Reduction of CaTiO_3 by Electrolysis in the Molten Salt $\text{CaCl}_2\text{-CaO}$

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ABSTRACT

The reduction of CaTiO_3 to generate Ti powder with a low content of oxygen was examined by electrolysis in a $\text{CaCl}_2\text{-CaO}$ melt. Using various sizes of the raw oxide particles, the concentration profile of the residual oxygen in the cathode basket suggests a reduction mechanism involving calcium from the melt. The residual oxygen content was influenced by the dehydration method. Vacuum dehydration above the melting temperature and decomposition of CaCl_2 hydrates below 550 K were required to eliminate water. Optimization of both water removal and the oxide particle size produced the lowest oxygen content (0.42 mass%O) in the powder.

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1. Introduction

Currently, the Kroll process is the primary industrial method to produce titanium metal.¹ As new energy-efficient refining methodologies have been explored, various attempts have examined the use of molten salts for this purpose.^{2–22} Notably, a calciothermic reduction of oxides in molten CaCl_2 , called the “OS process”, has been developed.^{6–11} The left side of Fig. 1 shows a flow sheet for the conventional Kroll process compared with that proposed herein, which is a modified version of the original OS process.^{16,17}

Magnesium is used as the reductant in the Kroll process,¹ and its by-product, MgCl_2 , is circulated by electrolysis to give liquid Mg and gaseous Cl_2 . Thus, the Kroll process consists of many synchronized processes. In contrast, the OS process uses Ca generated from the electrolysis as the reductant.^{6–11} That is, the CaO by-product is decomposed electrochemically in the same furnace as electrolysis to give Ca as the reductant. Accordingly, this strategy is expected to simplify the processes separated in the Kroll process and thus reduce the amount of consumed energy. The Kroll process produces metallic Ti sponge a few millimeters in particle size, which is subsequently melted and cast into ingots for further fabrication. The OS process forms a fine powder composed of coral-like particles a few tens of micrometers in size. This process is

favorable for the production of metallic powder and is expected to facilitate the preparation fine powders suitable for 3-dimensional printers.

Although TiO_2 is used as the raw material to refine Ti, ilmenite (mainly TiFeO_3) is used as the starting ore because of the relative scarcity of high-purity TiO_2 ores. The Kroll process uses the “up-graded” TiO_2 produced from ilmenite; likewise, the OS process requires high-quality TiO_2 . When the same treatments applied to the Kroll process were applied to the OS process, however, a small amount of iron in low-quality TiO_2 (before the chlorination step) can contaminate the metallic Ti product, making it brittle. This is because the OS process can reduce iron oxide to Fe as strongly as it can reduce TiO_2 . Therefore, complete removal of Fe from the starting oxide is needed to apply the OS process successfully. Some methods have already been developed to separate Fe from ilmenite,^{19–22} including the proposal that CaTiO_3 can be used as an alternative material for Ti production.^{16–18}

By modifying the OS process to include molten $\text{CaCl}_2\text{-CaO}$, as shown in the right-hand side of Fig. 1, this study examined the reductive preparation of Ti metal starting from CaTiO_3 rather than TiO_2 . Some attempts based on this concept have been partly reported.^{16–18} However, the residual oxygen level in the obtained Ti particles was so high that additional efforts were required.

2. Electrochemical Reduction of CaTiO_3 in the $\text{CaCl}_2\text{-CaO}$ Melt

The relevant reactions of the OS process have been reported previously.^{6–11} Briefly, solid CaO can dissolve ~20 mol% in a CaCl_2 melt^{23–25} and electrochemically decompose into Ca^{2+} and O^{2-} ions, as shown in Eq. (1). Ca^{2+} then receives two electrons to form metallic Ca and to dissolve as Ca in the melt near the cathode, as shown in Eq. (2). This precipitated Ca reduces CaTiO_3 to metallic Ti and simultaneously forms CaO (Eq. (3)). The formed CaO then decomposes as in Eq. (1), thereby perpetuating the reduction process. Notably, there is no need to supply a Ca reductant or source (such as CaO) once electrolysis begins. Note, however, that the generated O^{2-} emits an electron at the anode to form oxygen gas, as shown in Eq. (4). When carbon is used as the anode, which is stable in molten salts, the generated oxygen reacts with it to form CO or CO_2 gas, as shown in Eqs. (5) or (6), respectively.

