Reduction of Titanium Oxide in Molten Salt Medium

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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. The current flow through an external circuit between the feed and reductant locations was monitored during the reduction of TiO_2. The electrochemical potential of the feed electrode was intermittently measured during the reduction experiment to analyze 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 powder can be produced without direct physical contact between the feed and reductant. In certain experimental conditions, pure titanium powder with a purity of 99.5 mass% was successfully obtained.

1   Introduction

A new efficient reduction process that can serve as an alternative to the Kroll process [1] is being investigated by many researchers. Although various types of titanium reduction processes have been 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 of the reduction process.

Fray *et al.* have recently been trying to develop a new industrial reduction process, called the FFC process, based on the direct electrochemical reduction of TiO_2 to metallic titanium in a molten $CaCl_2$ salt [2]. The principle of the FFC process is schematically shown in Fig. 1 (a). The sintered TiO_2 feed electrode (cathode) is immersed in a molten $CaCl_2$ salt, and polarized cathodically to remove oxygen from the feed electrode. Metallic titanium is directly obtained by electrochemical technique. The main chemical reactions are expressed as equations in Fig. 2 (a1) and (a2). It is interesting to note that, according to Eq. (a1), the reduction of titanium oxides proceeds without the precipitation of metallic calcium. The features of the FFC process and other processes are listed in Table 1. This technique is simple and its advantage is that it makes the process semi-continuous. The product titanium, produced by electrolysis, using molten $CaCl_2$ salt as a medium, is deoxided down to 10 mass ppm oxygen levels after reduction of titanium oxides. The FFC process, however, has some disadvantages: impurities, such as carbon and iron, tend to accumulate in the titanium deposits because the feed electrode is

largely electronegative. Since it is difficult to achieve high current efficiency, the energy efficiency of the FFC process will also be a key factor affecting its commercial use. The extensive work conducted by Fray *et al.* has not only inspired academic research activities on titanium but has also stimulated related industries. As a result, a large variety of titanium reduction processes are currently under investigation [3-5]. For example, Ono and Suzuki are engaged in developing a commercial process, based on the calciothermic reduction of TiO_2 powder in a molten $CaCl_2$ salt [3]. The principle of their process, called the OS process, is schematically shown in Fig. 1 (b). The main chemical equations are shown in Eq. 2 (b1)-(b3). In the OS process, reductant calcium is produced by electrolysis, and titanium powder is obtained by metallothermic reduction using the calcium produced electrochemically. Along with the FFC process, it also has some advantages: the process is simple and can be semi-continuous, but it is also sensitive to carbon and iron contamination. Separation of excess calcium from the titanium powder product may also be a key technique for increasing energy efficiency. The excess calcium on the titanium deposit may affect leaching efficiency.

(a) FFC process

(b) OS process

(c) EMR / MSE process (Oxide system)
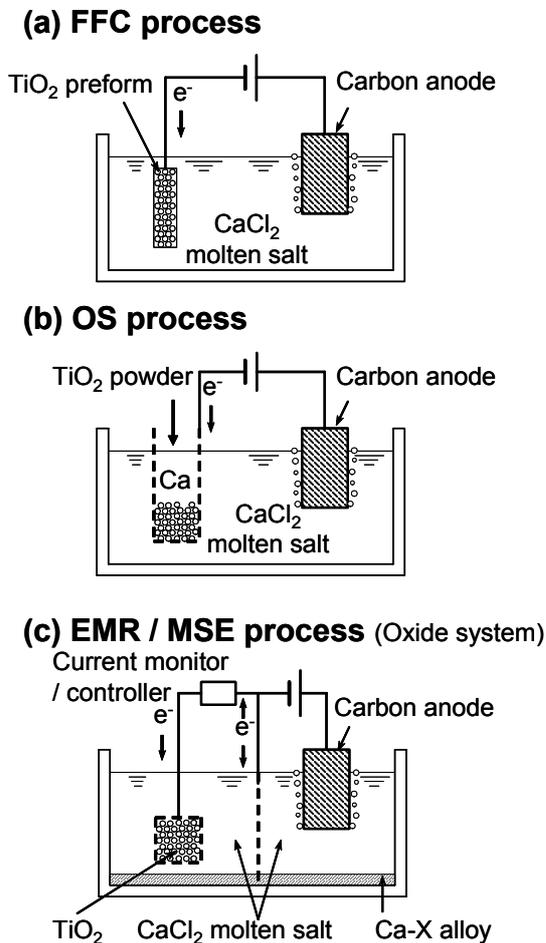
Figure 1: Comparison of various reduction processes of titanium oxide in molten calcium chloride medium.

