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Effect of the changed electrolytic cell on the current efficiency in FFC Cambridge process

Meilong Hu^{1*}, Qu Zhengfeng¹, Bai Chenguang¹, Di Hu², George Z. Chen^{2*}

1.College of Materials Science and Engineering, Chongqing University, China, 400044

2.Department of Chemical and Environmental Engineering, University of Nottingham Ningbo China, 315100

*Corresponding author, E-mail:hml@cqu.edu.cn; George.Chen@nottingham.ac.uk

Abstract: Low current efficiency of the FFC Cambridge process made it no obvious advantages in cost compared with the traditional process to produce metals. Effect of the changed electrolysis cell on the current efficiency has been studied. Put the cathode into an alumina tube with a hole can efficiently avoid short circuit and the cathode contaminated by carbon produced from graphite anode. The results show that the current efficiency can be improved greatly by reducing the electric field intensity in the electrolysis cell. The high background current is mainly caused by the electronic conductivity in the electrolysis cell. Otherwise, pollution of the cathode is avoided, the depletion of the anode sharply decreases and the deoxidation of the samples greatly improve when using the improvement electrolysis cell.

Keywords: FFC Cambridge process, current efficiency, changed electrolytic cell

1. Introduction

In metallurgy field, extracting metals from their oxides by FFC Cambridge process attracted a lot of attention due to its valuable advantages, for example, short process, environment friendly and metal powder obtained directly. Most of metals have been obtained by this process in laboratory, such as Ti, Mg, Si, V, Cr, Zr, Fe, Ta, Nb, and Mo¹⁻⁶). But the

development of the process is limited because of its high cost, namely low current efficiency. There are many reasons caused the low current efficiency of the FFC process. The first is the original nature of the metal oxides. Some metal oxides have good electric conductivity. The electro-deoxidization of these oxides is much easier than those have poor electric conductivity, liking semiconductor metal oxides. The second factor effected the current efficiency is the anode material. Normally, to accelerate the oxygen ions leaved from the electrochemical system, graphite rod always used as the anode in FFC process. Carbon powder, dropped from the graphite rod due to the reaction between oxygen ions and anode or produced by the reaction $O^{2-} + CO_2 = CO_3^{2-}$ (anode) and $CO_3^{2-} + 4e^- = C + 3O^{2-}$ (cathode), floats on the surface of the molten salt for the buoyancy. The cathode, anode and carbon powder can form the current circuit with the outside circuit, which made both of the resistance of cyclic circuit and the current efficiency of the electrochemical deoxidization decrease. The third factor is the impurities included in molten salt and metal oxides. There is no any chemical that is totally purity. These impurities will exhaust the electric energy during electrochemical deoxidization caused the current efficiency reducing. Otherwise, the metal products are probably contaminated due to much lower decomposition voltage of the impurities. The main factor influenced the current efficiency maybe is the electronic conductivity⁷⁾. Many kinds of multivalent anodic ions in the molten salt, liking anodic ions of the molten salt, anodic ions of the metal oxides, anodic ions of the impurities, will bring electronic conductivity for their transfer in site or valence.

Previous work has investigated the current efficiency for the FFC Cambridge process as a function of the electrolysis time, sintering conditions used for the cathode metal-oxide pellet, cell voltage, the molten salt temperature, and the anodic variables⁸⁻¹²⁾. The results of the studies show that the current efficiency can be improved by optimization of the electrolysis time, sintering conditions, cell voltage, the temperature and the inert anode. Although the current efficiency also can be improved using the inert anode, the cost of the anode prepared is the limited step. However, the effect of the changed electrolysis cell on the current efficiency has not been explored. In this paper, through changing the electrolysis cell to study the effect of the cell on the current efficiency in FFC Cambridge process.

2. Experimental procedure

Two kinds of electrolytic cells with two electrodes were used to measure the effect of them on the current efficiency of the FFC Cambridge process. The changed cell used is shown schematically in Fig.1. And using an alumina tube with a hole(diameter 8.0 mm) trapped the cathode in it to change the traditional FFC electrolysis cell. The cathodic metal oxide can face to face with the graphite anode through the hole. Above edge of the hole is lower than the molten salt surface about 10mm. The lower edge is higher than the bottom of the crucible about 15mm.

Fig.1. the changed electrolysis cell

Titanium oxide powder of 98% specified purity was selected as the oxide precursor. The titanium oxide was uniaxially pressed, at 6~7 MPa using a 7 mm diameter, into 0.4g preformed pellets. These pellets were subsequently sintered at 1173K for 2h, resulting the pellets had sufficient mechanical strength for wrapping on the metal wire. Then the pellet was attached to the steel rod served as cathode, and the graphite rod was used as the anode.

A dense alumina crucible of 100 mm internal diameter and 100 mm height was then placed inside the vertical tubular reactor. The crucible contained CaCl_2 salt. The water-cooled upper end of the reactor was sealed with a stainless steel cover with silicone-sealed feed. The sealed reactor system was vacuumed and then was continually flushed through with argon gas. Repeat 3 times. The reactor was then heated at a constant rate of 3 K/min by the furnace until a temperature of the target temperature was reached with argon flow of 120 ml/min. The carbon powder floated on the molten salt can be found. Using the molybdenum cathode collected the carbon and removed from the electrolysis cell.