Figure 1. Flowsheet of Kroll process and OS process.

As extensively reported,^{2–11,26,27} CaTi_2O_4 and CaTiO_3 are often found as intermediate phases during the reduction of TiO_2 to $\beta\text{-Ti}$ via $\alpha\text{-Ti}$. These intermediate phases delay the reduction process when TiO_2 is used as the starting material.^{3–5,15,26,27} This work will clarify this issue further by using CaTiO_3 as the starting material. In this case, a larger amount of CaO , produced from the starting oxide, is supplied to the melt. It is expected that a faster and more effective reduction will be realized on account of a high concentration of Ca viz. CaO . By using CaTiO_3 , this work seeks to obtain highly purified titanium metal with a relatively low content of oxygen. Our previous work¹⁷ reported the beneficial effects of removing water and the oxide particle size to the residual oxygen content in metallic titanium. Herein, these influences are examined more fully.

3. Experimental Procedures

Figure 2 illustrates the experimental apparatus used to generate metallic Ti from CaTiO_3 using electrolysis in a $\text{CaCl}_2\text{-CaO}$ melt. The stainless steel lid at the upper part of the vessel is equipped with the anode, cathode, and an argon gas inlet pipe, which can move vertically. The anode and cathode were immersed into the melt for the electrolysis and then pulled up after the reaction. The sample basket at the lower part of the cathode was pulled up and rapidly cooled inside a water-cooled pipe. The terminal end of the argon gas inlet pipe was placed 20 mm over the melt surface. The Ar gas was flowed at a rate of 350 mL/min to quickly eliminate the gases (i.e., CO and CO_2) generated at the anode.

A carbon bar of 10 mm in diameter was used as the anode. A cylindrical, metallic net basket consisting of Ti or stainless steel SUS316L was used as the cathode, where a certain mass of raw CaTiO_3 powder was filled. Approximately 600 g of anhydrous CaCl_2 lumps were filled in a dense Al_2O_3 or MgO crucible (90 mm ID, 100 mm OD, and 200 mm high). The stainless steel vessel was evacuated by a rotary pump and heated to dehydrate the system. After water electrolysis, constant voltage electrolysis of 3.0 V was conducted in Ar gas at atmospheric pressure at 1173 K. The rapidly cooled basket was removed from the vessel, and the sample was

sequentially washed with distilled water, a dilute acetic acid aqueous solution, ethanol, and acetone. The sample was then dried and kept in vacuum.

The surface of the obtained powder was observed by scanning electron microscopy (SEM, Hitachi TM-1000, Tokyo, Japan) and a LECO TC-600 analyzer (Michigan, USA) was used to measure the residual oxygen content. The crystalline phases were identified by X-ray diffraction measurements (XRD, Philips X'Pert Pro, Amsterdam, Netherlands). The raw material of the CaTiO_3 powder was commercially purchased; the #A, #K, #S, and #F powders were obtained from Alfa Aesar (Ward Hill, Massachusetts, United States), Kojundo Chemical Lab. (Saitama, Japan), Soekawa Chemicals (Tokyo, Japan), and Furuuchi Chemical (Tokyo, Japan), respectively. A Microtrac MT3000II instrument (Tokyo, Japan) was used to measure the size distribution of the oxide powders.

The Ar gas used for electrolysis was chosen from either a high-purity Ar source (>99.999%, <1.0 ppm oxygen) or an extra high-purity Ar source (>99.9995%, <0.2 ppm oxygen). These gases are designated as Pure-Ar and Ex-Ar, respectively.

The supplied electric charge Q was normalized by Q_0 , which is the theoretical charge necessary for full reduction of a filled amount of CaTiO_3 . The results are shown as the ratio Q/Q_0 in %.

4. Results and Discussion

4.1 Dehydrolysis

4.1.1 Vacuum heating

To eliminate water from the charged CaCl_2 prior to CaTiO_3 electrolysis, the vessel was evacuated by a rotary pump and heated continuously. A Pirani gauge, which was set between the pump and the vessel, was used to monitor the pressure. Figure 3 shows the pressure change inside the vessel during heating.

