temperature. Our group investigated the electrodeposition of Al-Ti alloy by using galanostatic on copper, titanium and stainless steel from an acidic $AlCl_3$-BMIC (2:1 molar ratio) ionic liquid containing $TiCl_4$ [27]. The substrates have great influence on the morphology and composition of the alloy deposits. The Ti content of Al-Ti alloys prepared at a current density of -5 mA cm^{-2} in this ionic liquid containing 0.2 mol L^{-1} $TiCl_4$ on copper, titanium and stainless steel is 4.9 at.%, 6.3 at.%and 9.0 at.%, respectively. The scanning electron micrographs show that the deposits on both copper and stainless steel are nodular, whereas deposits on titanium are sheet-like structures. Furthermore, the particle size on copper is smaller than that on stainless steel. It is observed that the Ti content in Al-Ti alloy deposited on these substrates decreases with increasing current density. Since

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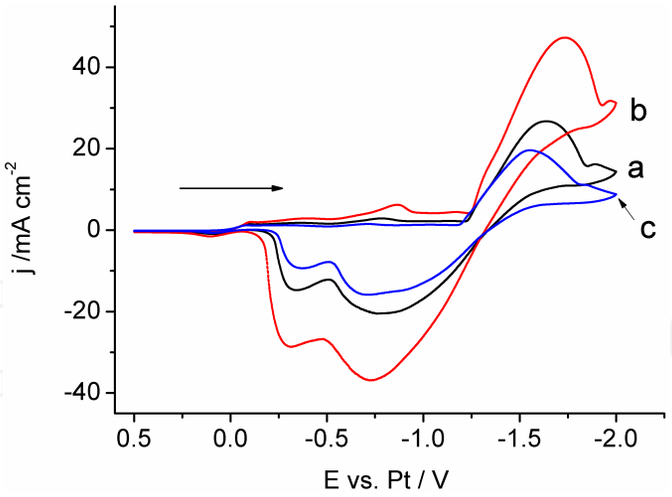


Figure 5. Cyclic voltammograms obtained at glassy carbon electrode at 50 mV s^{-1} in $AlCl_3$- BMIC-$TiCl_4$ (molar ratio 2:1:0.037) (a) and with the following additives: (b) 0.25 mol dm^{-3} toluene and (c) 0.25 mol dm^{-3} NH_4Cl

the reduction current of Ti(II) reaches limiting current condition more quickly than that of $Al_2Cl_7^-$, the partial current for the Al deposition remains increasing when partial current for the Ti deposition reaches a limiting current density, which results in a decrease in the Ti content of the alloys electrodeposited with an increase in current density [21]. Also, it is found that the content of Ti in Al-Ti alloys increases with increasing Ti(IV) concentration in ionic liquid. Results from SEM examinations reveal that the morphology of the Al-Ti deposits varies with the alloy composition. The deposit particle decreases in size with increasing Ti composition, decreasing current density and increasing Ti(IV) concentration.

The Al-Ti alloys can be successfully electrodeposited on different substrates in ionic liquids, but deposits are not very dense, smooth or bright, limiting its practically plating application. Quite recently we examined the addition of toluene and NH_4Cl additives and their effect upon the composition and morphology of electrodeposited Al-Ti alloys [28]. The cyclic voltammetric responses of $AlCl_3$-BMIC-$TiCl_4$ (molar ratio 2:1:0.037) in the absence and presence of equimolar quantities of the additives toluene and NH_4Cl indicate that the shape of the voltammograms and peak current densities is dependent on the additives used (see Figure 5). From these results it is evident that either the Al-Ti alloys deposition or stripping processes is affected by the addition of the additives. The onset of the Al-Ti alloy deposition potentials shifted anodically in the presence of NH_4Cl, suggesting that the NH_4Cl promotes the reduction of Al-Ti alloy. However, the opposite shiftis observed for the addition of toluene, suggesting that toluene restrains the deposition of Al-Ti alloy. Additionally, it should be noted that the charge passed during Al-Ti alloy reduction is greatly increased in the presence of toluene, but decreased in the presence of NH_4Cl relative to the additive free solution. These results indicate that the presence of the additives affects the Al-Ti deposition processes and various additives have different effect on Al-Ti electrodeposition, leading to change in the composition and morphology of Al-Ti alloy. The EDS analysis indicates that Ti content of Al-Ti alloy deposits increases in the presence of toluene, but decreases in the presence of NH_4Cl. The Al-Ti morphology is further modified upon the introduction of NH_4Cl or toluene to the solution. In contrast to the

deposits in the absence of additive, the deposits particles size obviously decreases and deposits become more smooth, dense, and uniform in the presence of additives.

