

Effect of Electrical Conductivity and Porosity of Cathode on Electro-Deoxidation Process of Ilmenite Concentrate

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Abstract: The performance of the cathode is always closely related to the electro-deoxidation process and its current efficiency. In this work, the effect of sintering temperature on the electrical resistivity of an ilmenite concentrate cathode was measured. The results show that the sintering temperature has a significant effect on the electrical conductivity of the cathode. The electrical resistivity of the ilmenite concentrate cathode decreases with increasing of the sintering temperature and increasing of the contact area. Besides, the influence of the cathode porosity on electrochemical process during preparation of Ti-Fe alloy in molten salt was studied. The results also reveal that the porosity of ilmenite concentrate cathode directly affects the electro-deoxidation process. The increasing of porosity is beneficial to the formation of intermediate product (CaTiO_3) and improvement of the current efficiency.

Key words: electrical resistivity; porosity; current efficiency; electro-deoxidation; ilmenite concentrate

FFC Cambridge process is a new technique by which pure metals and alloys can be directly prepared from their respective oxides^[1-6]. However, the FFC technology has not been industrialized due to its low current efficiency to achieve a low O content in the produced metal. In recent years, researches about improving current efficiency have been become a hot spot. Schwandt et al.^[7] proposed that a graphite pseudo-reference electrode combines with additions of calcium oxide to improve potential control. The speed and current efficiency of the experiment were significantly increased. Chen et al.^[8] attributed the overall rate of O from metal oxide to the lower metal/electrolyte interface. The reduction of TiO to Ti could be improved by increasing the pellet porosity. Fray et al.^[9] also compared the current efficiency by using either a graphite anode or an oxide based anode. Actually, current efficiency is affected by many factors in electro-deoxidation process, such as reaction process, the molten salt, property of the cathode and the anode. Among these factors, the cathode plays an important role in determining the current efficiency during electro-deoxidation process. However, the cathode performance is mainly influenced by the cathode conductivity and cathode porosity.

Although the importance of cathode has been realized, very few studies have examined the effect of the cathode resistivity and cathode porosity on electro-deoxidation process. Marques^[10] studied the effect of temperature on resistivity of two ceramic cathode materials (LSCFe_3 and LSCFe_7). Similarly, Zhao et al.^[11] indicated that the electronic conductivity of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$ cathode increased with the temperature decreasing. In regard to the study of cathode porosity, Fray^[12] used highly porous titanium oxide as precursors and studied the effect of porosity on the rate of reduction. Chen^[8] reported that the porosity of the TiO_2 cathode affects directly the morphology of the Ti produced by electro-reduction.

The above electrochemical reduction was studied using various cathode materials and mainly dominated by the oxide cathodes. The present work is focused on reducing ilmenite concentrate to prepare Fe-Ti alloy directly by the FFC-Cambridge process. The ilmenite concentrate cathode contains ilmenite phase, magnetite phase and few geikielite phase, which is more complicated than the pure oxide cathode. A high performance cathode is an important part to obtain high electrolysis efficiency.

Thus, the purpose of the present work is to study the effect

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of the sintering temperature on the electrical resistivity of the cathode, and the influence of the cathode porosity on the electrochemical process. It is expected that the conductivity of the cathode is improved by controlling the sintering parameters. Besides, the increasing of cathode porosity is beneficial to the electrolysis process. The results will provide a guiding significance for improving the cathode performance and increase the electro-deoxidation rate.

1 Experiment

Ilmenite concentrate from Pan Zhihua area in China was used as the raw material. The main composition of ilmenite concentrate cathode was FeTiO_3 . The ilmenite concentrate was mixed with a certain amount of binder and the mixture was compacted into cylindrical pellets under a load of 15 MPa. The pellets were 10 mm in diameter and 15 mm in thickness. After initial drying at room temperature for 12 h, the green pellets were sintered in a tube furnace to predetermined temperatures and durations in air atmosphere. The pellets were sintered under three different conditions: (i) 300 °C for 2 h, (ii) 600 °C for 1 h, and (iii) aim temperature for 3 h.

