Direct Extraction of Titanium Alloys/Composites from Titanium Compounds Ores in Molten CaCl$_2$

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Molten salt electroreduction process provides a simple approach for the facile production of alloys and composites. In this work, the solid oxide membrane (SOM)-assisted molten salt electroreduction process has been used to produce titanium alloys/composites directly from complex titanium compounds ores. The Ti-bearing blast-furnace slag, high titanium slag and natural ilmenite were used as raw materials. The SOM-assisted electroreduction process was carried out in molten calcium chloride (CaCl$_2$) at 950–1000°C and 3.8 V. The reaction mechanisms of the electroreduction process including the compounding process, the electroreduction process and the impurity-removal process were discussed. The results indicate that Ti$_5$Si$_3$, Ti$_5$Si$_3$/TiC, Ti$_5$Si$_3$/Ti$_3$SiC$_2$, Fe/TiC and TiAl$_3$ alloys/composites can be directly electrosynthesized from different titanium compounds ores. CaTiO$_3$ and Ca$_2$Al$_2$O$_3$ compounds will be commonly generated as intermediate products during the electroreduction process in molten CaCl$_2$. Impurities elements such as Ca and Mg can be removed during the electroreduction process. In addition, it is suggested that element Fe will be firstly generated during electroreduction process and thus can further improve the electronic conductivity of the ilmenite compounds pellets, Fe/TiC composites can be facilely produced from natural ilmenite.

Keywords: titanium compounds ores, electroreduction, molten salts, titanium alloys, composites

1. Introduction

Titanium and its alloys/composites possess many excellent properties and thus have various applications as structural materials and high-temperature materials, etc.$^{1,2}$ Recently, titanium alloys/composites such as Ti$_5$Si$_3$, Ti$_5$Si$_3$/TiC, Ti$_5$Si$_3$/Ti$_3$SiC$_2$, Fe/TiC and TiAl$_3$ have attracted much interest from researchers due to their unique properties. Ti$_5$Si$_3$ is a promising candidate material for high-temperature applications owing to its high melting point (2403 K), lower density (4.32 g cm$^{-3}$), excellent creep resistance, high oxidation resistance, and capacity to retain high strength at temperature beyond 1473 K.$^{3-5}$ In addition, the toughness and special strength of monolithic Ti$_5$Si$_3$ can be further improved through the addition of second-phase such as TiC. Therefore, Ti$_5$Si$_3$/TiC composites have been investigated, it was suggested that Ti$_5$Si$_3$/TiC composites possess higher fracture toughness compared with the monolithic Ti$_5$Si$_3$.$^6,7$ Besides, it is well known that Ti$_3$SiC$_2$ is a typical MAX phase, which possesses the advantages of both metals and ceramics, such as low density (4.5 g cm$^{-3}$), high strength and modulus (340 GPa), good thermal and electrical conductivity, damage tolerance at room temperature and excellent resistance to oxidation up to 1173 K.$^8-11$ However, the application of Ti$_3$SiC$_2$ was limited because of its poor wear resistance and low hardness.$^{12}$ Many studies have been conducted to improve the hardness and wear resistance of Ti$_3$SiC$_2$.$^{13-15}$ and it was found that Ti$_5$Si$_3$ can be used as reinforce particles for Ti$_3$SiC$_2$ due to their similar thermal expansion coefficients.$^{16,17}$ Ti$_5$Si$_3$/Ti$_3$SiC$_2$ composites exhibit higher hardness and improved wear resistance than pure Ti$_3$SiC$_2$.$^{17}$ In addition, TiC is one of the most suitable reinforcements for iron-based metal matrix composites (MMCs) due to its high hardness and chemical stability.$^{18-21}$ MMCs have many advantages compared with the monolithic metals, and Fe-based TiC composites have also attracted a lot of attention because of their special properties, such as good machinability, excellent wear resistance and strength retained at elevated temperature.$^{18-21}$ Moreover, there is a great deal of interest in developing lightweight structural materials, and Ti-Al intermetallic compounds (such as TiAl, Ti$_3$Al and TiAl$_3$) are a promising new generation of lightweight structural materials for high temperature applications in aerospace field due to their low densities, good mechanical properties and corrosion resistance at high temperature range.$^{22-25}$ TiAl$_3$ is the lightest (the density is 3.3 g cm$^{-3}$) among the Ti-Al intermetallics.$^{25}$ The main application of TiAl$_3$ is as reinforcement for discontinuously reinforced aluminum matrix composites (DRAMCs) because of its low coefficient of thermal expansion, high modulus and good recycling behavior.$^{23}$