3.2. Electrodeposition of Zn-Ti alloys

Zn-Ti alloys are used widely as metallic coatings in the corrosion protection of iron and steel due to their excellent corrosion resistance [29]. The electrodeposition is one of most promising techniques to prepare Zn-Ti alloy because it is simple and inexpensive, and is able to tailor the properties of the deposit by adjusting the deposition conditions. However, the electrodeposition of Zn-Ti alloys from aqueous solutions is impossible by the fact that hydrogen evolves before Ti deposition. The electrodeposition of Zn-Ti alloys were investigated by our group in a $ZnCl_2$-urea (1:3 molar ratios) eutectic-basedionic liquid containing 0.27 mol L^{-1} $TiCl_4$ [30]. Cyclic voltammograms recorded at glassy carbon electrode in the $ZnCl_2$-urea (1:3 molar ratios) eutectic-based ionic liquid are shown in Figure 6. Only a pair of redox peaks appears in the cyclic voltammogram of pure $ZnCl_2$-urea ionic liquid, which can be attributed to the deposition and stripping of Zn. After the addition of $TiCl_4$ to $ZnCl_2$-urea liquid, two additional reduction waves are observed in the voltammetry curve. Voltammetric data show that the first cathodic wave at -0.36 V (vs. Pt) corresponds to the reduction of Ti(IV) to Ti(III). It is noted that the violet passivating film is formed on the electrode surface after this reaction, indicating that Ti(III) is insoluble in $ZnCl_2$-urea eutectic-basedionic liquid. Thus, the reaction of Ti(IV) to Ti(III) in $ZnCl_2$-urea liquid involves the following sequence of reactions:

$$Ti(IV)_{solv} + e^- \text{ € } Ti(III)_{solv} \tag{3}$$

$$Ti(III)_{solv} + Cl^- \text{ € } TiCl_3 \downarrow \tag{4}$$

The second wave (B) at the more positive potential than that of Zn electrodeposition is contributed to the reduction of Ti(III) to Ti(II). Furthermore, the wave ascribed to the reduction of Zn(II) shows a small negative shift and the oxidation wave shifts to more positive potentials in the presence of $TiCl_4$. The positive shift of the stripping wave indicates formation of Zn-Ti alloy that is more stable toward oxidation than pure Zn.

The Zn-Ti alloys are electrodeposited on Cu substrate from $ZnCl_2$-urea deep eutectic ionic liquid with $TiCl_4$. The effects of deposition potential and temperature on the surface morphology and composition of electrodeposited Zn-Ti alloys are studied. The obtained alloys are adherent onto Cu substrate, but not very compact or dense. The EDX analysis shows that the deposits are composed of Zn and Ti, which are chloride-free. At the same temperature, the Ti content in Zn-Ti alloy increases with increasing potential from -1.3 to -1.8 V, but the Ti content tends to decrease as potential increased from -1.8 to -2.2 V. Because the initial deposition potential of Zn is more positive than that of Ti, the partial current for the electrodeposition of Ti metal would increase with increasing the deposition potential at lower deposition potential [8]. However, the Ti ion concentration (0.27 mol L^{-1}) is much less than Zn ion concentration

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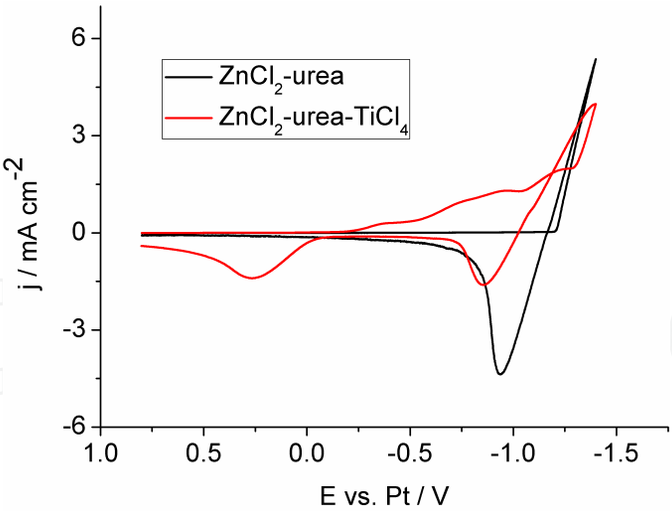


Figure 6. Cyclic voltammograms recorded at a glassy carbon electrode in the $ZnCl_2$-urea (1:3 molar ratios) eutectic based ionic liquid with and without $TiCl_4$ at 353 K. The sweep rate was 0.02 V s^{-1}. [Ref. 30]

