Electrochemical Behaviour of K$_2$TiF$_6$ at Liquid Metal Cathodes in the LiF–NaF–KF Eutectic Melt

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ABSTRACT

The electrochemical behaviour of Ti$^{4+}$ (K$_2$TiF$_6$) at liquid tin and bismuth electrodes has been investigated by cyclic voltammetry, square wave voltammetry and chronopotentiometry in the LiF–NaF–KF eutectic melt. Result shows that, on the liquid metal electrodes, the reduction reaction of the solvent occurs at more positive potential than that on the inert molybdenum electrode. There are two reduction steps including Ti$^{4+}$ + e$^{-}$ = Ti$^{3+}$ and Ti$^{3+}$ + 3e$^{-}$ = Ti (Ti–Sn alloys) on the liquid tin electrode within the electrochemical window of the melt. However, only one redox process corresponding to the redox of the Ti$^{4+}$/Ti$^{3+}$ couple is observed at liquid bismuth electrode.

Keywords: Molten Fluorides, Titanium, Liquid Metal Cathodes

1. Introduction

Titanium and its alloys have many excellent properties such as low density, high specific strength, good corrosion resistance, etc.1–4 Therefore, they are widely used in the aviation, aerospace, chemical, etc.5–8 Generally, titanium is extracted in the industry from titanium ore, like rutile or ilmenite, by the Kroll process.9 However, the Kroll process is a complex and batch process, which restricts the usage of the titanium and its alloys. Hence, many methods have been investigated for titanium production with low cost and high purity. Among them, molten salt electrolysis (such as FFC process,10 OS process,11 USTB process,12 etc.) is expected to replace the Kroll process.13,14

Up to now, in molten salt, researchers have successfully prepared titanium alloys by direct electrochemical reduction of oxide cathodes.15–17 However, the electrolysis time of the process is too long due to the bad conductivity of the oxide cathodes. In addition, titanium alloys may also be prepared by the electro-reduction of titanium ions at liquid metal cathodes in molten salt. So far, liquid metal cathodes have been successfully used to prepare aluminum alloys18 or magnesium alloys.19 Meanwhile, it is a critical technology in electrochemical reprocessing of actinide and lanthane elements from nuclear waste.20–23 Generally, the operating temperature of the molten salt electrolysis is lower than that of the direct mixing of various melting metals or thermal reduction of oxides. And the composition of the alloys prepared by this way is adjustable. Based on above discussion, molten salt electrolysis with liquid metal cathodes is a promising technology for titanium alloys preparation.

Over the past decades, many researchers focused on the electrochemical behaviour of titanium ions at inert or active metal electrodes24–26 because of the development of electrochemical extraction, refining and plating of titanium in molten salt. Meanwhile, the electrochemical behaviour of metal ions at liquid metal electrodes have also been performed.27–29 However, the reduction mechanism is still unclear and need to be further studied. In this work, liquid tin and bismuth were employed as working electrode due to very low melting points (504.9 K and 544.3 K). The electrochemical analyses including cyclic voltammetry and square wave voltammetry were carried out to study the electrochemical behaviour of Ti$^{4+}$ (K$_2$TiF$_6$) in the LiF–NaF–KF eutectic melt. For comparison, the electrochemical behaviour of Ti$^{3+}$ (K$_2$TiF$_6$) at a solid molybdenum electrode was also studied.

2. Experimental

The LiF–NaF–KF eutectic melt (46.5–11.5–42 mol%), reagent grade, Aladdin Industrial Corporation) was well mixed in a glove box under argon atmosphere, and was placed into a silicon nitride crucible. The electrolyte was pre-dried under vacuum atmosphere at 573 K for 24 h. Subsequently, the cooled and pre-dried electrolyte was placed and 5 wt% K$_2$TiF$_6$ (reagent grade, Aladdin Industrial Corporation) was added in a glove box for electrochemical test. The working temperature was measured by a thermocouple inserted into the melt. All experiments were carried out in a sealed vessel under dried argon atmosphere at 873 K.

A three-electrode system was applied to investigate the electrochemical behavior of titanium ions. The schematics of furnace cell assembly and working electrode were shown in previous work.30 Liquid tin or bismuth (99.99%, Alfa Aesar) was added in a quartz U-bent tube with a 4 mm inner diameter. The stability of the tube in the fluoride melt will be discussed in result and discussion section. For comparison, solid molybdenum wire (99.95%, Alfa Aesar) and glass carbon with a 1 mm diameter were served as working electrode as well. The counter electrode was high purity graphite rod (99.9995%, Alfa Aesar) with an 8 mm diameter. The reference electrode was high purity molybdenum rod with a 3 mm diameter.