Commonly, the above-mentioned titanium alloys/composites can be produced through various methods. For example, Ti$_5$Si$_3$, Ti$_5$Si$_3$/TiC and Ti$_5$Si$_3$/Ti$_3$SiC$_2$ can be synthesized by using the mechanical alloying (MA), self-propagating high-temperature synthesis (SHS) and hot isostatic pressing (HIP) processes, etc.$^{7,17,26-29}$ Fe/TiC composites can be conventionally produced through the powder metallurgy route.$^{30}$ Other methods such as the SHS, thermal plasma synthesis and field-assisted combustion synthesis (FACS) have also been investigated for the production of Fe/TiC.$^{31,32}$ Besides, the methods used to prepare TiAl$_3$ alloy generally include the thermal explosion (TE), vapor-phase magnesium reduction and arc melting, etc.$^{33-36}$ However, all above-mentioned methods are generally suffered from various problems, such as high-energy consumption, high cost and complex process.

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Therefore, searching for new alternative route for the production of titanium alloys/composites with low cost at relatively moderate conditions is still extremely needed.

In 2000, a novel route which is now called FFC Cambridge process was reported, the FFC process can be used to extract titanium metal from solid titanium dioxide in molten salts.\(^{37}\) In recent years, this method has attracted tremendous research interest towards electrochemical extraction of metals/ alloys from their metal oxides precursors in molten CaCl\(_2\) or CaCl\(_2\)-based molten salts.\(^{38,39}\) Generally, this novel method employs graphite-based anode as consumable electrode during the electroreduction process. However, it is known that the use of graphite-based anode will pollute the molten salts and decrease the current efficiency.\(^{39}\) In addition, the cathodic products will also be inevitably contaminated by the graphite-based anode because of the side reactions, e.g., CO\(_2\) + O\(^{-}\) + CO\(_3^{2-}\) and CO\(_3^{2-}\) + 4e\(^{-}\) → C + 3O\(^{2-}\).\(^{40}\) In order to avoid these side reactions, it is important to improve/modify the graphite-based anode.

The assembled yttria-stabilized zirconia solid oxide membrane (YSZ-SOM) electrode can be used as an inert anode to control the molten salt electroreduction process.\(^{41-51}\) During the SOM-assisted electroreduction process, the anodic reaction area can be separated from molten electrolyte by the SOM due to its selective permeability for only oxygen ions. Therefore, the anodic products-related side reactions can be avoided during the SOM-assisted electroreduction process.\(^{44}\)

In our previous work,\(^{44,45,47-51}\) various refractory metals/alloys/composites have been successfully prepared from their corresponding oxides/compounds precursors by using the SOM-based anode electrolysis process. In particular, the SOM process has the potential to be used to extract alloys/composites from complex multicomponent compounds in molten salts.\(^{47-50}\) Therefore, it is reasonable to expect that the SOM-assisted electroreduction process can be used for the electrochemical production of the above-mentioned titanium alloys/composites (i.e., Ti\(_5\)Si\(_3\), Ti\(_3\)Si\(_3\)/TiC, Ti\(_3\)Si\(_3\)/Ti\(_3\)SiC\(_2\), Fe/TiC and TiAl\(_3\)) from complex titanium compounds ores.

In this work, we report the SOM-assisted electroreduction of Ti-bearing blast-furnace slag, high titanium slag and natural ilmenite to produce titanium alloys/composites, i.e., Ti\(_3\)Si\(_3\), Ti\(_3\)Si\(_3\)/TiC, Ti\(_3\)Si\(_3\)/Ti\(_3\)SiC\(_2\), Fe/TiC and TiAl\(_3\). The products obtained from different titanium compounds ores were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX), etc. In addition, the reaction mechanisms including the electrochemical and/or chemical combusting reactions during the SOM-assisted electroreduction process were also discussed.

