



The equilibrium between metallic titanium and titanium ions in LiCl–KCl melts



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ABSTRACT

The equilibrium between metallic titanium and titanium ions (Ti^{2+} , Ti^{3+}) dissolved in LiCl–KCl melts and the influence of the electrolyte composition on the equilibrium were investigated. The accurate concentrations of titanium ions had been obtained based on a reliable approach for taking samples. Furthermore, accurate values of the equilibrium constants were calculated by the best-fitting method under the consideration of the TiOCl dissolution. The influence of the electrolyte composition on the equilibrium was evaluated by determining the equilibrium constant K_c between titanium metal and titanium ions in LiCl–KCl melts with different concentration of LiCl. It was shown that LiCl could affect the equilibrium and the K_c values decreased with the increase of concentration of LiCl.

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1. Introduction

The way of molten salt electrolysis used for electrowinning titanium has been studied for several years, which has been considered as the most promising way to replace prevailing Kroll process [1–3]. However, the electrolysis processes are complicated due to the variety of oxidation states of titanium ions. These oxidation states undergo disproportionation reactions leading low current efficiency and the formation of metallic muds in molten cells. The extent of a certain disproportionation reaction could be evaluated by the equilibrium of the reaction.

It has been reported that equilibrium exists between titanium ions and metallic titanium in most chloride melts, which can be expressed by the following reaction:



The equilibrium constant K_c is defined by the following equation:

$$K_c = \frac{x_{\text{Ti}^{3+}}^2 \cdot x_{\text{Ti}}}{x_{\text{Ti}^{2+}}^3} = \frac{x_{\text{Ti}^{3+}}^2}{x_{\text{Ti}^{2+}}^3} \quad (2)$$

where x_i is the molar fraction of a species i which is a cationic molar fraction defined by the following equation:

$$x_i = \frac{n_i}{\sum n_i} \quad (3)$$

The equilibrium between metallic titanium and titanium ions in different alkali chloride had been studied by some researchers. Mellgren et al., Kreye and Kellog, Li and Sekimoto et al. studied the equilibrium and determined the concentrations of Ti^{2+} and Ti^{3+} by H_2 volumetric analysis and titration respectively [4–10]. The results reported in their literatures are dispersed under different experimental condition and the concentration quotient K_c increased significantly with the decrease of the molar fraction of Ti^{2+} . In general, K_c should be a constant because the solutes (TiCl_3 , TiCl_2) obey Henry's law in the region where the concentrations of titanium ions are low. Such a tendency indicates that there is an underestimation of the concentration of Ti^{2+} or an overestimation of Ti^{3+} caused by some systematic errors or by the effect of some impurities in molten salt. According to the study of Sekimoto [8], the O^{2-} initially contained in molten salt could affect Eq. (1) and can cause the overestimation of Ti^{3+} . Ti^{3+} could react with O^{2-} and Cl^- to form TiOCl(s) in molten salt and TiOCl(s) would be dispersed in molten salts. TiOCl(s) could cause overestimation of Ti^{3+} during chemical analysis; because Ti^{3+} both in TiOCl(s) and in molten salt can be oxidized by the titrant agent and they cannot be distinguished. In previous paper [10], the concentration of O^{2-} in the molten salt was reduced to a low level by HCl treatment in the melts, and accurate concentrations of titanium ions in the melts were obtained based on a reliable approach for taking samples, which was confirmed via the comparison of different routes using the chemical analysis.

Actually, the values of equilibrium constants reflect the relative content of different oxidation states. It has been reported in some papers that the stability of the various oxidation states depends on the composition bath [11–13]. LiCl–KCl eutectic salt was one of the

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most common electrolytes in electrolyzing titanium. Little work about oxidation states of the titanium ions and the equilibrium between titanium metal and titanium ions in LiCl–KCl melts were reported.

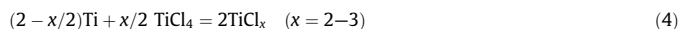
In this work, the equilibrium between metallic titanium and titanium ions (Ti^{2+} , Ti^{3+}) dissolved in LiCl–KCl melts and the influence of the electrolyte composition on the equilibrium were investigated. The accurate concentrations of titanium ions had been obtained based on a reliable approach for taking samples. Furthermore, the accurate values of the equilibrium constants were recalculated by best-fitting method under the consideration of the TiOCl dissolution. Finally, the influence of LiCl on the equilibrium constant and the average valence of titanium ions in the melts were discussed.

2. Experiment details

2.1. The preparation of electrolytes and samples

The electrolyte used in our experiments consisted of eutectic LiCl–KCl (59–41 mol%) (AR) melts was pre-dried in a vacuum chamber at 573 K for 10 h, and then heated up to 773 K under high purity argon atmosphere for 2 h. Hydrogen chloride gas was bubbled through the melts for 1 h to remove O^{2-} dissolved in the molten salt afterwards. At last, high purity argon gas was introduced into the fused salt to remove excess hydrogen chloride gas for 5 h. Temperature control within ± 2 K was achieved by a digital temperature controller (CHINO DZ3000, CHINO Corporation, Tokyo, Japan) and measured by a K-type thermocouple (Omega Engineering, Inc., Stamford, CT).

The LiCl–KCl obtained by the way described above was used as the reaction medium to prepare titanium subchloride (LiCl-KCl-TiCl_x) molten salt. The titanium subchloride salt was prepared by TiCl_4 (AR) which reacted with excess high pure titanium powder in the LiCl–KCl eutectic molten salt according to the following reaction:



After the reaction, the titanium subchloride salts were cooled to room temperature under argon atmosphere then transferred to the glove box, where the content of water and oxygen was maintained under 0.2 ppm. The detailed processes and devices of preparing LiCl–KCl– TiCl_x were the same as described in our previous paper [14].

