ELECTROCHEMICAL STUDY ON TITANIUM REDUCTION
IN EUTECTIC LiCl-KCl MELT

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ABSTRACT

Electrochemical reduction of Ti(III) and Ti(II) in eutectic LiCl-KCl melt has been investigated in three different modes of linear sweep voltammetry, cyclic voltammetry and potentiostatic voltammetry. Reduction of Ti(III) to Ti(II) took place from -0.6 V against the Ag/AgCl(10 mole%) reference electrode, whereas that of Ti(II) to metallic Ti, from -1.1V. Those reactions were reversible near the respective potential. The electrode deposit obtained at -1.2 V was metallic titanium of fine globular shape.

INTRODUCTION

Titanium has superior properties, such as high specific strength and high corrosion resistance. Its availability, however, is limited because of its relatively high production cost. One possible way to reduce the production cost might be the direct electrochemical reduction of titanium from a molten salt. Many papers have been published on the electrolysis of titanium from molten alkali or alkaline earth chlorides. Bockris et al.(1) and Dean et al.(2) reported that the alkaline earth cations were first electrochemically reduced and then the alkaline metal so formed reduced the titanium cations to produce metallic titanium. Nardins et al.(3) and Quemper et al.(4) reported the respective stepwise reduction potentials of Ti(IV) to Ti(III), Ti(III) to Ti(II) and Ti(II) to metallic Ti. From a practical view point, electroplating of titanium from molten salts has been investigated by several investigators(5,6). Cobel et al.(7) recently reported that metallic Ti of high purity was obtained in their pilot plant scale experiment. The reduction potentials reported by many investigators, however, disaccorded with each other (3, 4, 8-11). Therefore, it can be said that the reduction mechanism is still not well understood.

It is the intent of the present work to clarify the reaction mechanism associated with the electrochemical reduction of Ti(III) to Ti(II) and Ti(II) to metallic Ti in the LiCl-KCl eutectic melt.
EXPERIMENTAL

Figure 1 shows the schematic diagram of experimental apparatus. The atmosphere in the apparatus was kept inert by the flow of highly purified Ar gas deoxidized by using a titanium trap at 1073 K. Chlorine or hydrochloric acid gas was used for purification of the melt. Figure 2 shows the schematic diagram of electrolytic cell and the reference electrode. Reagent grade powders of LiCl and KCl were mixed to the composition of 59 mole% LiCl and 41 mole% KCl in a glove box. These salts were preheated for 24 hours at about 473 K in a purified Ar flow and then were melted together in an alumina crucible. Chlorine or HCl gas was injected into the melt for three hours to purify the melt and then purified Ar was injected to remove dissolved chlorine or HCl gas for another three hours. A certain amount of TiCl₃ and Ti chips in the case of Ti(II) reduction, were added to the melt. Then, three electrodes were dipped into the melt. The working electrode was either a nickel rod of 5 mm in diameter or a 8 mm x 15 mm nickel plate of 0.5 mm thickness, which was polished with dry abrasive papers down to # 1000. The reference electrode was Ag/AgCl(10 mole%). The construction of the latter is shown in Fig. 2. The counter electrode was either a graphite rod of 11 mm in diameter or Ti rods that were 2 or 5 mm in diameter. The experimental temperature was mainly 773 K, but occasionally 873 and 973 K were used. The experiments were carried out in three different modes, namely linear sweep voltammetry, cyclic voltammetry and potentiostatic voltammetry. In the former two, the sweep rate was mainly 0.0017 V/s, and occasionally 0.005, 0.017 and 0.05 V/s. After the experiments in the last mode, the electrode deposit was examined with SEM and EPMA.

RESULTS

Figure 3 shows the result of linear sweep voltammetry before adding TiCl₃. The residual current density of the melt was effectively lowered by chlorine gas injection. It was especially lower at potentials higher than -1.5 V, which made the reduction wave of Ti(II) clearer, as will be shown later. The increase in current density at potentials higher than -2.5 V was attributable to the reduction of Li⁺ to metallic lithium. So, most of the experiments were carried out after purification by chlorine gas injection.

