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ACTIVITIES OF TITANIUM IONS IN MOLTEN CALCIUM CHLORIDE

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Abstract

The subchloride titanium was prepared by sponge titanium and titanium tetrachloride in the $CaCl_2$ at 1173 K. The species were detected are mainly titanium dichloride, and the average valent in the melt are 2.05. The accurate equilibrium constants were obtained for the reaction $3Ti^{2+} = 2Ti^{3+}+Ti$ after the accurate activities of titanium chloride were evaluated with *emf* method, and the observed deviations from ideal behavior are discussed.

Introduction

The electrolysis processes for producing titanium are complicated due to the variety of titanium oxidation states [1-3]. These oxidation states undergo disproportionation reactions leading to a low current efficiency and formation of metallic muds in molten cells. Therefore, the research on the equilibrium between titanium ions and metallic titanium is very important for the process of electrodepositing titanium from fused electrolytes. In order to evaluate the equilibrium constant, K_c, of the reaction $3Ti^{2+}=2Ti^{3+}+Ti$, the concentrations of Ti^{2+} and Ti^{3+} were determined with chemical method. The K_c is defined by Eq. (2):

$$K_c = \frac{x^2_{Ti^{3+}} \cdot x_{Ti}}{x^3_{Ti^{2+}}} = \frac{x^2_{Ti^{3+}}}{x^3_{Ti^{2+}}} \tag{2}$$

Where x_i is the molar fraction of a species i , and it was defined by Eq. (3):

$$x_i = \frac{n_i}{\sum n_i} \tag{3}$$

The equilibrium constant was evaluated by Mellgren, Kreye, Li, Sekimoto *et al*. with determining the concentrations of Ti^{2+} and Ti^{3+} by H_2 volumetric analysis and titration, respectively [4-9]. The K_c was calculated with the concentration of titanium ions expressed by mole fraction which on the basis of the solutes ($TiCl_3$, $TiCl_2$) obey Henry's law under the condition of low titanium ions concentration. Actually, the activities of titanium ions in molten $CaCl_2$ are inconformity with the concentrations expressed by mole fraction when the initial concentrations of titanium ions are high. The relationship between activities and mole fraction is disclosed in this study in molten $CaCl_2$ at 1173 K. The observed deviations from ideal behavior are also discussed.

The activities of titanium ions in molten $CaCl_2$ are determined by *emf* method. The *emf* of the galvanic cell was measured as a function of $x_{Ti}{}^{2+}$ in the indicator half-cell [10-13]. The potential translated into potentials versus Cl_2/Cl^- even Ag/AgCl was used as reference.

$$\text{Ti}\ \Big|\ \begin{matrix}\text{TiCl}_2\\ \text{mole fraction}\\ \text{in molten salt}\end{matrix}\ \Big\|\ \text{Molten solvent}\ \Big|\ \text{Ag/AgCl}$$

Indicator half-cell   Reference half-cell

The measured values were corrected for the thermal *emf* of the electrodes system during the evaluation of the activities. The reversible cell *emf* of this cell is given by the Nernst equation.

$$-E = E^0 + \frac{2.303RT}{2F}\log\frac{a_{Ti^{2+}}}{P_{Cl_2}} \quad (1)$$

where E^0 is the standard electrode potential of the Ti^{2+}/Ti system, $a_{Ti}{}^{2+}$ is the activity of Ti^{2+}, and P_{Cl2} is the pressure of chlorine gas, other symbols have their usual significance. The activity of Ti^{2+} chloride will be given by the equation (2).

$$a_{Ti^{2+}} = \text{Anti}\log[-\frac{2F}{2.303RT}(E^{'} + E^0)] \quad (2)$$

where E' is the cell *emf* vs. a standard state (1 atom) chlorine reference.

Results and discussion

The concentrations of titanium ions were obtained by chemical analysis method. Samples were taken out from melt with the special quartz sampler and the concentrations were effective and accurate [9]. Then, the molar fraction of Ti^{2+} and Ti^{3+} ($x_{Ti}{}^{2+}$ and $x_{Ti}{}^{3+}$) can be calculated from the weight fraction, which varies from 1.6mol% to 11.0mol% (shown in Table 1).

Table. 1 Concentration of titanium ions and average valence in melt

$x_{Ti}{}^{2+}\times100$	$x_{Ti}{}^{3+}\times100$	Average valent, *n*	Deviation
13.08	0.58	2.05	0.011
10.29	0.41		
8.56	0.32		
5.08	0.24		
3.37	0.13		
1.79	0.08		

The average valence of the titanium ions in the molten salt is n, where n is calculated by equation (3):

$$\bar{n} = \frac{3x_{Ti^{3+}} + 2x_{Ti^{2+}}}{x_{Ti^{3+}} + x_{Ti^{2+}}} \quad (3)$$

Table 1 reveals that the average value of titanium ions in the molten salt is 2.05. The result indicates that the mainly species of titanium ions in molten $CaCl_2$ is Ti^{2+}. Therefore, the titanium rod (3mm) can be used as indicator electrode to measure $x_{Ti}{}^{2+}$ in equation (2).The results show in Fig. 1.

In Fig. 1, it can be seen that the activity of Ti^{2+} is shown as a function of its mole fraction. However, the deviation increases with the mole fraction increasing.

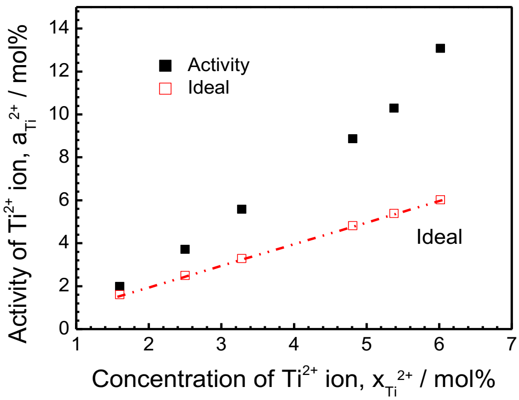

Fig. 1 Variation of the activity of Ti^{2+} with its mole fraction in $CaCl_2$.

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