

Influence of bath composition on Ti metal deposition in molten CaCl₂ containing calcium titanate

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Abstract

The dependence of the cathodic behavior of a Ti ion on the molar ratio of CaO to TiO₂ (R_{CaO/TiO_2}) was investigated in molten CaCl₂ above 1373 K, and the influence of R_{CaO/TiO_2} on Ti metal deposition was discussed. The reduction mechanism changed at $R_{CaO/TiO_2} = 1.5$; a three-step reduction of Ti was suggested in the melt of $R_{CaO/TiO_2} < 1.5$, while a two-step reduction seemed to occur above $R_{CaO/TiO_2} = 1.5$. Titanium metal deposition was also affected by R_{CaO/TiO_2} as well as by the cathode potential, and the suitable R_{CaO/TiO_2} was likely 1.5. Since this value was the same as the suitable value in the molten fluoride system, Ti metal was thought to be obtained only from Ti₂O₇⁶⁻. Silicon and Al metal were obtained electrochemically in molten CaCl₂ containing calcium silicate and aluminate more easily than Ti metal. The difficulty of the Ti metal deposition is likely to be caused by the so-called shuttle reaction; the shuttle reaction can occur in the Ti metal electrolysis because some ionic states of Ti are stable in the bath. To realize better Ti metal deposition, the control of the shuttle reaction should be important.

1. Introduction

A new Ti production process replacing the Kroll process is desired. Many researchers have been studying the innovative smelting process,[1-7] but those processes are still under development. In our laboratory, the direct electrowinning of liquid Ti has been studied in molten fluoride, and it was shown that Ti metal was obtained.[8] The Ti deposition strongly depended upon the molar ratio of CaO to TiO₂ (R_{CaO/TiO_2} , hereinafter), and $R_{CaO/TiO_2} = 1.5$ seemed suitable for Ti metal deposition.[9, 10] Based on these results in molten fluoride, Ti metal deposition in molten CaCl₂ containing some types of calcium titanate was attempted above 1300 K, and it was shown that Ti metal was deposited under a particular condition; R_{CaO/TiO_2} was dominant even in molten CaCl₂, and the electrolysis potential affected the deposition.[11-13] However, the Ti metal deposition in molten CaCl₂ seemed more difficult than that in molten fluoride.

In this study, Ti metal deposition in molten CaCl₂ containing some types of calcium titanate was attempted, and the influence of R_{CaO/TiO_2} on Ti metal deposition was discussed in comparison to that in molten fluoride. It is also discussed the differences from Ca and Al metal deposition in molten CaCl₂ above 1373 K which the authors have been studying.[14]

2. Materials and experiments

Calcium titanate was synthesized beforehand as follows; TiO₂ (Kishida Chem., >99.5%) and CaO (Kishida Chem., >98%) was mixed with a ball mill so that R_{CaO/TiO_2} became 1.0~2.0. The mixture was molded and sintered at 1573 K for 3 hours under an Ar atmosphere. The sintered compact was grinded into its powder. The main substances in the powder changed with R_{CaO/TiO_2} as shown in Table 1, which agrees with the reported phase diagram of the CaO-TiO₂ system.[15]

Table 1 Substances in synthesized calcium titanate.

R_{CaO/TiO_2}	substances	
	major	minor
1.0	CaTiO ₃	
1.325	Ca ₄ Ti ₃ O ₁₀ *	CaO, TiO ₂
1.5	Ca ₃ Ti ₂ O ₇ *	CaO
> 1.5	Ca ₃ Ti ₂ O ₇ , CaO	CaO, TiO ₂

* Ca₄Ti₃O₁₀ & Ca₃Ti₂O₇ are hardly distinguished

The apparatus for electrochemical measurement and electrolysis is almost the same in our former studies.[11-13] Calcium chloride (Kishida Chem., >95%) containing the calcium titanate powder was put in a Mo crucible, and vacuum dried at 373K for a day. The mixture with the crucible was set in an air-tight furnace and melted under a pure Ar atmosphere. In this paper, the electrolytic bath containing the calcium titanate of $R_{CaO/TiO_2} = 1.5$ is simply represented as “the bath of $R_{CaO/TiO_2} = 1.5$ ”, for example.

A Mo wire (Nilaco, ϕ 1.0mm) covered with pure Al₂O₃ sheath was used as a working electrode. A graphite rod (Nippon Techno-Carbon, MF-307, ϕ 5.0mm) was used as a counter electrode. Another Mo wire was used as a quasi-electrode, and its potential was calibrated with the Mo dissolution potential. The electrochemical behavior of Ti was investigated by cyclic voltammetry, and then potentiostatic electrolysis was carried out based on the results by cyclic voltammetry at 1373 ~ 1573 K. The electrodeposit was washed with distilled water, and then observed and analyzed by SEM-EDX (JEOL, JCM-6000/EX-5441) and XRD (Rigaku, RINT-2550V).