FFC Process (Fray *et al.*)

Electrolysis

Cathode: $TiO_2 + 4\ e^- \rightarrow Ti + 2\ O^{2-}$ (a1)

Anode: $C + x\ O^{2-} \rightarrow CO_x + 2x\ e^-$ (a2)

OS Process (Ono & Suzuki)

$TiO_2 + 2\ Ca \rightarrow Ti + 2\ O^{2-} + Ca^{2+}$ (b1)

Electrolysis

Cathode: $Ca^{2+} + 2\ e^- \rightarrow Ca$ (b2)

Anode: $C + x\ O^{2-} \rightarrow CO_x + 2x\ e^-$ (b3)
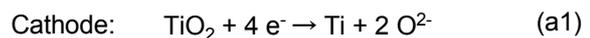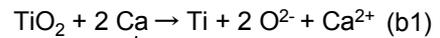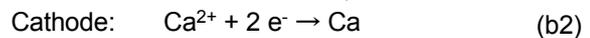
EMR / MSE Process (Okabe *et al.*)

Cathode: $TiO_2 + 4\ e^- \rightarrow Ti + 2\ O^{2-}$ (c1)

Anode: $2\ Ca \rightarrow 2\ Ca^{2+} + 4\ e^-$ (c2)

Electrolysis

Cathode: $Ca^{2+} + 2\ e^- \rightarrow Ca$ (c3)

Anode: $C + x\ O^{2-} \rightarrow CO_x + 2x\ e^-$ (c4)

Over all reaction

$TiO_2 + C \rightarrow Ti + CO_2$ (d)
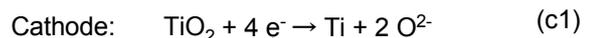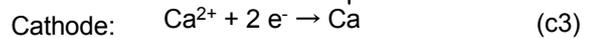
Figure 2: Various types of reactions during the currently investigated direct reduction process of titanium oxides.

In this study, we have carried out fundamental research on a new titanium reduction process with the aim of developing a new technology for preventing the accumulation of impurities in titanium deposits through an electronically mediated reaction (EMR) [6, 7]. The conventional representation of the calciothermic reaction of TiO_2 assumes that the reaction proceeds by the transport of reactants through the product phase. Contact between TiO_2 and calcium is achieved by diffusion of the reactants through the product phase, and therefore the product phases are often considered as barriers in metallothermic reactions. According to the concept of an EMR, a metallothermic reaction can be readily broken into two electrochemical steps as shown in Eq. 2 (c1) and (c2). When an electrically conducting medium exits to facilitate electron transfer and when local electroneutrality conditions are satisfied, reactions can, in principle, proceed at different locations. The feasibility of reducing an insoluble oxide in $CaCl_2$ by the EMR was demonstrated by Okabe *et al.* in 1999, where pure niobium powder was obtained by electrochemical reaction directly from Nb_2O_5 using a calcium alloy as reductant [7]. The EMR is effective in maintaining purity control when combined with the conventional molten salt electrolysis (MSE) of CaO in a molten $CaCl_2$ salt. It is also suitable for improving the energy efficiency in the production of calcium alloy reductant. 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 the electrons discharged from the reductant. By using the EMR/MSE process, the reduction of TiO_2 and the electrical 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. In this study the possibility of applying this EMR/MSE process for the reduction of TiO_2 was investigated.

