Preparation of Titanium Metal Using Titanium Suboxides in Molten Salt

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Perovskite is an inevitable phase formed in the cathode during electrolytic deoxidation using titanium dioxide as the raw material by FFC process. Here, titanium suboxides (Ti_3O_5 , Ti_2O_3 and TiO) are used as the raw materials to study whether perovskite can be avoided in the process. The results show that there is not perovskite formed during electrolysis using TiO and perovskite is appeared in the cathode when Ti_3O_5 and Ti_2O_3 are used as the raw materials. Perovskite is formed by combining Ca^{2+} in the molten CaCl_2 with the cathode materials after the voltage is applied between the electrodes. Perovskite is mainly produced by electrochemical deoxidation process and amount of it gradually decreases with oxygen content decreasing in the cathode. [doi:10.2320/matertrans.MA201807]

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1. Introduction

Titanium has a wide range of applications as an excellent structural and functional material. At present, the Kroll route is the main method for the preparation of titanium metal in industry. However, it has problems such as high preparation cost, complex process and serious pollution. Therefore, researchers have been seeking new technologies for efficient production of titanium. Electrolysis in molten-salt is been considered having great development prospects and has attracted worldwide attention. In 2000, Chen *et al.*¹⁾ carried out the direct electrochemical reduction of titanium oxide to titanium in molten CaCl_2 , which named the FFC (Fray-Farthing-Chen) Cambridge Process. In the FFC process, the mechanism of electro-deoxidation is that TiO_2 is electrolyzed into titanium and oxygen ions at the cathode, oxygen ions are dissolved in molten CaCl_2 and subsequently transferred to the anode under the electrolytic field. Finally, these ions discharged at the graphite anode in the form of CO or CO_2 .^{2,3)} In the OS process,⁴⁻⁷⁾ Suzuki *et al.* believed that the removal of oxygen via electrochemistry can be attributed to the calcium thermal reduction. There are different explanations about the mechanism of producing titanium by electrolysis process in molten salt.

Perovskite is the inevitable phase formed in the cathode during electrolysis process of stepwise deoxidization of TiO_2 .⁸⁻¹¹⁾ The formation of CaTiO_3 can causes expansion in the solid phase and decrease of cathode porosity, which will slows ion transport in the pores existing between the oxide particles and slow down the electrolysis speed.^{12,13)} In the later stage of electrolysis, reduction of TiO to Ti being another kinetically slow step. For the kinetic barrier caused by perovskite, Chen *et al.* studied the deoxidization effect of samples with different porosity, and found that increasing the porosity of samples can effectively reduce this barrier.¹⁴⁾ Therefore, one of the factors for improving the efficiency of electrolysis is to avoid the formation of perovskite as much as possible.

In all reported on electroreduction of solid oxides, such as TiO_2 ,¹²⁾ Nb_2O_5 ,¹⁵⁾ ZrO_2 ,¹⁶⁾ Ta_2O_5 ,¹⁷⁾ and SiO_2 ,¹⁸⁾ calcium-enriched oxide or perovskite phases of various compositions

are observed in partially reduced cathodes. However, the mechanism of formation of these intermediate products not fully understood. There are different views on the formation mechanism of perovskites. Schwandt and Fray *et al.*¹⁹⁾ believe that during the process of electro-deoxidation of titanium dioxide, the CaTiO_3 is formed when titanium dioxide was reduced to low-oxide. However, some other researchers²⁰⁾ believe that part of molten salt CaCl_2 can be hydrolyzed to form CaO , which reacts with TiO_2 to produced CaTiO_3 . In this paper, the formation mechanism of perovskites is determined by electrolysis using titanium oxides as the raw materials.

In previous studies, the results of different experiments using TiO_2 as raw materials show that perovskite is formed rapidly during the deoxidation of TiO_2 . Figure 1 shows the xrd patterns and SEM images of TiO_2 after electrolysis for 10 minutes. It shows that TiO_2 reduces to Ti_4O_7 in a short time, and at the same time, perovskite is rapidly generated.

Is there perovskite formed in the cathode if titanium suboxides are used as the raw material. In this paper, the main aim is to confirm the formation mechanism of calcium titanate in the cathode and the relationship between perovskite formed and raw material used in cathode.

2. Experimental

2.1 Materials and apparatus

The cathode raw materials used in this research including Ti_3O_5 , Ti_2O_3 , TiO powder with an average size of $40\text{ }\mu\text{m}$ – $50\text{ }\mu\text{m}$, and was wrapped by stainless steel gauze (400 mesh) as cathode for electrolysis. Anhydrous CaCl_2 of 96% specified purity, purchased from the Chengdu Hua Gong Company was the electrolyte. And the dense alumina crucible of 100 mm internal diameter and 100 mm height was placed in the vertical tubular reactor. The crucible contained approximately 600 g of anhydrous CaCl_2 salt. The KI solution (100 ml 0.2 g/L soluble starch and 0.08 g/L KI) was prepared to detect Cl_2 gas in the electrolysis process.