(4.79 mol L^{-1}) in the electrolyte. With further increasing of the deposition potential from -1.8 to -2.2 V, the partial current for the reduction of Ti (II) ions probably reaches a limiting value, whereas partial current for the reduction of Zn (II) ions continues to increase, and then Ti content in Zn-Ti alloys decreases. Under the same deposition potential, the Ti content in the deposits increases as the temperature increases. Ti ion concentration is very low in the electrolyte and the reduction of Ti is controlled by mass-transport process [25, 31]. An increase in the temperature would enhance the mass transport rate of Ti(II), and increase the deposition rate of Ti. The XRD patterns for electrodeposits show that the Zn-Ti alloy exhibits a chemically disordered hexagonal close-packed (hcp) structure very similar to that of pure zinc. The largest lattice parameters (a) corresponding lattice expansion ($\Delta a/a$) of 0.67% occur at an alloy with Ti content about 8.4 at.%, suggesting the formation of Zn-Ti alloys. The SEM images shown in Figure 7 demonstrate the particle size increases gradually as the deposition potential becomes more negative or temperature increases. When the deposition potential becomes negative to -2.0 V or temperature is increased up to 363 K, deposited grains grow quickly and the deposits become a little rough. At low deposition potentials or low temperature, the discharge rate of reducible ions on the electrode is lower and nucleation rate is faster than the crystal-growth rate, which results in fine-grained deposit.

In addition, the effect of substrates on the morphology and composition of the deposits was also investigated. The Ti content of Zn-Ti alloys on mild steel is significantly lower than that on copper and particle size on mild steel is obviously smaller than that on copper.

In contrast to DC plating, pulsed electrodeposition (PED) offers unique advantages, such as deposition of uniform and crack free coating with desirable characteristics. Recently, our group investigated that the electrodeposition of Zn-Ti alloys on mild steel in a $ZnCl_2$-urea (1:3 molar ratios) eutectic-based ionic liquid [32]. At constant current off-time and pulse current density, the grain size decreases with decreasing current on-time, deposits become more compact and refined grain structure (see Figure 8). In contrast, an increase in the current off-time at constant

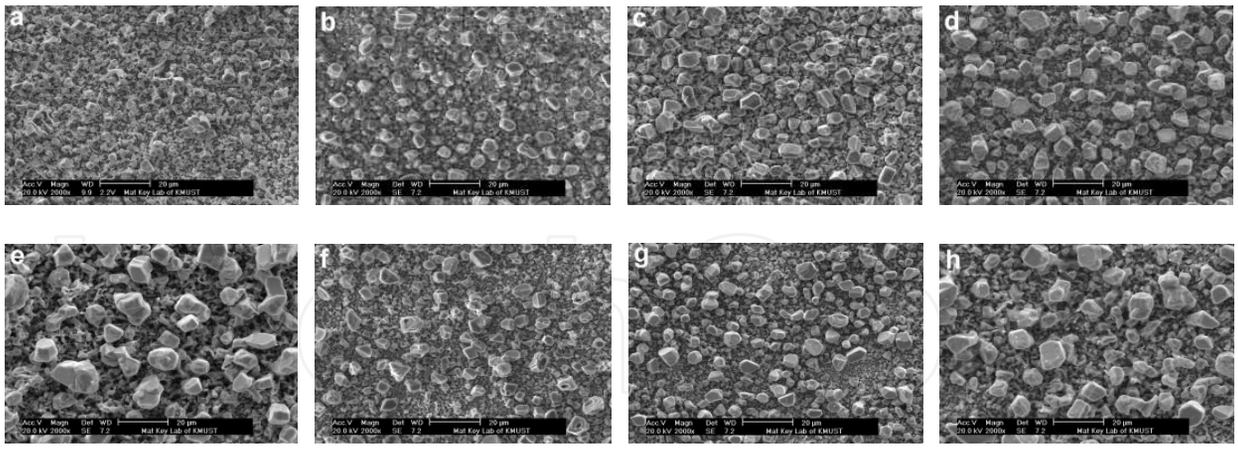


Figure 7. SEM images of the Zn-Ti alloys prepared in $ZnCl_2$-urea ionic liquid containing 0.27 mol L^{-1} $TiCl_4$ under different potentials and various temperatures: (a) -1.3 V, 353 K; (b) -1.5 V, 353 K; (c) -1.8 V, 353 K; (d) -2.0 V, 353 K; (e) -2.2 V, 353 K; (f) -1.8 V, 333 K; (g) -1.8 V, 343 K; (h) -1.8 V, 363 K. [ref. 30]

