

Preparation of titanium by electrochemical reduction of titanium dioxide powder in molten SrCl₂–KCl

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ARTICLE INFO

Keywords:

Electrochemical reduction
SrCl₂–KCl melt
TiO₂ powder
Titanium powder

ABSTRACT

SrCl₂ based molten salt system, i.e. SrCl₂–KCl, was selected to enhance the electrochemical reduction of TiO₂ powder via OS process, utilizing both high solubility of SrO and Sr in SrCl₂ melt and extremely high oxygen affinity of active metal (Sr). In this study, titanium dioxide particles were reduced in a three electrode cell consisting of a sinking Mo cathode in molten SrCl₂–KCl, and the reduction mechanism and reaction pathway of the oxide powder were explored by using cyclic voltammetry and potentiostatic electrolysis methods. Electrochemical tests showed that with small addition of SrO in the melt TiO₂ firstly transformed to SrTiO₃, then reduced to Ti–O solid solution and finally converted to metallic titanium; electro deoxidization of TiO₂ powder initiated only at the early stage of electrolysis and electro metallothermic reduction mechanism dominated the deoxidization reaction pathway. Metallic titanium powder containing 0.58 wt% oxygen with average particle size around 1 μm was produced in the 80 wt% SrCl₂–20 wt% KCl bath at 800 °C with 1 wt% SrO added to the melt.

1. Introduction

Kroll process represents the conventional metallurgical route for extracting some refractory metals from their principal ores, and one of the most representative applications is the production of metallic titanium [1]. However, this method has seriously restricted the extensive application of titanium due to time and energy consuming. Two novel, but similar processes, i.e. FFC Cambridge process [2] and OS process [3], have been developed for extracting titanium, as well as other metals, intermetallic and inorganic materials, via direct electrochemical reduction of solid oxide in molten salt, attracting intensive interest among academia and industry in recent two decades with advantages of easy operation and energy saving [4–8]. Molten CaCl₂ with small addition of CaO, and probably some other chlorides to decrease the melting point, is acted as the electrolyte and carbon is usually used as anode. The applied cell voltage is typical in the range of 2.8–3.2 V, lower than the theoretical decomposition voltage of chlorides but high enough to

obtain the active metal (liquid calcium). The evolution of carbon dioxide and/or carbon monoxide occurs at the anode during electrolysis. The apparent difference of the two processes is the design of the cathode, sintered TiO₂ pellet cathode in FFC process [9,10] and TiO₂ powder containing basket type cathode in OS process [3,8,11], respectively. Meanwhile, two different reduction mechanisms, direct electro deoxidization mechanism and electro metallothermic reduction mechanism, have been proposed and there are still some arguments about whether only one or both mechanisms involved throughout the reduction pathway [6,9,12–15].

The selection of molten CaCl₂ as the electrolyte relies on CaO thermodynamically more stable than the lowest valency oxide of titanium and on high solubility of CaO in molten CaCl₂ [16,17]. Previous studies have showed that deposition of liquid calcium is inevitable in both processes, however, solubility of Ca in molten CaCl₂ is small (2–4 mol%) [18] and density of liquid Ca is much lower than that of CaCl₂ at electrolysis temperature, resulting in deposited liquid Ca covering the surface of the oxide which can block the diffusion pathway or liquid Ca floating on the surface of electrolyte which increases the background current [3,19]. LiCl salt was also investigated for application of electrochemical reduction of TiO₂ to utilize its low melting point, 605 °C [20]. Same issues can emerge owing to much lower density of liquid lithium than that of molten LiCl [21] and minor solubility of lithium in molten LiCl (no

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more than 0.6 mol% at 650 °C) [22]. Intensive studies have been focused on improving process parameters, such as pre forming of cathode pellet, calcium oxide addition and applied cathode potential, to figure out reduction mechanism and reaction pathway in order to increase electrolysis speed, current efficiency and obtain high productivity of FFC Cambridge process [4,9,10,19,23–26]. It should be noted that relative long oxygen diffusive path from the inner of pellet to the melt demands quite long time electrolysis to remove the residual oxygen, restricting the improvement of reduction rate and yield [10,15]. It has been reported that acceleration of reduction rate and abatement of oxygen content were attained by using oxide powder as raw material owing to the diffusion path determined by the original oxide particle size [4,8,27]. However, only few studies have been performed to investigate the reaction pathway of OS process and some arguments still exist [28].

In this study, strontium with higher oxygen affinity compared to calcium was chosen as the active metal for the electrochemical reduction of TiO_2 powder via OS process. The solubility of SrO and Sr in molten SrCl_2 have been measured and estimated the order of 30 mol% [29] and 15 mol% [30] at 1000 °C (see phase diagrams in supplementary data), respectively, which suppose to avoid the problems mentioned above. Due to the high melting point of SrCl_2 , KCl was introduced to the melt system, considering the SrCl_2 –KCl system used to produce strontium by molten salt electrolysis [31]. The mass ratio of SrCl_2 and KCl in this study is 4 in order to obtain low melting point of the melt as well as ensure high solubility of SrO and Sr in the melt. The reduction mechanism and reaction pathway of the oxide powder have been explored by using cyclic voltammetry and potentiostatic electrolysis.