Table 1. Features of various reduction processes

	Advantages	Disadvantages
Kroll Process	◎ High purity titanium available ◎ Easy metal / salt separation ○ Established chlorine circulation ○ Utilizes efficient Mg electrolysis ○ Reduction and electrolysis operation can be carried out independently	× Complicated process × Slow production speed × Batch type process
FFC Process	◎ Simple process ○ Semi-continuous process	× Difficult metal / salt separation × Reduction and electrolysis have to be carried out simultaneously △ Sensitive to carbon and iron contamination △ Low current efficiency
OS Process	◎ Simple process ○ Semi-continuous process	× Difficult metal / salt separation △ Sensitive to carbon and iron contamination △ Low current efficiency
EMR / MSE Process	◎ Resistant to iron and carbon contamination ○ Semi-continuous process ○ Reduction and electrolysis operation can be carried out independently	× Difficult metal / salt separation when oxide system × Complicated cell structure △ Complicated process

2   Experimental

A schematic diagram of the reduction apparatus is shown in Fig. 3. Anhydrous $CaCl_2$, which

was used as the molten salt medium, was dried in a vacuum at 473 K for over 43 ks before the experiment. TiO_2 powder (99.9%, average particle size 2 μm) was used as the feed material, and in some cases it was made into a preform [8] with the aim of achieving effective salt/metal separation. The feed preform was fabricated from the slurry, which was made by mixing TiO_2 powder (5-10 g) and a binder solution (10-15 g). A collodion solution, which is a mixture of 5 mass% nitrocellulose in ethanol and ether, was used as a binder solution. In some experiments, flux such as $CaCl_2$ was added into the slurry. The synthesized slurry was cast into a stainless steel mold to make the preform. The fabricated preform was heated at 1073 K before reduction in order to remove the binder and water. TiO_2 powder or the preform containing TiO_2 powder (5-10 g) was kept in a sample holder and charged in a molten $CaCl_2$ salt (1300-1500 g) at 1127 K in an argon atmosphere. TiO_2 was electrochemically reduced by the electrons discharged from the reductant alloy. The holder containing the TiO_2 powder or preform was placed in the molten salt to prevent it from making physical contact with the Ca-18 mass% Ni reductant alloy (50-80 g). 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 mΩ. In order to monitor the driving force of the chemical reaction, the electrochemical potential ($\Delta E_{A/C}$) between the feed electrode and the reductant alloy was intermittently measured by opening the external circuit during the reduction experiment.
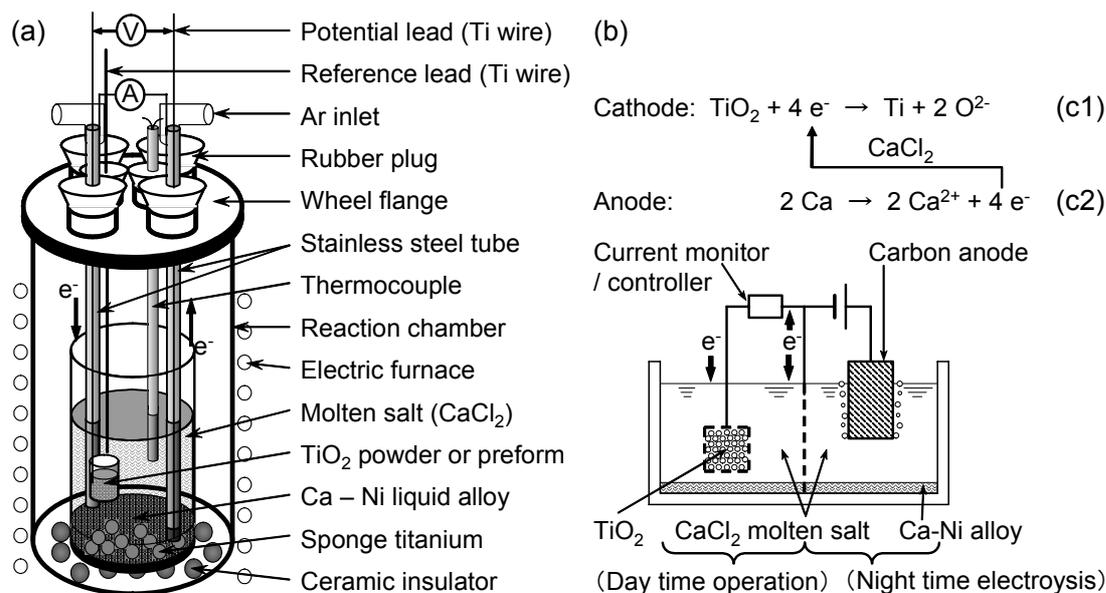
Figure 3: Schematic illustration of experimental apparatus for TiO_2 reduction though an EMR.

