

Production of titanium powder directly from TiO_2 in CaCl_2 through an electronically mediated reaction (EMR)

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Abstract

Production of titanium powder directly from titanium dioxide (TiO_2) through an electronically mediated reaction (EMR) using calcium as a reductant was investigated. Feed material (TiO_2 powder or preform) and reductant (Ca–Ni alloy) were charged in electronically isolated locations in a molten calcium chloride (CaCl_2) salt at 1173 K, and the current flow through an external circuit between the feed and reductant locations was monitored during reduction of TiO_2 . The voltage between feed electrode and reductant alloy was intermittently measured during the reduction experiment to monitor the reduction process. After the reduction experiment, pure titanium powder with low nickel content was obtained even though liquid Ca–Ni alloy was used as a reductant. These results demonstrate that titanium metal powder can be produced without direct physical contact between the feed and reductant. In some experimental conditions, pure titanium powder with 99.5 mass% purity was successfully obtained.

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1. Introduction

At present, titanium is industrially manufactured by the Kroll process [1], which is based on the magnesiothermic reduction of titanium chloride. Although the Kroll process is suitable for producing high-purity titanium, it is a labor-intensive, batch-type process with low productivity. Even when large-scale modern facilities are used [2], it takes over 10 days to produce 10 tons of sponge titanium. With this background, a new efficient reduction process that can serve as an alternative to the Kroll process is being investigated by

many researchers. Although various types of titanium reduction processes were studied in the past, none of them could be used for industrial purposes. The key factors in developing a commercial process, which can compete with the Kroll process, are the establishment of technology for effective purity control and/or speeding up the reduction process.

Fray et al. have recently been trying to develop a new industrial reduction process, called the FFC Cambridge process, based on the direct electrochemical reduction of TiO_2 to metallic titanium in molten CaCl_2 salt [3]. Their extensive work has not only inspired academic research activity on titanium but has also stimulated the related industries. As a result, a large variety of titanium reduction processes are currently under investigation [4–6]. For example, Ono and Suzuki are engaged in developing a commercial process, based on the calciothermic reduction of TiO_2 powder in molten CaCl_2 salt during electrolysis [4].

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In this study, we carried out fundamental research on a new titanium reduction process with the purpose of developing new technology for preventing the accumulation of impurities in titanium deposits using an electronically mediated reaction (EMR) [7,8]. The EMR is not only effective in maintaining purity control but is also suitable for improving energy efficiency when it is combined with the conventional molten salt electrolysis (MSE) of CaO in molten CaCl_2 salt, for producing reductant calcium alloy. One of the features of the EMR/MSE process is that the reduction of TiO_2 takes place without any direct contact with the reductant alloy because titanium is reduced by electrons released from the reductant. By using the EMR/MSE process, the reduction of TiO_2 and the electric power input for producing reductant alloy can be carried out separately. This makes it possible to carry out titanium reduction during the day and electrolysis for producing reductant alloy during the night. The possibility of applying this EMR/MSE process for the reduction of TiO_2 was investigated in this study.

2. Experiment

Experimental conditions of reductions are shown in Table 1, and a schematic diagram of the reduction apparatus is shown in Fig. 1. Anhydrous CaCl_2 was used as the molten salt medium, which was dried in a vacuum at 473 K for over 12 h before the experiment. TiO_2 powder or a preform containing TiO_2 powder (5–8 g) was kept in a sample holder and charged in molten CaCl_2 salt (1300–1500 g) at 1173 K in an argon atmosphere. The holder containing the TiO_2 powder was placed in the molten salt to prevent it from making physical contact with the Ca–18 mass% Ni reductant alloy (50–90 g). TiO_2 was thus electrochemically reduced using electrons discharged from the reductant alloy. The current flow ($i_{A/C}$) through an external circuit between TiO_2 and the Ca–Ni alloy was monitored using a standard resistance of 1 m Ω . In order to monitor the driving force of the chemical reaction, the voltage ($\Delta E_{A/C}$) between the feed electrode and reductant alloy was intermittently measured by opening the external circuit during the reduction experiment.

