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Study on Carbon Contamination to Prepare Titanium by Electrochemical Process

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Abstract

The carbonate parasitic reaction in the electrolysis process is one of the main reasons caused low current efficiency and serious carbon contamination. However, there are few reports discussed carbon contamination in molten salt electrolysis process. Here, carbon contamination and its harm to molten salt and the final product in FFC molten salt electrolysis process were systematically studied. The results show that when titanium is prepared using carbonaceous material as anode and $CaCl_2$ as molten salt, O^{2-} removed from the cathode oxides are dissolved in molten salt and transferred to the anode, CO/CO_2 gas is released from carbon anode and some CO_2 is dissolved in the $CaCl_2$ molten salt and reacts with O^{2-} to form CO_3^{2-}. Under the condition of the electrolysis, the electrochemical carbon evolution reaction of CO_3^{2-} will take place at the cathode, producing CO or C. Carbon contamination accumulated during electrolysis process, and C precipitated from the cathode was easy to fall into the molten salt because of its fine and porosity. These carbon particles float on the surface of the melt, which will be connected with the cathode and anode, resulting in decreasing of the current efficiency of the process. Carbon contamination of molten salt decreases the recycling efficiency of molten salt and increases the process cost. At the same time, the cathode product titanium easily reacts with the precipitated C to form TiC, which pollutes the metal product and causes the titanium product carbon content to exceed the standard.

Keywords: Carbon Contamination; The Parasitic Reaction; Electrochemical Process

Introduction

Kroll process is a long process and high-cost way to prepare titanium contamination. Many researchers have been searching for new low-cost processes to produce titanium. Twenty years ago, Chen, *et al.* proposed FFC Cambridge process to produce metallic titanium [1], which has received extensive attention. OS process, USTB process, SOM process, etc. have also carried out a lot of research work. In recent years, a lot of research work has been carried out on the improvement of the process of preparing titanium metal by molten salt electrolysis, including the basic thermodynamics of deoxidization, the optimization of process parameters, the course of deoxidization and the mechanism of deoxidization [2-7]. At present the current efficiency of the molten salt electrolysis process is low, and the cost advantage cannot be realized, so the industrial production has not been realized. There are many reasons for the low current efficiency, such as the low deoxidation efficiency of Ti-O solid solution, the parallel reaction in electrolysis process, the formation of conductive carbon layer in molten salt, etc. Carbon contamination is a difficult problem in the process of preparing titanium and its alloys by molten salt electrolysis, which is one of the main reasons for the low current efficiency of the process [8-10]. Some serious carbon contamination has been reported in the process of metal and alloy preparation by molten salt electrolysis with carbon as anode, as shown in table 1. The results show that carbon contamination is inevitable when carbon materials are used as the anodes in the molten salt. Firstly, the erosion and electrochemical reaction of the carbon anode in the molten salt lead to the stripping of the carbon powder [11,12]. On the other hand, CO_2 produced by the discharge of O^{2-} at the anode will be recaptured by O^{2-} in the molten salt to form CO_3^{2-} [8].

In a word, metal carbides are easily formed when carbon anode is used in molten salt electrolysis to prepare metal or alloy. Moreover, the fluffy carbon powder easily falls off and enters the molten salt in the electro-deoxidation process, forming a carbon layer on the surface of the molten salt, which causes the current efficiency reduced, high carbon content of products and the molten salt is polluted. Although the carbon contamination in electrolytic deoxidization process have been mentioned in many literatures, there are few systematic studies on the harm of carbon contamination. Here, carbon formation and carbon contamination in the process to produce titanium using TiO_2 as the raw material by FFC process are systematically studied, and the mechanism of carbon contamination in electrolysis process is clarified