The Ar with purity of 99.999% was flow into the vertical tubular reactor during all these experiments, the flowrate of gas is 200 mL/min. #304 Stainless Steel rods, 75 cm length, were selected as the current conductors. The dense graphite rod with purity of 99.9% and a diameter of 10 mm was

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Fig. 1 (a) XRD patterns of TiO_2 after electrolysis for 10 minute; (b) SEM image of TiO_2 after electrolysis for 10 minute.

Fig. 2 Schematic of the apparatus.

connected to the steel rod by threaded connection, which was selected as the anode.

The electrolysis process was performed in a tubular electrolytic furnace (show in Fig. 2). The stainless steel lid seals the upper end of the reactor, which was equipped with holes for the electrode rods and gas outlet. Argon gas continues to be introduced into the reactor from the bottom, and the gas exhaust was led into the starch KI solution to detect the released Cl_2 gas.

2.2 Electrochemical reduction of titanium suboxides

Put the corundum crucible into electrolytic furnace, which contains anhydrous calcium chloride, and the furnace lid was sealed. Then, the sealed reactor system was vacuumed and constantly flushed with high-purity argon gas, after the air in the furnace was completely discharged, argon gas was continuously introduced into the furnace to ensure an inert atmosphere. The furnace was heated from room temperature to 900°C , heating rate was $10^\circ\text{C}/\text{min}$, and keep it for 30 minutes to ensure calcium chloride completely melted and the stability of the furnace temperature. After that, two stainless steel rods were inserted into molten CaCl_2 as the

electrode rods, a stainless steel bar with graphite bar at the bottom was used as anode, and another stainless steel rod as cathode. Then a voltage of 2.8 V was applied between the cathode and the anode for pre-electrolysis to remove impurities in molten salt.

The titanium suboxides powder (Ti_3O_5 , Ti_2O_3 and TiO) was wrapped in stainless steel net as the cathode and graphite rod was used as the anode, a constant voltage of 3.1 V applied between the anode and the cathode. The electrochemical reduction was interrupted after different reaction times (10 minutes, 1 hour and 2 hours respectively), then the cathode was removed from the salt melt and locating it in the upper part of the reactor. The residual molten salt on the surface of the sample rapidly solidifies with decreasing temperature, and argon gas was kept in the furnace to ensure the inert atmosphere, these procedures can avoid increasing the oxygen content in sample during cooling. After cool down to room temperature naturally, put the samples into the water for several hours to remove the soluble residue CaCl_2 from sample surface and then dried. Finally, the dried samples were used for the XRD and SEM analyses.

2.3 Characterization of the cathodic products

The phase composition of the samples was determined through X-ray diffraction analysis (XRD: D/max 2500PC). Each scan was 10° to 90° . The microstructure and chemical composition of the samples were investigated using scanning electron microscopy (SEM, TESCAN VEGA II) and energy-dispersive X-ray analysis (EDS, Oxford INCA Energy 350). The acceleration voltage was 15 eK.

3. Results and Discussion

3.1 Phase transition during electrolysis

3.1.1 Electrolysis of Ti_3O_5

Figure 3(a) shows that Ti_3O_5 powder used as the cathode in the electrolysis process and XRD patterns.

According to the XRD patterns, it shows perovskites formed after electrolysis for 10 minutes and Ti_3O_5 completely reduced to Ti_2O_3 . With the prolongation of the reduction time, the Ti_2O_3 is reduced to Ti_2O after 1 hour and it is further

Fig. 3 Ti_3O_5 used as the cathode (a) the XRD patterns of Ti_3O_5 powder at different electrolytic time; (b) Changes of Starch KI solutions.

reduced to Ti_3O after 2 hours. Perovskite phase also appeared in the XRD pattern of the sample after electrolysis in 10 minutes and 2 hours. This is due to a large amount of Ca^{2+} from the molten CaCl_2 entered the cathode after the voltage was applied between the electrodes, these Ti_3O_5 are then reduced to Ti_2O_3 , with the perovskite produced as a byproduct.

When Ca^{2+} from the molten salt takes part in the reaction to form perovskite in the cathode, Cl^- may be forced to accumulate at the anode and finally be released as Cl_2 . The chlorine reacted with KI in the solution and replaced the iodine, so the replaced iodine produced a colour reaction with the starch in the solution. Figure 3(b) shows that the solution turns blue after electrolysis, which proves the formation of perovskite during electrolysis.

3.1.2 Electrolysis of Ti_2O_3

In the same way, the Ti_2O_3 powder as the cathode material, the phase compositions of partially reduced samples at different electrolysis time show in Fig. 4(a).

After the voltage was applied between the anode and cathode, the Ti_2O_3 is rapidly reduced to TiO in 10 minutes, and it is also accompanied by the formation of perovskite as the byproduct. CaTi_2O_4 can be found in the sample after electrolysis for 1 hour, which may be caused by chemical reaction occur between TiO and CaTiO_3 , and a part of the CaTi_2O_4 is deoxidized to form Ti_2O . In the XRD patterns electrolysis for 2 hour, it show Ti_2O was deoxygenated to produced Ti_3O , and there was no CaTiO_3 and CaTi_2O_4 in the

Fig. 4 Ti_2O_3 used as the cathode (a) the XRD patterns of Ti_2O_3 powder at different electrolytic time; (b) Change of Starch KI solutions.