## 2. Experimental Procedures

### 2.1 Fabrication of the titanium compounds ores mixture cathode

The titanium compounds ores used in this experiment include Ti-bearing blast-furnace slag (TBFS), high titanium slag (HTS) and natural ilmenite. The chemical compositions of these titanium compounds ores are listed in Table 1, and their corresponding phase compositions are shown in Fig. 1(a). It can be seen from Fig. 1 that TBFS mainly consists of perovskite (CaTiO\(_3\)) and diopside (CaMgSi\(_2\)O\(_6\)). HTS is mainly composed of M\(_2\)O\(_3\) (M = Ti, Fe), TiO\(_2\) and CaTi-SiO\(_2\). Natural ilmenite mainly contains ilmenite (FeTiO\(_3\)) and Fe\(_2\)O\(_3\). Obviously, these titanium compounds ores exhibit different colors (TBFS: brown color, HTS: black color, natural ilmenite: black-grey color), as shown in Fig. 1(b). In order to produce the predesigned stoichiometric titanium alloys/composites, the initial titanium compounds ores would be remixed with appropriate metal oxides components such as TiO\(_2\) or Al\(_2\)O\(_3\). The titanium compounds ores, appropriate metal oxides and carbon powder were mixed at the stoichiometric ratios (i.e., Ti : Si = 5 : 3 (75 mass% TBFS and 25 mass% TiO\(_2\)), Ti : Si : C = 6 : 3 : 1 (70 mass% TBFS, 29 mass% TiO\(_2\) and 1 mass% C), Ti : Si : C = 4 : 2 : 1 (71 mass% TBFS, 26 mass% TiO\(_2\) and 3 mass% C), Ti : C = 1 : 1 (94 mass% ilmenite and 6 mass% C) and Ti : Al = 1 : 3 (50 mass% HTS and 50 mass% Al\(_2\)O\(_3\)) corresponding to these predesigned titanium alloys and composites (i.e., Ti\(_5\)Si\(_3\), Ti\(_3\)Si\(_3\)/TiC, Ti\(_3\)Si\(_3\)/Ti\(_3\)SiC\(_2\), Fe/TiC and TiAl\(_3\)). These compounds ores mixtures were firstly ball-milled with anhydrous alcohol and PVB binder for about 10 h, and then about 0.6 g mixtures were pressed under 10 MPa to form porous cylindrical pellets (10 mm in diameter and 1–2 mm in thickness). The

![Fig. 1](image-url)
pressed pellets with porosity of approximately 21.7% have sufficient mechanical strength and thus can be directly used as the compounds pellets cathode in experiments. The pressed multicomponent mixture pellet was sandwiched between two porous nickel foils and fixed on a Fe-Cr-Al alloy wire to form a cathode, as shown in Fig. 2(a). The porous nickel foil with ~95% porosity has a uniform structure and thus can provide more electronic contact points to the pellet during the initial stage of electroreduction process.

2.2 Fabrication of the assembled SOM-based anode
The inert SOM-based anode consisted of a SOM tube (8 mol% yttria-stabilized zirconia (YSZ), 10 mm in diameter and 100 mm in length) filled with carbon-saturated liquid tin, and a Fe-Cr-Al alloy wire was inserted into the tube as the current conductor. The SOM tube was fabricated by the slip casting method, and it has been proved that the SOM tube can maintain excellent stability for a long-time electrolysis process in molten salts.47–50) During the electrolysis in this experiment, approximately 40 mm length of the SOM tube was immersed into the molten CaCl2. The liquid tin filled in the SOM tube was used as a medium to transport oxygen ions from the YSZ/tin interface to carbon, and the carbon saturated in the liquid tin was used as the reductant to react with oxygen \( \text{C} + x\text{O}^{2-} \rightarrow \text{CO}_x + 2\text{e}^- \) \( (x = 1, 2) \). It is noteworthy that the zero carbon emission production process can be realized by the further modification of the SOM-assisted electroreduction process.43) Due to the oxygen ions-conducting selectivity of the SOM, higher current efficiency and reduction speed can be facilely achieved using the SOM-assisted electroreduction process.48)

2.3 Electroreduction experiments
The assemble titanium compounds ores cathode and the SOM-based anode were placed in an alumina crucible which contained anhydrous CaCl2 to form an electrolytic cell. The schematic illustration of the SOM-assisted electrolytic cell is shown in Fig. 2(b). Pure CaCl2 was served as the electrolyte during the electroreduction process. The systematic experiments were carried out at 950–1000°C in a vertical furnace, and ultra-pure argon gas was continuously pumped into the reaction chamber to maintain an inert atmosphere during the electroreduction process. The pre-electrolysis was firstly carried out at 2.5 V for 2 h between the SOM-based anode and a Fe-Cr-Al alloy wire cathode to eliminate the electrochemical-ly-active impurities from the molten CaCl2. Then the electroreduction process was carried out at 3.8 V until the complete electroreduction of the compounds ores pellet cathode. During the SOM electrolysis process, the oxygen component contained in the cathode and the electrolyte can be continually removed through the SOM, as a result, the oxygen concentration can be lowered to a low level. More details about the key feature of the SOM-based anode electrolysis process can be found in our previous work.47–51) A Biologic HCP-803 electrochemical workstation was used to control the electrolysis experiment. After the electroreduction process was completed, the cathode pellet was lifted from molten CaCl2 and cooled in a stream of argon gas. Then the cathode pellet was taken out of the furnace, washed with tap water and dried in vacuum.