Table 1 Literatures about carbon contanmination during molten salt electrolysis

subject	**Carbon contamination**	**references**
Direct electrochemical production of Ti-10W alloys from the mixed oxides	The surface of the sample is carbon-rich and TiC is detected	Dring, *et al.*[13] (2006)
Electrochemical reduction mechanism of Nb_2O_5	There is NbC on the product surface	Vishnu, *et al.*[14](2013)
The influence of graphite anode and SnO_2-based inert anode on the current efficiency of Cr_2O_3 deoxidation	There is obvious carbon contamination in molten salt, and Cr_7C_3 appears in chromium products	Kilby, *et al.*[15] (2010)
Electrochemical reduction of K_2CrO_4 in molten salt using liquid zinc cathode	Liquid zinc cathode avoids product contamination, but there is still molten salt contamination	Weng, *et al.*[16] (2020)
Preparation of metal Ti in $CaCl_2$-based melt	Carbon powder is floating on the surface of molten salt and TiC in the titanium product is detected.	Suzuki, *et al.*[17] (2018)
Electrolytic reduction of V_3S_4 in molten $CaCl_2$	There is obvious molten salt contamination when electrolyzing V_2O_3	Matsuzaki, *et al.*[18] (2017)
One-step electrochemical preparation of metallic vanadium from sodium metavanadate in molten chlorides	Carbon contamination exists in molten salt and VC is mixed in vanadium products	Weng, *et al.*[19] (2016)
Electrodeoxidation of porous TiO_2 in molten calcium chloride	There is a large amount of carbon powder near the cathode and on the surface of the melt	Schwandt, *et al.*[9] (2009)
K_2CrO_4 electrolysis in $CaCl_2$-KCl molten salt	There is obvious carbon contamination on the surface and section of molten salt	Weng[20] (2017)

Experimental

Firstly, vacuum the furnace and then use high-purity argon gas to wash the furnace several times continuously to ensure the high-purity inert gas in the furnace. After heating to 900 °C and holding for 30 min to stabilize the system, the assembled anode rod and stainless-steel rod without sample were directly inserted into $CaCl_2$ molten salt for pre-electrolysis, which was carried out at a DC voltage of 2.8 V for 2 hours to reduce the impurity interference. After pre-electrolysis, the cathode was replaced by an assembled TiO_2 cathode, which was electrolyzed at a DC voltage of 3.1 V, and a time-dependent current curve was recorded. When the electrolysis was terminated, the samples washed in ultrasonic water bath for 30min and dried. Electrolytic products were analyzed by XRD (XRD: D/max 2500PC, Rigaku, Japan), SEM (SEM, TESCAN VEGA II) and EDS (EDS, Oxford INCA Energy 350) determination.

Results and Discussion

Carbon contamination of the molten salt

As we all know, carbon is the best option of the anode material in molten salt electrolysis, and it is widely used in the mature industrial process of molten salt electrolysis, such as aluminum prepare process using consumable carbon anode. In the process of electrolyzing titanium oxide in $CaCl_2$ based molten salt to produce metal, a layer of carbon black substance is found on the surface of molten salt after electrolysis, as shown in Figure 1[21]. It is seen from the section of molten salt that about one third of molten salt is contaminated and black after electrolysis. After electrolysis, cooled the crucible and washed. Collected the undissolved black substance, XRD results show that the main substance is $CaCO_3$, as shown in Figure 2. The main reason for the formation of $CaCO_3$ is that O^{2-} ions from the deoxidization of the cathode move to the vicinity of the graphite anode to form CO/CO_2. CO_2 dissolved in $CaCl_2$ molten salt reacts with O^{2-}ions removed from the cathode to form CO_3^{2-} ions. Therefore, there is a large amount of $CaCO_3$ on the surface of the frozen salt. At the same time, CO_3^{2-} can be reduced on the cathode by electrons and amount of carbon produced. These carbon falls into molten salt and carbon layer floats on the surface of the molten salt can easily connect the cathode and anode caused short-circuiting and reducing the current efficiency of the process [22]. However, the size of carbon is very small caused it is difficult to collect during washing. That why it is not carbon phase in XRD patterns. It can be seen that CO_3^{2-} formed from O^{2-} and CO_2 and carbon produced in deoxygenation process have serious contamination to the molten salt and decrease the current efficiency of the whole process.