Fig. 5 TiO used as the cathode (a) the XRD patterns of TiO powder at different electrolytic time; (b) Change of Starch KI solutions.

sample. In Fig. 4(b), the phenomenon of bluing of starch KI solutions also proves the production of perovskite in the process of electrolysis.

3.1.3 Electrolysis of TiO

The result show that there is no CaTiO_3 formed if TiO is used as the raw materials. Figure 5 shows the XRD patterns and the change of the gases released from the anode. In Fig. 5(b), the starch KI solutions also did not detect chlorine gas. Part of TiO has been reduced to Ti_3O after 10 minutes. It was completely reduced to Ti_3O in 1 hour, Ti_6O was produced after 2 hours.

The results show that perovskite formed in the cathode can be avoided only by using TiO as the raw materials during the electrolysis. Perovskite also appeared in the cathode when Ti_3O_5 and Ti_2O_3 are used as the raw materials. Comparing the results of Fig. 3 with Fig. 4, CaTiO_3 is still detected in the sample after electrolysis for 1 hour using Ti_3O_5 . However CaTiO_3 is completely converted to CaTi_2O_4 when using Ti_2O_3 . This means that using Ti_2O_3 as the raw materials produces less perovskite than that of Ti_3O_5 . The results demonstrate that as the oxygen content in the cathode raw material decreases, the amount of perovskite gradually reduced and there is not perovskite formed during electrolysis TiO .

We all know that CaCl_2 is easily hydrolysis in air to produce CaO . CaO can be react with TiO_2 formed CaTiO_3 . To prove that whether CaTiO_3 in the cathode produces during cooling, washing or drying in air after electrolysis. The comparison experiments of with voltage and without voltage are proceeded at here.

The results in Fig. 6 show that no perovskite produced when the sample soaks in the molten CaCl_2 compared with the sample electrolyzed in molten CaCl_2 at the same condition. It proved that perovskite in the cathode is only formed during electrolysis.

3.2 Transformation of sample morphology during electrolysis

In order to investigate the relationship between the changes of themorphology and the reaction of the samples during the deoxidization process, the partially reduced sample was measured by scanning electron microscope.

SEM image in Fig. 7(a) shows that there is a large number of perovskite electrolysis for 10 min using Ti_3O_5 ,

Fig. 6 (a) Comparisons of the XRD patterns of Ti_3O_5 powder electrolysis for 10 minutes and soak for 10 minutes; (b) Comparisons of the XRD patterns of Ti_2O_3 powder electrolysis for 10 minutes and soak for 10 minutes.

Fig. 7 SEM images using different titanium suboxides electrolysis at different time (a) using Ti_3O_5 as the raw material electrolysis for 10 min, 60 min and 120 min (b) using Ti_2O_3 as the raw material electrolysis for 10 min, 60 min and 120 min; (c) using TiO as the raw material electrolysis for 10 min, 60 min and 120 min.

which exhibit a crystal-like morphology and densely aligned with each other. In the initial stage of electrolysis, Ti_3O_5 reduces to Ti_2O_3 , the perovskite grows rapidly with terraced structure. Schwandt²¹⁾ believes that this terracing results from the CaTiO_3 “attempting” to form a uniform layer around the irregularly shaped sub-oxide particles, while maintaining faceted growth and one crystallographic orientation. It can be observed that the edge of the crystal structure becomes slippery gradually in 1 h shown as in Fig. 7(a). The change of microstructure is due to the chemical reaction between TiO and CaTiO_3 formed CaTi_2O_4 (reaction 3). CaTiO_3 or CaTi_2O_4 was not found in the sample electrolysis for 2 hours. It is consistent with the XRD results. Figure 7(b) is the SEM images using Ti_2O_3 electrolysis at different times. It can be found that the amount of perovskite produced is much when using Ti_3O_5 as the raw material in 10 min. Namely, oxygen content in titanium oxides is higher amount of perovskites is more. This is consistent with the dissolution behavior expected for a faceted material, which will grow by a ledge mechanism and preferentially dissolve at the corners.²¹⁾ It can be inferred that the stage of perovskite formation has ended and some perovskites have begun to react with TiO to form CaTi_2O_4 . It is obvious that the amount of perovskite produced decreases with the decreasing of oxygen content in the raw material and the reaction proceeds to the next stage faster.

The crystal-like morphology particles not appeared in Fig. 7(c). It is consistent with the results of the XRD pattern. The microstructure shows that the structure of samples becomes denser with the decrease of oxygen content.

4. Conclusions

- (1) Perovskites are still produced during electrolysis when both Ti_3O_5 and Ti_2O_3 were used as the raw materials. Perovskite can be avoided only when TiO is used as the cathode.
- (2) Perovskite is mainly produced by electrochemical deoxidation process which is formed by combining Ca^{2+} in the molten CaCl_2 with titanium oxides when the voltage is applied between the electrodes.
- (3) The amount of perovskite produced decreases with the decreasing of oxygen content in the raw material,

the crystal-like morphology of samples gradually weakened.

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