After the reduction experiment, the sample holder was taken out of the reactor, and was soaked in distilled water

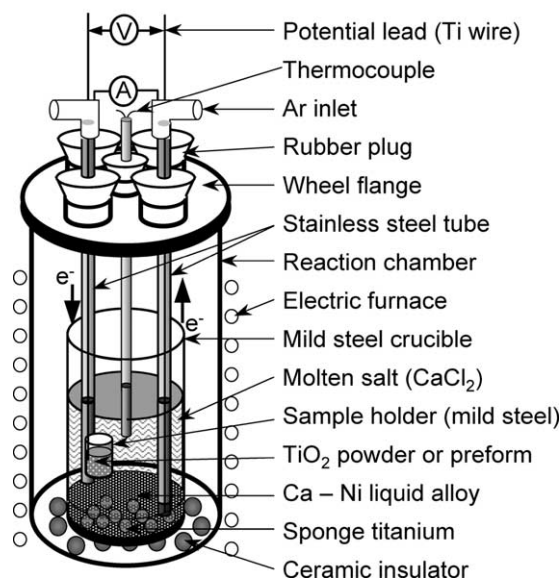
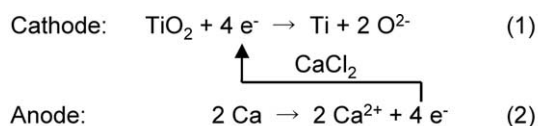


Fig. 1. Schematic illustration of experimental apparatus for TiO_2 reduction through an EMR.

for 24 h to dissolve the CaCl_2 . The titanium powder obtained after the experiment was recovered by leaching it with acetic acid and hydrochloric acid. The metal powder obtained was then rinsed with distilled water, alcohol, and acetone, and finally dried in a vacuum. The morphology of the metal powder was observed by a scanning electron microscopy (SEM). Phases in the sample were identified by an X-ray diffraction analysis (XRD). The composition of the sample was determined using an energy dispersive X-ray spectroscopy (EDS), and an inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The oxygen concentration of the powder deposit was determined by an inert gas fusion-infrared absorption spectroscopy.

3. Results and discussion

As shown in Fig. 2(a), an external current ($i_{A/C}$) of 0.2–0.4 A was observed between the anode and cathode for the first 500 s. Time zero corresponds to the moment when the feed TiO_2 powder in the sample holder (cathode) was charged into the molten CaCl_2 salt. The reductant Ca–Ni alloy (anode) was also charged into the molten salt at the same time. The external current, $i_{A/C}$, decreased to below 0.1 A after 3 ks. When the external current fell below 0.03 A, the sample holder was taken out of the molten CaCl_2 salt. In most cases, the reduction was completed within 7.2 ks (2 h). The value of the electric charge (Q_{exp}) that passed through the external path was calculated by means of time integration of the observed external current, and it was

Table 1
Experimental conditions in this study

Exp. no.	Exp. temp. (T/K)	Mass of sample (w/g)			Form of feed
		CaCl_2 molten salt	Ca–Ni alloy	Feed material	
C1	1173	1300	80	5.02	preform
C2	1173	1333	72	8.02	powder
C3	1173	1333	86	7.98	powder

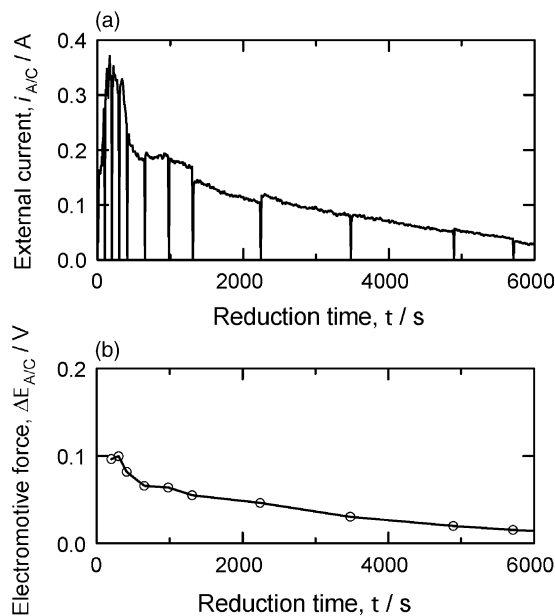


Fig. 2. Variation of the external current and electromotive force. (Exp. no. C1).