After the reduction experiment, the sample holder was taken out of the reactor and soaked in distilled water 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 scanning electron microscopy (SEM). Phases in the sample were identified by an X-ray diffraction analysis (XRD). The composition of the sample was determined by energy dispersive X-ray spectrometer (EDS), and analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The oxygen concentration of the powder deposit was determined by inert gas fusion-infrared absorption spectroscopy (LECO).

3   Results and Discussion

As shown in Fig. 4 (a), an external current ($i_{A/C}$) of 0.2-0.4 A was observed between the anode and the 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 in the molten $CaCl_2$ salt. In the experiment shown in Fig. 4, the reductant Ca-Ni alloy (anode) was also charged in the molten salt at the same time. The external current, $i_{A/C}$, fell 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 and the reduction experiment was terminated. In most cases, the reduction was completed within 2 h. The amount 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 about 650 C for the case shown in Fig. 4 (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, which was used as a feed material. The percentage of the obtained charge with respect to the theoretical charge, X_{EMR} ($= 100 \times Q_{exp.}/Q_{theo.}$), varied 1-9% depending on the experimental conditions. Figure 4 (b) shows the change in the electrochemical potential between the cathode and the anode, which was obtained by opening an external circuit periodically. For the initial 2 ks of the reduction experiment, the electrochemical potential was more than 0.05 V, and the $\Delta E_{A/C}$ decreased with time. The theoretical driving force of the reaction, $\Delta E_{theo.}$, calculated from the standard Gibbs energy change of the reactions shown in Eq. (c1) and (c2) in Fig. 2 (or Fig. 3 (b)) is 0.62 V at 1173 K [9]. The value of the $\Delta E_{A/C}$ observed during the reaction experiment was substantially smaller than that of the $\Delta E_{theo.}$. The reason for this is not clear at this stage, but it is possible that the dissolution of calcium in the $CaCl_2$ molten salt caused electronic conduction through the molten $CaCl_2$ under highly reducing atmosphere.
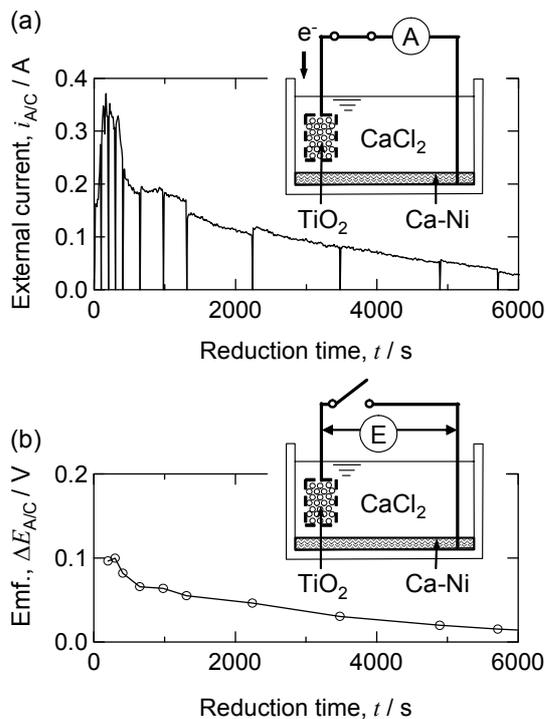
Figure 4: Variation of the external current and electromotive force.