After the operating temperature had been reached, the system was left to stabilise for 1h. Thereafter, the titanium oxide pellet sintered was slowly lowered into the electrolyte (when using the alumina tube put the tube into the salt slowly and then placed the cathode in the tube slowly). The graphite rod was then immersed to the molten salt. A constant voltage of 3.1 V was applied between the anode and the cathode.

Electro-deoxidation was terminated after 6 h, and the electrodes were removed from the melt into the part of the reactor. After the reactor was cooled the electrodes were removed from it and washed with water to remove salt in the electrolysed sample.

These procedures were repeated using the alumina tube to allow direct comparison with the without tube.

3. Results and discussion

3.1 Constant voltage electrolysis

Fig.2 Current changes with time at constant voltage of 2.8V with tube and without tube

- (a) titanium oxide electrolysis, weight of sample is 0.42g, electrolytic temperature is 1173K for 6h
 (b) chromium oxide electrolysis, weight of sample is 1.0g, electrolytic temperature is 1083K for 6h.

The current efficiency of the constant electrolysis can be described as equation (1). Here, Q_T is the theoretic electric quantity to electrochemical deoxidize of the cathodic metal oxide. Q_A is the actual electric quantity exhausted during deoxidization of the cathodic metal oxide, showed as equation (2). C and t are the current and the electrolysis time, respectively.

$$\text{Current efficiency: } \eta = \frac{Q_T}{Q_A} \quad (1)$$

$$\text{Actual electric quantity: } Q_A = \int_{t_1}^{t_2} C dt \quad (2)$$

From equation (1) it can be seen that the actual electric quantity is smaller and the current efficiency is bigger. Fig.2 shows that the shape and changes of the current curve are same with tube and without tube. But the area enclosed by the current curve with tube is much smaller and the background current is lower than that without tube. It means that the current efficiency increases when the cathode is trapped in the alumina tube. It is difficult to confirm the background current. The actual current efficiency can be calculated by the assistant of the oxygen content in metal obtained in the cathode. When the cathode trapped in the alumina tube the current efficiency is almost twice to the traditional electrolytic cell. Due to electric field has the great effect on the electronic conductivity, decreasing its intensity can reduce the electronic conductivity. One advantage of using the tube with the hole can cut most of the electric field between cathode and anode. The electric field just exist in the area of the hole on the tube. The electronic conductivity greatly decreases for the electric field intensity weakening. So the background current decreases and the current efficiency of the process increases. The other is cut off the current circuit caused by the carbon powder floating on the surface of the molten salt between two electrodes. Due to the hole on the tube is lower than the surface of the molten salt. The carbon powder cannot enter the tube to contaminate the product. It can reduce the current depletion and increase the current efficiency. As a result the whole current efficiency increases when the alumina tube is wrapped on the cathode. The electrodes pollution are also reducing.

3.2 Effect of the changed cell on cathode

Fig.3 Cathodes electrolysed without tube(a) and with tube(b) using chromium oxide

The final product—metal leaves on the cathode through the FFC Cambridge process using metal oxides as the precursor. So the cathode has a close relationship with the quality of the final product. Figure 3 is the cathodes electrolysed without tube(Fig.3a) and with tube(Fig.3b), which are the appearance taken from the salt and cooled in the top of the furnace. It shows that the final product is wrapped by the carbon powder and polluted heavily when the cathode put into the molten salt directly. However, the cathode electrolysed with tube is cleaner. The tube, which encloses the cathode, can prevent the carbon dropped off from the anode closing to the cathode. In fact, the carbon, produced during electrolysis, has two obvious drawbacks for electrolysis. Firstly, carbon powder will float to the cathode and cover it caused the final metal product polluted. Secondly, the carbon floating on the surface of the molten salt connects the cathode and the anode caused the current efficiency decreased. The cell with the tube can increase the current efficiency of the electrolysis and prevent the final product from polluting.

3.3 Effect of the changed cell on anode

The graphite anode is always used in the FFC Cambridge process to remove oxygen ions from the electrolysis cell. The carbon can easily react with the oxygen ions formed CO or CO₂ gases released from the electrochemical deoxidization system. But due to the sub-reaction and the depletion the carbon powder cause the current efficient decrease and the cathode contaminate. The anodes, after the constant voltage electrolysis with tube, show as Fig.4a(side faced the hole) and Fig.4b(off side faced the hole). The depletion of the anode, using the tube during electrochemical deoxidization in FFC Cambridge process, obviously extenuate. The back of the anode facing the hole of the tube almost does not consume. From Fig.4a the area of the graphite anode faced the hole is much reacted than the other zone. But the area on the anode close the bottom of the crucible has much bigger holes whatever with tube and without tube, which maybe produced by the diffusion of the oxygen ions from the lower edge of the alumina tube to the anode. This results show that the alumina tube limit the oxygen ions diffusion from cathode to anode maybe cause the current efficiency decrease. Fig.5 shows the side of the anode off the cathode with tube(a) and without tube(b),

respectively. The diameter of the anode obviously become small and the graphite depletion is very severely compared with the electrolysed anode with tube. The anode depletion is much lower than that without tube. These results show that the impurities and the electronic conductivity spend much energy during electrochemical deoxidization of FFC Cambridge process caused the current efficiency decrease. The alumina tube used in the FFC Cambridge process decrease the electronic conductivity largely by cutting down the electric field intensity. The depletion of the anode obviously lightens and the oxygen in metal reduces.