2. Experimental

Anhydrous SrCl_2 , KCl (99.99% purity, Sinopharm Chemical Reagent Co.,Ltd) and SrO , TiO_2 powder (99.6% purity, <2 μm particle size, Aladdin Industrial Inc.) were used as the raw materials. Fig. 1 illustrates a schematic illustration of the experimental arrangement for the cyclic voltammetry and potentiostatic electrolysis

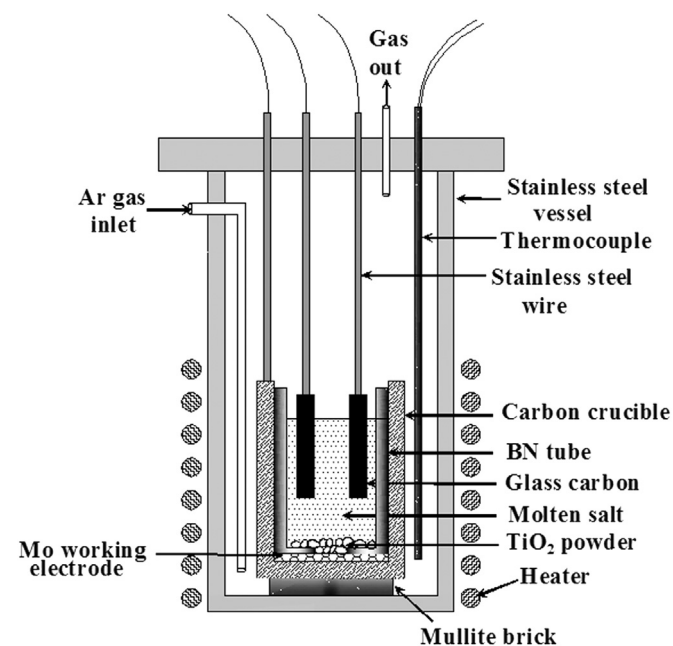


Fig. 1. Schematic diagram for electrochemical experiment.

measurements. A high purity graphite crucible (75 mm in outer diameter, 60 mm in inner diameter, and 120 mm in depth) with an order of molybdenum disk (60 mm in diameter, 3 mm thick) and BN crucible (60 mm in outer diameter, 50 mm in inner diameter, and 100 mm in depth, 10 mm or 50 mm bottom hole in diameter) inside was used as the electrolysis cell. The cyclic voltammetry was conducted within a 10 mm diameter hole on the bottom of the BN crucible, and the diameter was enlarged to 50 mm for the potentiostatic electrolysis. The exposure surface of molybdenum disk was employed as the working electrode and two glassy carbon rods (6 mm in diameter) were acted as the counter electrode and reference electrode, respectively. The electrolysis cell was located in a stainless steel sleeve, which was attached to the floor and was heated externally using an electric furnace in a glove box.

KCl was mixed with SrCl_2 , a mass ratio of 1:4, at room temperature. The mixed salt with a total mass of 300 g dried at 200 °C in a vacuum for 24 h to remove the residual moisture was used as the base electrolyte. Then the electrolyte was filled into the crucible and the apparatus was heated to 400 °C slowly in a purified Ar gas atmosphere, and held at that temperature for 4 h. The furnace was heated to operating temperature, i.e. 800 °C, with a heating rate of 5 °C/min after holding time. Pre electrolysis was conducted at 2.0–2.2 V with a graphite rod (6 mm in diameter) and a Ni–Cr alloy wire (3 mm in diameter) acted as anode and cathode, respectively. The pre electrolysis usually lasted for several hours, and it was stopped when the current reached a low and stable value. After pre electrolysis, these two electrodes were moved out and a certain amount of SrO and TiO_2 were added into the electrolyte according to experiment arrangement, following by two new glassy carbon rods hanged at the upper part of the furnace. Finally, the two glassy carbon rods were immersed into the melt salt after keeping for 1 h. All the electrochemical experiments were conducted using an IM6e electrochemical workstation (Zahner, Germany).

After electrolysis, the two glassy carbon rods were taken out from the melt and cooled down in Ar gas to room temperature. Subsequently, the graphite crucible was rinsed with distilled water to remove the detached carbon dust, and then was putted into distilled water to dissolve the solidified salt. The electrolytic product was collected by filtering using a 400 mesh stainless sieve and was washed in ultrasonic with a sequence of distilled water, acetic acid, distilled water and acetone, then dried in vacuum. The phase compositions of the obtained samples were characterized by X ray diffraction (XRD; Shimadzu/7000) in conventional $\theta/2\theta$ mode using Cu $K\alpha$ radiation and the morphologies were investigated by scanning electron microscopy (SEM; Shimadzu/SSX 550) equipped with an energy dispersive spectroscopy (EDS) for chemical analysis. The content of oxygen in the samples was determined by inert gas fusion infrared absorption method using an LECO TC436 oxygen/nitrogen analyzer.

3. Results and discussion

3.1. Electrochemical behavior of the SrCl_2 –KCl molten salt with SrO and TiO_2 additives

Table 1 lists some possible reactions with their Gibbs free energy change (ΔG^0) and theoretical decomposition voltage (E^0) at 800 °C in electrolytic system when graphite anode is adopted [32]. Based on Table 1, the decomposition voltage of SrCl_2 and KCl are much lower than those of SrO and TiO_2 , which makes it easy to restrict the evolution of Cl_2 gaseous. The decomposition voltage of SrO is located at the same level as those of titanium oxides. Meanwhile, the formation of CO is more preferable than that of CO_2 due to slight more negative decomposition voltage needed to form CO_2 .

Fig. 2 illustrates typical cyclic voltammograms in SrCl_2 –KCl base

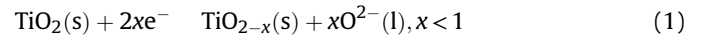
Table 1

Gibbs free energy change (ΔG^0) and decomposition voltage (E^0) of some reactions at 800 °C.