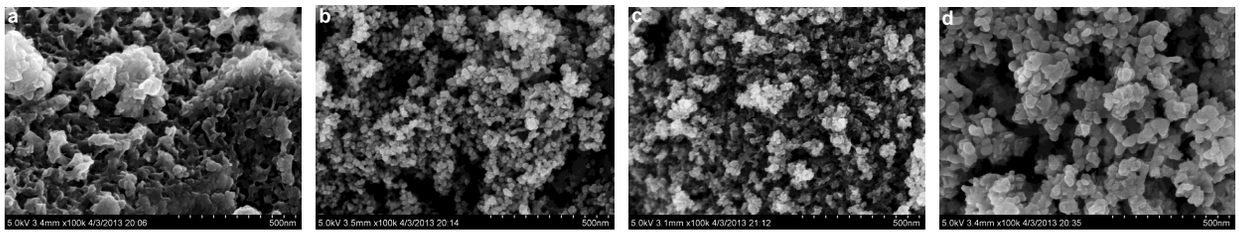


Figure 8. The scanning electron micrographs of Zn–Ti alloy coatings obtained by pulse electrodeposition plating. (a) j=10 mA cm^{-2}, t_{on}=4.0 ms; (b) j=10 mA cm^{-2}, t_{on}=2.0 ms; (c) j=10 mA cm^{-2}, t_{on}=1.0 ms; (d) j=5 mA cm^{-2}, t_{on}=2.0 ms.

current on-time and pulse current density results in the grain growth. The turned-on time is reduced and the turned-off time keeps constant, namely increasing the effective number of cycles (t_{on}+t_{off}), lead to an increase in the number of nuclei. As a result, the size of grain reduces. When the average current density in pulsed electrodeposition is equal to the current density applied in the continuous process, deposit obtained by pulsed electrodeposition shows a more refined granulation, due to the higher nucleation rate. At constant current on-time and off-time, the grain size of deposits decreases with increasing pulse current density.

Regarding the composition of deposits, higher on-time and current density causes a decrease in the content of titanium in the deposit. Furthermore, the Ti content in deposits obtained by continuous electrodeposition is smaller than that of the pulse deposited. This is important and should be taken into account when preparing deposits of a desired composition. It was also noticed that the proportion of Ti in the coating is higher than its proportion in the bath, indicating its preferential deposition. The reasons for this type of behavior are discussed in several works, without reaching a conclusion [33, 34]. Galvanic corrosion tests show that corrosion resistance of Zn-Ti alloy coatings increased with increasing Ti content.

The Zn-Ti alloys can be successfully electrodeposited from $ZnCl_2$-ureaeutectic-based ionic liquid, but deposits are not very compact or bright. So we investigated the effect of additives

on the composition and morphology of electrodeposited Zn-Ti alloys [35]. The cyclic voltammograms obtained in $ZnCl_2$-urea (molar ratio 10:1) containing 0.43 mol L^{-1} $TiCl_4$ in the absence and the presence of equimolar quantities of the additives LiCl, NaCl, KCl, NH_4Cl or etramethylammonium chloride (TMAC) demonstrate that the presence of the additive causes changes in the shape and position of the voltammograms. These results indicate that the presence of the additives affects both the Zn-Ti alloys deposition and stripping processes. The current crossovers in the cathodic region are evident in all the systems, indicating that nucleation and growth of Zn-Ti centre occur under the tested conditions. The deposition potential of the Zn-Ti alloy is negatively shifted in the presence of these additives, suggesting that the additives restrain the deposition of Zn-Ti alloy.

The EDX analysis indicates that Ti content of Al-Ti alloy deposits is almost unchanged in the presence of various additives. SEM images of Zn-Ti alloy deposits show that deposits become smooth and grain size decreases in the presence of NaCl or KCl additives (see Figure 9 a, c and d). In addition, the decrease in particle size is not obvious but deposits become more smooth in the presence of LiCl, NH_4Cl and TMAC (see Figure 9 a, b, e and f).