Figs. 5 (a) and (b) show the SEM image and the XRD pattern of the obtained titanium powder, respectively. It was found that after the reduction experiment, pure titanium powder was produced in the sample holder. The analytical results of the obtained titanium powder are listed in Table 2. These results clearly show 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 titanium was quite low, at just 0.2 mass%, even though a Ca-18 mass% Ni alloy was used as the reductant. The detailed mechanism of TiO_2 reduction in molten $CaCl_2$ through an EMR is currently under investigation because there are various interpretations for this reduction mechanism [2][3]. In the experiments investigated in this study, titanium with a high purity of 99.5% or more was obtained by using an EMR. In certain experimental conditions, titanium powder with 3500 ppm of oxygen was successfully obtained.

(a)

(b)
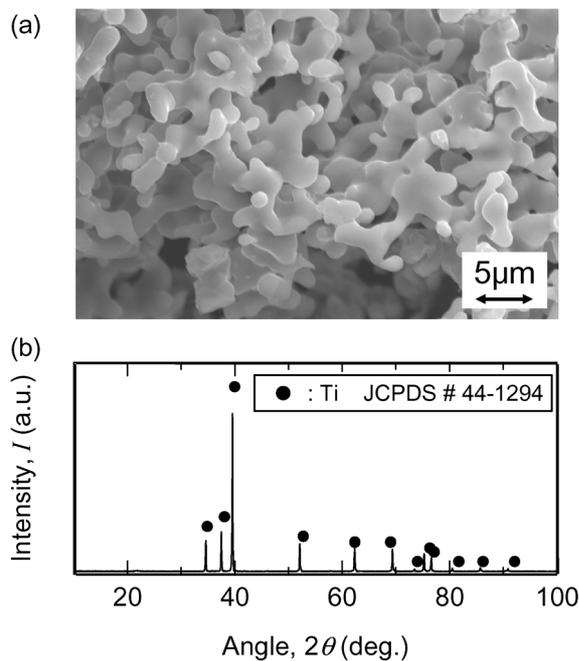
Figure 5: Titanium powder obtained after reduction. (a) SEM image. (b) X-ray diffraction pattern (Cu Kα).

Table 2. Analytical results of the titanium powder obtained using an EMR at 1173 K

Exp. #	Impurity content C_i [a](mass %)						EMR ratio X_{EMR}[b] (%)
	Ti	Ca	Fe	Ni	Cl	O	
B1	99.8	0.13	0.07	0.04	0.00	(0.00)	1.2
		0.23[c]	0.27[c]	0.16[c]			
B2	99.6	0.14	0.04	0.13	0.11	(0.00)	4.1
		0.26[c]	0.11[c]	0.23[c]			
C1	99.9	0.02	0.06	0.02	0.05	(0.00)	6.2
		0.17[c]	0.55[c]	0.11[c]		0.65[d]	
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]: $X_{EMR} = 100 \times Q_{exp.} / Q_{thoe.}$, where $Q_{exp.}$ is amount of electric charge passed through external circuit, and $Q_{thoe.}$ 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 (LECO) analysis.