A pressure increase was observed at three stages as the system was heated, classified as regions I, II and III. Region I occurs from ~ 330 K to 550 K, and regions II and III occur at ~ 900 K and 1050 K, respectively. It is noted that the melting temperatures of CaCl_2 hydrated with 6, 4, 2, and 1 crystalline water molecules are in the range of 302–473 K.²⁸ It is reasonable that the pressure increase in region I is caused by water removal from its adhesion to CaCl_2 and from the decomposition of hydrated CaCl_2 . The reasons for the pressure increases in regions II and III are not presently known.

To completely remove the water, this apparatus required a temperature as high as 1050 K, which is very close to the melting temperature of anhydrous CaCl_2 (1045 K). As shown in Fig. 3, sample (b), which was dried at 573 K in air for 230.4 ks, showed a lower pressure in the entire temperature range than the as-received

Figure 2. Experimental setup.

Figure 3. Pressure change during vacuum dehydration. Heating rate is 1/60 K/s. 600 g CaCl_2 was filled in the crucible. (a) Not pre-heated, and (b) pre-heated at 573 K for 230.4 ks in air.

Figure 4. Current and pressure during water electrolysis at 1173 K, where no CaO was mixed in CaCl_2 . Water electrolysis voltage = 2 V.

Table 1. Residual oxygen content in the samples obtained after the electrolysis using 0.1 mol% CaO. 2 g of CaTiO_3 (#A) was used. $Q/Q_0 = 200\%$.

Run No.	Dehydration temp. (K)	Dehydration time (ks)	Water electrolysis	Oxygen content (mass%)
A-1	873	19.8	none	5.62
A-2		45.9		1.80
A-3		83.1		1.61
A-4		259.9		1.92
B-1	1173	31.9	applied	1.48
B-2		23.5		1.77

sample (a). Clearly, heating above the hydrate melting temperature is required to dehydrate CaCl_2 fully.

4.1.2 Water electrolysis in vacuum

In addition to vacuum heating, water electrolysis at 1173 K in vacuum was applied to eliminate water from the molten salt. Carbon bars of 10 mm in diameter were used as both the anode and cathode, with 2.0 V applied between them. Figure 4 shows the current and pressure changes during this electrolysis. As seen, a large current flow occurred immediately after electrolysis commenced and soon dropped to a constant value. Likewise, the pressure was low initially but returned to the original pressure over time; it then remained constant during the water electrolysis process. The pressure change during electrolysis is caused by H_2 and O_2 gas evolution. Note, however, that the removal of water may still be insufficient with this process, even after electrolysis for 3.6 ks.

As reported previously,¹⁷ the residual oxygen in the obtained titanium powder was affected by not only the initial concentration of CaO in the melt but also by the dehydration process. The dehydration temperature and vacuum residence time were varied to obtain a Ti powder with a low content of oxygen. Table 1 lists the results of dehydration using an electrolyte bath containing 0.1 mol% of CaO. Starting from CaTiO_3 , the samples were electrochemically reduced and their oxygen concentrations were analyzed. Approximately 6 mass%O was detected in the sample dehydrated in vacuum at 873 K for 20 ks, whereas just 1.5 mass%O was obtained when it was dehydrated in vacuum at 1173 K for 30 ks followed by water electrolysis.

4.2 Sample morphology

Figure 5 shows the (a) basket before electrolysis, and (b) sample in the basket after electrolysis with $Q/Q_0 = 200\%$. As seen, the

Figure 5. View of stainless steel basket (15 mm in diameter) after the electrolysis of $Q/Q_0 = 200\%$ using 0.5 mol% CaO - CaCl_2 in Pure-Ar. (a) before electrolysis, and (b) after electrolysis, where the basket was opened, and the solidified salt remained at the lower part even after leaching.

