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Calciothermic Reduction of TiCl₄ Gas during the Electrolysis of CaCl₂ Melt

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The calciothermic reduction of TiCl₄ gas was studied firstly by using Ca-CaCl₂ melt, to whose surface the gas was blown. The fine Ti particles settled down in the crucible, when the concentration of dissolved Ca was > 2 mol% at 1173 K. When < 2mol%Ca, a part of TiCl₄ gas was dissolved probably as TiCl₃ or TiCl₂ into the CaCl₂ melt, and it precipitated as the lower Ti oxides. When TiCl₄ gas was blown to the molten CaCl₂, which was electrochemically decomposed into Cl₂ gas at the carbon anode and Ca at the Ti cathode, TiCl₄ gas was reduced to the dendritic Ti on the cathode surface. Because the electrolyzed Ca reacted preferentially with the oxide crucibles, most of the oxygen ions combined with Ti(II) and Ti(III), and they formed TiO and Ti₂O₃.

Introduction

Kroll process connects three reactions; chlorination of TiO₂, Mg reduction of TiCl₄, and molten salt electrolysis of MgCl₂ (1). It is industrially applied to produce Ti metal via pure TiCl₄ that is distilled several times, and the purity of its final product (sponge titanium) is high suitable for the aerospace applications. However, the sponge titanium formed by Mg reduction strongly adhered to the vessel and it is difficult to produce Ti continuously. Thermal waste due to the batch-type operation of the endothermic molten salt electrolysis and the exothermic Mg reduction is another demerit of the Kroll process. This work will connect the electrolysis and the Ca reduction in a single bath, using a high purity of TiCl₄ as starting material.

Concept of Proposal

A new method for production of metallic titanium is here proposed: TiCl₄ is continuously reduced by Ca, which is precipitated by the in-situ electrolysis of molten CaCl₂. An outline of this proposal is illustrated in Fig. 1(a). The electrolysis of the molten CaCl₂ forms liquid Ca and Cl₂ gas at the cathode and the anode, respectively. The operation will be done at about 1173 K, by considering the melting point of CaCl₂ and its evaporation.



The evolved Cl₂ gas can be industrially recycled for production of TiCl₄ from TiO₂. The precipitated Ca dissolves into the CaCl₂ melt; the solubility of Ca at 1173 K is reported to be 2.7 mol% at minimum and 4.0 mol% at maximum, although some variations have been reported (2-4). This dissolved calcium will be hereafter referred to

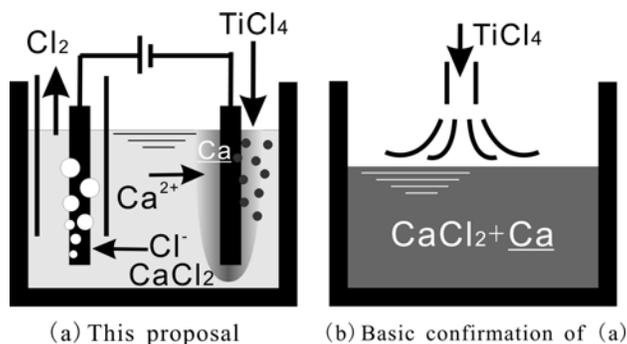
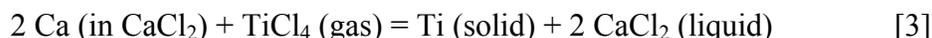


Figure 1. (a) Calciothermic reduction of TiCl_4 in the molten CaCl_2 and (b) its experimental confirmation.

as $\underline{\text{Ca}}$, which exists especially close to the cathode (5,6). When TiCl_4 gas is injected to $\underline{\text{Ca}}$, the metallic Ti is produced as,



Eq. [3] occurs at the interface between the liquid and the gaseous phase as illustrated in Fig.1(a), and the metallic powder is formed as the product. This powder formation is desirable for the continuous operation, and Ca neither reacts with Ti nor dissolves in Ti as the solid solution. The operation becomes simpler and this plant becomes more compact than that of the Kroll process. It is noteworthy that the electrolysis of MgCl_2 is operated in a separated plant. We expect that the energy consumed during Ti production can be saved because the exothermic and endothermic reactions are simultaneously conducted in a single cell. If we can realize the technique to extract Ti powder continuously from the molten salt, this proposal will be applied for the industrial operation.