Reaction	ΔG^0 (kJ/mol)	E^0 (V)
2KCl → 2K + Cl ₂	664.0	-3.44
SrCl ₂ → Sr + Cl ₂	669.5	-3.47
SrO + C → Sr + CO	280.1	-1.45
2SrO + C → 2Sr + CO ₂	577.6	-1.50
TiO ₂ + 2C → Ti + 2CO	335.3	-0.87
TiO ₂ + C → Ti + CO ₂	352.7	-0.91
TiO ₂ +1/2C → 3Ti ₃ O ₅ + 1/2CO ₂	67.5	-0.35
2Ti ₃ O ₅ +1/C → 3Ti ₂ O ₃ +1/2CO ₂	88.6	-0.46
2Ti ₂ O ₃ + C → 4TiO + CO ₂	388.8	-1.01
2TiO + C → 2Ti + CO ₂	436.7	-1.13

electrolytic with various SrO and TiO₂ additives for molybdenum electrode. When the melt is just SrCl₂-KCl (Fig. 2(A)), no cathodic reactions are observed, i.e. no Faradaic current flows through the cathode region, until the cathode potential reaches -1.4 V with respect to the glassy carbon reference electrode. It is obvious that the cathodic current increases sharply without appearance of peak (A1) when the cathode potential exceeds -1.4 V. One appropriate explanation of this fact is that metallic strontium, which has been proved to primarily deposit on the cathode from Sr²⁺, K⁺ and/or Na⁺ contained molten salt [33], deposits at the cathode region without diffusion control steps. The inconspicuous anodic peak, A2, at -1.3 V is supposed to correspond to the dissolution of the deposited strontium metal when the potential scan is reversed. Presumably because of high solubility of metallic strontium in strontium chloride, the deposited strontium has completely dissolved into the melt so the anodic peak current remains negative. The evolution of Cl₂ gaseous occurs at +1.4 V (A3) and the current curve fluctuates due to adsorption and desorption phenomenon of the gaseous molecular on the surface of the working electrode. The actual decomposition voltage of molten SrCl₂ from the voltametric result (2.8 V) is slight lower than the theoretical

decomposition voltage, which may be also attributed to high solubility of metallic strontium in its chloride and similar phenomenon is also observed in the CaCl₂ system [22]. Fig. 2(B) exhibits a similar curve, no oxidation current peak and redox current peak, with 1 wt% SrO added to the melt, except the oxidation and redox current peaks for O₂ evolution is observed at +0.4 V (B1, B2). In the 1 wt% TiO₂ containing molten salt, as shown in Fig. 2(C), a small oxidation peak current (C1) is observed during the cathodic scan. During the anodic sweep, the current reaches around 1 A when the potential locates at 0 V (C2) and some separation between the currents passed on the cathodic and anodic sweeps is observed. The phenomenon indicates that a weak electrochemical reaction occurs at this region. The solubility of TiO₂ in SrCl₂-KCl melt was measured using isothermal saturation method in our group and the result demonstrates it was insoluble. In the FFC Cambridge process, it was well accepted that sintered TiO₂ pellet firstly transferred to Magnelli phases (TiO_{2-x}) by removal of a small amount of oxygen through following reaction,



The small oxidation peak is supposed to origin from this reaction. Given that a good electric contact between the current collector and the oxide is the prerequisite for the initial stage of oxygen ionization and the insulating nature of TiO₂, as well as poor contact between TiO₂ powder and electrode, not unexpectedly, the direct electro deoxidization reaction of TiO₂ powder through reaction (1) via OS process is weak and slow. The relative high current during the anodic sweep may be due to the good electrical conductivity of Magnelli phases [2].

It is noteworthy that a much more positive reduction current peak at around -0.2 V (D1) emerges with addition of 1 wt% SrO and 1 wt% TiO₂ simultaneously in the melt, as exhibited in Fig. 2(D). It has been demonstrated that the formation of perovskite phases of various compositions at the early stage of electrolysis are

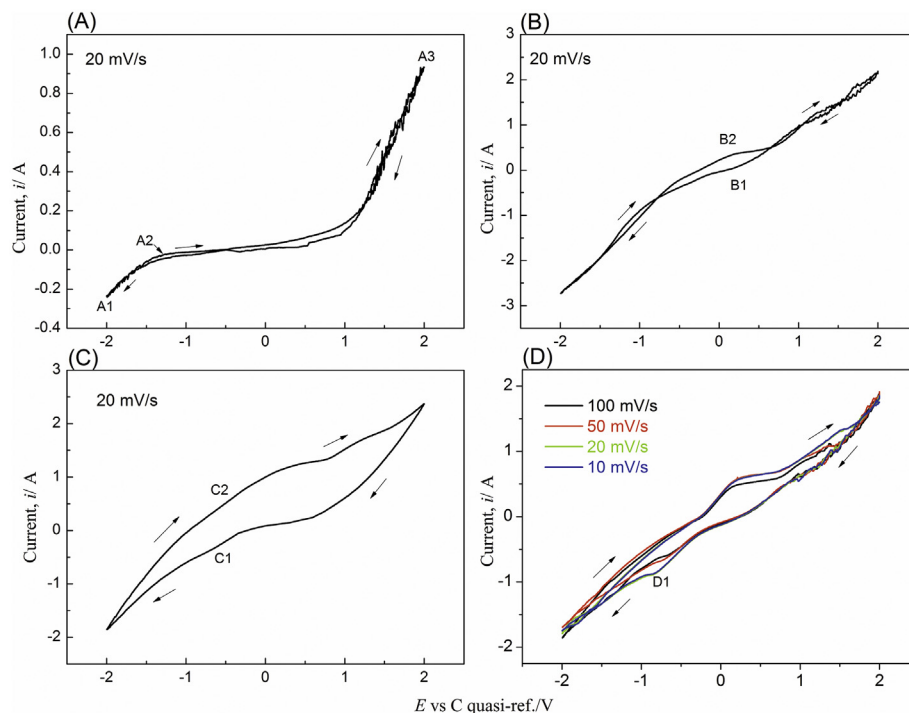
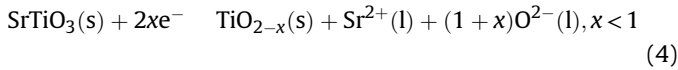
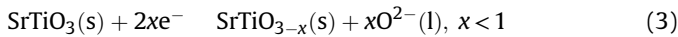


