

Direct electrochemical reduction of titanium-bearing compounds to titanium-silicon alloys in molten calcium chloride

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Abstract: Titanium-silicon alloys have been electrochemically extracted from the multi-component titanium compounds in molten calcium chloride electrolyte. Sintered pressed pellets of titanium-bearing compounds served as the cathode, and the electrochemical experiments were systematically carried out at 900 °C, 3.1 V and 1000 °C, 3.8 V using a graphite-based anode and an improved inert-oxygen-ion-conducting membrane-based anode, respectively. The mineral composition and morphology of the products were examined. The current feature and the reaction process are discussed, and the mechanisms involved in the electrochemical reduction of titanium-bearing compounds to titanium-silicon alloys are proposed. Comparison between the graphite- and membrane-based anode systems are also carried out, and the results show that the improved membrane-based anode electrolysis system exhibits higher current efficiency and reduction rate than the graphite-based anode electrolysis system. Interestingly, the other metallic impurities such as Ca, Mg and Al contained in the starting titanium compounds have been partly even completely removed during electro-deoxidation, and the removal mechanism is discussed in the paper too. The experimental results show that titanium-silicon alloy (Ti_5Si_3) can be directly extracted from titanium-bearing compounds using electro-deoxidation technology in molten CaCl_2 . Electrolysis of ~1.5 g titanium compounds using the membrane-based anode system can be finished within 6 h, and the current efficiency reaches approximately 50%.

Keywords: Electrochemical reduction, titanium alloys, molten salt, titanium-bearing compounds

1. Introduction

It is well known that titanium and its alloys possess many attractive properties, but the application of titanium and titanium alloys have been restricted because of their high processing cost. Titanium and titanium alloys are currently produced by the multi-step Kroll process [1] and conventional alloying methods [2,3], respectively. These methods suffer from low efficiency and high energy cost. Consequently, a large number of research initiatives are actively trying to address the problem of high production costs by searching for alternative processes. A number of processes have been developed in recent years [4-15], such as the Fray-Farthing-Chen (FFC) Cambridge process [4], the Ono-Suzuki (OS) process [5] and the solid oxide inert-oxygen-ion conducting membrane (SOM) process [6,14,15]. However, only a few studies have involved in the direct electrochemical reduction of complex multi-component titanium-bearing compounds to titanium and/or titanium alloys [11,13].

Transition metal silicide (Ti_5Si_3) has attracted interest from researcher in recent years [16,17], due to its low density (4.32 g/cm^3), high melting point (2130 °C) and excellent oxidation resistance [16]. Consequently, Ti_5Si_3

has being recognized as a promising candidate for high-temperature structural applications. At present, Ti_5Si_3 is normally prepared by reacting mixed stoichiometric elements of Ti and Si, using conventional powder metallurgy techniques [2] and self-propagating high-temperature synthesis (SHS) [17].

This paper reports the success of applying the SOM process and the FFC process to the extraction of Ti_5Si_3 silicide directly from complex Ti-bearing compounds. Comparison between the two processes is carried out systematically.

2. Experimental

2.1 Preparation of the cathode

The chemical compositions of the Ti-bearing blast furnace slag (TBFS) and high-titanium slag (HTS) are listed in Table 1, the two titanium compounds were mixed together in the appropriate stoichiometric ratio (Ti:Si = 5:3) corresponding to Ti_5Si_3 . The mixtures were ball-milled with anhydrous alcohol for approximately 15 h, the milled powder sized $< 5 \mu m$ with an average particle size of $2.7 \mu m$. Then approximately 1.5 g of the mixtures was pressed to form a cylindrical pellet under a pressure load of 15 Mpa. In order to obtain adequate strength for the electro-deoxidation, the pressed pellet was sintered in air at $1150 \text{ }^\circ\text{C}$ for approximately 2 h. The sintered pellet was finally wrapped with two porous nickel foils and then held together by Mo wires to form a cathode (as shown in Figure 1).