In the electrolysis of MgCl_2 as a part of Kroll process, the precipitated Mg metal adheres to the cathodic surface and it is not easy to react *in-situ* with the gaseous TiCl_4 . Deura *et al.* studied the combination of the electrolysis of MgCl_2 and the *in-situ* Mg reduction of TiCl_4 in the molten MgCl_2 (7,8). They showed that the metallic Ti preferentially precipitated at the open end of cathodic nozzle for TiCl_4 gas injection, and that the continuous supply of gaseous TiCl_4 was often terminated because the nozzle was inserted in the melt.

The purpose of this work is to verify experimentally this proposal combining eqs.[1]–[3] in a bath, and to find a suitable condition to form the metallic titanium powder in this bath. Firstly, this study verifies the feasibility whether $\underline{\text{Ca}}$ can reduce TiCl_4 gas, as shown in Fig. 1(b). Secondly this study verifies the combination with the electrolysis, as shown in Fig. 1(a).

Experimental

Reduction of TiCl_4 by Ca in Molten CaCl_2

As shown in Fig. 1(b), 660–700 g of CaCl_2 was melted in MgO or Al_2O_3 crucible at 1173 K, and several Ca grains were added to obtain the desired Ca concentration. TiCl_4 gas was then fed at a constant rate for 1.8–4.8 ks. The end of Al_2O_3 pipe was placed 10–

20 mm above the melt surface. After blowing, the white solidified salt and the residual Ca were removed by water.

Reduction of TiCl_4 by Ca from Electrolysis of CaCl_2

The apparatus as illustrated in Fig. 2 was used for the electrolysis to combine eqs.[1]-[3]. The cathode and the anode were made of Ti bar (6 mm ϕ) and carbon bar (10 mm ϕ), respectively. In several experiments, the anode was set inside the mullite pipe to exhaust the evolved Cl_2 gas efficiently to the outside of the vessel. The electrolysis was conducted by applying 4.0–5.0 V constantly. Although the theoretical voltage for decomposition of CaCl_2 is 3.21 V at 1173 K (7), the applied voltage was set enough high by considering a possible over-potential for Cl_2 gas evolution. TiCl_4 gas was constantly blown to the melt surface near the cathode for 4.1–25.0 ks after a certain amount of Ca was formed by the preliminary electrolysis.

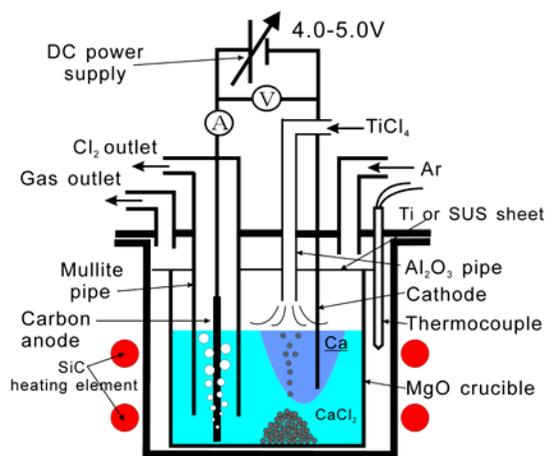


Figure 2. Experimental setup for *in-situ* reduction combined with the calciothermic reduction of TiCl_4 gas and the CaCl_2 electrolysis.

Results and Discussion

Formation of α -Ti

A part of the product was piled up as powder at the bottom of crucible, and the other was tightly sintered lumps at the surface of the solidified salt near the crucible wall. It is considered that the latter nucleated at the three-phase interface among the molten salt, crucible wall, and gas phase, and that it grew toward the melt on its surface. The former powder was a product of the reaction at the free surface between the molten CaCl_2 containing Ca and the gaseous TiCl_4 .

Fig. 3 shows a typical scanning electron microscope (SEM) image of the powdery sample recovered at the bottom of crucible. The Ti particles were spherical with a diameter of about 1 μm , and they were sintered slightly. However, the lumps at the free surface of molten salt were often sintered tightly on surfaces like the plate or bar. Most of these specimens consisted of the same size of Ti particles as shown in Fig. 3. No dendritic growth was found in the morphology.

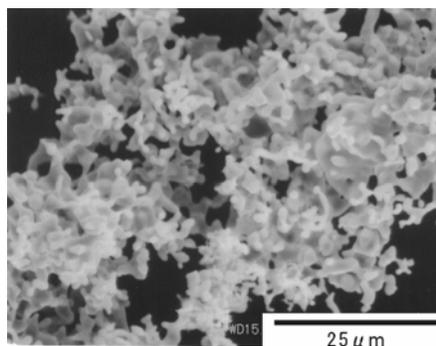


Figure 3. SEM image of the obtained powder in Run #D.

