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Direct Metal Production from Oxides by Using Molten Salt Electrolysis of CaO in CaCl₂

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Abstract

Molten salt electrolysis of CaO dissolved in the CaCl₂ melt can generate the reactive Ca atmosphere near the cathode, which has a strong reducing ability equivalent with pure Ca. When the oxide is set inside the basket-type cathode, it is reduced to the corresponding metal. The applied voltage should be controlled between 1.6 and 3.2 V above the melting temperature of CaCl₂ (1053K), when a carbon anode is used. The formed by-product CaO is removed as CO and CO₂ gas at the carbon anode. Within 3 hours we can obtain pure α -Ti from the starting TiO₂ powder in CaCl₂-0.5mol%CaO melt. As increasing the supplied charge, the residual oxygen in Ti decreased.

This simple mechanism has been successfully applied for production of 12 kinds of metals such as Ti, Zr, V, Nb, Cr, Fe, etc. However, the rare earth metals such as Y and Er could not be obtained due to thermodynamic limitation of calciothermic reduction. MgO, In₂O₃ and SnO₂ formed their metallic liquid.

Introduction

So-called valve metals such as Ti, V *etc* are presently produced from the oxide ores. These metals have a strong affinity with oxygen, and the oxygen is removed by forming an intermediate compound such as chloride or fluoride, and secondly by using a strong reductant such as

metallic magnesium. For example, TiO_2 is converted to TiCl_4 , which is later reduced by Mg to form metallic Ti. However, this conventional Kroll method can not produce Ti continuously. Its low productivity becomes the barrier for cost and energy saving. To produce the valve metals in the cheaper cost, we need an alternative refining method. An idea especially for TiO_2 refining, called as "OS process", has been developed by Ono and Suzuki as illustrated in Figure 1(a)[1-9]. The purpose of this work is to show the applicability of OS process to form the metals with a low oxygen concentration directly from the oxides.

OS Process

A brief outline of OS process is reported here [1-9]. When TiO_2 as the typical example of the oxide is selected as the raw material, a direct reduction to the metal is conducted, and simultaneously it is expected that the metallic Ti is deoxidized to the level of 0.3 mass% oxygen, which is required for the ductility. Only Ca can be chosen from the requisites of thermodynamics, the mutual solubility and the compound formation. The reduction and subsequent deoxidation are shown as,

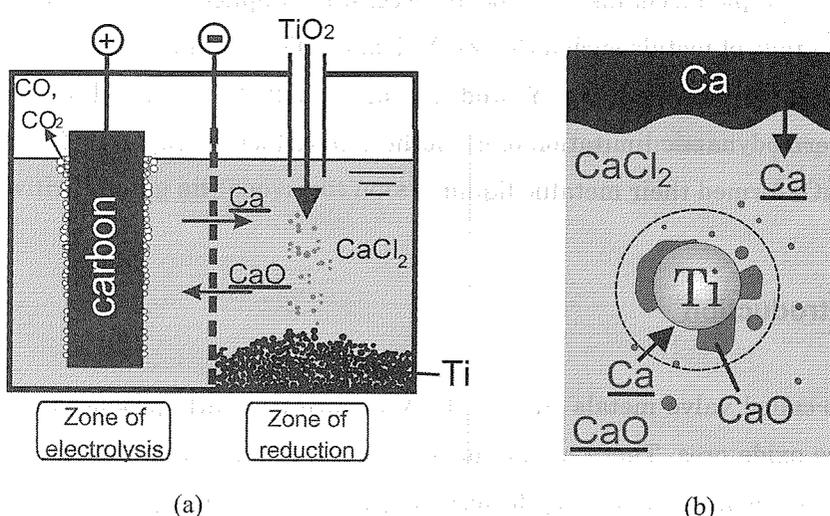
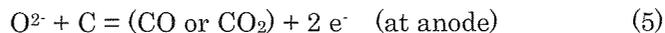


Fig.1 (a) Concept of OS process and (b) removal of CaO into molten CaCl_2 .

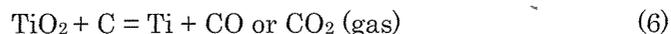


respectively, where Ca, CaO and O(inTi) are metallic Ca and CaO both dissolved in the molten CaCl_2 , and oxygen in Ti, respectively. The fundamentals for reduction and deoxidation in the molten CaCl_2 have been extensively studied for TiO_2 [1-4,6,7,12-14]. The byproduct CaO covers the surface of Ti and suppresses the complete reduction and deoxidation, as shown in Figure 1(b). Because the melt of CaCl_2 can dissolve about 20 mol%CaO above 1100K [10,11], it removes the solid CaO film from the Ti particles to promote the reactions [12-14]. The thermochemical activity of CaO is lowered by dissolution. When pure Ca coexists with CaCl_2 , TiO_2 is successfully reduced to α -Ti with <1000 mass ppm oxygen only for 3.6 ks at 1173K [1].