After sintering, the samples were polished by emery prior to measurement of resistivity of the cathode. The experimental apparatus is shown in Fig.1. Two copper sheets were put on the surface respectively to guarantee good contact with sample. A multimeter, connected with copper sheet, was used to measure the resistance of samples. To ensure sufficient contact between the sample and the copper sheet, the clamping device was introduced between the upper and lower surfaces of the sample and copper sheet. The electrical resistivity fluctuated in the beginning, while 30 min was necessary for stabilizing the values measured and obtaining the electrical resistance of sample. Meanwhile, the height and cross-section area of sample were measured. The dependence is expressed as follows:

$$\rho = RS/L \quad (1)$$

where, ρ is electrical resistivity, R represents resistance of the cathode after sintering; S represents the cross-section area of the cathode after sintering; L represents height of cathode after

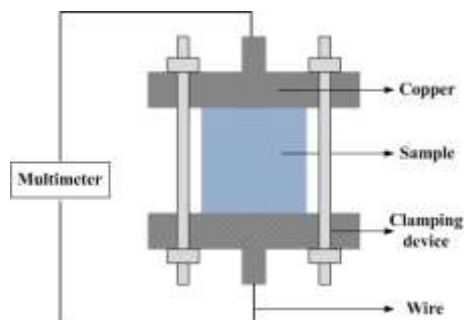


Fig.1 Apparatus for the measurement of electrical resistivity of sample

sintering. The mass of cathode is 10 g.

Porosity (θ) of the sintered ilmenite concentrate pellets was measured by the following mass-volume relationship.

$$\theta = \left(1 - \frac{M}{V\rho_s}\right) \times 100\% \quad (2)$$

where, M , V and ρ_s represent mass, volume, and density of the sintered pellet, respectively.

The electro-deoxidization experiment included both the pre-treatment to dry and purify the electrolyte and the electrolysis to decompose the oxide of the cathode. The pre-treatment process involved the thermal drying of the solid CaCl_2 and the pre-electrolysis of the molten CaCl_2 . The solid CaCl_2 was dried in an oven at about 100 °C for 2 h and at 300 °C for 3 h to remove physical water and crystal water, respectively. Electrochemical reduction experiments were carried out in graphite crucible, which was dried at 150 °C before the experiments. An ilmenite concentrate pellet was used as the working electrode and a graphite rod as the anode. The interior of reactor was purged with dry argon continuously. Pre-electrolysis was carried out at 850 °C for 2 h with 2 V to remove water and some impurities further. Then the ilmenite concentrate cathode was electrolyzed in CaCl_2 molten salt to prepare Fe-Ti alloy at 900 °C and the voltage was increased to 3.1 V. After electrolysis, the pellet and the graphite rod were removed from the electrolyte and cooled to room temperature at top in the furnace. The pellet sample was put into the distilled water for 12 h and then cleaned by Q2200E ultrasonic cleaner to remove the electrolyte which entered into the sample. The morphology and elements distribution were observed by SEM (scanning electron microscopy) and phase composition was analyzed by XRD (Rigak D/Max-2500). The schematic diagram of electrolytic apparatus is shown in Fig.2.

2 Results and Discussion

2.1 Electrical conductivity and porosity of cathode

The electrical resistivity of ilmenite concentrate cathode is presented as a function of the sintering temperature in Fig.3. The electrical resistivity of ilmenite concentrate cathode decreases remarkably with the sintering temperature increasing. In order to illustrate the influence of temperature

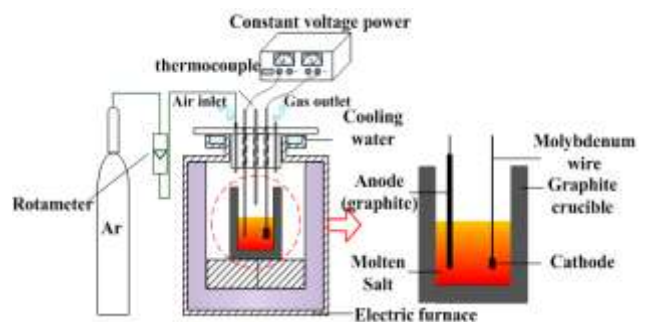


Fig.2 Schematic diagram of electrolytic apparatus

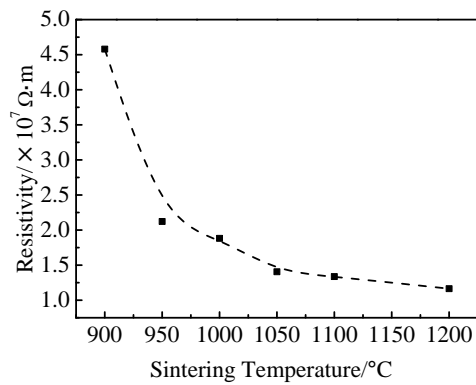


Fig.3 Effect of sintering temperature on the electrical resistivity of the sintered pellets

on electrical resistivity of ilmenite concentrate cathode, the metallographic images of the sintered ilmenite pellets obtained at different sintering temperatures are shown in Fig.4. With the temperature increasing, the resistivity between the particles is increased gradually.

