An investigation of electro-deoxidation process for producing titanium from dense titanium dioxide cathode

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Abstract: The electrolytic method for directly extracting metals from the cathode of their its oxide has been called as “electro-deoxidation”. TiO_2 cathode in molten $CaCl_2$ has been developed more than 10 years. Two different mechanisms (“FFC Cambridge” and “OS”) were proposed to describe this electrochemical process. In order to further explore the mechanism, a dense cathode was designed in the present study, and an electrical conductor (Mo bar) was connected with the cathode, but without direct connection with molten salt to get rid of the possible electrochemical reaction between electrical conductor and melt. The experiments were carried out in a vertical electric resistance furnace at 900 °C in argon atmosphere with molten calcium chloride as the electrolyte. The cathode was cylindrical in shape (about 35mm in height, and 8mm in diameter). The cathode after the electrolytic experiment was examined by using SEM technique. The SEM observation of the cathode showed a layer-structure with dense core and porous product in outer layer(s). The electrical resistance of the core was found much lower than that of the original cathode. The result of electro-deoxidation experiments by present authors indicated that the “FFC-Cambridge” mechanism may give a better explanation for the electro-deoxidation process of dense cathode at the initial time.

Keywords: Electro-deoxidation, titanium oxide, molten calcium chloride, reduction

1. Introduction

The electrochemical approach is a promising method for metals extraction not only from oxides [1, 2], but also from sulfides [3, 4]. The electrolytic method for directly extracting metals from the cathode of their its oxide has been called as “electro-deoxidation”. It would be a simpler, cheaper and more environmental friendly way to produce Ti metal using electro-deoxidation approach. As an important route of metals production, it has been studied in many laboratories [5-11]. However, the mechanism of the electro-deoxidation process is still not fully clarified.

Two mechanisms have been proposed to describe the electro-deoxidation process. The “FFC-Cambridge” mechanism points out that the deoxidation process is completed by the transport of oxygen anion from the cathode to the molten salt, and then to the anode [5]. The “OS” mechanism considers that Ti is obtained from the reduction of titanium dioxide by metal Ca produced in cathode reaction [6]. The fact that reductive electric potential of Ti^{4+} ion is lower than that of Ca^{2+} ion indicates “FFC-Cambridge” mechanism can be true [1, 5, 11, 12], while the metallothermic processing of Ca reacting with TiO_2 power in electrolyte near the cathode shows that the “OS” mechanism may be possible too [6, 13-15]. Therefore, work should continue to distinguish the foregoing two mechanisms of the electro-deoxidation process of TiO_2.

Porous cathode was usually used in the literatures [5, 8-12]. However, there would be electrochemical reaction on the interface between electrolyte and the electrical conductors (usually twisting metal wire, stick or net) when using porous cathode. Furthermore, the reaction interface in a porous TiO_2 cathode was so complicated that it is difficult to clarify the effect of the geometry on the reaction. In this case, a geometrically simple and dense TiO_2 cathode prepared by a stronger compacting pressure could simplify the study. For preparation a dense TiO_2 cathode, higher sinter temperature and longer sinter time is more appropriate.

2. Experimental

The experiments were carried out in a vertical electric resistance furnace at 900 °C in argon atmosphe molten calcium chloride as electrolyte. The cathode was cylindrical in shape (about 35mm in height, and 8mm in diameter) with a Mo wire of 1mm i. d. embedded in it as the electrical conductor. The dense cathode was made by iso-static pressing TiO_2 powder in A. R grade at 165MPa for 10min and sintering at 1450 °C for 10h. The cell for experiments was in a tubular shaped silica reactor. The reactor was open at one end and sealed with a rubber plug at the other end. Four holes were drilled in the plug, two of which were used as inlet and outlet of argon gas respectively. The others were respectively used as wires of cathode and anode. The electrode wires were connected to a CHI660A Electrochemical Workstation (Chenhua Co. Shanhai). A graphite crucible (45mm i. d, and 51mm o. d.) as reaction tank and anode was placed in the silica reactor. Molten $CaCl_2$ in the cell was about 40mm in depth. The applied voltage for the electro-deoxidation process was 3.0V. The schematic diagram of cell is illustrated in Fig. 1.