Fig. 2. Cyclic voltammograms of molybdenum electrode in SrCl₂-KCl (80 wt%:20 wt%) base electrolytic with various additives. (A) no additive; (B) 1 wt% SrO; (C) 1 wt% TiO₂; (D) 1 wt% SrO, 1 wt% TiO₂. Temperature 800 °C; working electrode: Mo, reference and counter electrode: glassy carbon.

unavoidable regardless of CaCl₂, LiCl or other chloride molten melts used, suggesting that perovskite phases are general thermodynamically more stable than the corresponding metal oxide [13]. The reaction between SrO dissolved in molten SrCl₂-KCl and TiO₂ is shown by reaction (2), and the Gibbs free energy of Reaction (2) at 800 °C is calculated as 134.95 kJ/mol [32].



Therefore, SrTiO₃ has already existed in the melt before the initiation of electrolysis. Furthermore, the reduction current peak gradually shifts to the more negative voltage with decreasing scan rates from 100 to 10 mV/s. Because SrTiO₃ possesses a good electrical conductivity [34], the reduction peak at 0.2 V can be attributed to the direct electro deoxidization reaction of SrTiO₃ to partially reduced oxides and/or intermediate oxides via reactions (3) and (4).



And the kinetics of these two reactions can be described based on the dynamic three phase reaction boundary models developed by previous studies [19,25]. Another assumption is that strontium titanate dissolves somewhat in the melt and the dissolution electrodeposition process occurs, in analogy with reduction of solid SiO₂ in molten CaCl₂ [35]. Unfortunately, no data was found on the solubility of strontium titanate in molten SrCl₂-KCl. Unlike the stepwise reduction routes following TiO₂-Ti₃O₅-Ti₂O₃-TiO-Ti as reported in the FFC Cambridge process [14], no other reduction current peaks at more negative potential are found in this study. It can be seen from the thermodynamic data shown in Table 1 that reduction of titanium sub oxides to metallic titanium requires larger cathodic polarization than that of titanium dioxide to sub oxides. Meanwhile, high thermodynamic barrier of solid diffusion of oxygen ions from the interior of the oxide particles to the surface combing with poor contact between the oxide particles and the electrode in OS process lead to deposition of active metal at the cathode area, following metallothermic reduction of the oxide powder more attractive at lower cathodic potential. Hence, it can be predicted that electro metallothermic reduction mechanism dominates the deoxidization reaction in OS process when cathode potential is more negative than the deposition potential of corresponding active metal.

3.2. Potentiostatic electrolysis at different cathode potentials

Potentiostatic electrolysis at five different cathode potentials, 0.5 V, 0.8 V, 1.2 V, 1.5 V, 1.7 V, was undertaken to further investigate the reduction mechanism and reaction pathway of the oxide powder in our study. The melt contained both 1 wt% SrO and 1 wt% TiO₂, and at the same time the diameter of the cylindrical working electrode increased to 50 mm to accelerate the reduction rate. Fig. 3 shows the current as a function of electrolysis time (Fig. 3(A)) and the stable current recorded at the final stage is plotted as a function of cathode potential (Fig. 3(B)), respectively. All the current curves at different cathode potentials have similar characteristics, i.e. an initial current peak is observed, then the current decreases rapidly at the first stage of reduction and finally continues to decrease gradually. The initial high current corresponds to transformation of TiO₂ and/or SrTiO₃ to sub oxides, like Ti₄O₇, Ti₃O₅ and Ti₂O₃, of decreasing valence, which is coincident with the reaction sequence for electrochemical reduction of TiO₂ in