Fig.4 Anode electrolysed with tube. (a. side faced the hole, b. off side faced the hole)
Fig.5 Anodes electrolysed with tube and without tube. (a. off side with hole, b. off side without hole)

4. Conclusions

Decreasing the electric field intensity between the cathode and the anode by using a tube wrapped the metal oxide cathode can not only increasing the current efficiency but also reducing the anode depletion, decreasing the cathode contamination and decreasing the oxygen content in the final metal. The current efficiency of the constant voltage electrolysis with tube increases more 10% than that without tube. Although the current efficiency increases when use the alumina tube in the cathode, the diffusion of the oxygen ions may be restricted in the tube and limit the current efficiency further increasing. The results of the constant voltage electrolysis show that the electronic conductivity is the main factor caused the high background current in FFC Cambridge process. How to effectively control the electronic conductivity is the key point to increase the current efficiency in this process.

Acknowledgement

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Captions List

Fig. 1 Caption The schematic of the changed electrolytic cell

Fig. 2 Caption Current changes with time at constant voltage of 2.8V with tube and without tube

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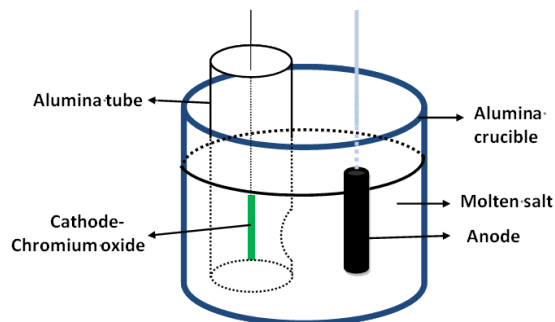


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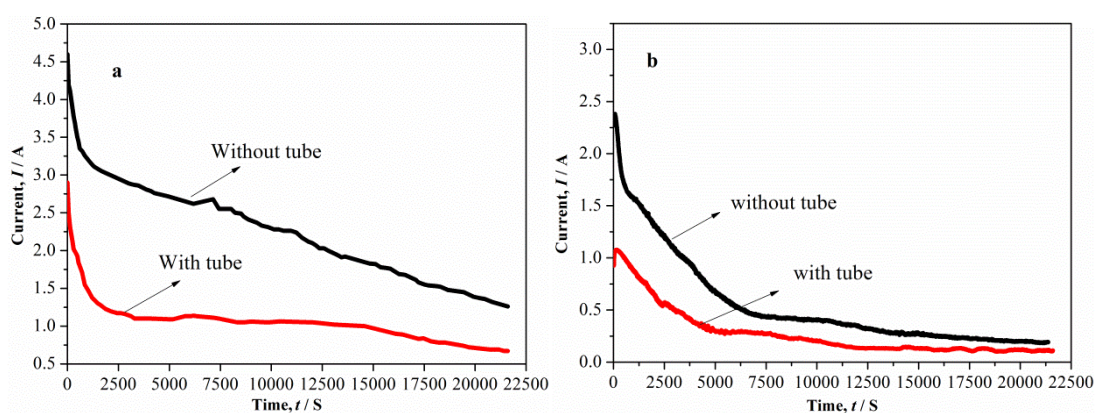


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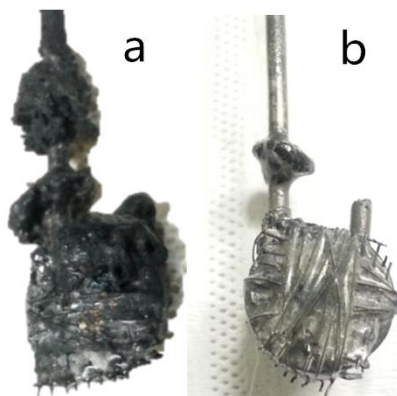


Fig.3 Cathodes electrolysed without tube(a) and with tube(b) using chromium oxide

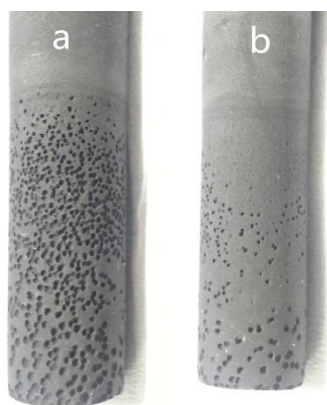


Fig.4 Anode electrolysed with tube.
(a. side faced the hole, b. off side faced the hole)



Fig.5 Anodes electrolysed with tube and without tube. (a. off side with hole, b. off side without hole)