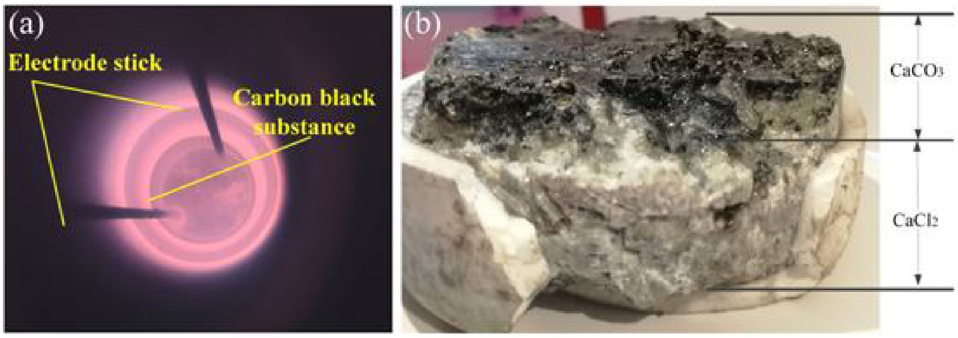

Figure 1: (a) Photo of molten salt surface; (b) Photo of molten salt after electrolysis

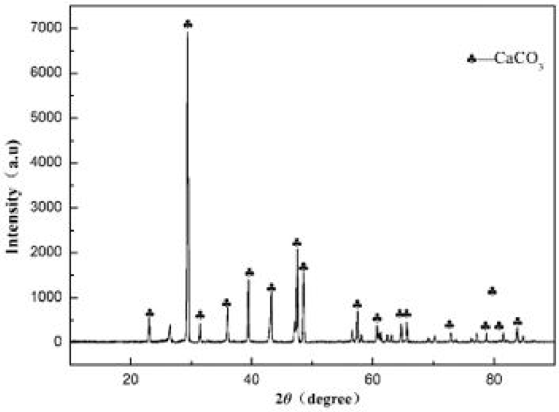

Figure 2: XRD patterns of the black salt

Effect of anode erosion current

Figure 3 shows the appearance of the anode before and after electrolysis in molten $CaCl_2$. It can be seen that the anode in molten salt is obviously consumed after the electrolysis, and the upper part is almost the same as before the electrolysis. Of course, the degree of anode consumption is closely related to the quality of cathode oxide, deoxidation time and deoxidation degree. Here, the anode morphology after electrolysis is given to explain the electrolysis process. Part of the anode mergence in molten salt is consumed by CO and CO_2 produced on the anode. With the increase of the reaction time, the anode consumption increases, the anode diameter decreases obviously, the surface presents honeycomb shape and the surface are rough and uneven. It can be seen that the consumption of carbon anode immersed in molten salt is obvious increase with the electrolysis time. The anode structure is damaged and looks loose and porous due to the reaction erosion, as shown in Figure 3(c). Is there free carbon from the corroded part of the anode falling off and soaking into the molten salt?

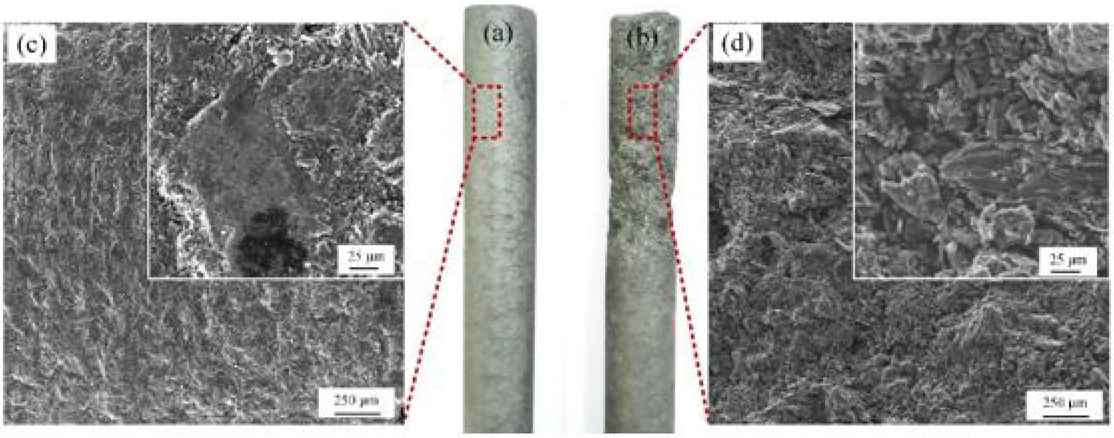

Figure 3: Photos of the graphite anode (a. before electrolysis, b. after electrolysis); SEM image of anode surface (c. before electrolysis, d. after electrolysis)