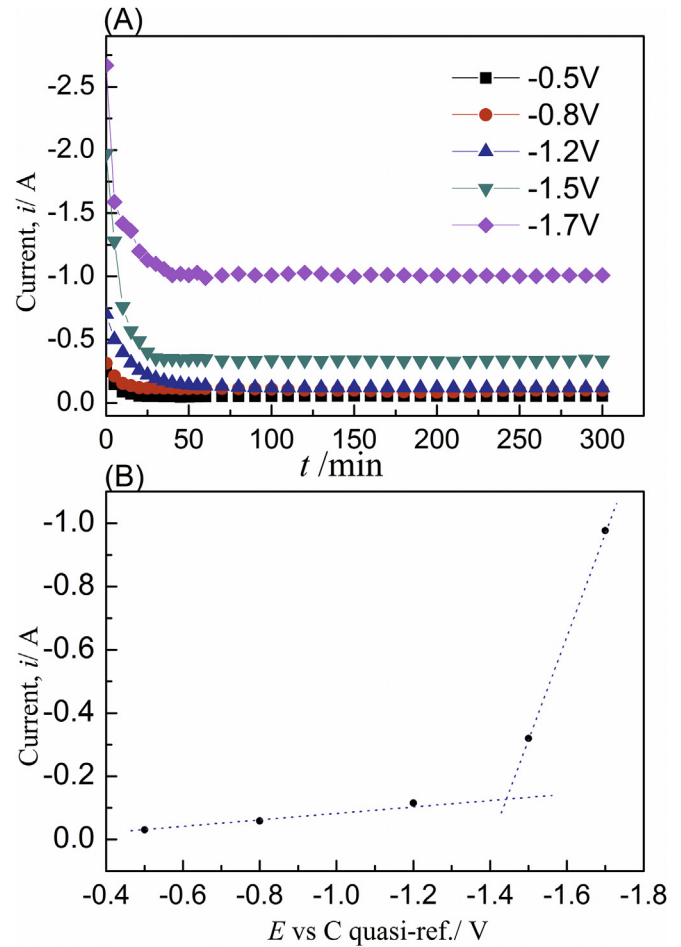


Fig. 3. (A) Chronoamperometry curves of different cathode potentials for Mo working electrode, (B) final stage stable current curves at different cathodic potential in potentiostatic electrolysis experiments. Melt: SrCl₂-KCl (80 wt%:20 wt%) with 1 wt% SrO and 1 wt% TiO₂, temperature 800 °C; reference and counter electrode: glassy carbon.

CaCl₂-CaO molten salt as established by Schwandt and Fray [9]. Because of electro deoxidization reaction of TiO₂ and/or SrTiO₃ to form these sub oxides without major reconstruction of the microstructure, hence, this reaction requires little kinetic barrier [10]. However, diffusion of oxygen ions becomes the rate controlling factor to obtain much lower valency oxides, like TiO, resulting in lower current and slower rate. As illustrated in Fig. 3(b), the final stable current increases extremely slowly before the cathode potential reaches around 1.4 V. However, the current increases sharply once the potential more negative than 1.4 V as shown in dotted lines, corresponding to the deposition of metallic strontium as discussed in last part.

Fig. 4 reveals the XRD patterns of the obtained electrolysis products and Fig. 5 shows the Ti-O-Sr phase stability diagram as functions of partial pressure of oxygen and strontium at 800 °C calculated by HSC CHEMISTRY 8.0 based on minimum Gibbs free energy law [36,37]. As we can see from Fig. 4, at more positive cathode potentials, i.e. 0.5 V, 0.8 V, 1.2 V, only two phases, SrTiO₃ and TiO are detected. A small quantity of SrTiO_{3-x} (*x* ≤ 1) phase was observed, which showed very similar peaks comparing with SrTiO₃, and were not displayed here. The peak intensity of TiO phase increases with the decreasing of cathode potential, indicating that diffusion of oxygen requires larger cathodic polarization. Due to the cathode potentials higher than the deposition potential of

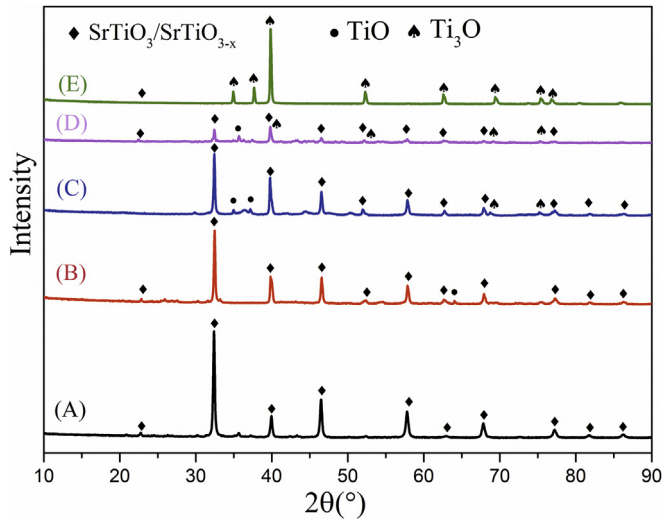


Fig. 4. X-ray diffraction patterns of samples obtained at different potentials for Mo working electrode with electrolysis time 5 h. A: -0.5 V, B: -0.8 V, C: -1.2 V, D: -1.5 V, E: -1.7 V. Melt: SrCl_2 KCl (80 wt%:20 wt%) with 1 wt% SrO and 1 wt% TiO_2 , temperature 800°C ; reference and counter electrode: glassy carbon.

corresponding active metal (strontium), the activity of strontium in the melt remains at a very low level. It can be claimed from Fig. 5 that the reduction pathway follows the $\text{TiO}_2/\text{SrTiO}_3 \rightarrow \text{Ti}_3\text{O}_5 \rightarrow \text{Ti}_2\text{O}_3 \rightarrow \text{TiO} \rightarrow \text{Ti-O solid solution} \rightarrow \text{Ti}$ (route 1), which is an electro deoxidization reaction pathway similar to

FFC process [9]. Upon the cathode potential more negative than the deposition potential of metallic strontium, TiO and Ti-O solid solution (Ti_3O) was obtained as shown in Fig. 4 (D and E). SrTiO_3 phase disappeared after 5 h electrolysis at 1.7 V. During electrolysis, metallic strontium deposits at cathode, then dissolves and well distributes in the melt. When using much more negative cathode potential, more metallic reducing agent will supply into the melt. Due to the high solubility of metallic strontium in SrCl_2 , the activity of strontium in the melt will increase simultaneously. The dissolved strontium acts as reducing agent to reduce the oxide. According to Fig. 5, the reduction pathway supposes to transfer to $\text{TiO}_2/\text{SrTiO}_3 \rightarrow \text{TiO} \rightarrow \text{Ti-O solid solution} \rightarrow \text{Ti}$ (route 2), which is in coincident with the XRD analysis. The formation of Ti-O solid solution after 5 h electrolysis at 1.7 V is that the residual oxygen concentration in the melt is still high enough to achieve thermo dynamic equilibrium between oxygen ions and Ti-O solid solution.