about 650 °C for the case shown in Fig. 2(a). It was found that this value was about 3% of the theoretical electric charge (Q_{theo}) necessary for reducing 5 g of TiO_2 as feed material. The percentage of the obtained charge in relation to the theoretical charge, EMR ratio ($X_{\text{EMR}} (= 100 \times Q_{\text{exp}} / Q_{\text{theo}})$), varied between 1–9% depending upon experimental conditions. Fig. 2(b) shows the change in the voltage between the anode and cathode obtained by opening an external circuit intermittently. Until 2 ks after beginning the reduction experiment, the voltage was above 0.05 V, and $\Delta E_{\text{A/C}}$ decreased with time. The theoretical electromotive force of the reaction, ΔE_{theo} , calculated from the standard Gibbs energy change ($\Delta G_r^\circ = -240.6 \text{ kJ [9]}$) in the reaction, $\text{TiO}_2(s) + 2 \text{ Ca}(l) \rightarrow \text{Ti}(s) + 2 \text{ CaO}(s)$, was 0.62 V at 1173 K. The value of $\Delta E_{\text{A/C}}$ observed during the reduction experiment was substantially smaller than that of ΔE_{theo} . The reasons for the values of EMR ratio and $\Delta E_{\text{A/C}}$ are smaller than the theoretical values were not clear at this stage, but it is possible that the dissolution of calcium in the molten CaCl_2 salt caused an electric conduction through the CaCl_2 . Fig. 3(a) and (b) show the SEM image and XRD pattern of the obtained titanium powder, respectively. It was found that pure titanium powder was produced in the sample holder after the reduction experiment. The analytical results of the obtained titanium powder and EMR ratio are listed in Table 2. Titanium with high purity of 99.5% or more was obtained using an EMR. In a certain experimental condition, titanium powder with 3500 mass ppm of oxygen was successfully obtained. This result clearly shows that the feed material (TiO_2) was reduced without any physical contact with the reductant (Ca–Ni alloy). It is worth noting that the nickel content in the titanium was quite low at just 0.2 mass%, even though a Ca–Ni alloy was used as the

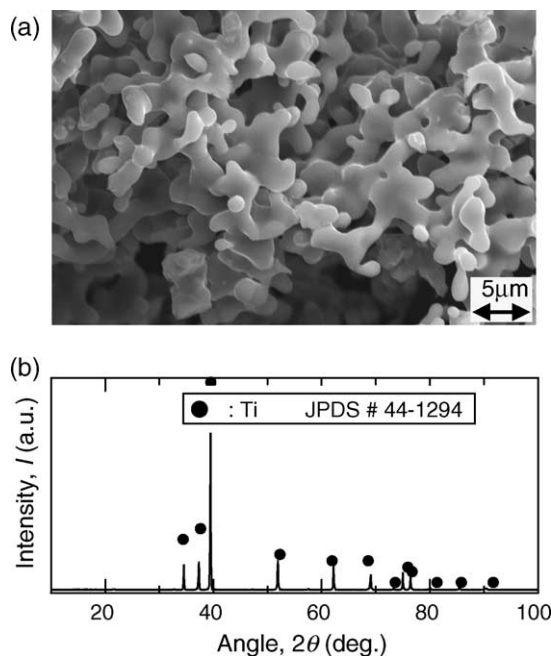


Fig. 3. Titanium powder obtained after reduction. (a) SEM image. (Exp. no. C3). (b) X-ray diffraction pattern ($\text{Cu K}\alpha$). (Exp. no. C3).

reductant. The detailed mechanism of TiO_2 reduction in molten CaCl_2 using an EMR is currently under investigation.