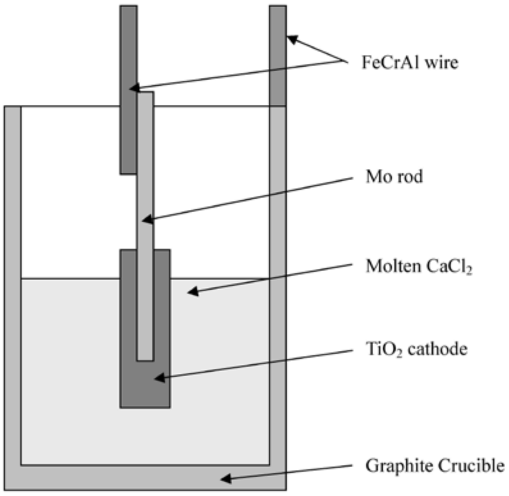

Fig. 1 Schematic diagram of experimental cell for titanium oxide electro-deoxidation

During the experiment, the cathode was immersed in molten $CaCl_2$ bath about 15mm for almost 6.6h at first, then 30mm about 1h. Therefore, two sections with different reduction times, 7.6h for the lower part and 1h for the upper part, would present in the cathode. After experiment, the cathode was taken away from the molten salt. The silica tube was pulled out of the furnace, and the reaction cell in the tube was quickly cooled to room temperature by flowing argon.

The quenched cathode was cut into different cross sections for SEM observation to identify the different layers formed during different reaction times. Resistances of the samples were measured too.

3. Results and Discussions

The current-time curve during the experiment is showed in Fig. 2. The curve was not smooth possibly for the short circuit of the carbon fractions， which was observed in electrolyte. It was also an important cause of the low current efficiency.

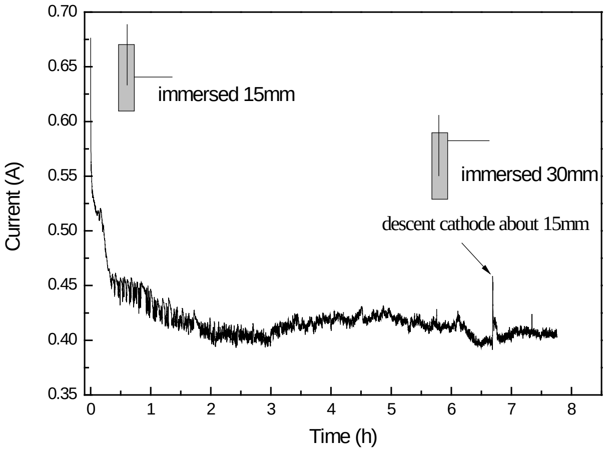

Fig. 2 Current versus time curve of titanium oxide electro-deoxidation

Fig. 3 is the SEM image of a cross section of the cathode reacted for 1h. It was found that this cathode was coated with a solidified $CaCl_2$ layer. The core of cathode was nonstoichiometric titanium oxides TiO_{2-x}, while the surface was a porous metallic titanium layer [16].

