

Chaoyi Chen, Chong Zhao, Junqi Li and Shufeng Yang*

Direct Extraction of Ti and Ti Alloy from Ti-Bearing Dust Slag in Molten CaCl_2

DOI 10.1515/htmp-2014-0235

Received December 21, 2014; accepted June 8, 2015

Abstract: Using process of solid oxygen-ion conducting membrane (SOM), titanium metal and its alloy can be prepared directly from Ti-bearing dust slag by immersing it in the molten CaCl_2 at $1,100^\circ\text{C}$, which has been proposed by constant voltage of 3.5 V for 2–6 h. The dust slag was ball-milled and pressed into pellets, then employed as the cathode, while the liquid copper, which was saturated with graphite powder and encased in yttria-stabilized zirconia (YSZ) tube, acted as the anode. The effect of forming pressure and electrolytic time on products was analyzed. The results show that the content of titanium increased with electrolytic time and the characteristic morphology presents as granule. Ti–Fe alloy can be obtained from Ti–Fe residue by 6 h electrolysis. For titanium-rich residue, when the forming pressure of pellets decreased from 6 to 3 MPa, only electrolysis for more than 4 h can completely remove the oxygen, and pure titanium is obtained by 6 h electrolysis. Besides, there is an unprecedented finding that the porous cathode is conducive to the removal of impurity elements.

Keywords: Ti-bearing dust slag, titanium, electrolysis, solid oxygen-ion membrane (SOM)

Introduction

At present, titanium sponge is industrially manufactured by Kroll process, which is a complicated, energy-intensive and environmentally harmful process [1, 2]. Besides, in the process of electric furnace smelting and the production of TiCl_4 , many Ti-bearing dust slags such as electric furnace dust (wt3.4%), iron-containing titanium slag (wt1.8%), superfine titanium-rich residue (wt4.6%), chloride residue (wt4.0%) and dust collection residue (wt6.0%) are generated as by-products. The content of

TiO_2 is 40–88 wt% [3, 4] and this means preparing 1 t TiCl_4 will produce about 200 kg waste residues. In the titanium branch in China, thousands of tons of waste residues are generated per year. Just in 2007, the production capacity of TiCl_4 in China reached 35.9×10^4 t, and the iron-containing titanium slag was 6,426 t, the superfine titanium-rich residue was 16,514 t [6]. And the production capacity of TiCl_4 has changed little in recent years. Therefore, how to treat these residues and realize recycling is a worthy subject. At present, the waste residues are directly discharged after simple chemical treatment in a few small-scale manufactures, which leads to enormous waste and pollution. It has been suggested that the residues can be directly poured back into the electric furnace for recycling [3, 5]. But because of the poor activities and gas permeability, the quantity of residues added is limited and the recovery rate is extremely slow. Some people utilized FFC Cambridge process to prepare titanium metal from this Ti-bearing dust slag [6], but the electrolytic reduction rate is slow.

This paper reports our investigation on using SOM process (solid oxygen-ion conducting membrane) to produce titanium metal or titanium alloy directly from different Ti-bearing dust slag, namely iron-containing titanium slag and superfine titanium-rich residue. And the effect of forming pressure of cathode pellets and electrolytic time on the products is discussed.

Experiment

The iron-containing titanium slag (about 1–3 mm in diameter), provided from a titanium plant of Guizhou province in China, was milled for 2 h at a rotation speed of 250 r/min in a high-energy ball-mill, while the superfine (< 0.5 mm in diameter) titanium-rich residue only needs milling for 0.5 h. Then these two kinds of milled slag powder (have the same size of 3–8 μm in diameter) were mixed with binder and compacted into pellets (10 mm in diameter and 5.0 mm in thickness) using 769YP-24B powder sampling machine under pressure of 3–6 MPa and sintered in air at $1,100^\circ\text{C}$ for 2 h. The sintered pellets, enwound tightly with molybdenum wires (0.2 mm in diameter) to molybdenum rods (2 mm in