Whether there is carbon powder entering the molten salt surface or not, different researchers have different understanding. Some people think that the carbon contamination of the molten salt surface is due to the consumption of the anode graphite rod during electrolysis [11,12], which causes the anode to be loose and porous, causing part of the carbon powder to fall off and enter the molten salt. The carbon powder can conduct electricity, causing a loss of the current efficiency. In above study it has also been reported that the formation of CO_3^{2-} in molten salt is caused by carbon falling into the molten salt from the electrochemical precipitation of the cathode. It also causes a black substance to float over the molten salt, contaminating the molten salt and the sample. Hence, carbon floating on the surface of the molten salt is one of the reasons for the low current efficiency of the whole electrolysis process.

In order to determine whether free carbon comes from carbon anode due to the reactive erosion, the relevant systematic studies has also carried out in the earlier period [21,23], the contamination can be verified by adding anode sleeve (Al_2O_3), cathode sleeve, corundum plate to isolate the cathode and anode area. The results show that the carbon contaminating in the molten salt mainly comes from the cathode region and is caused by the CO_3^{2-} ion electrochemical reduction reaction in the cathode region, while the carbon anode has less carbon falling off because of the reaction erosion. Anode carbon shedding is closely related to reaction time, anode consumption and deoxidation rate. Therefore, the key to solve the carbon contamination of molten salt and cathode products is to inhibit the carbon parasitic reaction. By isolating the cathode and anode with a sleeve or a corundum plate, the circuit of the two electrodes and the floating substance on the surface of molten salt can be avoided, and the current loss can be reduced to a certain extent, thus the current efficiency can be improved.

Wang, *et al.* described the mechanism of carbon contamination in the process of electrolytic preparation of metal Cr from K_2CrO_4 in molten salt $CaCl_2$-KCl, and proposed a new anode structure to prevent carbon contamination [20]. The results show that the surface erosion of the anode is much lower than that of the uncoated anode after the same electrolysis time. It is considered that the main reason for the decrease of carbon anode erosion is that the fluidity of molten salt around the anode decreases and the corrosion of the anode decreases.

It is concluded that carbon floating on the surface of the molten salt, which can decrease the current efficiency of the whole process, coming from both of the graphite anode and

CO_3^{2-}. It is the main reason of CO_3^{2-} electroreduction on the cathode.

Formation of TiC on the cathode

Figure 4 shows the morphology and elemental analysis of the sample electrolysis for 10 minutes. Figure 4a shows the appearance of the small particles on the surface of the sample, further phase analysis of the sample also proved that $CaCO_3$ existed in the sample electrolyzed for a short time. Figure 5 is SEM mage of the surface scanning of the sample cross section electrolyzed for 60 min. It can be seen that the sample is obviously layered, the outer layer is dense, the middle layer is loose porous layer, and the inner layer is denser. The main phase of the outer layer is $CaCO_3$.