According to the above results, the reduction mechanism of TiO_2 powder in the melt at different cathode potentials is shown schematically in Fig. 6. Firstly, the non conducting oxide was converted to Magnelli phases with the removal of a small amount of oxygen through the reaction (3) and (4) by electro reduction. If the applied cathode potential is higher than the theoretical deposition voltage of metallic strontium, the electro reduction will dominate the whole deoxidization process. The kinetics will be determined by the diffusion of the oxygen ions from the interior to the exterior, and several titanium sub oxides form, shown as route 1. When the applied cathode potential is more negative than the decomposition potential of SrO, metallic strontium deposits, following dissolves into the melt, which acts as an effective reducing agent. The high solubility of SrO and Sr in the SrCl_2 melt enables the continuous

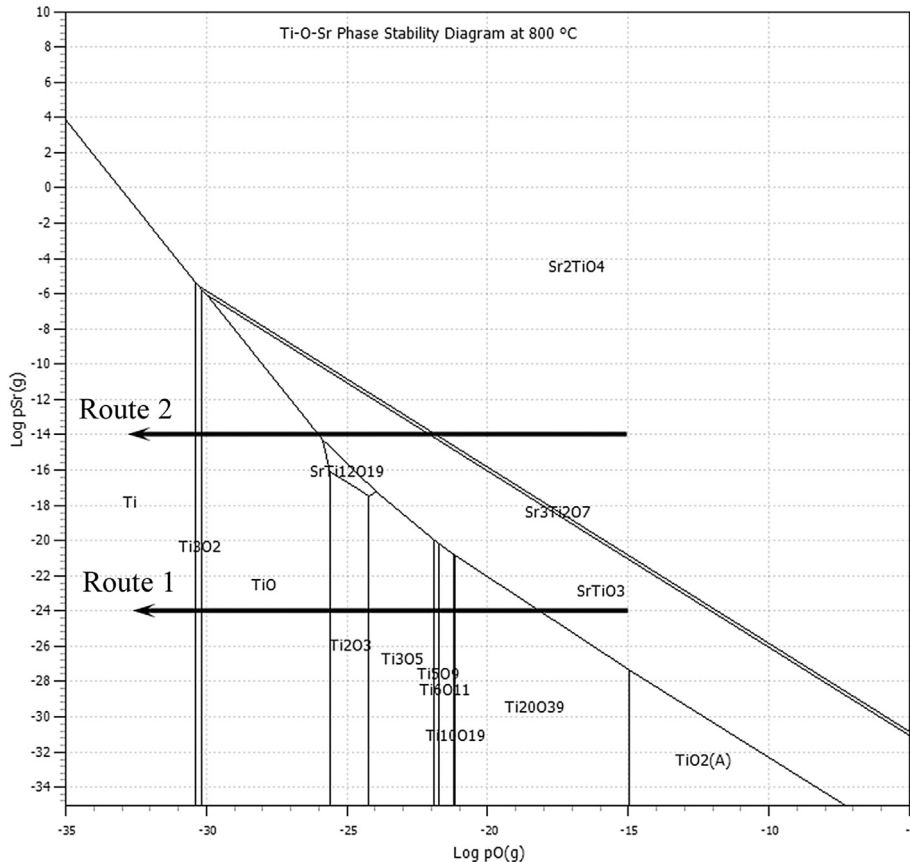


Fig. 5. Ti-O-Sr phase stability diagram at 800°C calculated based on minimum Gibbs free energy law.

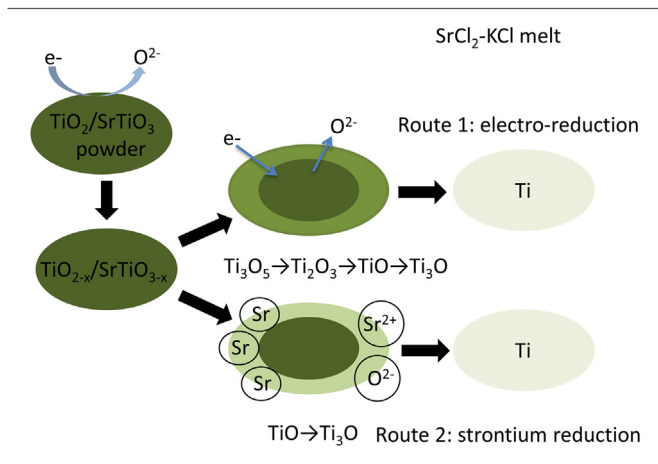


Fig. 6. Schematic diagram of reduction mechanism at different cathode potentials, route 1: electro-reduction without deposition of strontium and route 2: strontium reduction with generation of strontium. Electro-reduction occurs at the early stage regardless of applied potential.

supply of strontium and remove of oxygen ions in the reaction zone. Therefore, TiO_{2-x} and/or SrTiO_{3-x} are directly reduced to TiO , then Ti-O solid solution, and eventually titanium by electro metallothermic reduction following the route 2.