Figure 6. SEM images at each part as indicated in Fig. 5(b). The supplied charge $Q/Q_0 = 200\%$.

sample appeared as stacks of several layers. The layers were separately recovered and classified as upper, lower, inner, and outer and then observed with SEM (Fig. 6). Additionally, their oxygen content and phases were characterized, as listed in Table 2. A granular structure was often observed in the lower layer, whereas a sponge structure grew in the upper part of the basket. The oxygen level in the upper part was ~ 2 mass% lower than that in the lower part. Likewise, the oxygen content in the outer layer was slightly smaller than that in the inner layer; but no significant difference could be discerned in their corresponding SEM images. The identified phases in these layers corresponded well with their oxygen content; the volume fraction of lower oxides was found to increase in layers with lower oxygen contents. It should be noted that lower oxides such as Ti_6O are not generated at the temperature of electrolysis but are formed during the subsequent cooling process. According to the phase diagram of the Ti-O binary system,²⁹ only α -Ti or β -Ti phases are present at a dilute oxygen concentrations at 1173 K.

The distribution of the oxygen content in the basket reflects the upward motion of the calcium reductant, as reported previously.¹⁷ The densities of Ca and CaCl_2 are 1.36 Mg/m^3 and 2.0 Mg/m^3 , respectively.³⁰ The lighter Ca that was formed on the cathode and dissolved into the CaCl_2 melt floats upward, and the stream of Ca-rich material flows along the basket wall. The reductant Ca in this stream continues to reduce the raw oxide in the cathodic basket. Additionally, as shown in Eqs. (1)–(3), a larger amount (1.5 $\times$) of

Table 2. Oxygen contents and phases identified by XRD at each part in Fig. 5(b).

Area		Outer layer	Inner layer
Upper part	Oxygen	6.9 mass%	7.4 mass%
	Phase (XRD)	Ti ₆ O = 7%	Ti = 31%
		Ti ₃ O = 87%	Ti ₃ O = 40%
		TiO = 4%	Ti ₂ O = 27%
		TiC = 2%	TiC = 2%
Lower part	Oxygen	9.6 mass%	9.8 mass%
	Phase (XRD)	Ti ₆ O = 2%	Ti = 1%
		Ti ₃ O = 65%	Ti ₆ O = 30%
		Ti ₂ O = 33%	Ti ₃ O = 37%
			Ti ₂ O = 32%

Figure 7. View of Ti basket (12 mm in diameter) after electrolysis of $Q/Q_0 = 570\%$ in Ex-Ar. 1.7 g $\text{CaTiO}_3(\text{\#F})$ was reduced without CaO addition in CaCl_2 melt. (a) after salt removal, (b) after opening the basket (a).

Ca is formed and recycled than the amount of Ca consumed by reduction. Therefore, the Ca content in the upper part of the basket becomes higher and reduction occurs preferentially in this region. This relationship may explain why the top part of the basket contained the lowest oxygen content.

Figure 7 shows the morphology of the sample and the basket, where a larger electric charge was provided ($Q/Q_0 = 570\%$). As seen, this morphology differs considerably from that shown in Fig. 5(b). Figure 7(a) shows that the basket net peeled, exposing its inner layer. Figure 8 shows that the rind was partially removed, revealing its porous structure. The sample shown in Fig. 7(b) was leached by water, but the sample was not homogeneous; it consisted of an outer layer with a metallic raster and a porous sponge-like structure. The outer layer adhered to the inner surface of the basket net, as shown in Fig. 7(b); its oxygen content was as low as 0.25 mass%, which is very low and suitable for industrial materials. In contrast, the sponge structure located at the inner part close to the electrode rod, whose microstructure is shown in Fig. 9, has an oxygen content that is 0.96 mass% higher than that in the layered structure.

Figure 8. Leached sample recovered as shown in Fig. 7. **Figure 9.** SEM image of the sponge-like powder shown in Fig. 8. **Figure 10.** Oxide particle size dependency of residual oxygen in the samples after the electrolysis of $Q/Q_0 = 200\%$ and 600% .

4.3 Effects of oxide particle size

Figures 10 and 11 shows the oxygen content in the samples following reduction at supplied charges of $Q/Q_0 = 200\%$ and 600% using oxide powders with various size distributions. As seen, the residual oxygen content of the sample reduced at $Q/Q_0 = 200\%$ decreased when smaller particles were used, and it decreased at $Q/Q_0 = 600\%$ when larger particles were reduced. Although the experimental conditions such as the charged amount of initial oxide and the distance of electrodes were set as the same, the current were

Figure 11. Electrolysis time dependency of residual oxygen in the samples after the electrolysis of (a) $Q/Q_0 = 200\%$ and (b) 600% . Error bars show $\pm 2\sigma$ (σ : standard deviation). The errors in (b) were smaller than the plot size.

varied a little and the electrolysis time was varied to achieve a constant Q/Q_0 . As shown in Fig. 11, the residual oxygen in the obtained powder were nearly independent of time.