OS process additionally uses the molten salt electrolysis to recycle CaO into Ca, instead of the Ca supply from the outside of reactor. Because of small solubility of Ca in CaCl_2 (about 4 mol%Ca at 1173 K [15-18]), Ca formed near the cathode holds the high reducing ability during the electrolysis. When TiO_2 powder is exposed to this region, it is reduced to metallic Ti. The electrolysis of CaO is written as,



In total, the thermochemical reaction in the molten CaCl_2 can be expressed as,



Note that this over-all reaction (6) is equivalent with the conventional

process. OS process has several variations in the experimental setups, as shown in Fig. 2, but it is generally characterized by the following three points: (1) Ca is selected as the reductant of the oxide, (2) the byproduct CaO is electrolyzed into Ca in the molten CaCl₂, and (3) all the reactions are operated in the same molten salt. OS process holds the future potential of the simple and continuous operation such that the oxide, carbon and electricity are served for the starting materials and ideally that only the metal is recovered without any exhaust.

Current Density in Reduction of TiO₂

The authors reported that the Ti powder with 0.20 mass%O was successfully produced at 2.6-2.9V for 10.8 ks using 0.5 mol%CaO-CaCl₂ at the setup shown in Fig. 2(a)[2]. However, the detailed conditions to obtain a high purity Ti and the optimum operation parameters were not well studied. Here the current density was mainly studied. The TiO₂ powder was filled in the cylinder made of Ti net, and immersed in the molten salt as the cathode. Here the setups shown in Fig. 2(a) and 2(b) were compared.

As shown in Fig. 3, the oxygen concentration in the recovered samples decreased monotonically as the function of Q/Q_0 . The apparent cathodic current densities were 7.4 and 3.3kA/m² for the setup (a) and (b), respectively. The larger difference in the oxygen content was found at the deoxidation stage from α -Ti solid solution. The higher current density can generate the larger amount of Ca near the cathode, but it dissolves quickly to the bulk of the melt and does not work as the deoxidizing agent for the α -Ti solid solution. The dissolved Ca reacts with CO and CO₂ gas bubbles at the anode, and the black carbon powder was formed at the surface of the melt. These parasite reactions worsen the current efficiency. The higher and lower current densities

are more favorable at the reduction stage and deoxidation stage, respectively. For the more efficient operation, we need the control of current density adjusting the residual oxygen[19,20].

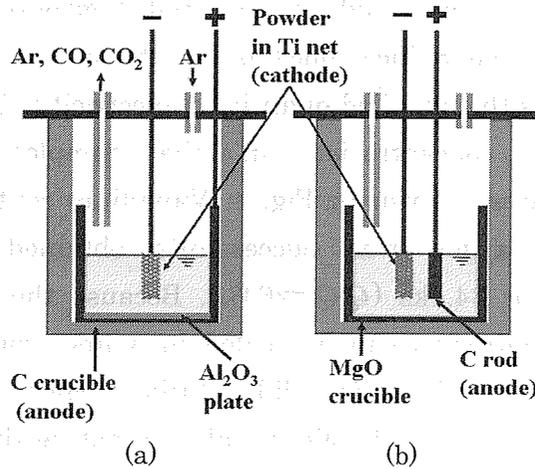


Fig. 2 Experimental setups. (a) a wide anodic area is obtained by carbon crucible, and (b) the closer electrode distance can be set.

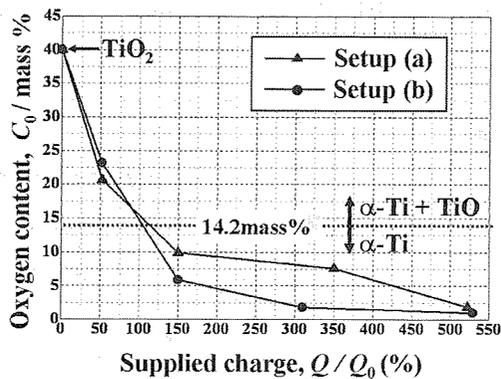


Fig. 3 Oxygen concentration in the samples. The supplied electricity Q is normalized by Q_0 , the theoretical electricity to form the necessary amount of Ca for the reduction. The Ti-O solid solution can be obtained below 14.2% at 1173 K according to the phase diagram[21].

Reduction of Liquid Oxide

The stable oxide, V_2O_5 , melts at 963K, which is below the melting point of $CaCl_2$ (1045 K)[22]. Namely, the oxide is served for OS process as the liquid. At the initial stage of the reduction, liquid sample was reduced once to the intermediate solid phase of CaV_2O_4 . As the supplied quantity of electricity, Q , increased, the oxygen concentration in the samples decreased exponentially, as shown in Fig. 4. Vanadium containing only 1800 ppm oxygen was successfully obtained after the electrolysis for 34.4ks ($Q/Q_0=264\%$). Because the decrease of oxygen concentration can be scaled in a line from the oxide stable region to the V-O solid solution region, the oxygen diffusion in the reduced solid metal may not be the dominant rate-determining step, but the diffusion such as oxygen from the solid particle surface to the $CaCl_2$ melt may play an important role. The surface oxidation of fine metallic particles during handling became critical to achieve the lower oxygen concentration[23,24].