Fig. 4 shows the phase identification of the powders by X-ray diffraction (XRD) measurements and it summarizes the changes in the Ca concentration during the reaction. The ends of the arrows show the initial and final concentrations which were evaluated by assuming the complete reaction. α -Ti powder was obtained in the experiments from Runs #A to #G. Because the gaseous TiCl_4 was simply fed to the free surface at a slow rate, a lower yield was expected due to incomplete reaction on the surface. However, the yield after leaching was as high as 50–70%.

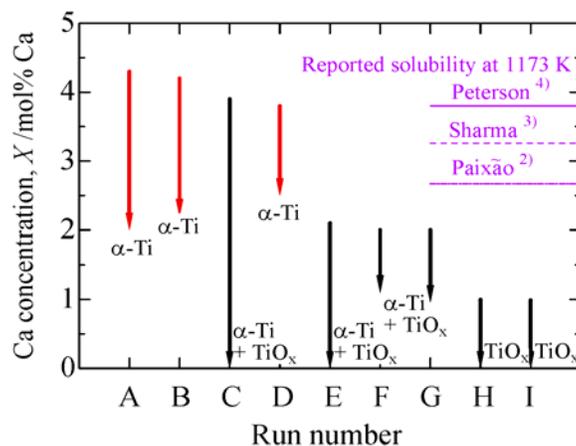


Figure 4. Change in Ca concentration during Runs #A-I, and the identified phases after the reaction with TiCl_4 and the salt removal in water.

The lower titanium chlorides such as TiCl_3 are converted to the lower oxides (TiO_x) such as Ti_2O_3 and TiO because of oxidation during aqueous treatment for CaCl_2 removal. The mixture of α -Ti and the lower oxides was obtained in Runs #C, #E–#G. In these runs, the final Ca concentrations were low, but a large amount of TiCl_4 was fed compared to the initial Ca concentration. Only the lower oxides were obtained in Runs #H and #I, where the Ca concentration was low considering the amount of TiCl_4 feed.

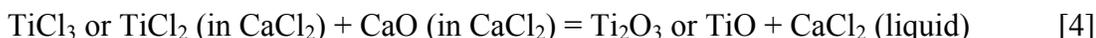
Calcium and TiCl_4 react stoichiometrically in a molar ratio of 2:1, as shown in eq.[3]. When the molar ratio of the supplied amount of Ca and that of TiCl_4 ($N_{\text{Ca}}/N_{\text{TiCl}_4}$) is larger than 2, it is expected that the entire amount of fed TiCl_4 can be reduced to α -Ti and some amount of Ca remains. The experiments approximately confirm this requirement. In terms of thermodynamics, this means that a strong affinity of Ca with Cl can decompose

TiCl₄ even if Ca dissolves as $\underline{\text{Ca}}$. In Runs #C and #E, however, the supplied TiCl₄ could not be reduced to Ti because $N_{\text{Ca}}/N_{\text{TiCl}_4}$ was smaller than 2. It is noteworthy that the lower oxides of titanium were formed when the Ca concentration decreased during the reaction to a level of <2 mol%. This shows that the thermochemical activity of $\underline{\text{Ca}}$ should be maintained higher than 2 mol%.

Formation of lower oxides

The other reasons for the formation of the lower oxides of titanium were the small leakage of air at the operation of Ca feed, the calciothermic reduction of oxide crucible, and a small amount of water in the used CaCl₂. They can serve oxygen to the melt.

TiCl₄ gas blown onto the molten salt may react with $\underline{\text{Ca}}$ to form firstly the lower chlorides such as TiCl₃ and TiCl₂. However, they are unstable if a small amount of oxygen exists (9), and react with oxygen to form the lower oxides



α -Ti was obtained as listed in Table 1. Porous α -Ti powder was recovered at Runs #ED and #EE as the slightly sintered particles at the bottom of crucible (Fig. 5(a)). The dendrite form adhered to the cathode was also obtained (Fig. 5(b)). This is probably because Ti(II) or Ti(III) ions were precipitated on the cathode during electrolysis, or because they were preferentially reduced to Ti metal by meeting with $\underline{\text{Ca}}$ near the cathode.

TABLE I. Estimation of $\underline{\text{Ca}}$ produced by the electrolysis and the phases after the reduction.