2.4 Characterization of the cathodic products
The phase compositions of the partially reduced products and the final products were analyzed using a D8 Advance X-ray diffractometer (Bruker Co. Germany). The phase contents of the final products were analyzed by Rietveld refinement using TOPAS. The microstructure of the products was examined by a JEOL JSM-6700F scanning electron microscope (SEM), and the local elemental composition of the products was determined by energy-dispersive X-ray (EDX) spectroscopy (Oxford INCA EDS system) attached to the SEM. The element composition of the final products was analyzed by Rietveld refinement using TOPAS. The microstructure of the products was examined by a JEOL JSM-6700F scanning electron microscope (SEM), and the local elemental composition of the products was determined by energy-dispersive X-ray (EDX) spectroscopy (Oxford INCA EDS system) attached to the SEM. The element composition of the final products was analyzed by X-ray Fluorescence (XRF).

3. Results and Discussion

3.1 Electrochemical production of Ti5Si3
Ti5Si3 has been electrochemically prepared from the TBFS/TiO2 (75 mass% TBFS and 25 mass% TiO2) precursors using the SOM-assisted electroreduction process at 950°C and 3.8 V (Fig. 3). TBFS used in this work typically contains Ca, Mg and Al impurities, as shown in Table 1. In order to investigate the variation of phase composition during the electroreduction process, the interrupted experiments with different electrolysis times were carried out. The XRD patterns of the products obtained at different electrolysis times are presented in Fig. 3(a). It can be seen that after 1 h electrolysis, the products contain CaTiO3, CaSiO3, Ca12Al14O33, MgAl2O4 and Ti2O3. It is suggested that the
complex compounds (such as CaMgSi2O6) are decomposed to simple oxides/compounds through chemical and/or electrochemical reactions. After being electrolyzed for 3 h, the products contain Ti5Si3, Ca12Al14O33, MgAl2O4 and Ti2O3, which imply that the simple oxides/compounds are reduced to metals/ alloys. Compounds Ca12Al14O33 and MgAl2O4 are relatively stable during the electroreduction process. As shown in Fig. 3(a), a small amount of MgAl2O4 still exists in the products when the electrolysis time is prolonged to 4 h. Finally, Ti5Si3 with trace of TiAl3 have been synthesized after 5 h electrolysis. Generally, the SOM-assisted electroreduction process has relatively fast reduction speed and higher current efficiency compared with the graphite-based anode process.47) The key feature of the SOM-assisted electroreduction process is that the anodic reaction area can be separated from molten CaCl2 by the SOM tube. Therefore, the side reaction caused by the carbon pollution in molten CaCl2 can be avoided. In addition, only O2 can migrate through the SOM tube, therefore, higher voltage (3.5–4.0 V) can be applied during the SOM-assisted electroreduction process.47,48) As a result, the higher current efficiency/reduction speed can be achieved by using the SOM-based anode process. Actually, the current features of the SOM-based anode electroreduction processes for titanium compounds have been described in our previous work.48) Generally, in this work, the typical current during the electrolysis process decreases rapidly from a higher level (around 2000 mA) to a lower level (approximately 800 mA) at the beginning of electrolysis, and then decreases gradually to a background value (~500 mA).

The main reaction mechanism of the electroreduction of TBFS/TiO2 to produce Ti5Si3 can be generally summarized by reactions (1)–(5). Titanium can be generated through the route: CaTiO3/TiO2 → CaO, Ti2O3 → Ti (reactions (1) and (2)). Silicon is formed by the electrochemical reduction of CaSiO3 (reaction (3)). Subsequently, Ti5Si3 is generated by a combination reaction between the formed Ti and Si (reaction (4)). In addition, Ti5Si3 can also be formed through reaction (5).
2TiO₂/2CaTiO₃ + 2e⁻ → Ti₂O₃ + O²⁻/2CaO (1)

Ti₂O₃ + 6e⁻ → 2Ti + 3O²⁻ (2)

CaSiO₃ + 4e⁻ → Si + CaO + 2O²⁻ (3)

5Ti + 3Si → Ti₅Si₃ (4)

6CaSiO₃ + 5Ti₂O₃ + 54e⁻ → 2Ti₅Si₃ + 6CaO + 27O²⁻ (5)

