Dissolution of Calcium Titanate in Calcium Chloride Melt and Its Application to Titanium Electrolysis

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The solubility of calcium titanate in CaCl2 melt was investigated above 1373 K, and electrodeposition of Ti metal in the melt was attempted. Many pits were formed on the surface of sintered CaTiO3 compact by the immersion in CaCl2 melt above 1373 K. The weight of the compact decreased with the increase in the immersion time, and the decrease got faster with the increase in temperature. Cathodic current in cyclic voltammetry increased with the addition of CaTiO3 powder in the bath, and the increase in the cathodic currents depended on the bath temperature and the added amount of CaTiO3. From the results by the electrochemical measurement, the solubilities of CaTiO3 in CaCl2 melt were estimated about 7 mol% at 1573 K, and less than 1 mol% at 1373 K. Metallic Ti was detected by XRD analysis in the electrodeposited obtained by potentiostatic electrolysis in the bath containing CaTiO3 above 1373 K, but the amount of Ti metal seemed a little. The similar results were obtained in CaCl2 melt containing Ca3Ti2O7 though the detailed study has not been completed. It was concluded that calcium titanate was soluble in molten CaCl2 above 1373 K, and that the CaCl2 bath containing calcium titanate could be applied to Ti electrolysis.

Keywords: titanium, calcium titanate, calcium chloride, molten salt, solubility, electrolysis

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1. Introduction

The current industrial smelting process of Ti metal is the Kroll process. Although the Kroll process is superb in the quality of the product and the simplicity of the total reaction, its productivity is not sufficient and hardly improved drastically. Therefore, the innovative smelting process is required to produce Ti metal more efficiently. Some new production processes of Ti metal have been investigated.1–6) Direct electrolysis in a molten salt bath is a possible candidate for the Ti metal production process, and some methods were proposed, actually.3,6)

The authors had also tried direct electrodeposition of liquid Ti metal in CaO-CaF2 melt containing TiO2 by using a direct-current electro-slag remelting (DC-ESR) unit, and showed that liquid Ti metal and Ti alloys were obtained under the suitable conditions.7–9) Through these investigations, it was suggested that a complex ion of Ti and O, i.e. a titanate ion, was preferentially formed in the bath and affected the electrochemical reduction of a Ti ion.10–12)

The formation of a Ti-O complex ion in a fluoride melt implies that a titanate ion can exist in a chloride melt containing an oxide ion considering the affinity of a Ti ion with Cl and F ions. TiO2 is said not to dissolve in CaCl2 melt below 1200 K,3,4) but there is a possibility that a titanate ion dissolves in the same bath at higher temperature. A Ca ion is thought more stable electrochemically than a Ti ion in molten chloride, and it was reported that CaCl2 melt was compatible with liquid Ti metal above the melting point of Ti metal, 1941 K.25) If a titanate ion is soluble in a CaCl2 melt, the CaCl2 bath containing a titanate ion can be applied to Ti electrolysis.

In this study, the change in the surface morphology and the weight of a sintered compact of calcium titanate by the immersion in CaCl2 melt was investigated above 1373 K. The change in cathodic behavior in the bath with calcium titanate powder was also studied, and the solubility of calcium titanate was estimated at various temperatures from the results of the electrochemical measurement. The electrodeposition of Ti metal in CaCl2 melt with calcium titanate powder was attempted under various conditions. Meta calcium titanate, CaTiO3, was mainly used in this study.

2. Experimental Procedure

2.1 Immersion test

A sintered compact of CaTiO3 was prepared using commercial CaTiO3 (Kishida Chem., > 99%) or a ball-milled mixture of CaO (Kishida Chem., > 98%) and TiO2 (Kishida Chem., > 99.5%) of 1:1 in mole; the powdery sample was molded with about 60 MPa for 20–30 sec, and sintered at 1573 K for 3 hours under an Ar (5N) atmosphere. A Ca3Ti2O7 compact was also prepared using a mixture of CaO:TiO2 = 3:2 with the same procedure. A rectangular specimen of about 15 × 10 × 10 mm was quarried from the compact, and polished with emery paper. The surface of the specimen was observed by an optical microscope (OM) and a scanning electron microscope (SEM, Nihon Denshi, JCM-6000), and then analyzed by a X-ray diffractometer (XRD, Rigaku, RINT-2550V).