3.3. Electrolysis at 1.7 V with different time

To confirm the reduction mechanism and pathway described above, we further performed electrolysis experiment at 1.7 V for Mo working electrode with different electrolyzing time, 0.5 h, 1.5 h, 4 h, 6 h. Fig. 6 shows the XRD patterns of obtained samples. No other phases were detected, otherwise $\text{SrTiO}_3/\text{SrTiO}_{3-x}$, with 0.5 h electrolysis as demonstrated in Fig. 7(A). Direct electro deoxidization of TiO_2 powder to titanium sub oxides is supposed to happen at the early stage of electrolysis, despite of the cathode potential more negative than deposition potential of metallic strontium as discussed in the last parts. However, those sub oxides,

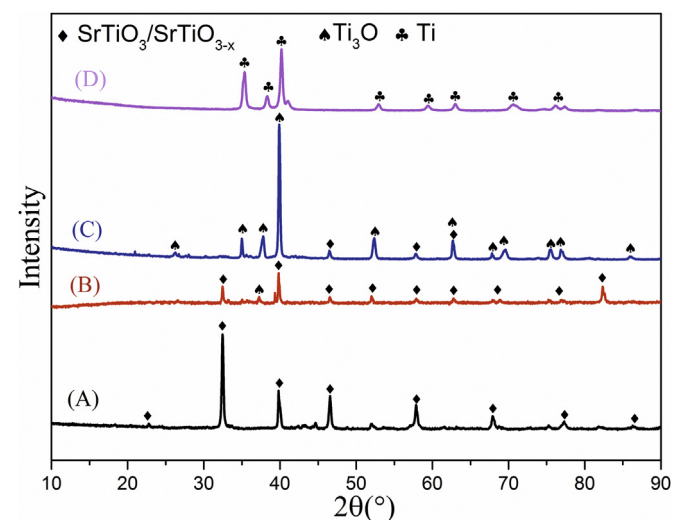


Fig. 7. X-ray diffraction spectra of samples obtained at -1.7 V for Mo working electrode with various electrolyzing time. A: 0.5 h, B: 1.5 h, C: 4 h, D: 6 h. Melt: SrCl_2 -KCl (80 wt%:20 wt%) with 1 wt% SrO and 1 wt% TiO_2 , temperature 800°C ; reference and counter electrode: glassy carbon.

such as Ti_3O_5 , were not detected probably because of the concentration below the analytical limit of XRD. With increasing electrolyzing time, SrTiO_3 just directly transforms to Ti_3O , finally converts to metallic titanium, as shown in the Fig. 7(B)–(D), and this is consistent with the findings discussed in previous part. It is important to note that good control of the oxygen ions concentration in the melt, namely additive content of SrO, has significant influence on the reduction rate from Fig. 5. Relative high oxygen ions concentration favors the decomposition of SrO to provide sufficient metallic strontium as reducing agent, however, transformation of Ti-O solid solution to metallic titanium requires low enough oxygen ions concentration to shorten the electrolysis time to obtain minimal oxygen containing titanium metal.

3.4. Evolution of morphology and oxygen concentration

The obtained electrolytic products after 0.5 h and 6 h electrolysis at 1.7 V was also observed and analyzed by SEM and EDX, as shown in Figs. 8 and 9. After 0.5 h electrolysis, as can be observed in Fig. 8 (a), the dimension of the powder is of the same order of magnitude as that of TiO_2 feedstock. The vast majority of the particles are smaller than $3\ \mu\text{m}$, except for a slight sintering for some particles. The EDS measurement reveals that the content of Sr, Ti, O is close to their stoichiometric ratio in SrTiO_3 . However, the content of O decreased somewhat and of Ti corresponding increased slightly compared to that in SrTiO_3 , suggesting that the particles were partial reduced.

The appearance of the obtained metallic titanium after 6 h electrolysis is shown in Fig. 9. More spherical morphology was found, and fine titanium powder was prepared. It seems that the titanium particles slightly sinter, but the average particle size is just about $1\ \mu\text{m}$, similar to that after 0.5 h electrolysis. The observations demonstrate that there is no apparent growth of the particle size during the electrolysis process despite of the reaction between SrO and TiO_2 . This means the diffusion pathway can be maintained at a considerable short level, depending on the original grain size of oxide particles. The large specific surface area of the particles also provide sufficient reaction sites of strontium reduction to accelerate the deoxidization rate. The EDS result demonstrated that the product consisted of almost pure titanium phase, except that some white particles were shown in the SEM picture and were confirmed as enrichment in oxygen by EDS, which may be a mixture of SrO and other oxygen containing strontium compounds. The undesired impurity oxide contaminations may be attributed to rinsing and acid leaching process thanks to their insoluble character in water and slow leaching rate [38].

The concentration of oxygen in the obtained metallic titanium powder was 0.58 wt% determined by the oxygen/nitrogen analyzer. The results show that micro sized titanium powder with high purity was successfully produced in our study. It can be claimed that the residual strontium oxides contribute to certain amount of oxygen remained in the product. Hence, a more effective post treatment process is required to remove the mixed oxide impurities and also to avoid re oxidation of the obtained product.

4. Conclusions

Metallic titanium with low oxygen content was produced by the electrochemical reduction of titanium dioxide powder via OS process in new molten salt system, i.e. SrCl_2 -KCl with addition of 1 wt% SrO at 800°C . The reduction mechanism and reaction pathway of the oxide powder were detailed studied by cyclic voltammetry and potentiostatic electrolysis methods. It was demonstrated that direct electro deoxidization reaction of TiO_2 powder hardly took place owing to poor contact between the current collector and the oxide