The results of Ti deposition in a molten CaF₂-MgF₂ eutectic mixture containing some types of calcium titanate[9-10] are mentioned to compare the difference between the Ti in molten CaCl₂ and in molten fluoride. It is also discussed the difference in the cathodic behaviors and metal depositions of Si [14] and Al in molten CaCl₂. Commercial CaSiO₃ powder (Wako Pure Chem., CaO:40.0~48.0%, SiO₂: 51.0~57.0%) was used in the Si electrolysis, while the sintered CaAl₂O₄ powder by the same procedure above was used for the Al electrolysis.

3. Results and Discussion

3-1. Influence of R_{CaO/TiO_2} on Ti electrolysis in molten CaCl₂

Cathodic current during cyclic voltammetry increased with the increase in the added amount of the calcium titanate. From the current increase with the addition of CaTiO₃ or Ca₃Ti₂O₇, their solubilities in molten CaCl₂ were estimated as more than 5 mol% at 1573K.[16] Three cathodic current peak/humps appeared around -1.1 V, -1.3 V and -1.6 V (vs. Mo diss.) in the bath of $R_{CaO/TiO_2} < 1.5$, while two peak/humps were seen around -1.4 V and -1.7 V (vs. Mo diss.) in the bath of $R_{CaO/TiO_2} \geq 1.5$. However, clear current peaks were hardly observed, and their shapes became more indistinct with the rise in bath temperature. The current of the peak/humps were not proportional to the square root of the potential scan rate, but showed a linear relationship to them. These result suggest that the so-called residual current by convection in the bath affected the voltammetry.

Table 2 shows the summary of Ti metal deposition by potentiostatic electrolysis under various conditions. In the bath where R_{CaO/TiO_2} was not 1.5, Ti metal was obtained only at lower electrolytic potential, and Ca metal seemed to co-deposit. In these conditions, it is not denied that Ti metal was obtained by the reduction by electrodeposited Ca metal. In the bath of $R_{CaO/TiO_2} = 1.5$, Ti metal was detected without the co-deposition of Ca metal as shown in Fig.1 [12] contrarily. However, only a few and small Ti metal particles were seen in the deposit, and the O content was not low enough.

It was shown that Ti metal could directly electrodeposit only in the bath of $R_{CaO/TiO_2} = 1.5$, and that the yield of Ti metal deposition seemed very low. A Mo-Ti alloy layer was not observed on the Mo cathode under any condition, which is a contrast to the cases in the Ca and Al electrolysis mentioned after.

Table 2 Summary of Ti metal deposition by potention-static electrolysis in molten CaCl₂ containing calcium titanate at 1573 K.

		R_{CaO/TiO_2}										
		1.0		1.325		1.5		1.6	1.8	2.0		
PE	E_{cath} (V vs. Mo _{dis})	-2.1	-1.6	-1.8	-1.7	-1.9	-1.8	-1.9	-1.9	-1.9	-1.8	-1.7
	Ti deposition	△	×	×	○	⊙	⊙	×	○	×	△	×
CV	reaction step	3					2					

⊙ Ti without Ca ○ Ti without Ca (depend on concentration)
△ Ti with Ca × no Ti

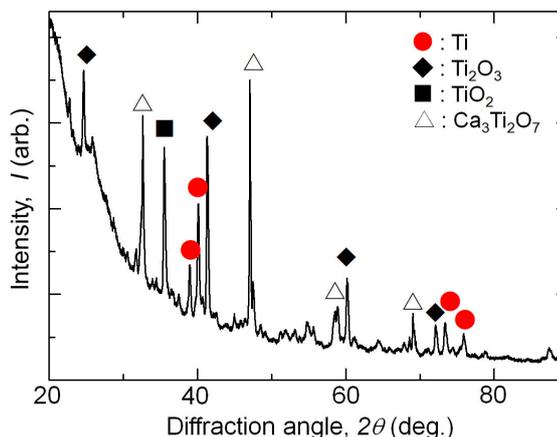


Fig. 1 XRD pattern of electrodeposit by potention-static electrolysis in bath of $R_{CaO/TiO_2} = 1.5$. (1573K, [12] $C_{Ca_3Ti_2O_7} = 5\text{mol}\%$, $E_{cath} = -1.9\text{V}$ (vs. Mo diss.))