The resistivity of cathode is explained by the compactness between the particles. It mainly depends on the liquid formation and solid phase reaction. In order to illustrate starting temperature of generating the liquid phase, phase's change of ilmenite concentrate as a function of temperature was calculated by FactSage, as shown in Fig.5. The liquid phase is generated when temperature is higher than 1000 °C. With the temperature increasing, silicate phase begins to decrease and the amount of liquid increases. When the temperature is higher than 1100 °C, ilmenite begins to decrease and pseu phase appears, which is stable in the

temperature range 1100~1300 °C. Silicate phase almost completely disappeared and liquid slag is produced in large quantities when the temperature is higher than 1200 °C. Thus when the sintering temperature was raised to 1200 °C, the liquid formation in the local area make local structure more compact so that connectivity between particles improves.

The electrical resistivity of the cathode depends on both the contact resistance between the particles and characteristic intrinsic electrical resistivity of the fully dense ilmenite phase. The contact resistance is determined by the contact area between the particles, so the influence of the contact area between particles on the electrical resistivity was investigated. The shape of the particles was considered as a sphere.

The relationship between electrical resistance and contact area can be explained by Fig.6, which is the equivalent circuit of different sintering temperatures. From Fig. 6, it can be obtained that the total electrical resistance includes R_m (ilmenite concentrate characteristic electrical resistance) and R_c (contact resistance).

The contact resistance depends on contact area between particles in a cross-section of the cathode. The number of contact points between particles has a significant influence on the contact area, and the contact points on a cross-section depend on the connectivity between particles. For instance, in Fig.6, the number of contact points changes with sintering temperature increasing from small to large in cross-section A. It can be obtained that the total electrical resistance is equal to the sum of mineral characteristic electrical resistance and contact resistance when contact between particles is the point contact. At this condition, the contact resistance is the largest. With sintering temperature increasing, ilmenite concentrate

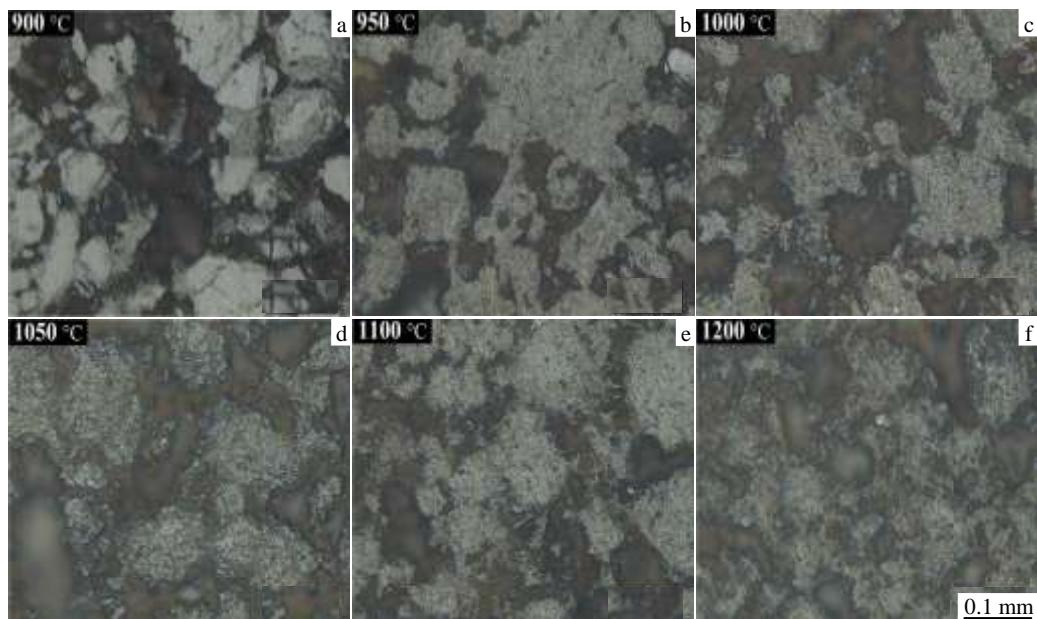


Fig.4 Metallographic images of the sintered ilmenite pellets obtained at different sintering temperatures: (a) 900 °C, (b) 950 °C, (c) 1000 °C, (d) 1050 °C, (e) 1100 °C, and (f) 1200 °C