Calcium chloride (Kishida Chem., > 95%) of about 30 g was put into a Mo crucible, and then dried at 373 K for a half day in a vacuum drier. The titanate specimen was set on the dried salt, and settled in an air-tight furnace tube in an electric furnace (Motoyama, MS-2821). The salt with the compact was heated under a pure Ar flow, held at 1573–1573 K for 2–8 h, and cooled to room temperature. The heating and cooling rate was 5 K/min due to the limitation of the experimental equipment. Although the time length of the heating...
and cooling should have been taken account into the real immersion time, the temperature-holding time is called as “immersion time” in this paper.

The calcium titanate specimen after cooling was taken by dissolving the solidified salt in distilled water. The specimen after careful washing with distilled water was weighed, observed by OM and SEM, and analyzed by XRD.

2.2 Electrochemical measurement

The apparatus is schematically illustrated in Fig. 1. A mixture of CaCl₂ and calcium titanate powder was put in a Mo crucible, where the commercial CaTiO₃ itself or the crashed powder of the titanate compact described before was used. The vacuum-dried mixture with a Mo crucible was settled in the air-tight furnace tube, and held at 1373−1573 K under a pure Ar flow.

A Mo wire (Nilaco, 99.9%, φ1 mm) was used as a working electrode, and it was covered with an Al₂O₃ sheath (Nikkato, SSA-S) except for 3−4 mm of its end. A graphite rod (Nippon Techno-Carbon, MF-307, φ5 mm) was used as a counter electrode. Since a common reference electrode using a porous mulite membrane could pollute the bath, another Mo wire was used as a quasi-reference electrode. The potential of the quasi-reference electrode was calibrated with the Ca/Ca²⁺ potential which was estimated by the zero current potential in cyclic voltammetry. All the potential hereinafter was represented versus this Ca/Ca²⁺ potential.

Measuring the cathodic current and the corresponding anodic current by cyclic voltammetry, the change in the electrochemical behavior with calcium titanate addition was examined. The dependence of the electrochemical behavior on the added amount of calcium titanate and temperature was investigated. Referring the results by the cyclic voltammetry, potentiostatic electrolysis was performed at various potentials. The electrodeposit obtained was washed with distilled water, observed by OM and SEM, and analyzed by XRD and energy dispersive X-ray spectrometer (EDX) attached to the SEM equipment.

3. Results and Discussion

3.1 Change in surface morphology and weight of calcium titanate compact by immersion test

Figure 2 shows the XRD pattern of the titanate specimen from the CaO-TiO₂ (1:1) mixture. It was shown that CaTiO₃ was synthesized by the sintering, though the color of the specimen changed from white to black by sintering. Almost the same result was obtained with the compact made from commercial CaTiO₃ reagent. It was also ascertained that Ca₃Ti₂O₇ was synthesized by the sintering with the CaO-TiO₂ (3:2 in mole) mixture.

Figure 3 shows the change in the surface morphology of the CaTiO₃ specimen by the immersion in CaCl₂ melt for the 2-hours holding at 1573 K. The surface before the immersion looks flat and smooth, while many pits appear on the surface after the immersion. The weight of the CaTiO₃ specimen decreased by the immersion, and the weight loss became rapid with the increase in the bath temperature. The weight loss increased with the immersion time as shown in Fig. 4. White compound precipitated from the solution obtained by dissolving the solidified CaCl₂ salt after the immersion test in dis-

![Fig. 1](image1)

![Fig. 2](image2)

![Fig. 3](image3)
tipped water. The precipitate was identified as CaTiO$_3$ by XRD, and its amount almost agreed with the weight loss of the titanate specimen.

The change in the surface morphology of the CaTiO$_3$ specimen and the dependence of the weight loss on the bath temperature and the immersion time clearly indicate that CaTiO$_3$ dissolved in CaCl$_2$ melt above 1373 K. However, the dissolved amount was not large; the concentration by the immersion for the 8-hours holding at 1573 K was estimated about 0.2 mol% from the weight loss and the amount of the precipitate. It was thought that the dissolution rate of CaTiO$_3$ was not fast in the case the sintered compact was used.