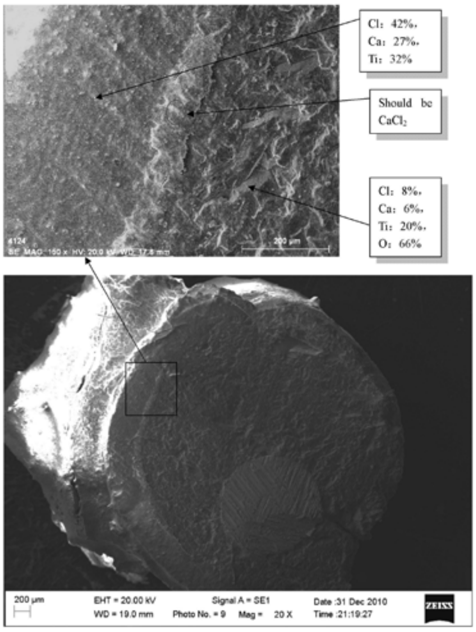

Fig. 3 SEM image of the cross section of cathode reduced for 1h

Fig. 4 is the SEM image of a vertical section of the cathode reacted for 7.6h. From Fig. 4, three layers were found in the cathode, including an inner TiO_{2-x} layer, a middle $Ti_xO_y/Ca_zTi_xO_y$ layer as well as a surface metallic titanium layer [16]. The middle and surface layers were so porous that they could be easily stripped from the core. In molten $CaCl_2$, outside the cathode surface, the high concentration of the dissolved oxygen can be observed from the left up figure with EDS data in Fig. 4. In "FFC-Cambridge" mechanism, this may attribute to the diffusing of O^{2-} ions from the cathode to the melt. While in the veiwpoint of "OS" mechanism, the oxygen may from the dissolved CaO produced by the metallothermic reduction reaction between TiO_2 and Ca (Ca is deposited first in the cathode).

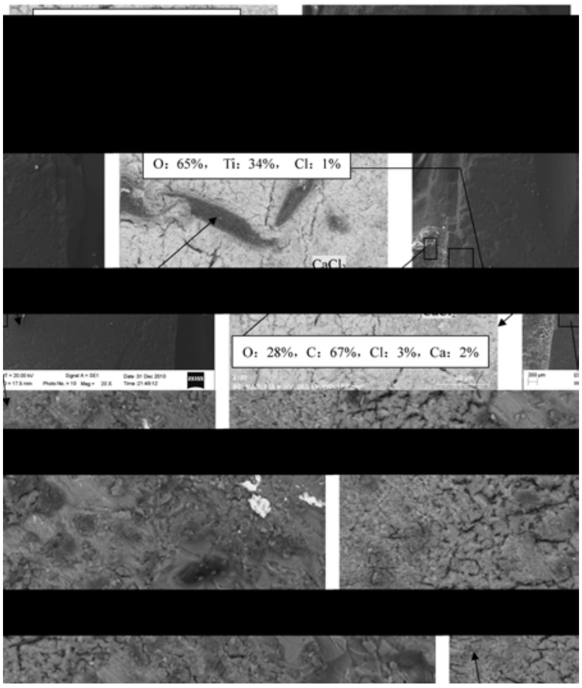
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Fig. 4 SEM image of the longitude section of cathode reduced for 7.6h

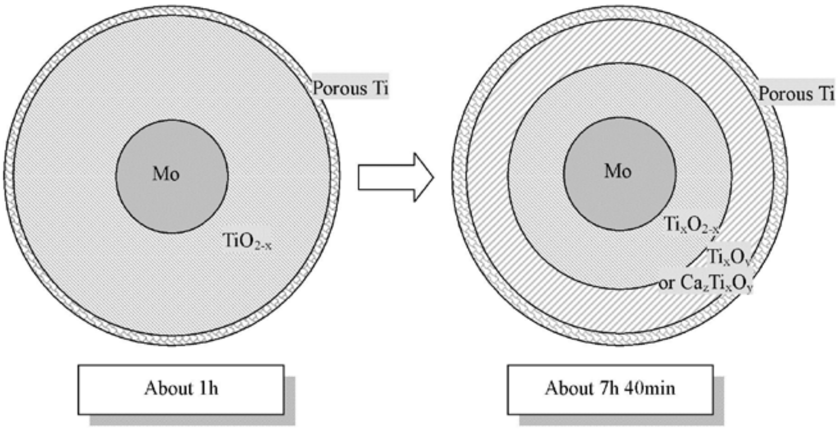

Fig. 5 Schematic diagram of cathode reduction for different times

According to Fig.3 and Fig.4, the reaction mechanism may be described as follows. At the initial stage, a porous Ti layer was formed, and then a middle layer formed between Ti and core. The middle layer might be protoxides of titanium, or calcium-containing species. Thickness of titanium layer did not change much during the reduction process. At room temperature, the resistance of the inner (core) layer measured by four-probe method was about 10~50Ω, while it was about 200~300Ω for the original TiO_2 cathode. These imply that the core was TiO_{2-x} [17]. Because molten salt $CaCl_2$ was not found in the inner layer of cathode, the reduction of the core should not be caused by the in-stiu calciothermic reduction, but oxygen anion can be transferred out. According to the above analyses, schematic diagrams of cathode reduction can be given as shown in Fig. 5.