The electroanalytical techniques including linear polarization, cyclic voltammetry, square wave voltammetry and chronopotentiometry were performed under the same conditions (873 K, dried argon atmosphere) at the solid molybdenum, liquid tin and bismuth electrodes using a PAR Model 263 potentiostat/galvanostat communicated with Powersuit software. The product was collected by breaking the working electrode. It is easy to remove the residual electrolyte on the surface of the product because of the weak adhesion between metal and electrolyte. Then, the product was washed by deionized water and dried at a temperature of 60°C. The product was analyzed by Scanning Electron Microscopy (JSM-6701F) equipped with an EDS probe (Thermo NS7).
Figure 1. Linear polarization curves of the glass carbon, solid molybdenum, liquid tin and bismuth electrodes in the blank melt at 873 K, scan rate: 100 mV s$^{-1}$.

Table 1. Theoretical decomposition potential of the solvent at 873 K, assuming that all species are in standard state, at unit activity.

| Reaction          | $E^\circ$ (V) |
|-------------------|--------------|
| 2LiF $\rightarrow$ Li$_2$F$_2$ | 5.52         |
| 2NaF $\rightarrow$ Na$_2$F$_2$ | 5.03         |
| 2KF $\rightarrow$ K$_2$F$_2$ | 4.97         |
| C + 2KF $\rightarrow$ K$_2$CF$_2$ | 3.88         |
| C + 4KF $\rightarrow$ K$_2$CF$_4$ | 2.89         |

3. Results and Discussion

Figure 1 shows the linear polarization curves of the glass carbon, solid molybdenum, liquid tin and bismuth electrodes in the LiF–NaF–KF eutectic melt. Table 1 is the theoretical decomposition voltage of the solvent, calculated from the HSC Chemistry 6.0 software. It shows that the theoretical voltage for the evolution of CF$_4$ or CF$_2$ resulting from the fluorination of the graphite is much lower than that of the evolution for the fluoride gas (F$_2$). It further indicates that the anode reaction shown in Fig. 1 is the fluorination of the electrodes instead of the generation of the fluoride gas. Based on above analysis, Fig. 1 displays that the fluorination of the glass carbon occurs at $\sim$1.0 V (vs. Mo-QRE), solid molybdenum at $\sim$0.0 V (vs. Mo-QRE), liquid tin at $\sim$0.1 V (vs. Mo-QRE) and liquid bismuth at $\sim$0.0 V (vs. Mo-QRE). It indicates the fluorination of liquid tin, bismuth and solid molybdenum electrodes is more negative than that of glass carbon electrode. The inset of Fig. 1 shows that, on the positive sweep, the current increases monotonically within the potential region of 1.0–1.5 V (vs. Mo-QRE), which may result from the formation of the CF$_x$ passivating layers on the fresh glass carbon electrode.\(^{31,12}\) Subsequently, the current begins to fluctuate in the potential region of 1.5–3.0 V (vs. Mo-QRE), which suggests the generation, coalescing and detaching of bubbles (such as carbon-fluoride or fluorine) at the surface of the electrode.\(^{33}\) Meanwhile, the stability and influence of the SiO$_2$ tube used to place the liquid metal are studied by cyclic voltammetry in the fluoride melt. Figure 2a is the CV curves of the Mo electrode in the black melt and the melt after immersing SiO$_2$ tube (6 mm in outside diameter, 4 mm in inner diameter and 30 mm in length) for 10 and 30 min. Figure 2b, the magnified voltammogram of the Fig. 2a, shows that, comparing with the CV obtained in the black melt, there are two weak reduction peaks (a and b) in the melt after immersing SiO$_2$ tube for 10 and 30 min. Peak a and b may relate to the generation of the SiO$_2$ tube for 10 and 30 min. Peak a and b may relate to the reduction of Si(IV)/Si and CaSi$_2$/Si. However, the reduction currents ($\approx$0.05 A cm$^{-2}$) of the peak a and b are much smaller than that ($\approx$0.25 A cm$^{-2}$) of the reduction current of Ti$_4$$^{14+}$/Ti (alloy), shown in Fig. 5. It indicates that SiO$_2$ tube is hardly dissolved into fluoride melt in the short measurement time. Therefore, the effect of SiO$_2$ tube can be neglected due to high K$_2$TiF$_6$ (5 wt%) concentration.