Table 1 Chemical compositions of the titanium-bearing compounds (wt. %)

Compounds	TiO ₂	SiO ₂	CaO	Al ₂ O ₃	MgO	Total FeO _x	MnO
TBFS	21.00	26.57	26.52	13.09	9.98	2.14	0.65
HTS	73.41	5.60	0.85	1.20	2.01	14.73	1.20

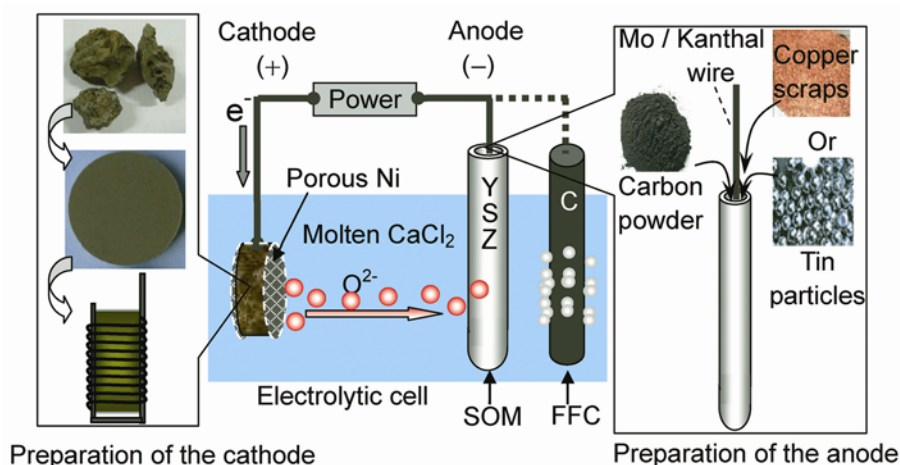


Fig. 1 Schematic illustration of the electrolytic cell and the processes of the fabrication of the electrodes

2.2 Preparation of the anode

The anodes used in our experiments include two different types of anodes, one is a graphite rod as used in the

so-called FFC process [4], and another is an SOM (8 mol. % yttria-stabilized zirconia (YSZ) tube) filled with carbon-saturated liquid copper/tin, and a Mo/Kanthal wire was inserted into the YSZ tube as a current conductor [6,14,15]. The key feature of the SOM-based anode and the relevant details about the SOM process can be found in our previous work [14,15], and also is shown in Figure 1.

2.3 Electro-deoxidation experiments

The schematic illustration of the electrolytic cell is shown in Figure 1, and the schematic illustration of the fabrication of anode and cathode are also inserted in the figure. The two assembled electrodes were placed in a graphite crucible which contained analytical grade anhydrous CaCl_2 as electrolyte to form an electrolytic cell. Ultra-high purity argon gas was continuously led into the crucible to form an inert atmosphere during the electro-deoxidation experiments. A Bio-Logic HCP-803 electrochemical workstation was used to control the experiments and record the current-time curves during the electro-deoxidation process. Systematic experiments were carried out at 900 °C, 3.1 V and 1000 °C, 3.8 V using the graphite-based anode and the SOM-based anode, respectively. After the experiment finished, the cathode was lifted from the electrolyte and cooled naturally under the protection of the inert atmosphere, then washed thoroughly in flowing water and dried in vacuum. More details about this experiment including pre-electrolysis process can be found elsewhere [15].

2.4 Characterization of the cathode products

The mineral composition, morphology and impurity content of the products were carefully examined by means of different methods including X-ray diffractometer (XRD, Rigaku D/Max-2550), inductive-coupled plasma spectroscopy (ICP, Perkin Elmer PE400) and scanning electron microscope (SEM, JEOL JSM-6700F).