The electro-deoxidation experiments for only 10min when immersing the cathode 20mm were also carried out. Fig. 6 shows the SEM result for sample of 10min, where the layer-structure was not observed in this cathode. However, the resistance of the cathode at room temperature measured was as high as 10~50Ω, same as that of the inner layer for samples in Figs. 3 and 4. The foregoing results may indicate that the resistance of the cathode dropped sharply after a short time deoxidization, and then the resistance of inner layer almost unchanged during the consequent reduction. It has been found that the resistance of titanium oxide is a decreasing function with the increase of oxygen vacancy[18, 19]. So the decrease of the resistance could be due to the oxygen diffusing to the molten $CaCl_2$ which increases oxygen vacancies.

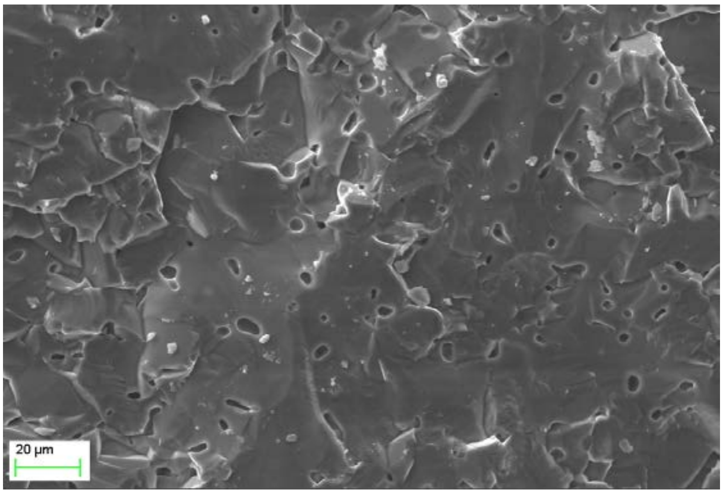

Fig. 6 SEM image of a cathode reduced 10min

At the present experimental temperature, the electric resistivity of polycrystalline TiO_2 (measured in Ar atomsphere) is as high as 10^4 Ω·cm [20], while it is 10^{-1} to 10^1Ω·cm for TiO_{2-x} [21]. This means, at the initial stage of the deoxidation, the high resistance of cathode would result in large voltage drop within the cathode. However, the applied voltage was a constant value (3V). So, the metallic Ca could not be generated because the potential was not negative enough to reduce the calcium ions. Only if the resistance of cathode is decreased, it may be possible to produce metallic calcium. So the theory of "FFC-Cambridge" process could be used to explain the mechanism of electro-deoxidation process at the initial stage.

4. Conclusions

Experiments of the electro-reduction for extracting titanium directly from TiO_2 cathode in molten $CaCl_2$ were carried out using a dense cathode. The following conclusions are drawn.

(1) Metallic titanium can be produced from dense TiO_2 cathode through a simple electro-deoxidation process, and in this process, a layer-structure of cathode was formed.

(2) At the initial stage of electro-deoxidation process, the resistance of inner layer decreased quickly compared to that of the initial sample indicating that the “FFC-Cambridge” mechanism could be dominated at this stage.

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References

[1] K. S. Mohandas, D. J. Fray. FFC Cambridge process and removal of oxygen from metal-oxygen systems by molten salt electrolysis: an overview. *Trans. Indian Inst. Met*., 2004, 57(6), p579-592.

[2] A. J. Fenn, G. Cooley, D. J. Fray, et al. Exploiting the FFC Cambridge Process. *Adv. Mater. Processes.*, 2004, 162(2), p51-53.