The similar procedure was applied to the Ca$_3$Ti$_2$O$_7$ compact. However, the Ca$_3$Ti$_2$O$_7$ compact came apart in distilled water, so its change by the immersion in CaCl$_2$ melt could not be examined.

3.2 Change in cyclic voltammogram with calcium titanate addition

The shape of the voltammogram in the bath containing the calcium titanate did not change with time after more than 1 hour past from the system temperature reaching the scheduled experimental temperature. The electrochemical measurement was performed following this criterion.

Figure 5 shows the change in voltammograms with the addition of CaTiO$_3$ powder in CaCl$_2$ melt. The cathodic current clearly rose with CaTiO$_3$ addition all over the scanned potential range, and the cathodic current tended to increase with the added amount of CaTiO$_3$ as mentioned afterwards. Three cathodic current humps were seen around 1.1 V, 0.55 V and 0.2 V, though clear cathodic current peaks were not observed. The cathodic currents at these humps showed the linear relationship with the square root of the potential scan rate, which suggests that the cathodic reactions seemed diffusion-controlled. In the reverse scan, three anodic current peaks appeared at 0.5 V, 1.1 V and 1.3 V.

The results described above indicate that CaTiO$_3$ powder dissolved in CaCl$_2$ melt above 1373 K within 1 hour, and that three cathodic reactions of the species relating to titanate occurred in the bath. Although the reaction mechanism has not been discussed well yet, this behavior, i.e., 3-step reduction, seems similar to that in the fluoride melt with CaTiO$_3$.\(^{11}\)

Figure 6 shows the change in voltammogram with temperature. The cathodic current increased with the increase in temperature. This tendency is reasonable considering the acceleration of the mass transfer in the bath with temperature, but the remarkable increase in current at 1573 K is hardly explained only by this reason.

Figure 7 shows the change in voltammogram with the added amount of CaTiO$_3$ at 1573 K. The current tended to increase with temperature in the case the CaTiO$_3$ content was below 7 mol%, while the shape almost unchanged in the bath of above 7 mol% CaTiO$_3$. Since clear cathodic current peaks due to the CaTiO$_3$ addition were not observed in the system, the relationship between the cathodic current at 0.45 V and the CaTiO$_3$ content in the bath was plotted as shown in Fig. 6. Although the reproducibility on cyclic voltammetry seemed insufficient, the plots in Fig. 8 can be explained well by considering that the solubility of CaTiO$_3$ in CaCl$_2$ melt at 1573 K is about 7 mol%. The solubility of CaTiO$_3$ at 1473 K is also estimated about 5 mol% in the same way from Fig. 8, but that at 1373 K is hardly found from the result in Fig. 8. The solubility at 1373 will be mentioned later.

The cathodic current by cyclic voltammetry remarkably increased with Ca$_3$Ti$_2$O$_7$ addition at 1573 K, which indicates
that \( \text{Ca}_3\text{Ti}_2\text{O}_7 \) is also soluble in \( \text{CaCl}_2 \) melt at high temperature. The solubility of \( \text{Ca}_3\text{Ti}_2\text{O}_7 \) has not been estimated yet, however. Although the solubility product of calcium titanates should be essential to understand their dissolution, they have not been discussed yet. To estimate the solution product, the investigation should be carried out in \( \text{CaCl}_2 \) melt containing calcium titanate made from \( \text{CaO} \) and \( \text{TiO}_2 \) of various molar ratio.

### 3.3 Attempt at Ti electrodeposition in \( \text{CaCl}_2 \) melt containing calcium titanate

Figure 9 shows the change in the cathodic current density during potentiostatic electrolysis at 0.1 V in the bath of 3 mol%-\( \text{CaTiO}_3 \). After the current attenuation at the beginning of electrolysis, current gradually increased with irregular current drops. This current increase is thought due to the increase in the surface area with electrodeposition, and the irregular drops seem to have been caused by the exfoliation of the deposit. The current behaviors at 1473 K and 1573 K were almost the same, whereas the current at 1373 K was obviously smaller than those at 1473 K and 1573 K. Since the solubility of \( \text{CaTiO}_3 \) at 1373 K was suggested to be small as shown in Fig. 8, the added amount of \( \text{CaTiO}_3, \) 3 mol\%, is thought to have exceeded the solubility at 1373 K. Considering the difference in the current shown in Fig. 9, the solubility of \( \text{CaTiO}_3 \) was deduced as 1 mol\% or less. In addition, these results indicate that the cathodic current at this potential was mainly caused by the reduction of the species derived from \( \text{CaTiO}_3 \).