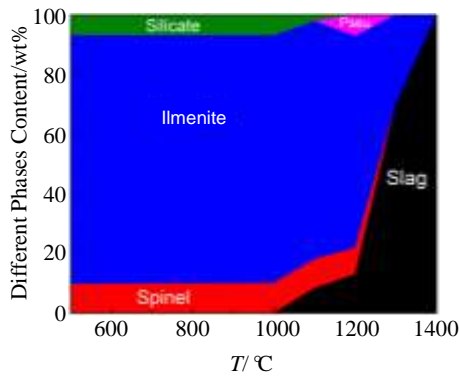


Fig.5 Phases change of ilmenite concentrate as a function of temperature

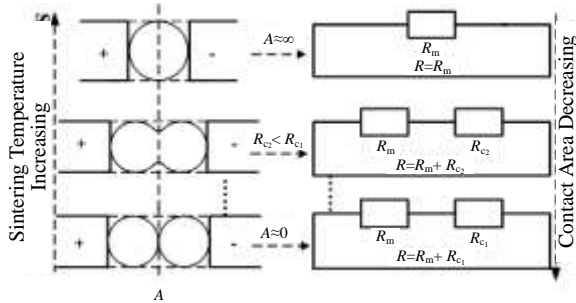


Fig.6 Equivalent circuit at different sintering temperatures

begins to soften, and thus the local structure becomes compact. The contact area and the cathode porosity increase, which

results in the contact resistance decreasing. The total electrical resistance equals to the mineral characteristic electrical resistance when the contact area is large enough.

According to the above analysis, the electrical resistance of the cathode mainly depends on the contact area between the particles. However, since the contact area is difficult to measure directly, the porosity of the cathode is always used to reflect the contact area. Besides, the cathode porosity is related to the de-oxidation process. Thus it is necessary to investigate the influence of porosity on electrolysis de-oxidation process and the current efficiency. The cathode with different porosities was prepared at 1200 °C.

2.2 Effect of the cathode porosity on the electro-deoxidation process

The porosity of the sample, which was prepared by the molten casting method at 1500 °C under Ar protection, is approximately zero. Other samples with different porosities were prepared by the powder metallurgic method with addition of different pore-forming agents NH₄HCO₃.

Fig.7 shows the microstructures of sintered ilmenite concentrate cathodes with different porosities. As can be seen, there is almost no porosity in the cathode prepared by the molten casting method, shown in Fig. 7a. The connection between particles appears when sintered at 1200 °C. With pore-forming agent increasing, the porosity and the porosity's diameter increase, as shown in Fig.7d.

The ilmenite concentrate cathodes with different porosities were electrolyzed in CaCl₂ molten salt for 6 h at 900 °C and 3.1 V. To reflect the electrolytic process of cathode, two parts