3. Results and discussion

3.1 Current feature of the electro-deoxidation processes and mineral composition of the products

In order to achieve relatively high reduction rate, a high cell voltage is necessary, but there is a voltage limit, i.e. the decomposition voltage of the molten electrolyte (CaCl_2 , ~3.2 V). Therefore, 3.1 V was chose as the applied voltage for the graphite-based anode system, and 3.8 V was chose as the applied voltage for the SOM-based anode system. It should be noted that the SOM process can be conducted at applied voltage higher than the decomposition voltage of the molten CaCl_2 [6]. Figure 2a shows the variations of the current during the electro-deoxidation in the two different processes. As can be seen from the figure, the electro-deoxidation of ~1.5 g compounds pellet can be finished within 5-6 h using the SOM process, and the background current is about 300 mA. In contrast, approximately 12-14 h is needed to electro-deoxidize a similar cathode pellet using the FFC process, and the residual current maintains at approximately 500 mA, which is higher than that of the SOM process. The current efficiency of the SOM process is calculated to be approximately 50-60%, it is obvious that the current efficiency and reduction rate of the SOM process is higher than that of the FFC process. The photos of the YSZ membrane inserted in Figure 2a shows that the outer surface (interface of YSZ/molten

CaCl₂) of the membrane is corroded by the molten CaCl₂ electrolyte, whereas the inner surface (interface of carbon-saturated liquid metal/YSZ) of the membrane is unaffected. Figure 2b shows the XRD patterns of the products obtained from the two different processes. As evidence in the figure, the similar mineral composition of the products can be achieved through electro-deoxidation using different processes, only a small amount of Ti₅Si₄ and TiSi₂ are coexisted in the products. It should be noted that the stable phase Ti₅Si₃ would finally form if there is sufficient electrolysis time, as we discussed recently elsewhere [15].

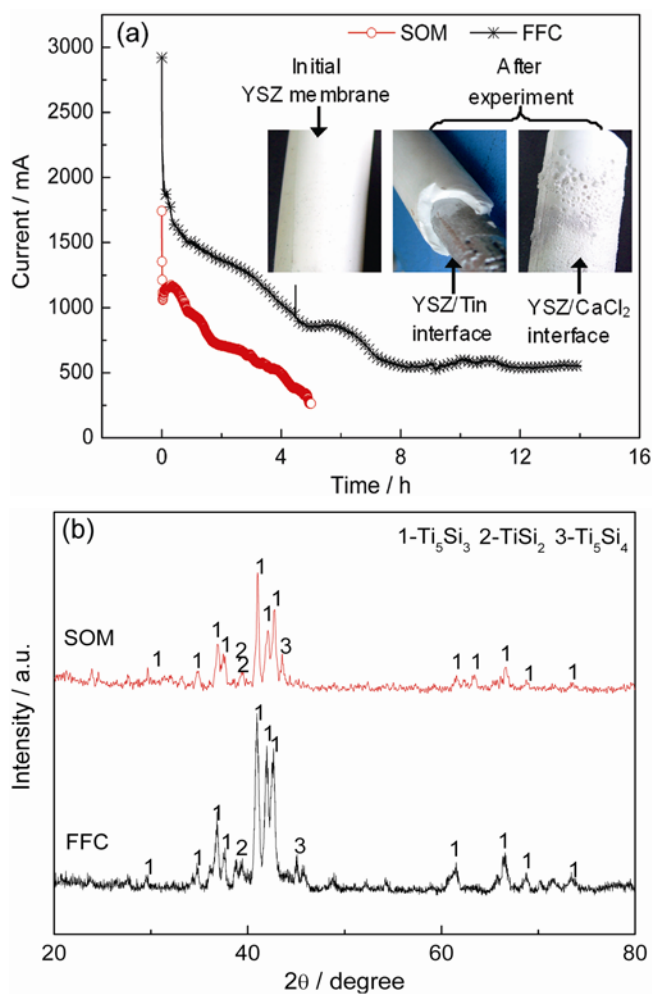


Fig. 2 Current-time curves (a) during the electro-deoxidation in the two different processes and XRD patterns (b) of the products obtained from the two different processes. The inset in (a) is the photos of the YSZ membrane before and after experiment

3.2 Microstructure observations

SEM images of the products produced in the FFC process and the SOM process are shown in Figure 3. The particles in the figure exhibit a good uniformity and their sizes are approximately 0.5-1 μm. The particles in the product of the SOM process are slightly bigger and smoother than that of the FFC process, which might attribute to the different applied voltages and electrolysis times in the two different processes. Moreover, these

particles typically possess smooth and uniform morphology that have begun to interconnect and increase in size. It should be noted that our previous work [15] has shown that the particles generated from electro-deoxidation typically possessing smooth surfaces, which is beneficial to the high-temperature oxidation resistance.