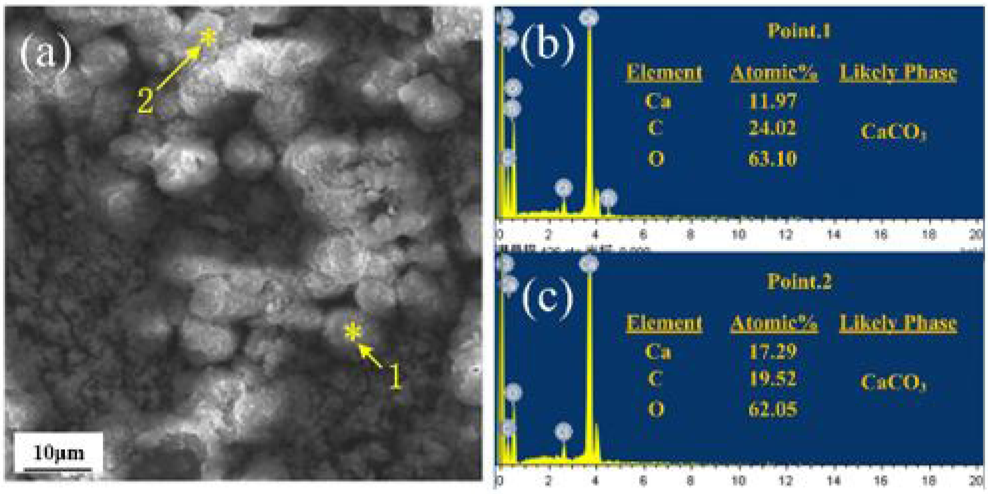

Figure 4: SEM-EDS results of the samples electrolysized for 10 minutes (a SEM image of the sample surface morphology; b. EDS results of point 1; c. EDS results of point 2)

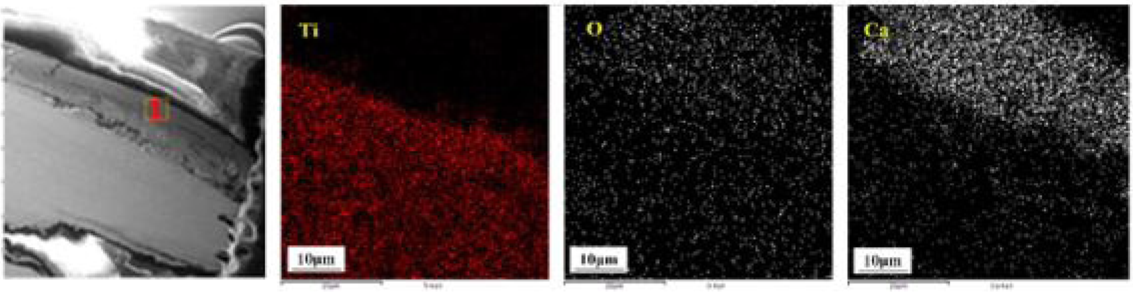

Figure 5: Mophology element and its content of the sample electrolysis for 60min

The results of the discontinuity electrolysis study show that there are a large number $CaCO_3$ formed on the samples surface in the initial stage of electrolysis. It is inferred that carbon in $CaCO_3$ comes from CO_2 in air when washing [24]. CaO in this stage is mainly obtained by the reaction of Ca^{2+} in molten salt with O^{2-} removed from the cathode. There is no titanium metal in cathode and TiC was not found at in this stage.

Before electrolysis, TiO_2 powder was wrapped with the mesh nickel screen and then tied to the cathode with molybdenum wire, as shown in Figure 6a. After electrolysis the cathode is lifted off the molten salt surface and cooled. It is found that the sample is wrapped by a lot of black material, as shown in Figure 6b. The black substance on the cathode surface was analyzed by SEM and XRD. It was found that the main phase is carbon. The material enclosed in the outer layer of the cathode is unconsolidated and porous structure carbon, as shown in Figure 6(c), which is easily fall into molten salt. It was found that the cathode product was completely covered by carbon powder. Where does carbon on the cathode come from? It is found that O^{2-} can capture CO_2 to form CO_3^{2-}in molten salt. CO_3^{2-} can be reduced to C or CO at the controlled electrolysis voltage. There are lots of researches about utilization of carbon and reducing carbon dioxide emissions. It shows that carbon which is product of carbon evolution reaction of CO_3^{2-} wrapped on the cathode. In order to determine whether the product titanium was polluted by carbon, the samples were analyzed by XRD. The results showed that TiC phase appeared in the cathode product, as shown in Figure 7. The electrochemical reduction behavior of parallel side reactions in the cathode will affect the purity of metal products, which is one of the main reasons that lead to the content of titanium carbon exceeding the standard.