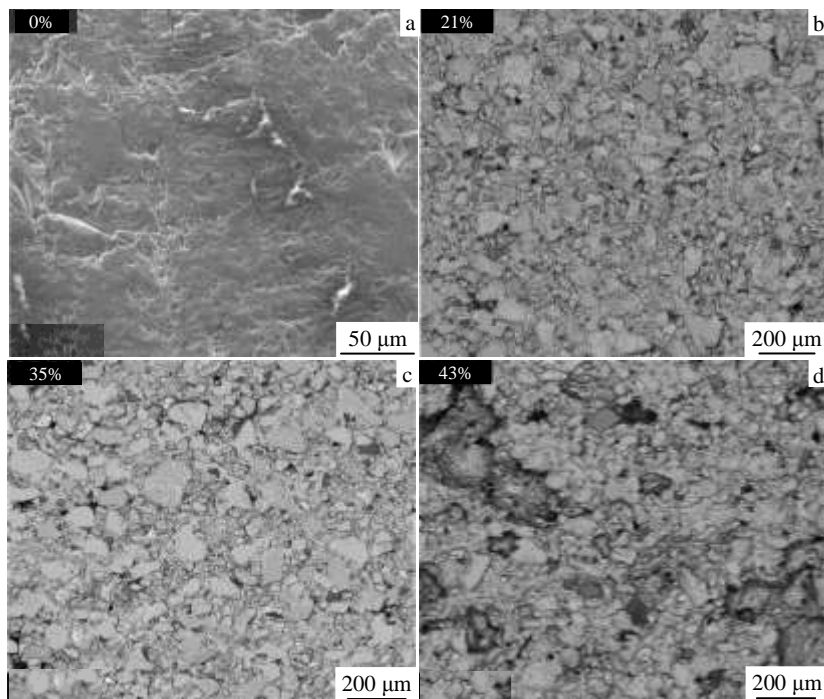


Fig.7 SEM images of the cathode with different porosities: (a) 0%, (b) 21% (c) 35%, and (d) 43%

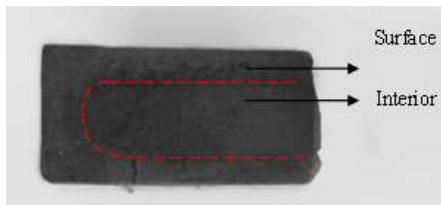


Fig. 8 Picture of ilmenite concentrate cathode after electrolyzed in CaCl_2 molten salt

of the pellet were selected as shown in Fig. 8 and analyzed by X-ray diffraction with the results collected in Fig. 9 and Fig. 10. The sample after electrolyzed for 6 h has an obvious boundary between reduction area and unreduced area, which uses a red line to show the boundary in Fig. 8. Thus the cross-section of the cathode is defined as the total plane, which includes the interior and surface of the cathode. But the surface of cathode is only referred to the product layer.

Fig. 9 shows the XRD patterns of the electrochemically reduced samples with different porosities. After 6 h of electrolysis, the main phases are FeTiO_3 , TiO_2 and the compound of Ca, Fe and O on cross-section of the cathode with 0% porosity. However, when the porosity is higher than 21%, the Fe phase, CaTiO_3 phase, Fe_2Ti phase, titanium sub-oxides and FeTi phase are formed. Besides, with the porosity increasing, CaTiO_3 phase has become the main phase. These differences illustrate that the porosity has a great influence on de-oxidation process of the metal oxides.

In the initial stage of reduction, Fe is first to be reduced from FeTiO_3 due to the lower theoretical decomposition voltage of FeO in comparison with TiO_2 . The second stage of the electrochemical reduction of ilmenite concentrate is characterized by the formation of the different mixtures of titanium sub-oxide and CaTiO_3 . According to the previous study^[13,14], CaTiO_3 phase is the inevitable intermediate product during de-oxidation process. The formation of CaTiO_3 is partly due to the reaction between Ca^{2+} present in molten CaCl_2 , which decomposes further to generate the titanium sub-oxides. In the third stage, CaTiO_3 decomposes to give rise to a combination of products that involve sub-oxides of titanium and Ti-Fe alloy. Finally, Fe-Ti alloy is formed through diffusion.

Fig. 10 shows the phase of cathode surface prepared by different porosities after electrolysis which was detected by XRD. The main phase is CaTiO_3 and Fe when porosity is zero. The Fe, CaTiO_3 , Fe_2Ti , titanium sub-oxides and FeTi phase are formed on the surface during the electro-deoxidation of ilmenite concentrate pellet with 21% porosity. When the porosity of cathode is 0% only the surface contacts with molten salt. Thus deoxidation of the cathode occurs on the surface, which leads to the low efficiency and forms the thin thickness of reaction layer. That is why CaTiO_3 and titanium sub-oxides only form on the surface. When the porosity increases, the pellets could be effectively penetrated by the molten CaCl_2 , which enters through the pores to form CaTiO_3 , and subsequently was reduced to form the sub-oxides of titanium (Ti_3O_5 and Ti_2O_3) no matter on the surface or interior.