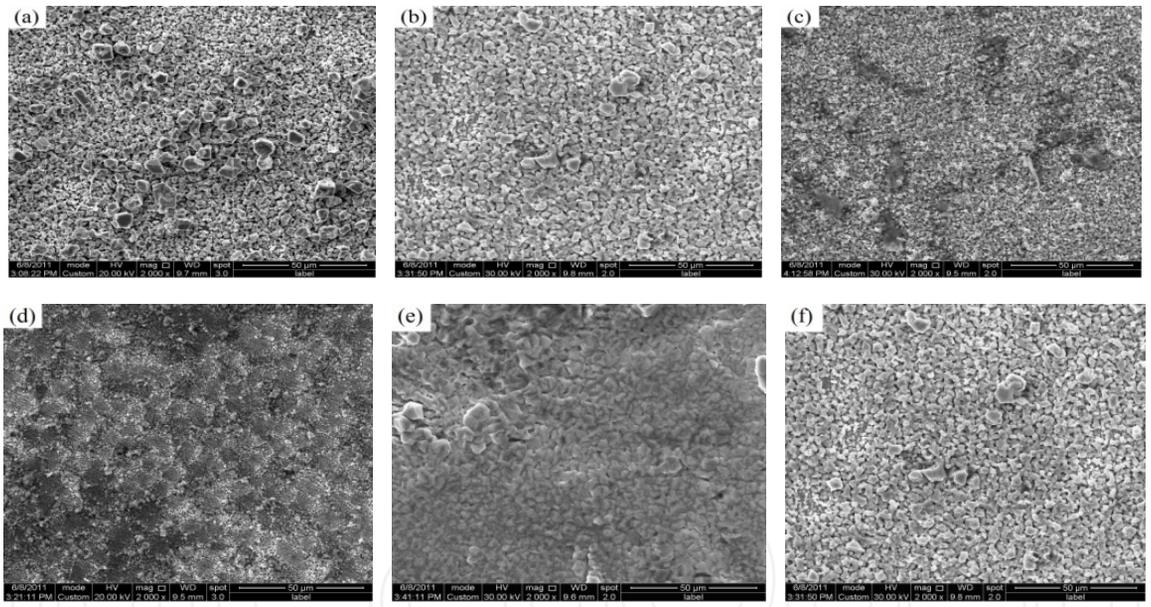


Figure 9. Representative scanning electron micrographs of Zn-Ti alloys electrodeposited on mild steel from $ZnCl_2$-urea (molar ratio 10:1) containing 0.43 mol L^{-1} $TiCl_4$ (a) and with 1.67 mol L^{-1} following additives: (b) LiCl, (c) NaCl, (d) KCl, (e) NH_4Cl and (f) TMAC.

The electrodeposition of Zn-Ti alloy from $ZnCl_2$-urea-$TiCl_4$ in the presence of NaCl was further investigated at different deposition potential and temperature. The Ti content of the electrodeposited alloys increases with increasing current density and temperature under our experimental conditions. As the reduction potential of Zn (II) is more positive than that of Ti (II), the partial current for the deposition of Ti increases quickly with increasing current density. As a result, the Ti content of the electrodeposited alloys increases with increasing current density. It is also noted that the Ti content in Zn-Ti alloys increases with increasing Ti

(IV) concentration in ionic liquid. Results from SEM examinations reveal that the structure of the Al-Ti deposits varies with the alloy composition. The deposit particle decreases in size with increasing Ti composition, resulting from the increase in current density, temperature and Ti (IV) concentration.

3.3. Electrodeposition of Al-Mn-Ti alloy

The Ti addition to Al-Mn alloy can effectively improve high temperature oxidation and pitting corrosion resistance. Since both Al-Ti [21] and Al-Mn [36] alloys can be electrodeposited from Lewis acidic $AlCl_3$-EMIC (or BMIC) ionic liquid, we investigated the electrodeposition of the Al-Mn-Ti ternary alloys in the $AlCl_3$-BMIC (2:1 molar ratios) ionic liquid at the temperature range from 80 to 100℃ [37]. Mn(II) and Ti ions were introduced into the ionic liquid by dissolution of $MnCl_2$ and anodic dissolution of titanium sheet, respectively. Based on the relationship between the charge passed and weight loss of titanium sheet, the number of electrons involved in the reaction was calculated from Faraday's law to be approximately 4, indicating that the anodic oxidation of metal Ti produced Ti(IV) ions in $AlCl_3$-BMIC ionic liquid. It was found that Ti(IV) was reduced to Ti(II) in two one-electron steps.

$$\mathrm{Ti(IV)} + e^- \text{ €} \quad \mathrm{Ti(III)} \tag{5}$$

$$\mathrm{Ti(III)} + e^- \text{ €} \quad \mathrm{Ti(II)} \tag{6}$$

As discussed previously, Al deposition occurs by the electrochemical reduction of the coordinately unsaturated $Al_2Cl_7^-$ ion in Lewis acidic $AlCl_3$-BMIC ionic liquid [38]

$$4Al_2Cl_7^- + 3e^- = 7AlCl_4^- + Al \tag{7}$$

However, when Mn(II) or Ti(II) is present in the ionic liquid, this reaction becomes

$$xM\left(AlCl_4\right)_p^{(p-2)-} + 4(1-x)Al_2Cl_7^- + (3-x)e^- = Al_{1-x}M_x + \left[7(1-x) + px\right]AlCl_4^- \tag{8}$$

Where $M(AlCl_4)_p^{(p-2)-}$ represents Mn(II) or Ti(II) solvated in the chloroaluminate ionic liquid by $AlCl_4^-$ and $Al_{1-x}M_x$ denotes the resulting aluminum-transition metal alloy. In the pure melt, a stripping wave for electrodeposited Al begins at ~0 V, but this wave is replaced by waves corresponding to the stripping of the electrodeposited Al-Mn and Al-Ti alloys in the solutions containing Mn(II) or Ti(II), respectively [21, 36].