To understand the local reaction, a three-dimensional (3-D) chemical potential diagram of the Ti-Ca-O system at 1173 K was constructed [9, 10], and is shown in Fig. 6 (a). The diagram provides an insight into the phase relationship during the EMR. Point "α" in Fig. 6 (a), corresponds to the Ti / Ca / CaO (in molten salt) equilibrium and can be connected to point "β", which corresponds to the Ti / TiO / CaO (in molten salt) equilibrium, through the metal/molten salt interface (solid two-phase equilibrium shown by the line between point "α" and "β"). Fig. 6 (b) is a schematic representation of the EMR pathway which is consistent with the chemical potential diagram. The metal/molten salt interface, which corresponds to the line connecting points "α" and "β" in Fig. 6 (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 may be the major steps in this reduction process when molten salt exists in the system.
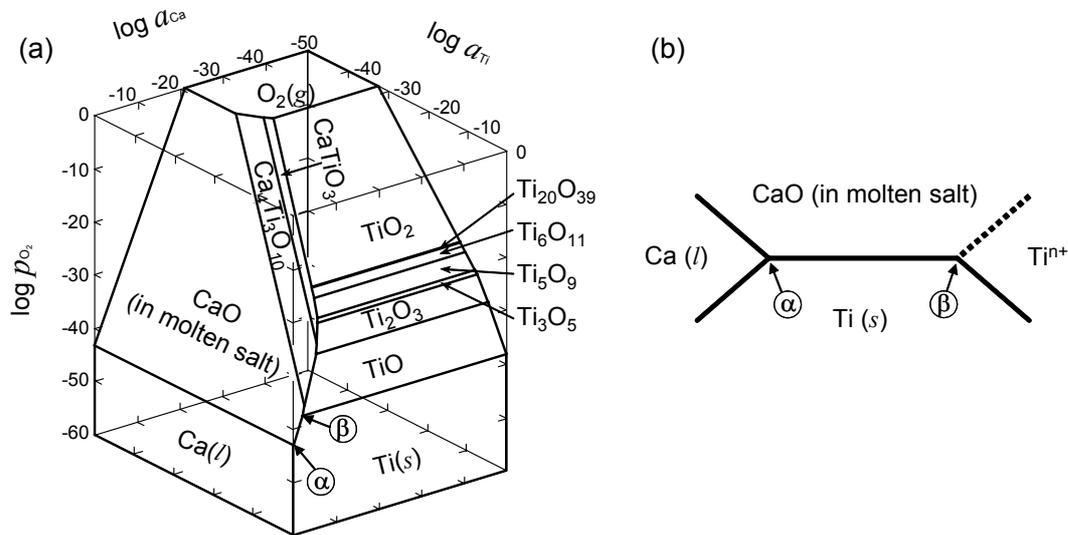
Figure 6: (a) Three-dimensional chemical potential diagram of the Ti-Ca-O system at 1173 K. (b) Depiction of the reaction pathway consistent with the chemical potential diagram.

4 Conclusions and Future Remarks

The experimental results for the calciothermic reduction of TiO_2 in a molten $CaCl_2$ salt showed that the electronically mediated reaction (EMR) can be applied to the direct reduction process of titanium oxide. The reduction of TiO_2 proceeds without direct physical contact with the reductant Ca-Ni alloy, and contamination of titanium can be effectively prevented by utilizing an EMR. This approach may be applied to develop a (semi-)continuous process for the production of titanium powder.

When considering industrial electrolysis, the most compromised issue is the energy efficiency of the electrolysis, and its efficiency in the direct reduction of titanium oxides is low at present. However, the industrial electrolysis process of manufacturing reductants, such as calcium or magnesium, is established and it is possible to produce them with a comparatively high efficiency. Using the process cell of the EMR/MSE process shown in Fig. 3 (b), it is possible to manufacture and stock the reductant by a molten salt electrolysis at night when the

cost of power is low, and the titanium reduction process using labor power can be performed during the day. In this study, the reduction of titanium dioxide as a feed material was investigated. This reduction technique is also suitable for the reduction of halogenides, in which case the application of the EMR/MSE process may extend to recycling of the molten salt or efficient separation of the metal/salt.

5   Acknowledgements

6   References

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