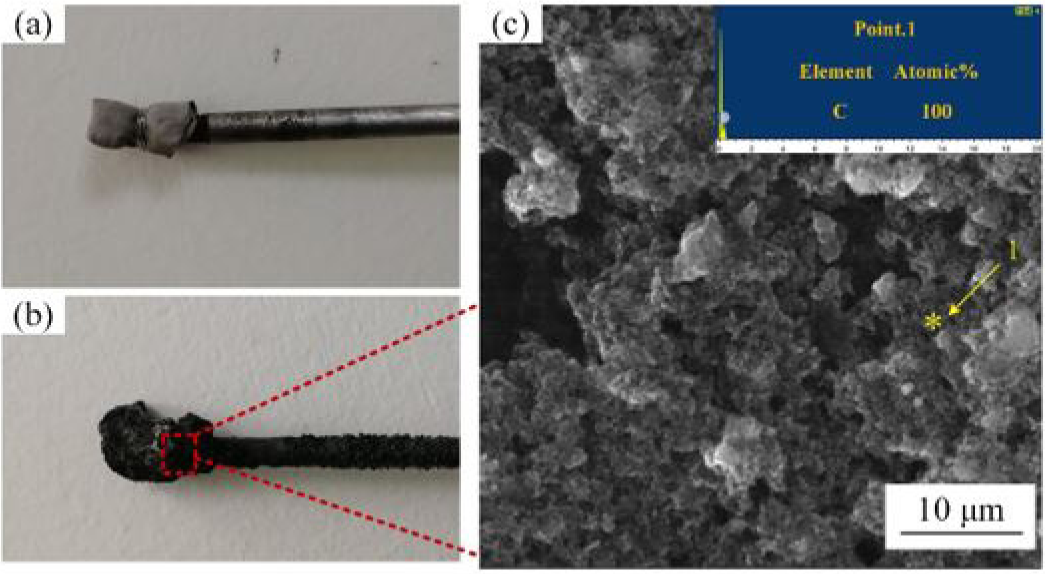

Figure 6: The photo of the cathode (a) before electrolysis; (b) after electrolysis ;(c) SEM image of the cathode surface substance

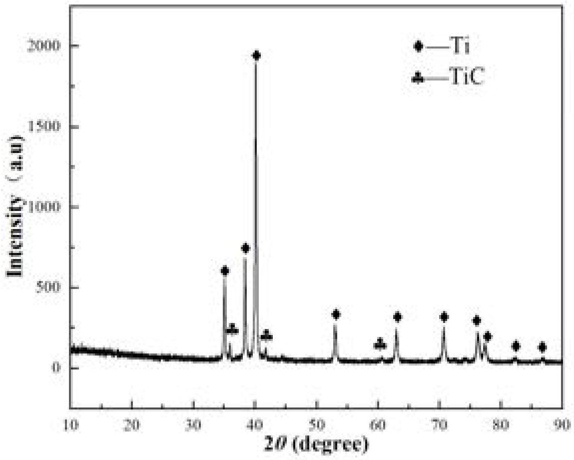

Figure 7: XRD patterns of the sample (a. XRD patterns of the product; b. XRD patterns of the cathode surface substance)

It can be seen that the final titanium product includes some TiC due to carbon evolution of CO_3^{2-} in the electrolysis process. The carbon evolution of carbonate is accompanied by the whole deoxidation process of titanium oxides, which is the main cause of carbon pollution in the final product. Based on the study it can be known that CO_3^{2-} produced form the reaction of O^{2-} and CO_2 in the molten salt are the main reason caused contamination of the molten salt and the final product titanium. Hence, how to promote CO_2 releasing fast from the anode is the key way to decrease carbon continuation.

Conclusion

(1) Both molten salt and the cathode products will be polluted by carbon when the carbon material is used as anode in FFC process.

(2) TiC is formed in the final titanium metal due to the reaction of carbon and titanium metal.

(3) When the carbon is precipitated from the cathode, it forms a fine fluffy product. With the time prolonging in the electrolysis process, the carbon powder on the surface gradually accumulates and it will lead to short circuit of current and decrease of current efficiency.

(4) The main reason for the existence of large amount of $CaCO_3$ in molten salt is that the O^{2-} ion reacts with the CO_2 dissolved in molten salt to form CO_3^{2-} ion, which is always accompanied by the whole process of electrolytic deoxidation.

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