Figure 4 shows the results of linear sweep voltammetry, after the addition of 1.2 mole% of TiCl₃ to the melt. Figure 5 is the magnification of Fig. 4 near -0.6 V. The rest potential was about -0.2 to -0.3 V. The reduction waves appeared at -0.6 and -1.1 V at 773 K. The broken line in this figure shows the residual current density. The increase in current density, and hence, the reduction wave due to the formation of titanium metal can be seen clearly following the addition
of TiCl$_3$ to the melt. The same reduction waves were obtained at 873 K, although the current density was higher in magnitude. The reduction waves at -0.6 and -1.1 V were considered to correspond to the reduction of Ti(III) to Ti(II), and to the reduction of Ti(II) to metallic Ti, respectively, as follows:

\[
\text{Ti}^{3+} + e = \text{Ti}^{2+} \quad (1)
\]

\[
\text{Ti}^{2+} + 2e = \text{Ti} \quad (2)
\]

In order to reduce Ti(III) to Ti(II) in the melt prior to the experiment, metallic Ti chips were added to the melt simultaneously with the addition of TiCl$_3$. Thermodynamic calculations show that the equilibrium of equation (3) is shifted far to the right(12).

\[
2\text{TiCl}_3 + \text{Ti} = 3\text{TiCl}_2 \quad (3)
\]

Therefore, the melt must contain mostly Ti(II) when TiCl$_3$ and Ti chips are simultaneously added to the melt. Figure 6 shows the result of linear sweep voltammetry in the Ti(II) containing melt. The rest potential shifted to -0.8 or -0.9 V. The reduction wave corresponding to equation (1) disappeared and only the wave at -1.1 V can be seen. The current density increased with an increase in temperature, but the reduction potential did not change much regardless of the temperature. The increase in current density seen close to the rest potential has not been clarified yet. It might be attributable either to the reduction of impurities in the melt such as Al$^{3+}$ or to the reduction of residual Ti(III). Figure 7 shows the effect of the Ti$^{2+}$ content on the current density. The current density increased with an increase in the amount of TiCl$_3$ and Ti chips added. The current density at -1.2 V is plotted in Fig. 8. The current density increased linearly with the amount of added TiCl$_3$. Figure 9 shows the effect of sweep rate on the polarization curve. The current density increased with an increase in sweep rate. But the reduction potential was unchanged, regardless of the sweep rate. Figure 10 shows the result of cyclic voltammetry near -1.1 V. Both the reduction and oxidation current densities started to increase at -1.1 V, regardless of the sweep rate. The oxidation current is due to the oxidation of the metallic Ti electrode deposit which is formed in cathodic sweep. This shows that the reduction reaction of equation (2) is reversible.

In potentiostatic voltammetry, a Ti rod was used as the counter electrode. Figure 11 shows the change in current density with time in
potentiostatic voltammetry at -1.2 V in which a nickel rod was used as the working electrode at 773 K. The amount of TiCl$_3$ and Ti chips added (mole%) were respectively, a)2.01 and 1.27, b)3.88 and 2.11, c)4.03 and 2.32, d)5.55 and 2.76. The current density increased in a), c) and d), but was almost constant in b). Except for a), the current increased with an increase in the amount of added TiCl$_3$ and Ti chips. Figure 12 shows the change in current density with time in similar potentiostatic voltammetry experiments in which a nickel plate was used as the working electrode. The amount of added TiCl$_3$ and Ti chips were 3.83 and 2.04 mole%, respectively, in all experiments. The current density was almost constant and of the same order of magnitude in all experiments. However, it was smaller than in the experiments with the nickel rod as the working electrode. Photograph 1 shows the SEM image of the electrode deposit. Although at low magnifications the electrode surface was smooth, the photo shows that the surface was actually the agglomeration of small globular particles that were several microns in diameter. Table 1 shows the composition of electrode deposit. The electrode deposit was mainly composed of metallic Ti, which showed that the reduction wave at -1.1 V was attributable to the reduction reaction of equation (2). The deposit also contained a certain amount of aluminum. This is because the TiCl$_3$ powder originally contained 25 mole% of AlCl$_3$. Both Ti and Al were homogeneously distributed over the surface.