3.2 Electrochemical production of Ti₅Si₃/TiC

Ti₅Si₃/TiC composites have also been electrochemically produced from the TBFS/TiO₂/C (70 mass% TBFS, 29 mass% TiO₂ and 1 mass% C) mixture precursors using the SOM-assisted electroreduction process. The electroreduction process for the TBFS/TiO₂/C mixture was carried out at 1000°C and 3.8 V. Figure 4(a) shows the macrostructures of the initial pressed TBFS/TiO₂/C mixture pellet and the obtained Ti₅Si₃/TiC powder. It is obvious that the initial mixture pellet displays a grey color, and the obtained final Ti₅Si₃/TiC products exhibit a grey-yellow color. After being electroreduced for 5 h, the TBFS/TiO₂/C mixture precursors have been reduced to Ti₅Si₃/TiC (with a trace amount of TiAl₂), as evidenced in Fig. 4(b). The intermediate products obtained at 4 h mainly contain MgAl₂O₄ and Ti₅Si₂, MgAl₂O₄ will be reduced to liquid metal Al and Mg, which can be further removed from the cathodic products. The content of TiS₂ also decreases with the increase of electrolysis time. The main intermediate products obtained at early stage (1–2 h) consist of Ca₁₂Al₁₄O₃₃, CaTiO₃, Ti₂O₃ and CaSi₂O₅. Therefore, based on the XRD analysis, it can be seen that the electroreduction process can be generally divided into two periods, i.e., (i) the compounding/reduction processes, such as the electroreduction of CaSiO₃, Ti₂O₃, CaSi₂O₅ and the formation of Ti₅Si₃/TiC; (ii) the impurities removal processes including the electroreduction of Ca₁₂Al₁₄O₃₃ and MgAl₂O₄ compounds. It should be noted that the two periods are not strictly proceeded, they may coexist in the electroreduction process. Figure 4(c) and 4(d) show the microstructures of the cathodic products obtained at 2 h and 5 h, respectively, and their corresponding EDX spectra were shown in Fig. 4(e) and 4(f), respectively. As shown in Fig. 4(c), the cathodic products obtained at 2 h mainly contain large irregular particles. Besides, elements Ti, Si, C, Ca, Mg, Al, O and Cl are found in the products (Fig. 4(e)), and their corresponding compounds are Ca₁₂Al₁₄O₃₃, MgAl₂O₄, Ti₅Si₃, TiC and CaCl₂. The impurity elements (such as Ca, Mg, Al and O) can be gradually removed with increasing electrolysis time, as revealed in Fig. 4(e) and 4(f). The elements contained in the final products are Ti, Si, C and Al (due to the formation of TiAl₂) (Fig. 4(f)). The obtained Ti₅Si₃/TiC composites particles typ-
ically possess smooth surfaces and uniform morphology (Fig. 4(d)).

The main reaction mechanism of the electroreduction of TBFS/TiO$_2$C to produce Ti$_5$Si$_3$/TiC can be generally summarized by reactions (6)–(10). The reaction mechanism is similar to the electrochemical synthesis of Ti$_5$Si$_3$ as discussed above. Titanium is formed by the reduction of CaTiO$_3$. Silicon is formed by the reduction of CaSi$_2$O$_5$ to form TiSi$_2$, Ti$_5$Si$_3$, Ti$_3$SiC$_2$ and TiC. The main reaction mechanism is expressed by reactions (6) and (7).

\[
\text{(6)} \quad \text{CaSi}_2\text{O}_3 + 8e^- \rightarrow 2\text{Si} + \text{CaO} + 4\text{O}_2^{2-}
\]
\[
\text{(7)} \quad 3\text{TiSi}_2 + 7\text{Ti} \rightarrow 2\text{Ti}_5\text{Si}_3
\]

In addition, Ti$_5$Si$_3$/TiC can also be formed through reactions (9) and (10).

\[
\text{(9)} \quad 12\text{CaTiO}_3 + 3\text{CaSi}_2\text{O}_3 + 2\text{C} + 72e^- \rightarrow 2\text{Ti}_5\text{Si}_3 + 2\text{TiC} + 15\text{CaO} + 36\text{O}_2^{2-}
\]
\[
\text{(10)} \quad 6\text{Ti}_2\text{O}_3 + 3\text{CaSi}_2\text{O}_3 + 2\text{C} + 60e^- \rightarrow 2\text{Ti}_5\text{Si}_3 + 2\text{TiC} + 3\text{CaO} + 30\text{O}_2^{2-}
\]