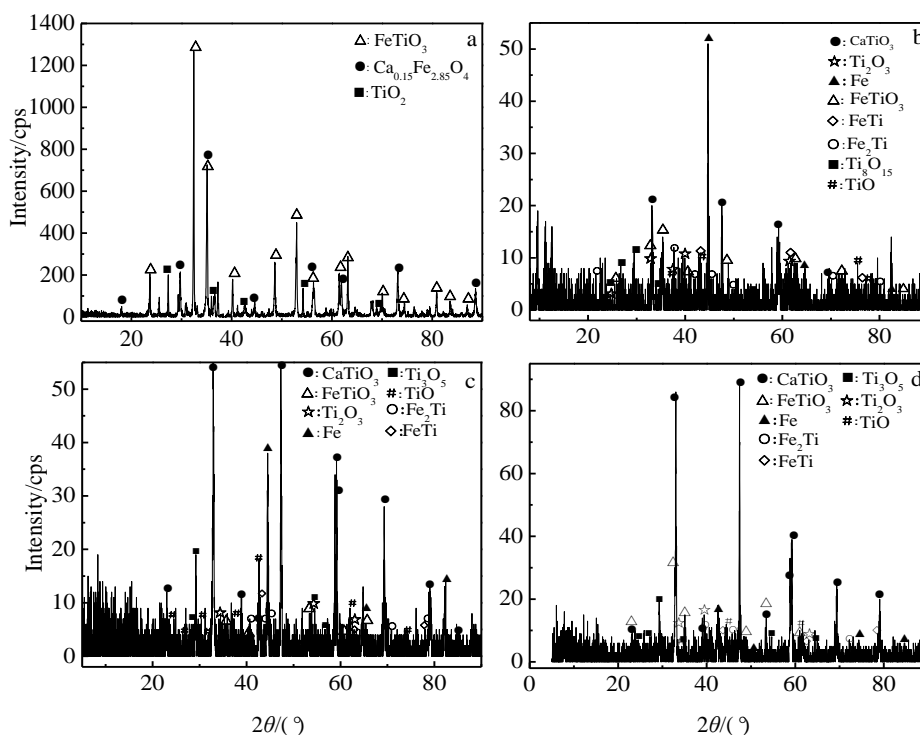


Fig. 9 XRD patterns of cross-section of cathode with different porosities after electrolysis: (a) 0%, (b) 21%, (c) 35%, and (d) 43%

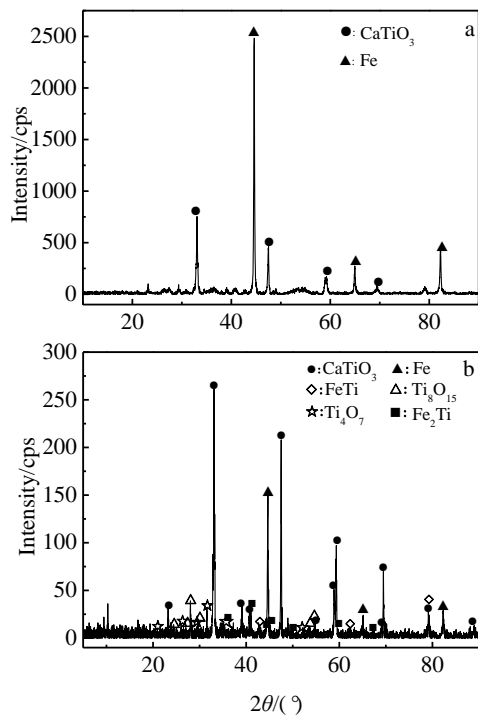


Fig. 10 XRD patterns of surface of cathode with porosities of 0% (a) and 21% (b) after electrolysis 6 h at 3.1 V and 900 °C

As discussed above, the cathode porosity plays an important role in the formation of intermediate product of CaTiO_3 . Since the formation of intermediate product (CaTiO_3) is the necessary process, the increasing of cathode porosity is beneficial to increase reaction area and further accelerating the formation of subsequent compounds. However, it is necessary to choose a cathode with suitable porosity. If the porosity is too high, the cathode is not adequate mechanical strength and is not benefit the product recycling.

The current curve for ilmenite concentrate cathode with different porosities is given in Fig. 11. It reveals that the current drops rapidly within few minutes and then decreases slowly. At the beginning of electrolysis, the electro-deoxidization was carried mainly through electrochemical reaction, which determines the speed of process and large initial current. The oxygen in cathode was removed gradually and forms a compact product layer on the surface, which further prevented the penetration of the molten salt and the migration diffusion of oxygen ion. The electro-deoxidization speed is mainly dependent on the diffusion of ions from the interior of pellet to the interface of metal and molten salt, which results in a drop in current.