The electrochemical windows of the blank LiF–NaF–KF eutectic melt have been obtained by a potential scanning at the solid molybdenum, liquid tin and bismuth electrodes and are given in Fig. 3. The results show that the reduction potential\(^{34}\) of the fluoride at the solid molybdenum electrode is $\approx$1.75 V (vs. Mo-QRE). The reduction potentials at liquid tin and bismuth electrodes are $\approx$0.6 V and $\approx$0.25 V (vs. Mo-QRE), respectively. The values are much more positive than that at the solid molybdenum electrode. In general, the phenomenon results from the alloying effect between the electrodeposited metals and liquid cathode. Moreover, it also shows that the reduction potential of potassium at the liquid bismuth is more positive than that at liquid tin. The result indicates that bismuth is easier than tin to form alloys with reduced metals. The similar result for electrochemical reduction of Pr$^{3+}$ at liquid cadmium and bismuth electrodes was also reported in literature.\(^{35}\)

Figure 2a shows cyclic voltammograms and fitting data at the solid molybdenum electrode in the LiF–NaF–KF eutectic melt without and with 5 wt% K$_2$TiF$_6$. It is found that an obvious redox peak is observed and the difference between cathodic peak potential and the starting reduction potential of K$^+$ ion is about 1.75 V. The result is different from that by F. R. Clayton who disclosed the reduction of Ti$^{4+}$ to Ti$^{3+}$ at both platinum and pyrolytic graphite electrodes in LiF–NaF–KF melt at 500°C.\(^{36}\) In that work, the
The deviation of Ti⁴⁺/Ti³⁺ is about 2.0 V. The reason for the deviation may be related to the temperature. The theoretical potentials of Ti⁴⁺/Ti³⁺ and K⁺/K are calculated at different temperature. Although the standard reduction potentials of the metal ions in aqueous solution and molten salts are different, the change trend of the standard reduction potentials with the temperature will be the same. The results are shown in Table 2. The theoretical potential of K⁺/K (vs. F₂/F⁻) shifts to the positive direction with increase of temperature. However, the theoretical potential of Ti⁴⁺/Ti³⁺ (vs. F₂/F⁻) decreases about 0.2232 V, which approximates to the deviation (about 2.5 V) between Ref. 36 and this work, due to the increase of temperature from 500 to 600°C. Therefore, the redox peak at 0.0 V (vs. Mo-QRE) shown in Fig. 4a should be the redox of the Ti⁴⁺/Ti³⁺ couple. In addition, the redox peak is further investigated by calculating the transfer electron number. Figure 4b is the gauss fitting of the reduction wave shown in (a). According to the Faraday constant, n the electron exchange number, R the ideal gas constant and T the temperature. The result shows that the reduction potential of the solvent is nearly unchanged. It indicates that the potential of the Mo-QRE is stable and reproducible.

### Table 2. The theoretical potentials of K⁺/K (vs. F₂/F⁻) and Ti⁴⁺/Ti³⁺ (vs. Cl₂/Cl⁻) at 500 and 600°C.

|           | 500°C  | 600°C  |
|-----------|--------|--------|
| K⁺/K      | -5.0732| -4.9681|
| Ti⁴⁺/Ti³⁺ | -2.6822| -2.8003|

The electrochemical behaviour of Ti⁴⁺ (K₂TiF₆) at liquid tin electrode

Figure 5 shows cyclic voltammograms at liquid tin electrode in the melt without and with 5 wt% K₂TiF₆ scan rate: 100 mV s⁻¹.
appeared in the electrochemical window of the melt. Figure 6 shows square wave voltammograms recorded at different frequencies (5 and 10 Hz) in the melt with 5 wt% K₂TiF₆, scan rate: 25 and 50 mV s⁻¹.

Figure 7. Chronoamperometry recorded at the liquid tin electrode in the LiF–NaF–KF–5 wt% K₂TiF₆ melt at the potential of −0.6 V (vs. Mo-QRE).

2') appeared in the electrochemical window of the melt. Figure 6 shows square wave voltammograms recorded at different frequencies (5 and 10 Hz) in the melt with 5 wt% K₂TiF₆. The result is consistent with that obtained by cyclic voltammogram. The potentials of cathodic peak 1 and cathodic current 2 are about −0.40 V and −0.05 V (vs. Mo-QRE), respectively. The potential of cathodic current 2 is similar to the potential of the peak (at about −0.0 V (vs. Mo-QRE)) obtained at the molybdenum electrode (Fig. 4a). The cathodic current 2 is attributed to the reduction from Ti⁴⁺ to Ti³⁺. However, the peak 1 is not observed at the molybdenum electrode. Nevertheless, according to our previous work, Ti³⁺ ions can be reduced by one-step reaction at liquid tin cathode to synthesis Ti–Sn alloys, despite the valence state of Ti ions in chloride melt includes +2, +3 and +4. Therefore, the peak 1 is more likely to represent the one-step reduction of Ti³⁺ and the formation of Ti–Sn alloys because the valence state of Ti ions in fluoride melt includes +3 and +4, does not includes +2. In order to verify this surmise, the chronoamperometry was used subsequently.