3.3 Electrochemical production of Ti$_5$Si$_3$/Ti$_3$SiC$_2$

Besides Ti$_5$Si$_3$/TiC composites, Ti$_5$Si$_3$/Ti$_3$SiC$_2$ composites have also been prepared from the TBFS/TiO$_2$C (71 mass% TBFS, 26 mass% TiO$_2$ and 3 mass% C) mixture precursors using the SOM-assisted electroreduction process at 950°C and 3.8 V. The XRD patterns of the mixture cathodic pellets after being electrolyzed for different times are shown in Fig. 5(a). The XRD analysis reveals that the TBFS/TiO$_2$C mixture precursors can be completely reduced to Ti$_5$Si$_3$/Ti$_3$SiC$_2$ within 7 h electrolysis. The main intermediate compounds occurred during the electroreduction process generally contain Ca$_{12}$Al$_2$O$_{33}$, CaTiO$_3$, MgAl$_2$O$_4$, CaSiO$_3$ and Ti$_2$O$_3$. The products obtained at 1 h consist of CaTiO$_3$, CaSiO$_3$, Ca$_{12}$Al$_2$O$_{33}$ and a small amount of Ti$_5$Si$_3$. With prolonging the electrolysis time to 3 h, a large amount of Ti$_5$Si$_3$ and TiC are formed, however, no Ti$_3$SiC$_2$ has been detected in the products. The TiC content gradually decreases with the increase of electrolysis time (i.e., 3 h, 5 h and 7 h, as shown in Fig. 5(a)), and no TiC has been found in the products obtained at 7 h electrolysis. On the contrary, Ti$_3$SiC$_2$ occurs in the products obtained at 5 h and 7 h. It is suggested that TiC plays an important role in the formation of Ti$_5$Si$_3$/Ti$_3$SiC$_2$. The electroreduction process generally proceeds through the route: CaTiO$_3$, MgAl$_2$O$_4$, CaSiO$_3$, Ti$_2$O$_3$, C $\rightarrow$ TiSi, Ti$_5$Si$_3$, TiC, SiC, TiO$_2$, C $\rightarrow$ Ti$_3$Si$_3$, Ti$_3$SiC$_2$. Figure 5(b) shows the typical SEM image of the obtained Ti$_5$Si$_3$/Ti$_3$SiC$_2$, and its corresponding EDX spectrum is shown in Fig. 5(c). Obviously, the obtained Ti$_5$Si$_3$/Ti$_3$SiC$_2$ particles show smooth surfaces and porous structure due to the interconnection of particles. The EDX analysis shows that the final products contain element Al, which is mainly attributed to the formation of TiAl (Ti + Al $\rightarrow$ TiAl, $\Delta G^{950°C}_{\text{f}}$ = −61.27 kJ mol$^{-1}$).

The main reaction mechanism of the electroreduction of TBFS/TiO$_2$/C to produce Ti$_5$Si$_3$/Ti$_3$SiC$_2$ can be generally expressed by reactions (11)–(14). Firstly, Ti$_5$Si$_3$/TiC is formed through the electroreduction process as expressed by reactions (11) and (12). In addition, TiSi can also convert into Ti$_3$SiC$_2$ via the reaction 3TiSi + 2Ti $\rightarrow$ Ti$_3$SiC$_2$. The generated TiC and Ti$_5$Si$_3$ will react with C or SiC to form Ti$_3$SiC$_2$, as expressed by reactions (13) and (14).

\[
\text{(11)} \quad 6\text{CaTiO}_3 + 3\text{CaSi}_2\text{O}_3 + 3\text{C} + 36e^- \rightarrow 2\text{Ti}_5\text{Si}_3 + \text{TiC} + 9\text{CaO} + 18\text{O}_2^{2-}
\]
\[
\text{(12)} \quad 3\text{Ti}_2\text{O}_3 + 3\text{CaSi}_2\text{O}_3 + 3\text{C} + 30e^- \rightarrow 2\text{Ti}_5\text{Si}_3 + \text{TiC} + 3\text{CaO} + 15\text{O}_2^{2-}
\]
\[
\text{(13)} \quad \text{Ti}_5\text{Si}_3 + 4\text{TiC} + 2\text{C} \rightarrow 3\text{Ti}_3\text{SiC}_2
\]
\[
\text{(14)} \quad \text{Ti}_5\text{Si}_3 + 7\text{TiC} + \text{SiC} \rightarrow 4\text{Ti}_3\text{SiC}_2
\]

3.4 Electrochemical production of Fe/TiC

The electroreduction of the ilmenite/C (94 mass% ilmenite and 6 mass% C) mixture precursors using the SOM-assisted electroreduction process has also been systematically carried out in molten CaCl$_2$ at