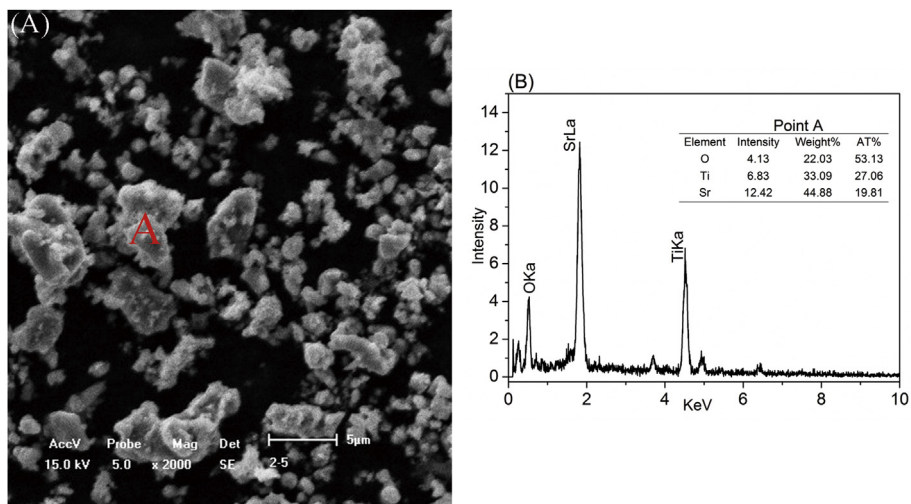


Fig. 8. SEM (A) and EDS at A point (B). The sample was obtained with 0.5 h electrolysis at -1.7 V for Mo working electrode.

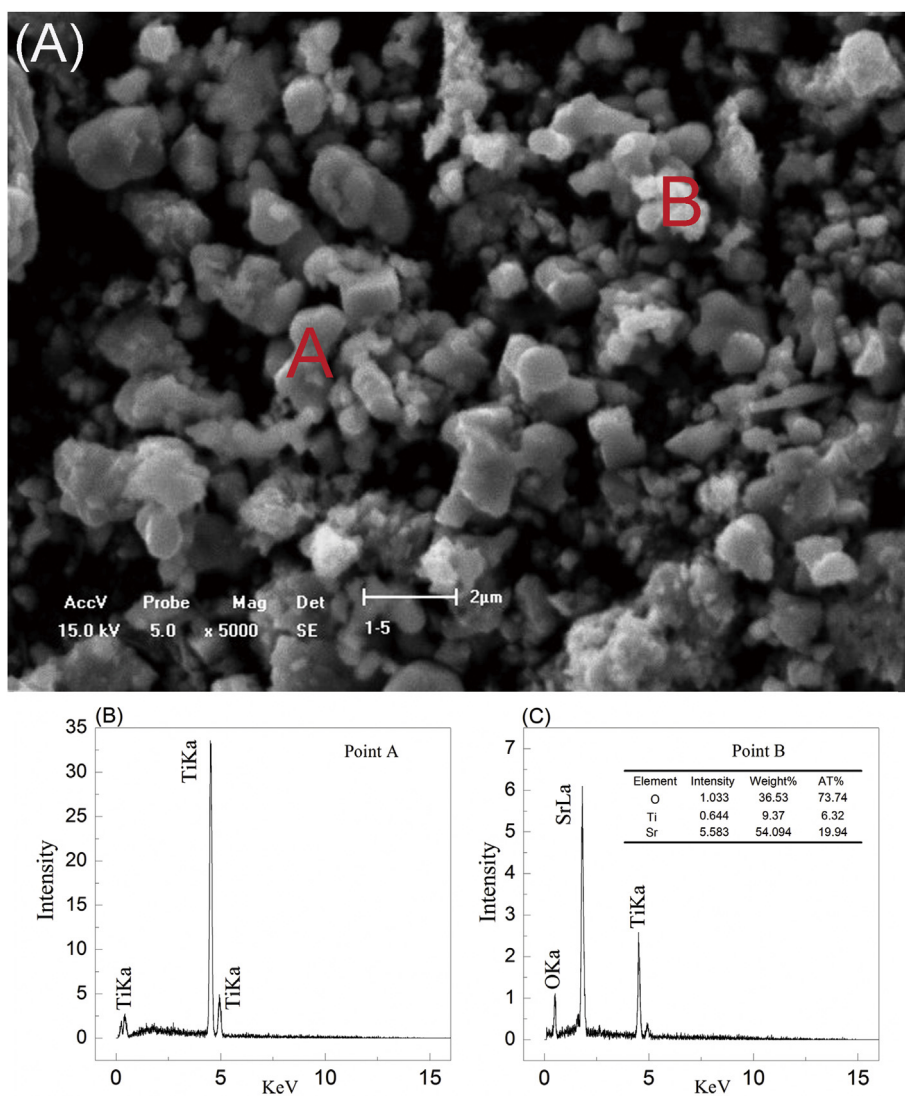


Fig. 9. SEM (A) and EDS at A point (B) and B point (C). The sample was obtained with 6 h electrolysis at -1.7 V for Mo working electrode.

powder. Formation of SrTiO₃ stimulated the electro deoxidation reaction of TiO₂ and/or SrTiO₃ to form sub oxides at the early stage of electrolysis with small addition of SrO in the melt, regardless of the applied cathode potential. Electro metallothermic reduction mechanism was confirmed when the applied cathode potential was more negative than the decomposition potential of SrO. Metallic strontium deposited at cathode region, then dissolved and well distributed in the melt, directly reducing TiO₂ or SrTiO₃ powder to Ti–O solid solution due to strong oxygen affinity of strontium and finally to metallic titanium. Good control of the oxygen ions concentration in the melt, namely quantity of additive SrO, may improve the reduction rate and efficiency. No apparent growth of the oxide particles' size during electrolysis process was demonstrated. The average grain size of obtained metallic titanium powder was about 1 μm, similar to the raw material powder, suggesting that the diffusion pathway depended on the original grain size of the oxide particles.

Acknowledgements

The authors acknowledge the essential discussion from our colleagues and groupmates and the contribution of the Analysis and Testing Center in Northeastern University.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jallcom.2016.05.206>.

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