*Corresponding author: Shufeng Yang, State Key Laboratory of Advanced Metallurgy, University of Science and Technology Beijing, Beijing 100083, China, E-mail: yangshufeng@ustb.edu.cn
Chaoyi Chen, Chong Zhao, Junqi Li, School of Materials and Metallurgy, Guizhou University, Guiyang 550025, China

diameter), acted as the cathode. The liquid copper saturated with carbon powder and filled in SOM tube (yttria-stabilized zirconia (YSZ)) acted as the anode. The YSZ tube can separate the anode from molten electrolyte. Only O^{2-} are able to migrate across and be oxidized at the anode, which reacts with carbon powder in the YSZ tube. Anhydrous $CaCl_2$ was adopted as molten salt and graphite crucible was used as the reactor in a vertical cylindrical tube furnace. The schematic of the cell setup for SOM process is illustrated in Figure 1.

The experiment was performed under the condition with 1,100°C at 3.5 V for 2–6 h, and the highly purified argon as protective gas was purged into the sealed reactor continuously. When the electrolysis was terminated, the cathode was lifted from the molten salt, cooled in the argon stream, removed from the reactor and then washed and dried. The morphology and structure of the electrolytic products were analyzed by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) (JSM-6700F), and the phase was examined by x-ray diffraction (XRD) (D/max22500PC).

The chemical composition of the iron-containing titanium slag and superfine titanium-rich residue in the original waste residue are shown in Table 1. The principle

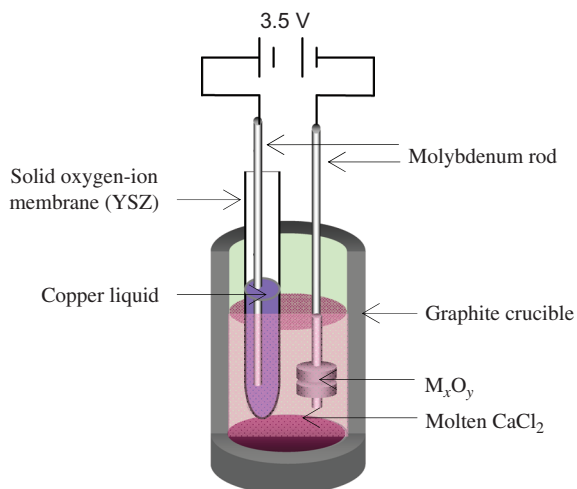


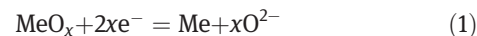
Figure 1: Schematic illustration of SOM experimental apparatus.

Table 1: Chemical composition of the original materials (wt%).

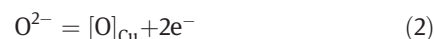
Phase	TiO ₂	TiFe	CaO	MgO	SiO ₂	Al ₂ O ₃	MnO
Fe–Ti residue	46.7	44.7	0.98	0.51	1.79	1.83	3.51
Ti-rich residue	87.3	5.19	0.86	0.42	1.86	1.13	3.24

of the SOM electrolytic process to extract metal, based on the direct electrochemical reduction theory, has been illuminated in detail in previous works [7–9]. The electrodes reaction can be expressed as follows:

At the cathode,



At YSZ/copper interface,



At the anode,



Overall cell reaction,



Results and discussion

Electrolysis of Fe–Ti residue

Figure 2 shows the SEM images and EDX spectra of cross section with electrolytic products for the iron-containing titanium slag pellets pressed at 6 MPa, which are electrolyzed at the operation temperature of 1,100°C for different times (2, 4 and 6 h). It can be seen clearly that the product structure becomes loose with the increase of electrolysis time, and the morphology converts from massive to graininess after electrolysis for 6 h. The loose structure will be the advantage to remove the melts inside the pellet.