Run	X'_{Ca}	X_{Ca}	$N_{\text{Ca}}/N_{\text{TiCl}_4}$	$V_{\text{Ca}}/V_{\text{TiCl}_4}$	Identified phase by XRD *	
					at the bottom of crucible	on the cathode
EB	1.1	0	1.8	1.3	Ti _{1.9} O ₃ , Ti ₂ O ₃ , TiO	TiO, α -Ti, Ti ₂ O ₃
EC	0.99	0	1.8	1.3	Ti ₂ O ₃ , TiO, Fe ₃ Ti ₃ O	TiO, α -Ti, Fe ₃ Ti ₃ O, Ti ₅ Si ₃
ED	0.64	5.6	6.7	6.2	Ti ₅ Si ₃ , α -Ti, TiO	Ti ₈ C ₅ , α -Ti
EE	1.0	2.2	6.0	4.1	α -Ti, TiO, Ti ₅ Si ₃	α -Ti, TiO, CaTiO ₃

X'_{Ca} and X_{Ca} : Ca concentrations after the preliminary electrolysis (before the gas blowing), and after the reaction, respectively (mol%Ca).

N_{Ca} and N_{TiCl_4} : the total amount of formed Ca, and the amount of blown TiCl₄ (mol).

V_{Ca} and V_{TiCl_4} : Ca forming rate after TiCl₄ blowing, and the supplying rate of TiCl₄ (mol/s).

*: listed as the dominant phases, minor phases, and faint phases, in this order.

By assuming that all the supplied current was used only for the electrolysis of CaCl₂, the total amount of $\underline{\text{Ca}}$ during the electrolysis, N_{Ca} , was evaluated. Using the amount of blown TiCl₄ gas, N_{TiCl_4} , the ratio of $N_{\text{Ca}}/N_{\text{TiCl}_4}$ is listed in Table 1. The final $\underline{\text{Ca}}$ concentration in the molten salt after the reaction, X_{Ca} , was also shown in Table 1.

Because TiCl₄ and $\underline{\text{Ca}}$ react by the molar ratio of 1:2 to form Ti as shown in eq.[3], all the amount of blown TiCl₄ should be reduced completely when $N_{\text{Ca}}/N_{\text{TiCl}_4} > 2$. Run #ED and #EE satisfied conditions of $N_{\text{Ca}}/N_{\text{TiCl}_4} > 2$ and of $X_{\text{Ca}} > 2$ mol%. However, the intermediate product, TiO, was included as well as α -Ti. This suggests that a significantly large difference in Ca concentration might be generated in the melt. This is because the dissolution and diffusion of precipitated Ca at the cathode toward the bulk

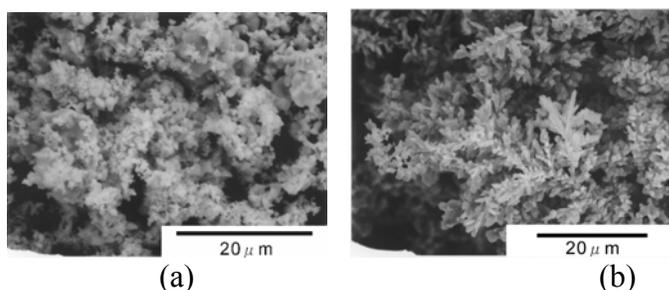


Figure 5. SEM images of (a) the powder at the bottom of the crucible and (b) the powder adhered to the cathode.

seems slow. More probably this is because Ca was consumed by the back-reaction, where the Cl_2 gas evolved at the anode reacts with Ca near the cathode as reported (6).

Conclusion

A new approach was proposed to produce metallic Ti continuously by the calciothermic reduction using the dissolved calcium, Ca , and the gaseous TiCl_4 . For the fundamental confirmation of this proposal, metallic Ca grains were dissolved in molten CaCl_2 in advance, and the TiCl_4 gas was blown onto the free surface of the molten CaCl_2 . α -Ti powder and its sinter were recovered when the Ca concentration was above 2 mol%. The lower oxides of titanium were obtained in addition to α -Ti when the Ca concentration was below 2 mol%.

In the combined molten salt electrolysis of CaCl_2 , α -Ti was formed as the powder at the bottom of the MgO crucible, when $N_{\text{Ca}}/N_{\text{TiCl}_4} > 2$ and $X_{\text{Ca}} > 2$ mol%. A faint amount of oxygen polluted Ti(II) and/or Ti(III) to form the lower oxides.

Acknowledgments

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