![Fig. 5](image-url)
1000°C and 3.8 V. Figure 6(a) presents the XRD patterns of the products obtained at different times during the electroreduction of ilmenite/C. The raw materials (ilmenite/C) are composed of FeTiO$_3$ and a small amount of Fe$_2$O$_3$ phases. The XRD pattern of the mixture precursors after being electrolyzed for 1 h shows a significant difference compared with the XRD pattern of the raw materials (0 h), as observed in Fig. 6(a). The main phases of the products obtained at 1 h are CaTiO$_3$ and Fe. Obviously, no iron oxides have been detected. It is suggested that iron oxides can be facilely reduced to iron due to their lower decomposition voltages at 1000°C (FeO: 0.94 V, Fe$_3$O$_4$: 0.92 V, Fe$_2$O$_3$: 0.85 V). The first generated Fe will act as the electronic conductor and further accelerate the electroreduction process because of its good electronic conductivity. Therefore, Fe/TiC can be facilely produced, only 3 h is needed to completely reduce the ilmenite/C pellet to Fe/TiC, as shown in Fig. 6(a). The phase contents of the obtained Fe/TiC composites were determined by Rietveld refinement using TOPAS. As shown in Fig. 6(b), the contents of Fe (PDF# 65-4899) and TiC (PDF# 71-0298) phases are 44.89 mass% and 55.11 mass%, respectively. In order to further investigate the electroreduction of the ilmenite/C precursor, a partially reduced cathodic pellet (after being electrolyzed for 0.5 h) was analyzed using XRD, and the variation of the phase composition from the pellet’s surface to its interior is shown in Fig. 6(c). Obviously, the phase composition of the surface of the pellet mainly consists of Fe and CaTiO$_3$. CaTiO$_3$ can be generated through chemical and/or electrochemical compounding processes. Besides Fe and CaTiO$_3$, Fe$_3$C, Ti$_3$O$_5$ and Ca$_3$Fe$_2$Si$_3$O$_{12}$ are generated in the interior of the cathodic pellet. The small amount of Ca$_3$Fe$_2$Si$_3$O$_{12}$ can be reduced to Fe and CaSiO$_3$. It should be noted that the Si content of the final Fe/TiC product is determined to be 0.91 mass%, which implies that the trace amount of CaSiO$_3$ may loss through the dissolution in molten CaCl$_2$. Actually, the dissolution of CaSiO$_3$ in molten CaCl$_2$ has been confirmed in the previous work and the solubility is determined to be 1.56 mass% at 850°C. However, no obvious results show that the formation of CaSiO$_3$ can affect the production of Ti-Si alloys/composites from titanium/silicon compounds, as shown in Figs. 3–5, these observations are consistent with the previous work. The reason responsible for the loss of Si during the electrolysis of ilmenite/C may be attributed to the different porosities. During the electroreduction of ilmenite/C, Fe can be facilely formed and thus large amount of pores can be generated in the cathode due to the removal of oxygen. These pores provide sufficient channels for molten CaCl$_2$, which means that the generated CaSiO$_3$ can be easily and sufficiently dissolved into molten CaCl$_2$. The generated Fe can react with C to form Fe$_3$C according to the reaction: $3Fe + C \rightarrow Fe_3C$ ($\Delta G_{1000°C}^{\circ} = -2.52 \text{ kJ mol}^{-1}$). Generally, the electroreduction of the ilmenite/C mixture precursors to produce Fe/TiC can be simply expressed as the reaction: $FeTiO_3 + C + 6e^- \rightarrow Fe + TiC + 3O^{2-}$, as schematically shown in Fig. 6(d).

Figure 7 shows the typical microstructures of the products obtained at different times. Obviously, the products obtained at 1 h exhibit a large amount of cubic particles (Fig. 7(a)). On the basis of the XRD analysis (Fig. 6(a)) and the previous work, the cubic particles are CaTiO$_3$. The obtained final Fe/TiC composites particles possess porous and sponge-like structure, as shown in Fig. 7(b). The corresponding EDX analysis (the inset in Fig. 7(b)) measured over the SEM imaging area confirms that the ilmenite/C mixture precursors have...
been completely electroreduced to Fe/TiC.

The main reaction mechanism of the electroreduction of ilmenite/C to produce Fe/TiC in molten CaCl₂ can be generally summarized by reactions (15)–(20), which mainly contains the compounding/electroreduction processes (reactions (15)–(18)). In addition, the small amount of TiFe and Fe₃C generated during the electroreduction process can react with C or Ti to form Fe and TiC, respectively, as expressed by reactions (19) and (20).

\[
\text{FeTiO}_3 + \text{CaO}/(\text{Ca}_2^++\text{O}_2^-) + 2e^- \rightarrow \text{CaTiO}_3 + \text{Fe} + \text{O}_2^- \tag{15}
\]

\[
4\text{FeTiO}_3 + \text{Ca}_2^+ + 10e^- \rightarrow \text{CaTiO}_3 + \text{Ti}_2\text{O}_3 + 4\text{Fe} + 4\text{O}_2^- \tag{16}
\]

\[
3\text{CaTiO}_3 + 2e^- \rightarrow \text{Ti}_2\text{O}_3 + 3\text{CaO} + \text{O}_2^- \tag{17}
\]

\[
\text{Ti}_2\text{O}_3 + 3\text{C} + 10e^- \rightarrow 3\text{TiC} + 5\text{O}_2^- \tag{18}
\]

\[
\text{TiFe} + \text{C} \rightarrow \text{TiC} + \text{Fe} \tag{19}
\]

\[
\text{Fe}_3\text{C} + \text{Ti} \rightarrow \text{TiC} + 3\text{Fe} \tag{20}
\]