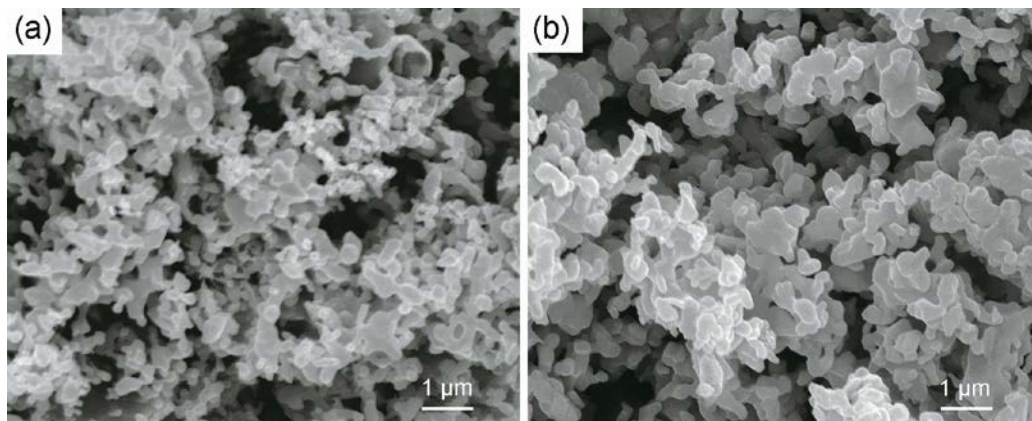


Fig. 3 SEM images of the products obtained from the FFC process (a) and the SOM process (b)

3.3 Impurity element analyses

The typical product produced in the SOM process was used to analyze its impurity content, and the result is shown in Figure 4. As can be seen from the figure, the impurity elements such as Ca, Mg, Al, Fe and O were removed effectively, and their contents lowered to a small level. It should be noted that the removal mechanism involving the elements Ca, Mg and Al was discussed in the previous work [14,15], which mainly involves the physical and chemical properties of these elements, such as their considerable solubilities in molten CaCl_2 , and their melting points are lower than the electrolysis temperature. The significance of the phenomenon that the removal of Ca, Mg and Al from titanium-bearing compounds during the electro-deoxidation is at least two-fold: it can be negative for synthesis of the desired stoichiometric ratio alloys involved these metallic elements, but may also be positive for separation of metallic elements from a multi-component mineral.

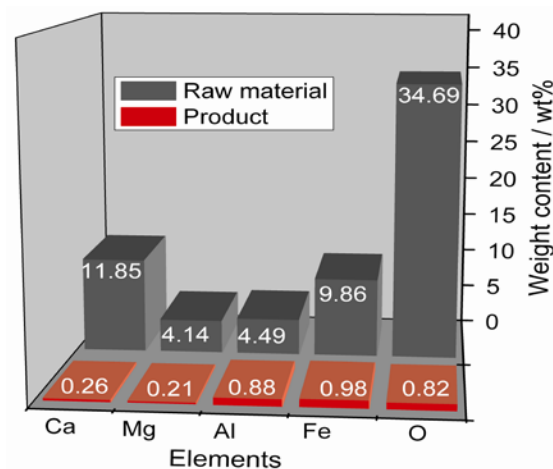


Fig. 4 Impurity elements contents of the typical product obtained from the SOM process