[3] G. Li, D. Wang, X. Jin, et al. Electrolysis of solid MoS_2 in molten $CaCl_2$ for Mo extraction without CO_2 emission. *Electrochem. Commun.,* 2007, 9(8), p1951-1957.

[4] X. Ge, X. Wang, S. Seetharaman. Copper extraction from copper ore by electro-reduction in molten $CaCl_2$-NaCl. *Electrochim. Acta.*, 2009, 54(18), p4397-4402

[5] G. Z. Chen, D. J. Fray, Farthing T. W. Direct electrochemical reduction of titanium dioxide to titanium in molten calcium chloride. *Nature*., 2000, 407, p361-364.

[6] K. Ono, R. O. Suzuki. A new concept for producing Ti sponge: Calciothermic reduction. *JOM.,* 2002, 54(2), p59-61.

[7] I. M. Ashraf. The 11th world conference on Titanium (Ti-2007). *JOM.*, 2008, 60(5), p40-44.

[8] M. Ma, D. Wang, W. Wang, et al. Extraction of titanium from different titania precursors by the FFC Cambridge process. *J. Alloys Compd.*, 2006, 420(1-2), p37-45.

[9] S. L. Wang, Y. Li. Reaction mechanism of direct electro-reduction of titanium dioxide in molten calcium chloride. *J. Electroanal. Chem.*, 2004, 571(1), p37-42.

[10] K. Dring, R. Dashwood, D. Inman. Voltammetry of titanium dioxide in molten calcium chloride at 900℃. *J. Electrochem. Soc.*, 2005, 152(3), pE104-E113.

[11] G. Chen., D. J. Fray, Farthing T.. Cathodic deoxygenation of the alpha case on titanium and alloys in molten calcium chloride. *Metall. Mater. Trans. B*., 2001, 32 (6), p1041-1052.

[12] D. J. Fray. Emerging molten salt technologies for metals production. *JOM*., 2001, 53(10), p27-31.

[13] R. O. Suzuki, K. Ono, K. Teranuma. Calciothermic reduction of titanium oxide and in-situ electrolysis in molten $CaCl_2$. *Metall. Mater. Trans. B*., 2003, 34(3), p287-295.

[14] R. O. Suzuki. Calciothermic reduction of TiO_2 and in situ electrolysis of CaO in the molten $CaCl_2$. *J. Phys. Chem. Solids*., 2005, 66(2-4), p461-465.

[15] R. O. Suzuki. Direct reduction processes for titanium oxide in molten salt. *JOM.*, 2007, 59(1), p68-71.

[16] D. T. L. Alexander, C. Schwandt, D. J. Fray. The electro-deoxidation of dense titanium dioxide precursors in molten calcium chloride giving a new reaction pathway. *Electrochim. Acta.,* 2011,56(9), p3286-3295.

[17] U. Balachandran, N. G. Eror. Electrical conductivity in non-stoichiometric titanium dioxide at elevated temperatures. *J. Mater. Sci.,* 1988, 23(8), p2676-2682.

[18] J. R. Smith, F. C. Walsh, R. L. Clarke. Electrodes based on Magnéli phase titanium oxides: the properties and applications of Ebonex® materials. *J. Appl. Electrochem.*, 1998, 28(10), p1021-1033.

[19] H. Gruber, E. Krautz. Magnetoresistance and conductivity in the binary system titanium–oxygen. II. Semiconductive Titanium Oxides. phys. Stat. Sol. (a), 1983, 75(2), p511-518.

[20] T. Bak, J. Nowotny, J. Stranger. Electrical properties of TiO_2: equilibrium vs dynamic electrical conductivity. Ion., 2010, 16, p673-679.

[21] A. Stokiosa, G. Wilczyński, Electrical Conductivity of $TiO_{2-\delta}$ and Non-stoichiometric Phases of TiO_x at Low Oxygen Pressure and Temperature Range 900-1280 K. *High Temp. Mater. Processes,* 2010, 29(1-2), p1-18.