3-2. Comparison between Ti depositions in molten CaCl₂ and in molten fluoride

The results of cyclic voltammetry in the molten fluoride were similar to those in molten CaCl₂; some cathodic current peak/humps appeared with the addition of calcium titanate, and their shapes became unclear with the temperature rise. The ratio $R_{CaO/TiO_2} = 1.5$ seemed the border in the cathodic reaction of Ti; the number of the reduction step seemed three in the bath of $R_{CaO/TiO_2} < 1.5$ and two in the bath of $R_{CaO/TiO_2} \geq 1.5$.

Figure 2 shows the XRD patterns of the electrodeposit obtained by potention-static electrolysis at -1.8V (vs. Mo diss.). Ti metal was detected in the electrodeposit obtained in the bath of $R_{CaO/TiO_2} = 1.5$ though the electrolysis potential where Ti metal was obtained was limited.[10] The Ti peaks are hardly found in the XRD pattern of the deposit from the bath of $R_{CaO/TiO_2} = 1.45$, and the Ti peaks are not seen in that of the deposit of $R_{CaO/TiO_2} = 1.55$. Many Ti metal particles were observed in the deposit from the bath of $R_{CaO/TiO_2} = 1.5$ as shown in Fig.3. However, their amount were very little in comparison to that calculated from the quantity of the electricity during potention-static electrolysis.

The electrodeposition of Ti metal both in molten CaCl₂ and in molten CaF₂-MgF₂ strongly depends on R_{CaO/TiO_2} , and the optimum value for Ti metal deposition is concluded as 1.5. Considering the difference in the chemical affinity between Ti-F and Ti-Cl, it is thought that a titanate ion preferentially formed instead of their oxychloride or oxyfluoride ion. Titanium metal seems to deposit only from Ti₂O₇⁶⁻, though its actual structure in the bath has not been clarified.

The electrodeposition of Ti metal was difficult even in each bath of $R_{CaO/TiO_2} = 1.5$, and the current efficiency was negligibly small. In the Ti electrolysis using a DC-ESR unit, Ti metal in liquid was forcedly deposited and the current efficiency reached about 25% in the bath of $R_{CaO/TiO_2} = 1.5$. [8] The electrodeposited Ti metal is thought to be lost easily unless its potential is well controlled by the adhesion on the cathode.

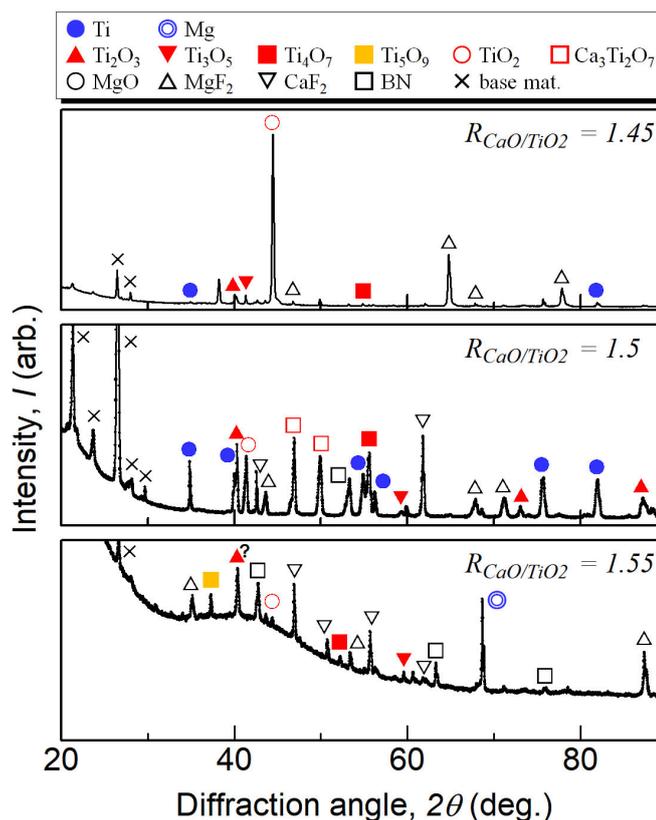


Fig. 2 XRD patterns of electrodeposit by potentiostatic electrolysis in bath of various R_{CaO/TiO_2} . (1573K, $C_{TiO_2} = 5$ mol%, $E_{cath} = -1.8V$ (vs. Mo diss.))