The cyclic voltammograms recorded at a glassy carbon electrode for the solutions revealed that the presence of Mn(II) in the solution inhibits the nucleation of Al (see Figure 10a and b). The cyclic voltammograms recorded at glassy carbon electrode in the ionic liquid containing

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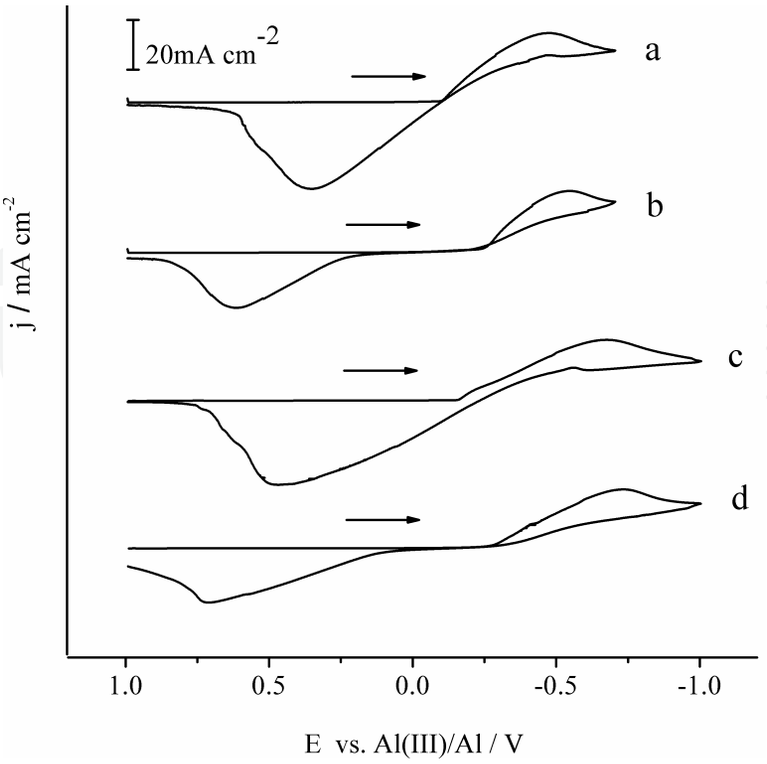


Figure 10. Cyclic staircase voltammograms recorded at a glassy carbon in Lewis acidic $AlCl_3$-BMIC ionic liquid: (a) pure ionic liquid, (b) 25 mmol L^{-1} Mn(II), (c) 25mmol L^{-1} Ti(IV), (d) 25 mmol L^{-1} Mn (II) +25 mmol L^{-1} Ti(IV). The scan rate was 0.05 V s^{-1}, and the temperature was 323 K.

both Mn(II) and Ti(II) is similar in appearance to that recorded in the Mn(II) solution (see Figure 10b and d). This implies that the formation of Al-Mn dominates the ternary Al alloy deposition process. In fact, the Ti content of all of the Al-Mn-Ti alloys produced during this investigation was less than 3.8 at. %.

Controlled current techniques were employed to prepare Al-Mn, Al-Ti and Al-Mn-Ti alloy samples at a copper substrate. In the case of the binary alloys that were prepared in solutions containing only one of the two transition metal precursors [i.e., either Mn(II) or Ti(II)], the Mn content of the Al-Mn alloys is always greater than the Ti content of the corresponding Al-Ti alloys when the two binary alloys were prepared under identical conditions such as applied current density, concentration of the precursor ions, and temperature. This same result carries over to the ternary alloys, including those prepared with $C_{Mn(II)} = C_{Ti(II)}$, because the Ti content of these alloys is always smaller than the Mn content. The j_t signifies the total applied current density, and j_{Ti}, j_{Mn}, and j_{Al} express the partial current densities for Ti, Mn, and Al, respectively. From plots of $-j_{Ti}$, $-j_{Mn}$, and $-j_{Al}$ against $-j_t$, it can be seen that $-j_{Al}$ depends linearly on j_t, whereas the variations of $-j_{Mn}$ and $-j_{Ti}$ with $-j_t$ show more complex behavior. $-j_{Ti}$ increases at low values of $-j_t$, but reaches a limiting value as $-j_t$ is increased. This behavior explains why the Ti content of the Al–Ti and Al–Mn–Ti alloys decreases as $-j_t$ is increased, because once $-j_{Ti}$ reaches a limiting value, it becomes a smaller fraction of $-j_t$, whereas $-j_{Al}$ becomes an increasingly larger fraction of $-j_t$ as the latter is increased. This result was noted during previous studies of the electrodeposition of Al-Ti in a similar ionic liquid, and it is based on the fact that the concen-