When the time of electrolysis was 2 h, the structure of product was more compact and the obvious peaks of O, Cl and Ca were measured by SEM and EDX (see Figure 2(a)). The EDX analyzed results of selected typical area are also given in Table 2. When electrolyzed for 4 h, the O and Ca peaks declined clearly, and the Cl peak disappeared (see Figure 2(b)). When the electrolytic time increased to 6 h, the morphology structure of cathode products presented typical sponge morphology (see Figure 2(c)), in which the O peak disappeared and the main peaks were Ti, Fe and a small amount of other impurity elements such as Si, Ca and Mn. From the results mentioned above, it is found obviously that the O in cathode pellets can be removed completely in 6 h. This may be explained as follows: the YSZ membrane was used to separate the anode from the

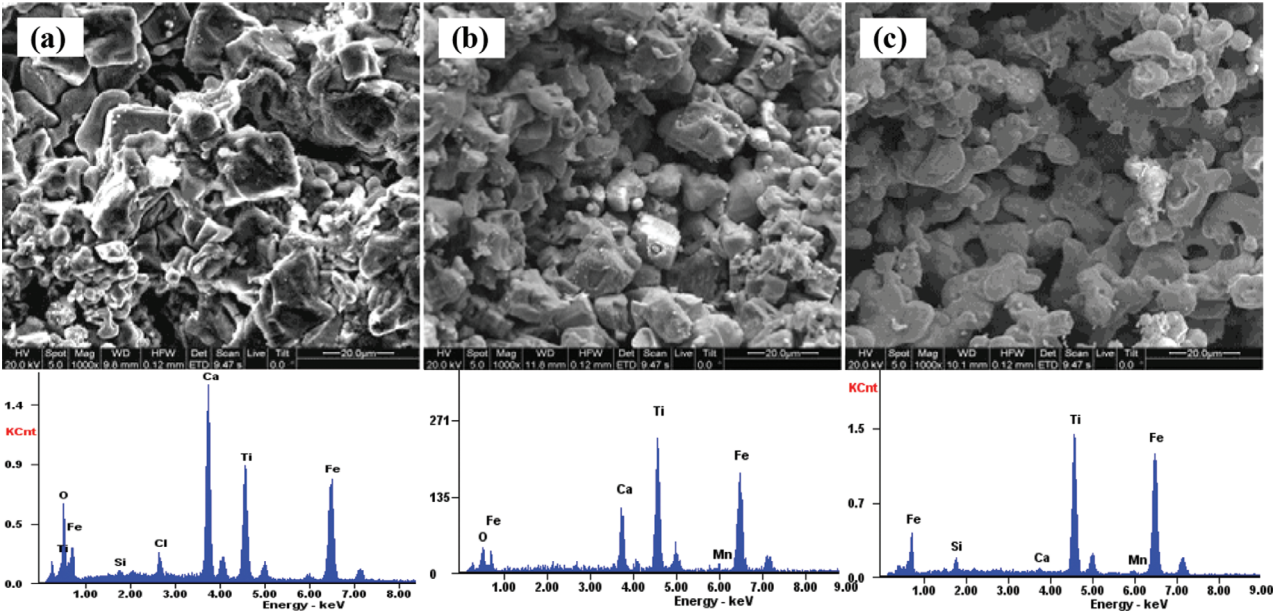


Figure 2: SEM images and EDX spectra of the Fe–Ti residue pellets after electrolysis for different times: (a) 2 h, (b) 4 h and (c) 6 h.

Table 2: EDX results of the electrolytic products for Fe–Ti residue pellets after different times (wt%).

Electrolysis time (h)	Ti	Fe	Ca	Mg	Si	Al	Mn	O	Cl
2	19.23	34.51	20.18	0	0.47	0	0	23.79	1.83
4	30.10	48.16	9.24	0	1.01	0	2.03	10.36	0
6	32.86	62.82	0.68	0	2.14	0	1.50	0	0

ionic melt and thus a higher potential can be obtained between the anode and cathode, which means a larger overvoltage. Therefore, SOM process has predominance compared with the FFC process at the rate of reduction [9].