To understand the local reaction, a three-dimensional (3D) chemical potential diagram of the Ti–Ca–O system at 1173 K was constructed, and is shown in Fig. 4(a) [9,10]. As the Ca–Ni alloy was used in the reduction experiment, the activity of Ca was not unity in theory, therefore, the stability plane of Ca (l) in Fig. 4(a) shifts to lower activity region. But this shift can be neglected considering the scale of the diagram. The diagram provides an insight into the phase relationship during the EMR. Point ‘α’ and ‘β’ in Fig. 4(a), corresponding to Ti/Ca/CaO and Ti/TiO/CaO equilibrium can be connected through the metal/molten salt interface

Table 2

Analytical results of the titanium powder obtained using an EMR and EMR ratio at 1173 K

Exp. no.	Composition, C_i^a (mass%)						EMR ratio, X_{EMR}^b (%)
	Ti	Ca	Fe	Ni	Cl	O	
C1	95.6	4.16	0.05	0.16	0.06	(0.00)	2.8
C2	99.9	0.10	0.00	0.00	0.04	(0.00)	3.6
		0.16 ^c	0.27 ^c	0.05 ^c		0.57 ^d	
C3	99.9	0.01	0.00	0.00	0.00	(0.00)	5.1
		0.15 ^c	0.20 ^c	0.04 ^c		0.35 ^d	

^a Determined by EDS analysis. Values in parenthesis are listed for reference.

^b $X_{\text{EMR}} = 100 \times Q_{\text{exp}} / Q_{\text{theo}}$, where Q_{exp} is amount of electric charge passed through external circuit, and Q_{theo} is the theoretical electric charge necessary for reducing TiO_2 .

^c Determined by ICP-AES analysis.

^d Determined by inert gas fusion-infrared absorption spectroscopy analysis.

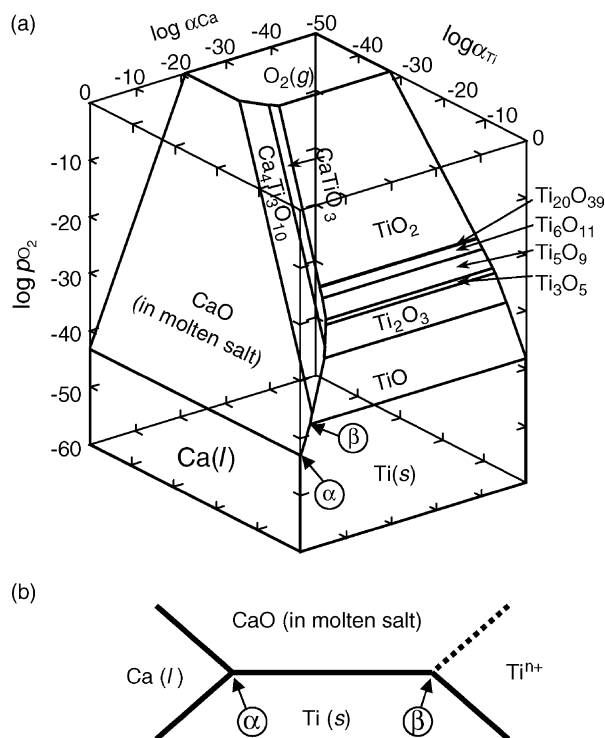


Fig. 4. (a) Three-dimensional chemical potential diagram of the Ti–Ca–O system at 1173 K. (b) Depiction of the reaction pathway consistent with the chemical potential diagram.

(solid two-phase equilibrium shown by the line between point α and β). Fig. 4(b) is a schematic representation of the EMR pathway, consistent with the chemical potential diagram. The metal/molten salt interface, which corresponds to the line connecting points α and β in Fig. 4(a), connects the two three-phase fields. In this situation, the reductant calcium need not necessarily make physical contact with the titanium oxides; rather electron and ion transfer can be considered to be the major step especially in the process with molten CaCl_2 .

4. Conclusion

The experimental results for calciothermic reduction of TiO_2 in molten CaCl_2 salt showed that the electronically mediated reaction (EMR) plays an important role in

the reduction process. The reduction of TiO_2 proceeds without direct physical contact with the reductant Ca–Ni alloy, and contamination of titanium can effectively be prevented by utilizing the EMR. This approach may be applied to develop a (semi-)continuous production of titanium powder.

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