Figure 7 is the chronoamperometry recorded at the liquid tin electrode in the LiF–NaF–KF–5 wt% K₂TiF₆ melt at the potential of −0.6 V (vs. Mo-QRE). The current density is about 0.3 A cm⁻². The large current density means that faradic reaction happens during electrolysis. Figure 8 shows SEM image and EDS analysis of the products obtained by chronoamperometry at the potential of −0.6 V (vs. Mo-QRE) for 600 s. The content of titanium, potassium and tin obtained by EDS analysis are presented in Table 3. It indicates that metal titanium is electroreduced. The result further verifies that the peak 1 obtained at liquid tin electrode is attributed to the reduction of Ti³⁺. Therefore, Ti–Sn alloys are obtained.

As discussed above, it is inferred that Ti³⁺ is reduced to Ti–Sn alloys at the liquid tin electrode by consecutive two-step reduction reactions: Ti³⁺ to Ti⁴⁺ and Ti⁴⁺ to Ti–Sn alloys.

### Table 3. The content of titanium, potassium and tin obtained by EDS analysis.

| Point | Atom % | Weight % |
|-------|--------|----------|
|       | Ti     | K        | Sn       |
| 1     | 4.30   | 0.32     | 95.38    |
| 2     | 6.49   | 0.76     | 92.75    |
| 3     | 4.50   | 0.60     | 94.90    |

3.2 Electrochemical behaviour of Ti⁴⁺ (K₂TiF₆) at liquid bismuth electrode

Figure 9 and Fig. 10 are cyclic voltammogram and square wave voltammogram at liquid bismuth electrode in the melt without and with 5 wt% K₂TiF₆. There is only a couple of redox current (1 and 1'). It is easy to conclude that the redox current is attributed to the redox reaction of Ti⁴⁺/Ti³⁺ couple according to the potential. However, it is worth noting that, in the reduction region, the cathodic current (shown in Fig. 9, red solid line) increases rapidly in the potential region of −0.25 to −0.6 V (vs. Mo-QRE) after
dissolving 5 wt% K2TiF6. It may result from the formation of Ti–Bi alloys. Then, the chronoamperometry was employed to study this phenomenon. Figure 11 shows chronoamperometry recorded at the liquid bismuth electrode in the LiF–NaF–KF+5wt% K2TiF6 melt at the potential of −1.0 V (vs. Mo-QRE). It shows that the current density is about 0.25–0.40 A cm⁻², and a faradic reaction happens during electrolysis. Figure 12 shows SEM image and EDS analysis of the cathodic product obtained by chronoamperometry at the potential of −1.0 V (vs. Mo-QRE) for 300 s. The content of titanium, potassium and bismuth obtained by EDS analysis are presented in Table 4. The results show that there are titanium and potassium at the surface of the liquid bismuth electrode, which means that the titanium and potassium will be electro-reduced at liquid bismuth electrode at the potential of −1.0 V (vs. Mo-QRE).

Table 4. The content of titanium, potassium and bismuth obtained by EDS analysis.

| Point | Atom %  | Weight % |
|-------|---------|----------|
|       | Ti      | K        | Bi       | Ti | K | Bi |
| 1     | 1.40    | 1.13     | 97.47    | 0.33| 0.22| 99.46|

4. Conclusions

In summary, the electrochemical behaviors of Ti⁴⁺ (K₂TiF₆) at solid molybdenum, liquid tin and bismuth electrodes are studied in the LiF–NaF–KF eutectic melt. The result shows that, on the liquid metal electrodes, the reduction of the solvent or titanium ions occurs at more positive potential than that on the inert molybdenum electrode. Meanwhile, it is confirmed that Ti⁴⁺ is electroreduced to metal and form Ti–Sn alloy by two-step reduction reactions at the liquid tin electrode: Ti⁴⁺+e⁻=Ti³⁺ and Ti³⁺+3e⁻=Ti (Ti–Sn alloys). However, only one redox process corresponding to the Ti⁴⁺/Ti³⁺ couple is observed at liquid bismuth. That is titanium and potassium can be electro-reduced at the liquid bismuth electrode at the potential of −1.0 V (vs. Mo-QRE).
Conflicts of interest

There are no conflicts to declare.

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