From Table 2, the metallic impurities of Mg and Al were completely removed during electrolysis, and these observation results agreed well with those of Ma et al. [6]. It can also be found that the Ti and Fe content increased gradually with electrolysis time. CaTiO_3 , FeTiO_3 and titanium protoxide formed first in the process of electrolysis. Then, due to the decomposition voltage of FeO is low, Fe is reduced preferentially, which increases the conductivity of the cathode and contributes to the reduction of titanium dioxide [6]. The atomic ratio of Fe:Ti is 1.64:1 when electrolysis time is 6 h. The corresponding XRD pattern is shown in Figure 3, in which the main alloys are TiFe and

TiFe_2 , and a few diffraction peaks of metallic Ti and Fe. This result is in accord with the EDX results.

Electrolysis of titanium-rich residue

Pressure at 6 MPa

Figure 4 shows the SEM images and EDX spectra of products from titanium-rich residue at 6 MPa pressure after 2, 4 and 6 h electrolysis, respectively. It can be found that the product has a compact structure for electrolysis of 2 h, which has obvious peaks of O, Cl, Ca (see Figure 4(a)). The EDX results in Table 3 show high content of O (29.2%), Cl (11.16%) and Ca (21.37%). The content of Ca can be reasonably attributed to the Ca in melts participated in electrochemical reaction to form perovskite during the initial electrolysis [10]. The XRD spectrum shows the low valence oxides of Ti, CaTiO_3 , CaCl_2 and

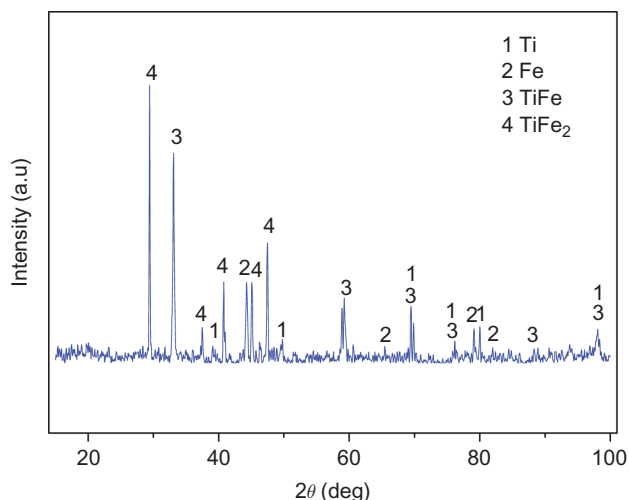


Figure 3: XRD spectra of the Fe-Ti residue after electrolyzing 6 h.

FeTiO₃. CaCl₂ is caused by the compact structure of product which makes it difficult to remove the melts from inside of the sample.

The content of O, Cl and Ca in product decreased greatly after 4 h electrolysis, but the content of Ti increases. When the electrolysis time is prolonged to 6 h (see Figure 4(c)), the morphology structure of product is uniform, and typical spongelike metallic powders with particle size around 1–4 μm are also obtained. The content of impurities further declined and with no detectable oxygen content in products.

Pressure at 3 MPa

For the direct electrochemical reduction, the microstructure of cathode pellet is a crucial factor to influence the rate of reduction, which is mainly represented by the porosity and particle size of pellets. That is to say, the bigger the porosity and smaller the particle size, the higher the electrochemical reduction rate [11]. During the preparation of the cathode, once the sintering temperature and time are given, to a certain degree, the range of particle size and porosity of pellets are mainly determined by forming pressure [12]. From Figure 5 it can be seen that the particle size is smaller at the pressure of 3 MPa, while the porosity is bigger. The purity of electrolytic cathode pellets pressed at 3 MPa should be researched as follows.