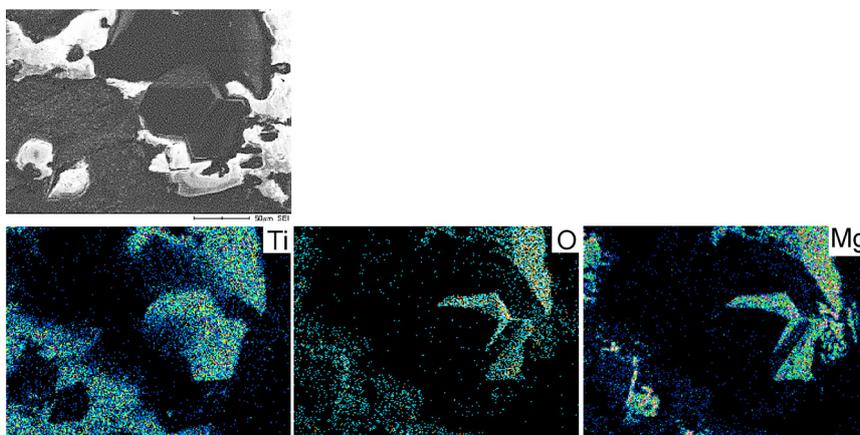


Fig. 3 SEM image and EDX map of electrodeposit by potentiostatic electrolysis in bath of $R_{CaO/TiO_2} = 1.5$. (1573K, $C_{TiO_2} = 5$ mol%, $E_{cath} = -1.8V$ (vs. Mo diss.))

3-3. Comparison with Si and Al deposition in molten $CaCl_2$

A clear cathodic current peak appeared in cyclic voltammogram in molten $CaCl_2$ with the addition of either $CaSiO_3$ [14] or Ca_2SiO_4 though the shape became indistinct with the rise in bath temperature. A thick $MoSi_2$ layer was formed on Mo cathode by potentiostatic electrolysis in the bath containing $CaSiO_3$ when the potential was set more negative than the potential of the cathodic current peak.[14] By the potentiostatic electrolysis using $MoSi_2$ as cathode in the bath containing either $CaSiO_3$ or Ca_2SiO_4 , many Si metal particles were observed in the electrodeposit as shown in Fig. 4. Cathodic current in cyclic voltammetry increased with the addition of $CaAl_2O_4$ in molten $CaCl_2$, but no clear cathodic current peak/hump was seen. A thick layer of intermetallic compound of Al and Mo was formed on Mo cathode as shown in Fig. 5, and Al metal was also detected on its surface by XRD analysis.

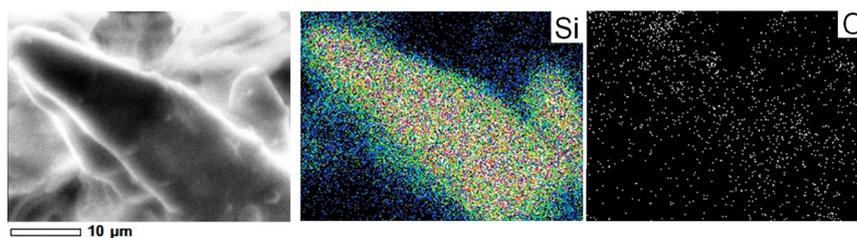


Fig. 4 SEM image and EDX map of electrodeposit by potentiostatic electrolysis in bath containing CaSiO_3 . (1573K, $C_{\text{CaSiO}_3} = 5 \text{ mol\%}$, $E_{\text{cath}} = -1.5\text{V}$ (vs. Mo diss.))

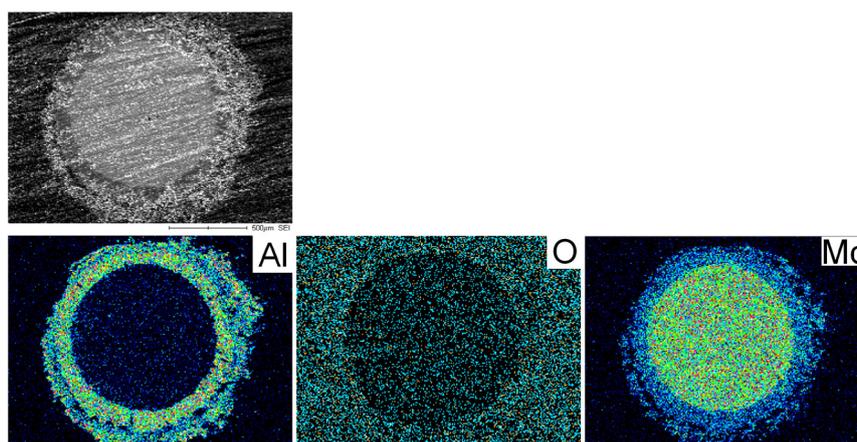


Fig. 5 SEM image and EDX map of cross section of Mo cathode after potentiostatic electrolysis in bath containing CaAl_2O_4 . (1573K, $C_{\text{CaAl}_2\text{O}_4} = 7 \text{ mol\%}$, $E_{\text{cath}} = -1.8\text{V}$ (vs. Mo diss.))