3.4 Mechanism of the electrochemical process

The mechanisms of the electro-deoxidation process involved in electrolysis of single or mixed oxides have been intensively studied [4,5,9,11,13]. There are two representative mechanisms related to these deoxidation processes, as shown in Figure 5a and b, i.e. the electro-deoxidation mechanism [4] and the calciothermy mechanism [5,9]. The electro-deoxidation mechanism describes the reaction: $\text{MeO}_x + 2xe^- = \text{Me} + x\text{O}^{2-}$; the calciothermy mechanism describes the reaction: $\text{MeO}_x + x\text{Ca} = \text{Me} + x\text{CaO}$, then CaO will dissolve in molten CaCl_2 and be reduced to metal Ca in the cathode. In our experiment, the starting materials (as shown in Table 1) contain a considerable number of CaO component, consequently, the calciothermy mechanism is logically presented in the electrolysis process, and this calciothermy process also lead to the removal of CaO component from the solid cathode into molten electrolyte. The two mechanisms coexist in the electro-deoxidation process in this experiment, as shown in Figure 5c. It should be noted that the details about the mechanism of the electro-deoxidation process is discussed elsewhere [15], the reaction procedure is well in agreement with the published three-phase interlines (3PIs) theory [18,19]. The reactions firstly occur at the three-phase-contact points of current conductor/oxide compounds/molten salt, and then expand along the surfaces of the pressed cathode pellet, as schematically exhibited in Figure 5c.

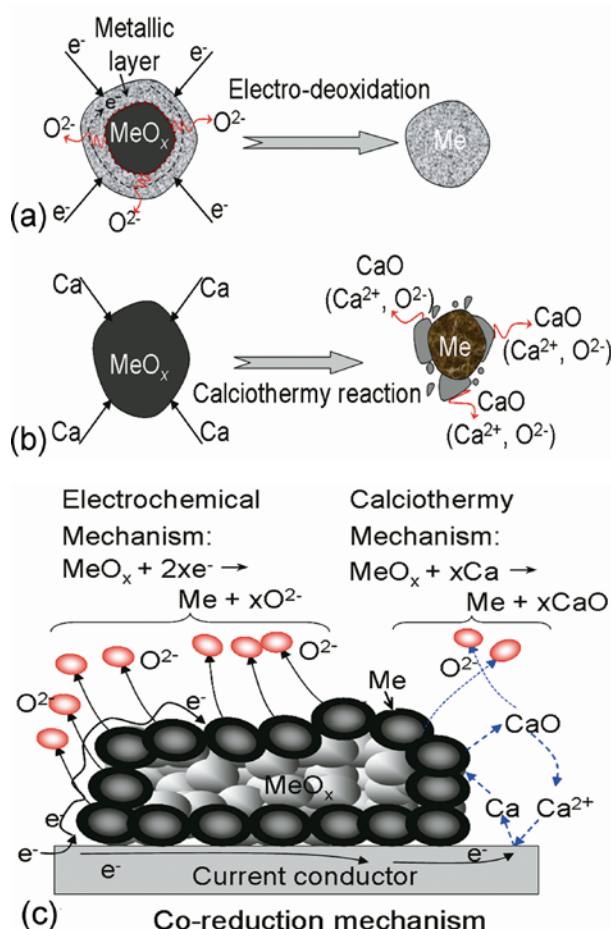


Fig. 5 Schematic illustrations of the electro-deoxidation mechanism (a) and the calciothermy mechanism (b) as well as the co-reduction mechanism involved in this experiment

4. Conclusions

Ti₅Si₃ silicide has been successfully electrochemically extracted from complex multi-component titanium-bearing compounds by two different electro-deoxidation processes in molten calcium chloride. The current-time curves of the two processes and the products obtained from the two processes were compared, and the morphology as well as the impurity content of the products were also examined. The results show that the SOM process possesses higher current efficiency and reduction rate than the FFC process; oxygen and impurity elements such as Ca, Mg and Al can be removed effectively and their contents can be lowered to a small level, and Ti₅Si₃ can be produced as the final product in the cathode. The product Ti₅Si₃ particles typically possess smooth surface and good uniformity. The mechanisms involved in the removal of impurities and oxygen have been roughly discussed in the paper too. The SOM process is a promising alternative process for the extraction of titanium alloys direct from titanium-bearing compounds.

Acknowledgements

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