Figure 12 shows SEM images of the starting samples #A and #F and their reduced states. Note that the particle size of #A is very fine, whereas that of #F is coarser. The morphology of the reduced samples is granular at $Q/Q_0 = 200\%$, and their structures grew as sponge-like particles at $Q/Q_0 = 600\%$. Particle sintering resulted in slight coarsening of the samples. These morphologies correspond well to the oxygen levels in the samples; good values below 1 mass%O were analyzed at $Q/Q_0 = 600\%$, whereas ~ 7 mass%O were observed at $Q/Q_0 = 200\%$.

Because the reductant Ca precipitates on the cathodic surface and dissolves into the melt, it exists near the cathodic basket. Reduction of the raw material begins at the basket surface, and the particles near its inner surface will be strongly reduced in the early stages of electrolysis. Because finer particle sizes offer the largest surface area per unit mass, the finer oxide powder is more easily reduced. Therefore, in the early stage of electrolysis, in which a small amount of electric charge is supplied and the reduction and deoxidation have scarcely progressed, the oxygen content of the finer powder is relatively low, such as that at $Q/Q_0 = 200\%$.

However, with more electric charge (e.g., $Q/Q_0 = 600\%$), the oxygen content decreased to less than 1.0 mass%O as the reduction and deoxidation progressed. The morphology of the layered structure shown in Figs. 7–9 became characteristic; the layered

Figure 12. SEM images of the raw materials and the reduced samples at $Q/Q_0 = 200\%$ and 600% . Their oxygen contents were showed in Fig. 10.

Figure 13. Illustration of oxygen removal when two kinds of initial powder were applied.

structure formed close to the basket surface and the sponge-like structure was generated in the inner regions. Overall, these findings suggest the reduction mechanism shown in Fig. 13. That is, relatively fine starting powders cause the reduction to proceed more quickly in the early reduction stage (i.e., small Q/Q_0), with the reduced Ti particles adhering to the basket inner surface as a layer-like structure. This metallic film disturbs the spatial exchange of Ca and O^{2-} in the melt, thus delaying the reduction within the region inside this layer. In contrast, when the starting particles are relatively large, reduction is initially delayed compared with the finer particles, and more time is required to form the Ti film in the area close to the basket net. However, due to slow film formation, the interspace among the oxide particles can persist for longer time, thereby facilitating the exchange of Ca and O^{2-} . Overall, this mild coarsening of the outer layer promotes reduction and deoxidation of residual oxygen in the lower parts of the basket.

5. Conclusions

The electro-reduction of CaTiO₃ in a CaCl₂ melt was examined to prepare good-quality metallic titanium powder with a very low content of oxygen. In particular, the effects of water removal from the starting CaCl₂ reagent and the oxide particle size were experimentally studied.

The pressure inside the vessel was examined during evacuation and heating. Pressure fluctuations were observed at ~ 900 K and near the melting point of anhydrous CaCl_2 (1045 K). Although these changes were not fully investigated, the cause of these fluctuations appears to be gas evolution resulting from water adhered to the strongly hygroscopic CaCl_2 reagent and thermal decomposition of hydrate impurities. For effective water removal by evacuation, it was necessary to use temperatures higher than those leading to gas evolution.

Additionally, the particle size of the raw oxides was found to influence the residual oxygen content in the reduced samples. When the electric charge was insufficient, such as $Q/Q_0 = 200\%$, the oxygen content decreased as the particle size decreased. In contrast, the sample oxygen content decreased at $Q/Q_0 = 600\%$ as the particle size increased. This is because of a dense Ti film formed at the basket inner surface. In addition, since the formation rate of layered Ti is slower when relatively large raw oxide particles were used as the starting materials, the particles did not sinter well and a wider interspace occurred among them. Further, the exchange of Ca and O^{2-} in the melt was not greatly affected by the large particle size, and the inner part of the basket was reduced rather well. The resultant oxygen content of the sample decreased to 2500 ppm, which matches the Japanese Industrial Standard.

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