### 3.5 Electrochemical production of TiAl₃

TiAl₃ intermetallic has also been prepared from the HTS/Al₂O₃ (50 mass% HTS and 50 mass% Al₂O₃) mixture precursors using the SOM-assisted electroreduction process in molten CaCl₂ at 950°C and 3.8 V. The products obtained at different electrolysis times are analyzed by XRD, as shown in Fig. 8(a). It can be seen that the tetragonal TiAl₃ and the cubic TiAl₃ type compound Ti₅Si₃Al₃ with a small amount of Ti₅Si₃ are generated as the final products at approximately 4–5 h. The intermediate phases are composed of Ca₁₂Al₁₄O₃₃, \(\text{CaTiO}_3\), \(\text{Ti}_2\text{O}_3\) and TiO, which suggest that the reduction pathway for \(\text{CaTiO}_3\) is: \(\text{CaTiO}_3 \rightarrow \text{CaO}, \text{Ti}_2\text{O}_3 \rightarrow \text{TiO} \rightarrow \text{Ti}\). In addition, partially Al₂O₃ can react with CaO to form Ca₁₂Al₁₄O₃₃ through chemical compounding process, \(\text{CaTiO}_3 \rightarrow \text{CaO}, \text{Ti}_2\text{O}_3 \rightarrow \text{TiO} \rightarrow \text{Ti}\). The partially electroreduced products display a dark grey color (Fig. 8(b)-ii). The color of the electroreduced products gradually changes to silvery grey with the increase of the electrolysis time (Fig. 8(b)-ii, iii and iv). The SEM image (Fig. 8(c)) shows that the prepared TiAl₃ particles possess large particle sizes. Elements Ti, Al, Fe and Si are found in the final products according to the EDX analysis (Fig. 8(d)), which further confirms the formation of Ti₅Si₃Al₃ and Ti₅Si₃.

The main reaction mechanism of the electroreduction of HTS/Al₂O₃ to produce TiAl₃ can be generally expressed by reactions (21)–(25). Ca₁₂Al₁₄O₃₃ can be formed through a compounding process (reaction (21)). Then the formed Ca₁₂Al₁₄O₃₃ can be reduced to Al (reaction (22)). The generated Ti reacts with Al to form TiAl₃ (reaction (23)). In addition, TiAl₃ can also be formed through the compounds electroreduction processes (reactions (24) and (25)). It should be noted that these discussed reactions (reactions (1)–(25)) can only be considered as the general guidelines for the electroreduction of the titanium compounds ores.

\[
7\text{Al}_2\text{O}_3 + 12\text{CaO}/(\text{Ca}^{2+}, \text{O}^{2-}) \rightarrow \text{Ca}_{12}\text{Al}_{14}\text{O}_{33} \tag{21}
\]

\[
\Delta G^{\text{θ}}_{950°C} < -150.0 \text{kJ} \cdot \text{mol}^{-1} \tag{22}
\]

\[
\text{Ca}_{12}\text{Al}_{14}\text{O}_{33} + 42e^- \rightarrow 14\text{Al} + 12\text{CaO} + 21\text{O}^{2-} \tag{22}
\]
4. Conclusions

The SOM-assisted electroreduction process has been used to extract titanium alloys/composites from different complex titanium compounds ores including TBFS, HTS and natural ilmenite. The systematic experiments were carried out in molten CaCl$_2$ at 950–1000°C and 3.8 V. The phase composition and microstructure of the obtained products were characterized, and the element composition of the final products was analyzed. In addition, the reaction mechanisms of electroreduction of titanium compounds ores to titanium alloys/composites have been discussed on the basis of the experimental results. The results show that Ti$_2$Si$_2$, Ti$_3$Si$_2$/TiC and Ti$_2$Si$_2$/Ti$_3$SiC$_2$ can be electrochemically produced from TBFS; Fe/TiC can be electrosynthesized from natural ilmenite; TiAl$_3$ can be produced from HTS. The impurities elements Ca and Mg can be removed during the electroreduction process. Element Fe will be firstly generated and then can act as electronic conductor to accelerate the electroreduction process. It is suggested that the SOM-assisted electroreduction process has the potential to provide an efficient and facile route for the production of titanium alloys/composites from the titanium compounds ores. More detailed investigations on the electroreduction of titanium compounds ores to titanium alloys/composites are ongoing and will be reported in due course.

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REFERENCES

9–13.
53) K. Chen, Y. Hua, C. Xu, Q. Zhang, C. Qi and Y. Jie: Ceram. Int. 41
173–182.