Table 1 Composition of the electrode deposit

|    | a   | b   | c   | d   | e   | f   | g   |
|----|-----|-----|-----|-----|-----|-----|-----|
| Ti (wt%) | 86.4 | 93.5 | 91.5 | 73.7 | 71.7 | 70.6 | 72.2 |
| Al (wt%)  | 13.6 | 6.5  | 8.5  | 26.3 | 28.3 | 29.4 | 27.8 |

The symbols correspond to those in Figs. 11 and 12.

DISCUSSION

As shown above, the reduction of Ti(II) to metallic Ti was reversible and the current density increased linearly with the concentration of Ti(II) cation. This suggests that the reduction is controlled by mass transfer in the melt. Generally, if the electrode reactions are controlled by mass transfer, the electrode potential can be represented in terms of the chemical potential difference of the anion-forming species between the reference and working electrodes, namely, the
chemical potential difference of chlorine in the present case.

\[ E = \frac{RT}{2F} \ln \frac{P_{\text{Cl}_2} \text{(W.E.)}}{P_{\text{Cl}_2} \text{(R.E.)}} \]  \hspace{1cm} (4)

where, \( P_{\text{Cl}_2} \text{(R.E.)} \) and \( P_{\text{Cl}_2} \text{(W.E.)} \) are the partial pressures of chlorine at the reference and working electrodes. At the reference electrode, the following equilibrium can be considered.

\[ \text{Ag} + \frac{1}{2}\text{Cl}_2 = \text{AgCl} \]  \hspace{1cm} (5)

\[ \Delta G^\circ(5) = -RT \ln \frac{a_{\text{AgCl}}}{a_{\text{Ag}}} \]  \hspace{1cm} (6)

Therefore, \( P_{\text{Cl}_2} \text{(R.E.)} \) can be calculated, using the datum of \( \Delta G^\circ(5) \) and taking \( a_{\text{Ag}} = 1 \) and \( a_{\text{AgCl}} = 0.1 \). Similarly at the working electrode, the following equilibrium must be considered in order to calculate the potential of the Ti(III) to Ti(II) reduction process.

\[ \text{TiCl}_2 + \frac{1}{2}\text{Cl}_2 = \text{TiCl}_3 \]  \hspace{1cm} (7)

\[ \Delta G^\circ(7) = -RT \ln \frac{a_{\text{TiCl}_3}}{a_{\text{TiCl}_2} a_{\text{Cl}_2}^{1/2}} \]  \hspace{1cm} (8)

Using the datum of \( \Delta G^\circ(7) \) and assuming \( a_{\text{TiCl}_3}/a_{\text{TiCl}_2} = 1 \), \( P_{\text{Cl}_2} \text{(W.E.)} \) can be calculated. Putting these partial pressure of chlorine at the two electrodes into equation (4), the Ti(III) to Ti(II) reduction potential was calculated as \(-0.62 \text{ V} \) at 773 K. This value is in good accord with the experimental value of \(-0.6 \text{ V} \). In order to calculate the potential for the reduction of Ti(II) to metallic Ti, the following equilibrium must be considered.

\[ \text{Ti} + \text{Cl}_2 = \text{TiCl}_2 \]  \hspace{1cm} (9)

\[ \Delta G^\circ(9) = -RT \ln \frac{a_{\text{TiCl}_2}}{a_{\text{Ti}} a_{\text{Cl}_2}^1} \]  \hspace{1cm} (10)

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Using the datum of $\Delta G°(9)(12)$, and taking $a_{Ti} = 1$ and $a_{TiCl_2} = 0.1$, $P_{Cl_2}$ for the reduction can be calculated. Putting this partial pressure of chlorine into equation (4), the reduction potential of Ti(II) to metallic Ti was calculated as $-1.10 \text{ V}$. This value is also in good accord with the experimental value. In the same way, the reduction potential of $Li^+$ to metallic lithium was calculated to be as $-2.5 \text{ V}$, which is in good accord with the experimental value.