Figure 6(a) shows the SEM images and EDX spectra of reduction products for titanium-rich residue with pellets pressed at 3 MPa after electrolysis for 4 h. The microstructure is of sponge morphology and similar to Figure 4(c). The main EDX peaks are of Ti and a little Si, and the content of Ti is as high as 98.98% (see Table 3). When the electrolysis time is prolonged to 6 h, the metallic Ti is sintered further and recrystallized, display the uniform granules and porous morphology (see Figure 6(b)). This structure is advantageous to eliminate the melts and other impurities inside electrolyzed pellet. The characteristic morphology of the nodular Ti metal is similar to that of

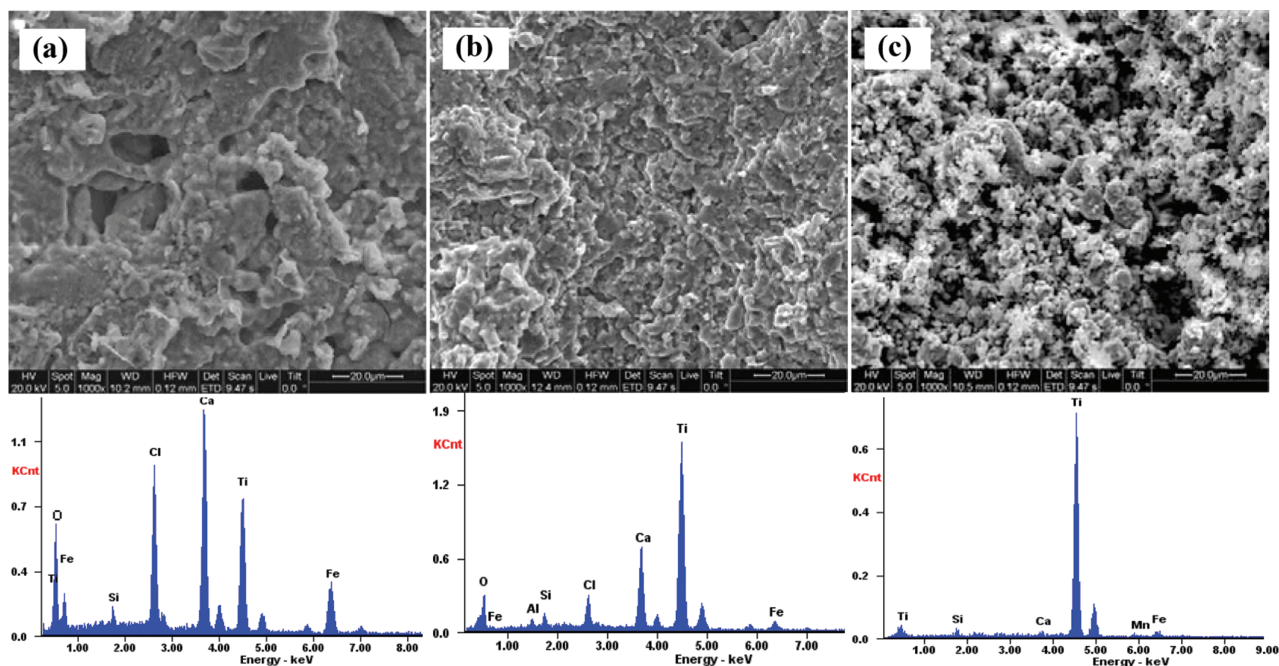
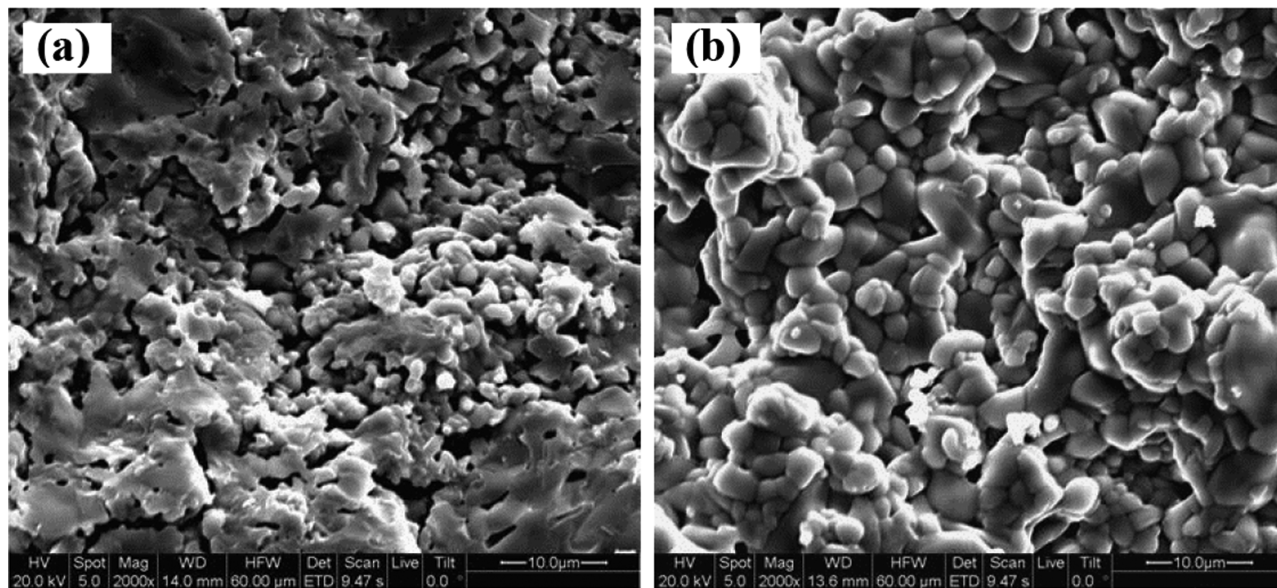