Black electrodeposit was obtained by the potentiostatic electrolysis at 0.1 V at 1373 \(-\) 1573 K. Titanium metal was detected in it by XRD as shown in Fig. 10, and some Ti lower oxides were also contained. From the increase in the cathodic current in the voltammograms and the existence of Ti metal and its lower oxides in the electrodeposit, it is concluded that the reduction of a titanate ion occurred in \( \text{CaCl}_2 \) melt containing \( \text{CaTiO}_3 \). However, the amount of Ti metal seemed a very little, and a Ti metal particle was not found by SEM-EDX analysis. Although the influence of the cathode potential on the Ti electrodeposition was examined, better electrodeposit was not obtained at any cathode potential. Moreover, \( \text{Ca} \) metal was detected in the deposit as shown in Fig. 10, which implies that the reduction by the so-called OS mechanism\(^5\) cannot be denied.

It was reported that the Ti electrolysis in \( \text{CaF}_2\)-\( \text{CaO}\)-\( \text{TiO}_2 \) bath was strongly affected by the bath composition; Ti metal was specifically obtained by the electrolysis in the bath where the molar ratio of \( \text{CaO} \) to \( \text{TiO}_2 \), \( \text{R}_{\text{CaO}}/\text{TiO}_2 \), was 3:2, while Ti metal was hardly electrodeposited in the bath of \( \text{R}_{\text{CaO}}/\text{TiO}_2 = 1:1.\)\(^9\) The \( \text{CaCl}_2 \) bath containing \( \text{CaTiO}_3 \) corresponds to the
molar ratio \( \frac{R_{CaO}}{TiO_2} = 1:1 \), which may have caused the hardness of Ti deposition in the melt with \( \text{CaTiO}_3 \).

Electrodeposit containing Ti metal was also obtained in \( \text{CaCl}_2 \) melt containing \( \text{Ca}_3\text{Ti}_2\text{O}_7 \), while lower oxides of Ti and Ca metal were not detected in the deposit. Since the bath containing \( \text{Ca}_3\text{Ti}_2\text{O}_7 \) corresponds to the molar ratio \( \frac{R_{CaO}}{TiO_2} = 3:2 \), the chemical type of titanate ions may cause the difference between the electrodeposits in the baths with \( \text{CaTiO}_3 \) and \( \text{Ca}_3\text{Ti}_2\text{O}_7 \). However, the detailed examination in the bath containing \( \text{Ca}_3\text{Ti}_2\text{O}_7 \) has not been completed yet. The dependence of Ti deposition on the chemical types of titanate must be investigated in detail, and the influence of the electrolysis condition on the current efficiency should be discussed.

4. Conclusion

It was shown from the immersion test and the electrochemical measurement that both \( \text{CaTiO}_3 \) and \( \text{Ca}_3\text{Ti}_2\text{O}_7 \) dissolved in \( \text{CaCl}_2 \) melt above 1373 K. The solubility of \( \text{CaTiO}_3 \) was estimated about 7 mol% at 1573 K from the electrochemical measurement. It is also shown that the electrochemical reduction of a titanate ion occurred in \( \text{CaCl}_2 \) melt containing \( \text{CaTiO}_3 \), and Ti metal was detected in the electrodeposit obtained by potentiostatic electrolysis. However, the amount of Ti metal seemed a very little, and some Ti lower oxides were also detected. Considering the reported results in \( \text{CaF}_2-\text{CaO}\text{-TiO}_2 \) melt, it was suggested that the chemical type of a titanate ion in the bath affected its reduction mechanism and strongly influenced the electrodeposition of Ti metal.

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