Many investigators have reported the reduction potentials of the different Ti electrode reactions. They are listed in Table 2, together with the present results.

Table 2 Comparison of the reduction potentials resulting from the present work with those of other workers.

| Authors | Melt | Electrode | Sweep Rate | Reduction Potential |
|---------|------|-----------|------------|---------------------|
| Present | LiCl-KCl | WE: Ni | 0.0017 | Ti(III) to Ti(II) $-0.6 \text{ V}$ |
| Authors | (TiCl$_3$) | CE: graphite | | Ti(II) to Ti $-1.1 \text{ V}$ |
|         | (TiCl$_2$) | RE: Ag/AgCl | 0.05 V/s | |
| A       | BaCl$_2$ | WE: Ni | 0.0017 | Ti(IV) to Ti(III) $0.0 \text{ V}$ |
| Ref. 3  | LiCl-KCl | CE: graphite | 0.0034 V/s | Ti(III) to Ti(II) $-0.5 \text{ V}$ |
|         | (TiCl$_4$) | RE: Ag/AgCl | | Ti(II) to Ti $-1.2 \text{ V}$ |
| B       | LiCl-KCl | WE: graphite | 0.001 V/s | Ti(IV) to Ti(III) $+0.4 \text{ V}$ |
| Ref. 4  | (TiCl$_4$) | CE: graphite | | Ti(III) to Ti(II) $-0.6 \text{ V}$ |
|         |         | RE: Ag/AgCl | | Ti(II) to Ti $-1.4 \text{ V}$ |
| C       | LiCl-KCl | WE: W | ? | Ti(IV) to Ti(III) $+0.6 \text{ V}$ |
| Ref. 8  | (TiCl$_3$) | CE: W | | Ti(III) to Ti(II) $-0.9 \text{ V}$ |
|         |         | RE: Ag/AgCl | | Ti(II) to Ti $-1.1 \text{ V}$ |
| D       | LiCl-KCl | WE: Pt | ? | Ti(IV) to Ti(III) $-0.9 \text{ V}$ |
| Ref. 9  | (TiCl$_4$) | CE: graphite | | Ti(III) to Ti(II) $-1.0 \text{ V}$ |
|         |         | RE: Ag/AgCl | | Ti(II) to Ti $-1.5 \text{ V}$ |
The potentials of the data in C (8) were originally given with respect to the Cl₂/Cl⁻ reference electrode. This data were converted to the Ag/AgCl reference electrode by considering the potential difference of 1.0 V between the Ag/AgCl and Cl₂/Cl⁻ electrodes obtained in the present work. Further, Ti(IV)/Ti(III) potential given by the authors in C is the oxidation potential, rather than the reduction potential, because they used TiCl₃ as the starting species. The Ti(III)/Ti(II) reduction potential measured by the present authors is in good accord with those measured by authors A and B. The Ti(II)/Ti reduction potential measured by the present authors is in good accord with those measured by authors A and C. Many authors reported the latter reduction potential to be less positive than that found by the present authors. Presumably, they noticed that the wave positive to that for Li⁺ reduction arises from the reduction of Ti(II) to metallic Ti. Actually, the wave appeared near -1.5 V in the present experiments also. But the electrode deposit composed mainly of Ti was obtained at -1.2 V, and the theoretical calculations showed that this reduction can take place at -1.1 V. Thus, it can be said conclusively that the Ti(II)/Ti reduction potential is -1.1 V with respect to the Ag/AgCl reference. The reduction process is reversible, although Ferry et al. (8) reported to be irreversible process based on impedance measurements.