tration of Ti(II) in the solvent is much smaller than the concentration of the reducible Al(III) species. On the other hand, $-j_{Mn}$ increases with $-j_t$, so that the Mn content of the alloys increases with increasing $-j_t$. Furthermore, the $-j_{Ti}$ derived from the solution containing Mn(II) and Ti(II) is generally smaller than the value observed in the solution containing Ti(II), but no Mn(II), suggesting that the deposition of Ti is inhibited by Mn(II). Overall, the Al-Mn-Ti alloys rich in Ti are obtained at small $-j_t$, whereas the alloys rich in Mn are obtained at large $-j_t$. The inhibition of the deposition of the nobler component, Ti, by the less noble component, Mn, makes the codeposition of Al, Ti, and Mn an anomalous process.

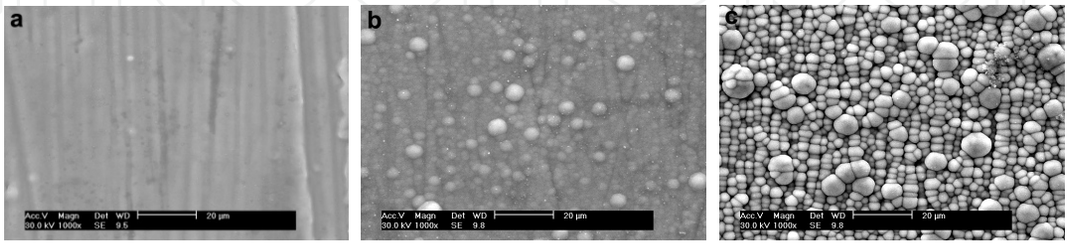


Figure 11. SEM micrographs of electrodeposited Al-Mn-Ti alloy samples at 80℃ by different current density. (a) 4mAcm^{-2}, (b) 6mAcm^{-2}, (e) 8mAcm^{-2}

SEM images of the Al-Mn-Ti alloy deposits reveal that the morphology varies from spherical nodules to a shining surface, depending on the current density and the Mn concentrations (see Figure11). The EDX analysis of the Al-Mn-Ti alloy deposits indicates that Al, Mn and Ti were distributed uniformly in the deposits. XRD analysis revealed that the Al-Mn-Ti alloy deposits are an amorphous phase similar to Al-Mn deposits [36]. Pitting potential measurements of the electrodeposited Al-Mn-Ti alloys revealed that the addition of relatively modest amounts of Ti and Mn to the alloy resulted in a significant increase in corrosion resistance, compared with pure Al and the comparable binary alloy containing only titanium metal components.

3.4. Electrodepositin of Ni-Ti alloy

Ni-Ti alloys are widely used in industrial and medical devices because of their unique shape memory, excellent corrosion resistance, and good biocompatibility [39]. The electrodeposition is an effective, cheap and ready method to prepare alloy coating. However, the electrodeposition of Ni-Ti alloy is very difficult owing to the larger difference of electrode potential between Ni and Al. Recently, our group preliminarily investigated thecodeposition of Ni-Ti alloy from the BMIC-EG (molar ratio 1:2) eutectic based ionic liquid containing $TiCl_4$ and $NiCl_2$. The total concentration of $TiCl_4$ and $NiCl_2$ in the bath kept 0.15 mol/L while the $TiCl_4$/$NiCl_2$ mole ratio was varied. The cyclic voltammograms recorded at a glassy carbon electrode in BMIC-EG, BMIC-EG-$NiCl_2$ and BMIC-EG-$TiCl_4$ solution are shown in Figure 12. For the BMIC-EG-$NiCl_2$ liquid, only one redox couple due to the cathodic deposition and anodic stripping of Ni was observed in the cyclic voltammograms. It is noted that reduction potential of BMIC-EG positively shifted in the presence of Ni(II), suggesting Ni(II) may promote the decomposition of ionic liquids. The addition of $TiCl_4$ produced an additional reduction wave at a potential more negative than reduction potential of Ni(II). Multiple stripping waves

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appeared in the presence of $TiCl_4$ and relative magnitude of these stripping waves depends on the reversing potential, indicating the codeposition of Ti and Ni. The dense and compact Ni-Ti alloys could be electrodeposited by potentiostatic electrolysis at Cu substrate (see Figure 13). The XPS analysis showed that the deposits contained Ti metal in addition to Ni. The EDS analysis indicated that the Ni and Ti were distributed uniformly in the alloy. It was found that the Ti content of electrodeposited Ni-Ti alloy is increased with an increase in current density (or cathodic overpotential), suggesting that the Ti is deposited at a more negative potential as compared to pure Ni. In addition, the composition of the alloy could also be controlled by the ionic liquid bath composition.