Silicon and Al metal were easily obtained by the electrolysis in molten CaCl_2 containing calcium silicate and aluminate, whereas Ti metal was hardly electrodeposited in the bath containing calcium titanate. One of major differences of a Ti ion from a Si and Al ions in molten salt bath is the number of their stable ionic state; Ti(IV), Ti(III) and Ti(II) are said to be stable in molten chloride, while Ti(IV) and Ti(III) are said stable in molten fluoride.[17] Only one ionic state, Si(IV) and Al(II), is thought to be stable in Si and Al. The number of the cathodic current peak/humps in their cyclic voltammograms should be related to the number of stable ionic state(s). When there are plural stable ionic states in electrolytic bath and electrochemical reaction proceeds with multi-step, the so-called shuttle reaction can occur. Since the shuttle reaction badly prevents an efficient electrodeposition of metal, the difficulty of the electrodeposition of Ti metal is considered to be caused by its shuttle reaction. The difference in the Ti electrolysis between in molten CaCl_2 and the molten fluoride can be also explained by the shuttle reaction, though other factors, such as $R_{\text{CaO/TiO}_2}$ and the solubility of Ti compound, should strongly influence it.

To improve the current efficiency of Ti metal deposition, the shuttle reaction should be controlled. The direct deposition of liquid Ti metal should be effective to prevent the deposit from flaking away from cathode. It is also potential to use a diaphragm for electrolysis.

4. Conclusion

It is concluded that the molar ratio of CaO to TiO_2 , $R_{\text{CaO/TiO}_2}$, strongly affects the electrochemical reaction of a Ti ion in molten CaCl_2 containing calcium titanate, and that the optimum $R_{\text{CaO/TiO}_2}$ for Ti metal deposition is 1.5. Considering the results of Ti metal in molten fluoride containing calcium titanate, Ti metal seems to deposit only from $\text{Ti}_2\text{O}_7^{6-}$. However, Ti metal deposition is more difficult than Si or Al metal deposition, which is likely to be due to the so-called shuttle reaction.

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6. References

- [1] G. Chen, D. Fray, T. Ferthing, *Nature*, 407 (2000) 344–361.
- [2] K. Ono, R.O. Suzuki, *JOM*, 54 (2002) 59-61.
- [3] R. O. Suzuki, H. Noguchi, H.Hada, S. Natsui, T. Kikuchi, *Material Trans.*, 58 (2017) 341-349.
- [4] K. Weil, Y. Hovanski, C. Lavender, *Journal of Alloys and Compounds*, 473 (2009) 139-143.
- [5] D. Fray, C. Schwandt, *Material Trans.*, 58 (2017) 306-312.
- [6] O. Takeda, T. Okabe, *Journal of Japan Institute of Light Metals*, 67 (2017) 257-263.
- [7] C. Schwandt, G. Dougherty, D. Fray, *Key Engineering Materials Online*, 436 (2010) 13-25.
- [8] T. Takenaka, M. Sugawara, H. Matsuo, A. Matsuyama, M. Kawakami, *ECS Trans.*, 16 (2009) 139-143.
- [9] Y. Yamanaka, T. Morishige, T. Takenaka, *ECS Trans.*, 64 (2014) 275-283.
- [10] K. Nishikawa, H. Sawada, T. Morishige, T. Takenaka, *ECS Trans.*, 75(15) (2016) 199-206.
- [11] T. Takenaka, K. Shimokawa, K. Nishikawa, H. Okada, T. Morishige, *Material Trans.*, 58 (2017) 350-354.
- [12] H. Okada, K. Shimokawa, T. Morishige, T. Takenaka, *Material Trans.*, 59 (2018) 690-693.
- [13] H. Okada, M. Murata, T. Morishige, T. Takenaka, *ECS Trans.*, 86(14) (2018) 117-122.
- [14] T. Takenaka, R. Shimokawa, H. Okada, T. Morishige, *ECS Trans.*, 86(14) (2018) 29-35.
- [15] R.S. Roth, J.R. Dennis, H.F. McMurdie; *PHASE DIAGRAMS FOR CERAMISTS VOLUME VI*, p.110-111, American Ceramic Society, U.S.A, 1987.
- [16] C. Schwandt, D. Alexander, D. Fray; *Electrochim. Acta*, 54 (2009) 3819–3829.
- [17] T. Takenaka, M. Kawakami, N. Suda, *Material Science Forum*, 449-452 (2004) 453-456.