Fig. 1 shows the experimental apparatus to determine the equilibrium between the titanium ions and titanium metal. The prepared titanium subchloride salts and excess metallic titanium were held at a designed temperature to reach equilibrium. High-purity argon gas was used to stir the molten salts for making the reaction of titanium ions and titanium metal adequately. Samples were taken by extracting the melts up into a piece of quartz tube ($\varnothing 8 \text{ mm} \times 500 \text{ mm}$). A quartz filter was welded at the end of the quartz tube, and the fused salt could pass through it but titanium particles were filtered out. Meanwhile, titanium wire ($\varnothing 0.3 \text{ mm}$) was placed into

the quartz tube to avoid breaking of the equilibrium reaction between metallic titanium and titanium ions when the dispersed titanium powders were filtered out by the quartz filter. After rapid-quenching, samples were transferred to the glove box to await analysis. Four parallel samples were taken from fused salt for analysis in each experiment. The average values were considered to be the measured values of the concentration of titanium ions.

2.2. The determination of titanium ions concentration

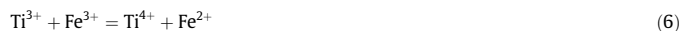
The quantitative analysis of different oxidation states of titanium ions consists of three main steps. The concentrations of Ti^{2+} , Ti^{3+} and Ti^{4+} in each sample were determined by H_2 volumetric analysis, titration and spectrophotometry respectively. The process of quantitative analysis was described as follows.

First, the concentration of Ti^{2+} was measured by H_2 volumetric analysis. The method is based on the fact that TiCl_2 can react with hydrochloric acid and generates H_2 gas in hydrochloric acid solution which is expressed by the following reaction:



The oxygen dissolved in diluted hydrochloric acid can oxidize Ti^{2+} in the process of determination of Ti^{2+} , which can cause the underestimation of Ti^{2+} concentration in the sample. Vacuum-deaeration was used to remove the O_2 dissolved in deionized water then the deoxygenated water which was used to prepare diluted hydrochloric acid (1.0 mol/L) and $\text{NH}_4\text{Fe}(\text{SO}_4)_2$ aqueous solution (0.05 mol/L) was obtained. The deoxygenated hydrochloric acid solution was saturated by bubbling of high purity H_2 to prevent the H_2 generated by Re. (5) dissolving in the hydrochloric acid solution before the reaction. After the reaction, all of the Ti^{3+} in the solution consists of Ti^{3+} which is original in the sample and the Ti^{3+} generated by Re. (5).

The concentration of Ti^{3+} in the solution was determined by the titrimetric analysis using $\text{NH}_4\text{Fe}(\text{SO}_4)_2$ aqueous solution which was acidified with sulfuric acid. The Ti^{3+} in the solution reacts with Fe^{3+} as the reaction follows:



The titration process was conducted in high purity argon atmosphere. Finally, the total titanium ions (Ti^{2+} , Ti^{3+} and Ti^{4+}) amount in the other solution was determined by diantipyryl methane spectrophotometry. The concentration of Ti^{4+} from Re. (6) was equal to the concentration of Ti^{2+} plus Ti^{3+} .

3. Results and discussion

3.1. The study for equilibrium between titanium ions and metallic titanium in LiCl–KCl salt

The time for reaching the equilibrium between the titanium and titanium ions has been studied by some researchers [4,6]. Li pointed out that it took longer time of about 2.5–4 h to reach the equilibrium when the reaction was from left to right than the opposite direction at 973 K [4]. Kreye et al. also studied the

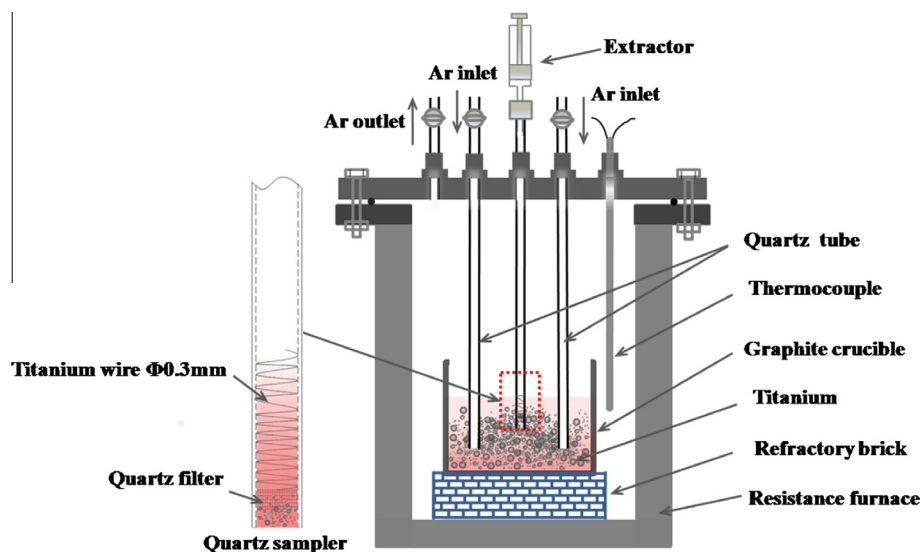


Fig. 1. Experimental setup: schematic diagram of equilibration apparatus and sampling device.

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