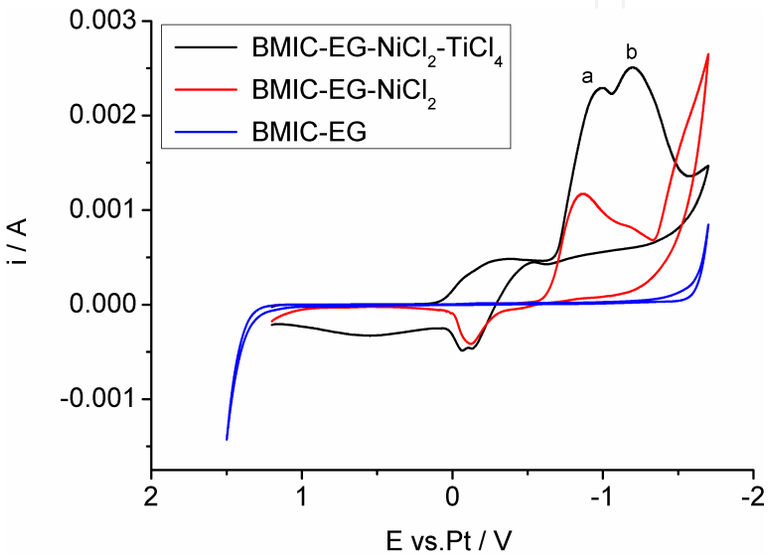


Figure 12. cyclic voltammograms recorded at a glassy carbon electrode in BMIC-EG containing $NiCl_2$, $TiCl_4$ and a mixture of $NiCl_2$ and $TiCl_4$ at 353 K. The scan rate is 10 mV s^{-1}.

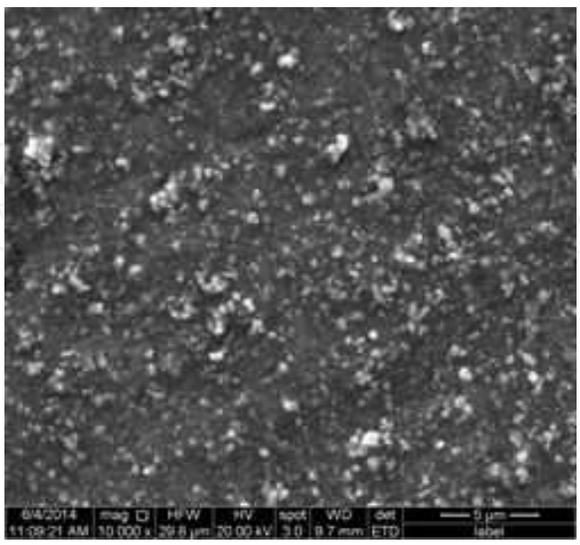


Figure 13. SEM micrograph of the deposits formed potentiostatically on Cu in BMIC-EG containing $NiCl_2$ and $TiCl_4$ at a potential of -1.3V (vs. Pt) and 353 K.

4. Conclusion

In this chapter we have summarized the findings from literature and our studies on the electrochemical preparation of titanium and its alloys in ionic liquids. It has been demonstrated that elemental titanium can not be electrodeposited from ionic liquid in the presence of chloride. The successful deposition of titanium in ionic liquids will require the development of tailored titanium precursors. In addition, it is difficult to preparation of titanium by direct electrochemical reduction of titanium dioxide in ionic liquid due to very slow reduction rate. However, it is shown that titanium could be co-deposited in ionic liquid with aluminum and transition metal, such as zinc and nickel. Some titanium alloys like Al-Ti, Zn-Ti, Al-Mn-Ti and Ni-Ti can be successfully electrodeposited from ionic liquid. In this context, ionic liquids are very promising for titanium alloys preparation. Both wide electrochemical window and high thermal stability allow these processes of Ti and its alloy electrodeposition which are impossible in aqueous or organic solvents.

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Author details

Cunying Xu* and Yixin Hua

*Address all correspondence to: xucunying@aliyun.com, xucunying@kmust.edu.cn

Department of Metallurgy, Kunming University of Science and Technology, P. R. China

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