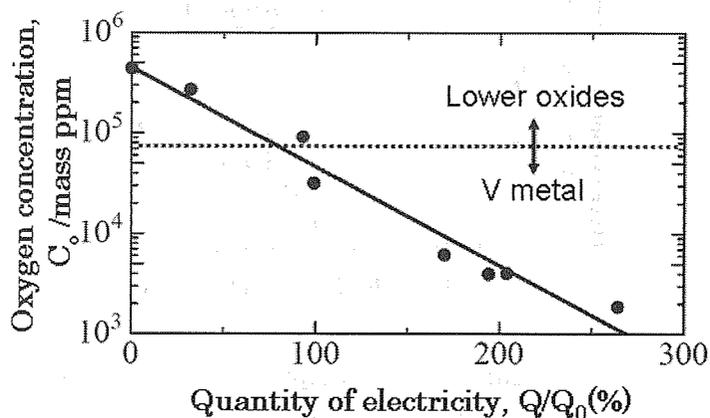


Fig. 4 Oxygen concentration in the obtained samples. The V-O solid solution was obtained below 7 mass% at 1173 K, which corresponded to the phase diagram[21].

Reduction of Other Oxides

1.0 g of 14 kinds of oxide powder (Table 1) was reduced by OS process in the cathode made of stainless steel net. The carbon and Ti crucibles were used for MgO and In_2O_3 , respectively because the melting points of Mg and In are lower than 1173K. Most of the oxides were successfully reduced to their metallic states, although some intermediate phases such as CaTiO_3 and some lower oxides coexisted. The relatively high oxygen concentration was therefore analyzed. They are simply because the electrolysis was conducted only for 1 hour at

Table 1 Experimental conditions and results.

Sample	Time (ks)	Phases identified by XRD	Oxygen concentration (mass%)	Carbon concentration (mass%)
Fe_2O_3	3.6	Fe	2.21	0.275
Cr_2O_3	3.6	Cr	3.73	0.673
CoO	3.6	Co	1.12	0.591
MoO_2	3.6	Mo, Mo_2C	4.94	0.528
Nb_2O_5	3.6	Nb	3.96	0.363
WO_3	3.6	W, $\text{Fe}_3\text{W}_3\text{C}$	1.32	—
NiO	3.6	Ni, $\text{Ca}(\text{OH})_2$	2.80	1.04
TiO_2	3.6	Ti_3O , CaTiO_3	15.7	0.247
ZrO_2	3.6	Zr, Zr_3O , CaZrO_3	16.2	0.0626
MgO	3.6	Mg, MgO	6.60 ?	0.488
In_2O_3	7.2	In, $\text{InTi}_3\text{C}_{0.5}$	4.24	0.617
Bi_2O_3	7.2	Bi, Bi_2O_3	12.4	0.388
Y_2O_3	3.6	Y_2O_3	21.4	0.364
Er_2O_3	3.6	Er_2O_3	10.9	0.103

1173K. As mentioned above, the oxygen concentration would decrease as the longer time was applied.

The carbide formation was due to the cell arrangement that the anode was set close to the cathode. The carbon powder formed from the parasite reaction and reacted with the product. The formation of Ca(OH)_2 after removal of CaCl_2 in aqueous solutions indicates that a small amount of Ni might make an alloy with Ca. Most of Mg floated as the spherical particles at the surface of CaCl_2 melt. In and Bi were contaminated by the crucible and accidental air leakage. The author believes that the OS process can be applied also for the liquid metal.

It is noteworthy that Y_2O_3 and Er_2O_3 remained unreacted. The characteristic color of the powders was kept even after the electrolysis. Because the free energy changes of the calciothermic reduction only for Y_2O_3 and Er_2O_3 are positive in the studied oxides, it is natural that they were not reduced. The theoretical decomposition voltages of Y_2O_3 and Er_2O_3 to the metal and oxygen gas are 2.70 and 2.69V, and those to the metal and CO_2 gas are 1.68 and 1.67V, respectively. If O^{2-} transfer in CaCl_2 melt is due to the reduction, the applied 3.1V was large enough to form the metal. These evidences well confirmed the mechanism of OS process.

Conclusions

The OS process consisting of the electrolysis of CaO in the molten CaCl_2 and the calciothermic reduction in the same bath could produce the metals directly from their oxides. The exceptions are rare earth metals whose oxides are thermodynamically more stable than CaO. The calciothermic reduction could not reduce these oxides without any suitable activity control. The rates of reduction and deoxidation might be determined by the diffusion in the CaCl_2 melt, and a high Ca

concentration near the cathode was the important factor to obtain the high current efficiency.

Acknowledgments

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