The current efficiency in the potentiostatic voltammetry experiments with the nickel plate as the working electrode was calculated as follows. Since the electrode deposit was composed of Ti and Al, the efficiency was calculated for each metal and summed up to obtain the total efficiency,

\[ \text{Eff.}(i) = \left( \frac{W_i}{W_0} \right) \times 100 \% \]  

(11)
where \( \text{Eff.}(i) \) is the efficiency for metal \( i \), \( W_i \) is the mass of the deposit of metal \( i \) obtained from the total amount of deposit and the composition of the deposit, \( W_{10} \) is the theoretical mass of the deposit of metal \( i \) calculated with the following equation.

\[
W_{10} = \int \frac{M_i}{z_i F} I \, dt
\]

(12)

where \( M_i \) and \( z_i \) are molar mass and balance of \( i \), respectively, \( F \) is the Faraday constant, \( I \) is the total current, and \( t \) is time. Table 3 shows the calculated results.

Table 3 Current efficiency

| specimen | Eff.(Ti) % | Eff.(Al) % | Eff. total % |
|----------|------------|------------|--------------|
| e        | 6.9        | 7.3        | 14.2         |
| f        | 5.5        | 6.0        | 11.5         |
| g        | 6.4        | 6.6        | 13.0         |

The symbols for each specimen correspond to those shown in Fig. 12.

The current efficiency was very low. This is partly because some part of electrode deposit was lost during washing with water before weighing. But also, it is likely that some of the deposit was lost during the electrolysis, considering the fluctuation of current density with time. From careful observation of Photo. 1, the slow increase in current density seems attributable to an increase in the interfacial area and, the sudden drop in current density seems to result from the loss of the deposit.

**CONCLUSION**

The electrochemical reduction of Ti(III) to Ti(II) and the reduction of Ti(II) to metallic Ti was investigated in LiCl-KCl melt. The reduction wave of the former appeared at \(-0.6\) V, whereas that of the latter appeared at \(-1.1\) V against the Ag/AgCl(10 mole%) reference. These experimental potentials are in good accord with the calculated ones based on thermodynamic considerations. The latter reduction was
shown to be reversible by cyclic voltammetry. An electrode deposit was obtained by potentiostatic voltammetry at -1.2 V. The deposit was composed of metallic Ti and Al with a globular shape. The current efficiency was as low as 15%, because of the loss of material during washing before weighing and presumably due to the loss of material during the electrolysis.

ACKNOWLEDGEMENT

The present work is financially supported by Chubu Electric Power Co. LTD.

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Fig. 1 Schematic diagram of the experimental apparatus; 1. Ar cylinder, 2. chlorine or HCl gas cylinder, 3. calcium chloride, 4. silica gel, 5 activated Ti tower, 6. gas flow meter, 7. mass flow controller, 8. electric furnace, 9. electrolytic cell, 10. NaOH trap.

Fig. 2 Schematic diagram of the electrolytic cell and construction of the reference electrode.

1. Working electrode
2. Reference electrode
3. Counter electrode
4. Thermocouple
5. Pyrex tube
6. Alumina crucible
7. Rubber plug

Fig. 3 Effect of purification on the residual current density.
Fig. 4 Cathodic polarization curves in Ti$^{3+}$ containing melt.

Fig. 5 Magnification of Fig. 4 near -0.6 V.

Fig. 6 Cathodic polarization curves in Ti$^{2+}$ containing melt.
Fig. 7 Effect of the Ti$^{2+}$ content on the cathodic polarization curve.

Fig. 8 Effect of the Ti$^{2+}$ content on the current density at -1.2 V.

Fig. 9 Effect of sweep rate on the cathodic polarization curve in Ti$^{2+}$ containing melt.
Fig. 10 Cyclic polarization curve in Ti$^{2+}$ containing melt near -1.1 V.

Fig. 11 Change in current density with time during the potentiostatic polarization at -1.2 V with a nickel rod electrode.

Fig. 12 Change in current density with time during the potentiostatic polarization of a nickel plate electrode at -1.2 V.
Photograph 1. Surface morphology of the deposit obtained at -1.2 V on a nickel plate electrode.