It is an interesting phenomenon also noticed that with porosity increasing of the ilmenite concentrate cathode the current decreases. This seems to be contradictory with the expected results. However, it can be explained if the products have much higher resistance in the high porosity case. Due to the poor electrical conductivity of CaTiO_3 , with the

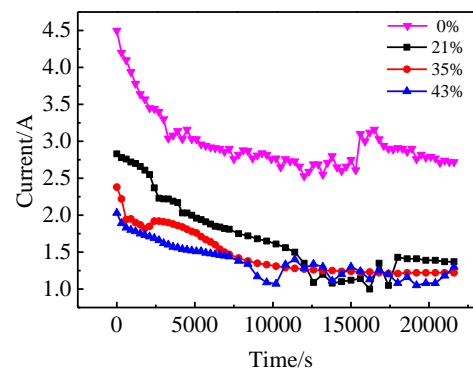


Fig. 11 Current versus time for ilmenite concentrate cathode with different porosities

Table 1 Current efficiency (η) versus porosity

Porosity/%	0	21	35	43
η /%	16.18	28.89	33.06	35.58

proceeding of the electro-deoxidization, the cathode resistance increases and current decreases. Thus the current with higher porosity is larger than that with small porosity.

The characterization of current efficiency is described as follows:

$$\eta = \frac{Q_{\text{theoretical}}}{Q_{\text{actual}}} \times 100\% \quad (3)$$

where, η is current efficiency, $Q_{\text{theoretical}}$ and Q_{actual} is the required theoretical quantity of electricity and the actual consumption quantity of electricity, respectively. Q_{actual} is obtained by the time integral of current. The theoretical charge required to remove the oxygen from the ilmenite concentrate is expressed by oxygen content level after electrolysis. As the oxygen content after electrolysis is not detected, the reduced metal content after electrolysis 6 h cannot be obtained. In order to compare the effect of porosity on current efficiency, the $Q_{\text{theoretical}}$ is just estimated. Assuming metal oxide is reduced completely, the total mole of electrons can be required. According to the Faraday constant, the $Q_{\text{theoretical}}$ when metal oxide in the cathode are reduced completely can be calculated. Actually, the value of $Q_{\text{theoretical}}$ is smaller than the calculated value, resulting in the current efficiency calculated by Eq. (3) is smaller than the actual value.

Table 1 is the relative current efficiency calculated with different porosities. The calculated value is higher than the actual value. However, the tendency of current efficiency at different porosities can be illustrated. It can be seen that with porosity increasing, the current efficiency increases, which illustrates that the porosity increasing is beneficial to the formation of intermediate product, thus further improving current efficiency.

3 Conclusions

1) The sintering temperature has a significant effect on the electrical conductivity of the ilmenite concentrate cathode. The electrical resistivity decreases from $4.58 \times 10^7 \Omega \cdot m$ to $1.16 \times 10^7 \Omega \cdot m$ when the sintering temperature increases from 900 °C to 1200 °C.

2) With the sintering temperature increasing, the liquid formation increases the contact area between ilmenite concentrate particles, which results in the decreased contact resistance.

3) The porosity of the ilmenite concentrate cathode has a direct effect on the reduction process and is related to the available surface area in contact with the electrolyte.

4) Increasing of the porosity is beneficial to the formation of intermediate product (CaTiO_3) and improvement of the current efficiency. The current efficiency will increase by about 50% when the porosity increases to 43%.

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阴极电导率和孔隙率对熔盐电解钛精矿脱氧过程的影响

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摘要: 阴极的性能通常是和电解过程与电解效率有着密切的关系。测量了焙烧温度对钛精矿阴极电导率的影响。结果表明焙烧温度对钛精矿阴极导电性影响很大。钛精矿阴极电阻率随着焙烧温度升高和接触面积的增加而增大。另外也研究了阴极孔隙率对熔盐电解制备 Ti-Fe 合金还原过程的影响。结果表明阴极的孔隙率对还原过程有着直接的影响。孔隙率的增加有利于中间化合物 CaTiO_3 的形成, 从而改善电解过程中的电流效率。

关键词: 电阻率; 孔隙率; 电流效率; 电解脱氧; 钛精矿

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