Figure 4: SEM images and EDX spectra of the electrolytic conducts at 1,100°C for different times: (a) 2 h, (b) 4 h and (c) 6 h. Pellets were pressed with 6 MPa.

Table 3: EDX results of the electrolytic products for titanium-rich residue under different conditions (wt%).

Electrolysis time	(h)	Ti	Fe	Ca	Mg	Si	Al	Mn	O	Cl
Pressure at 6 MPa,	2	20.67	16.40	21.37	0	1.19	0	0	29.20	11.16
	4	49.76	4.09	13.52	0	1.39	1.11	0	26.45	3.69
	6	88.57	6.03	1.30	0	1.17	0	2.33	0	0
Pressure at 3 MPa,	4	98.98	0	0	0	1.02	0	0	0	0
	6	100	0	0	0	0	0	0	0	0

**Figure 5:** SEM images of the cathode pellets of titanium-rich residue after sintering at 1,100°C for 2 h. (a) Pressure at 3 MPa and (b) pressure at 6 MPa.

the reduction product from TiO_2 [13]. Only Ti peak can be found by EDX. The result in Table 3 also reveals that the content of Ti is up to 100%. XRD (Figure 7) and EDX analyses proved that the electrolyzed pellet is pure Ti metal.

The XRD analysis in Figure 6 presents that there are a few unidentified diffraction peaks for 4 h electrolysis. However, there are only Ti metal peaks for 6 h electrolysis. Increasing the electrolysis time can remove the impurities in pellets to obtain Ti metal.

Analysis of impurities behavior

It can be found that there are absent Mg and Al impurities in products from the data in Table 2. From Table 3, all the impurity elements are completely removed during electrolysis, especially under the pressure of 3 MPa condition to electrolyze for 6 h. This unprecedented finding

is scientifically interesting and commercially important, which has not been reported in previous literatures. Meng Ma et al. [6] agreed that Al and Mn could be partly or completely removed during the electrolysis of titanium-rich slag using FFC process, and although the TiO_2 and Al_2O_3 were mixed to electrolyze in the laboratory, the loss of Al was observed. They also suggested that the interactions between different metal atoms were important factors effecting the final composition of an alloy. The concentration of the metallic elements must come up to a certain extent for forming alloy. Another report [14] pointed out that the reduction of solid cathode in molten CaCl_2 has been known to be capable of removing some non-metallic elements but alloying the metallic elements [15].

The experimental results show that the nonferrous metal elements, even all the impurity elements, can be removed under the optimum formation pressure of pellets. The reasons should be considered that some metal

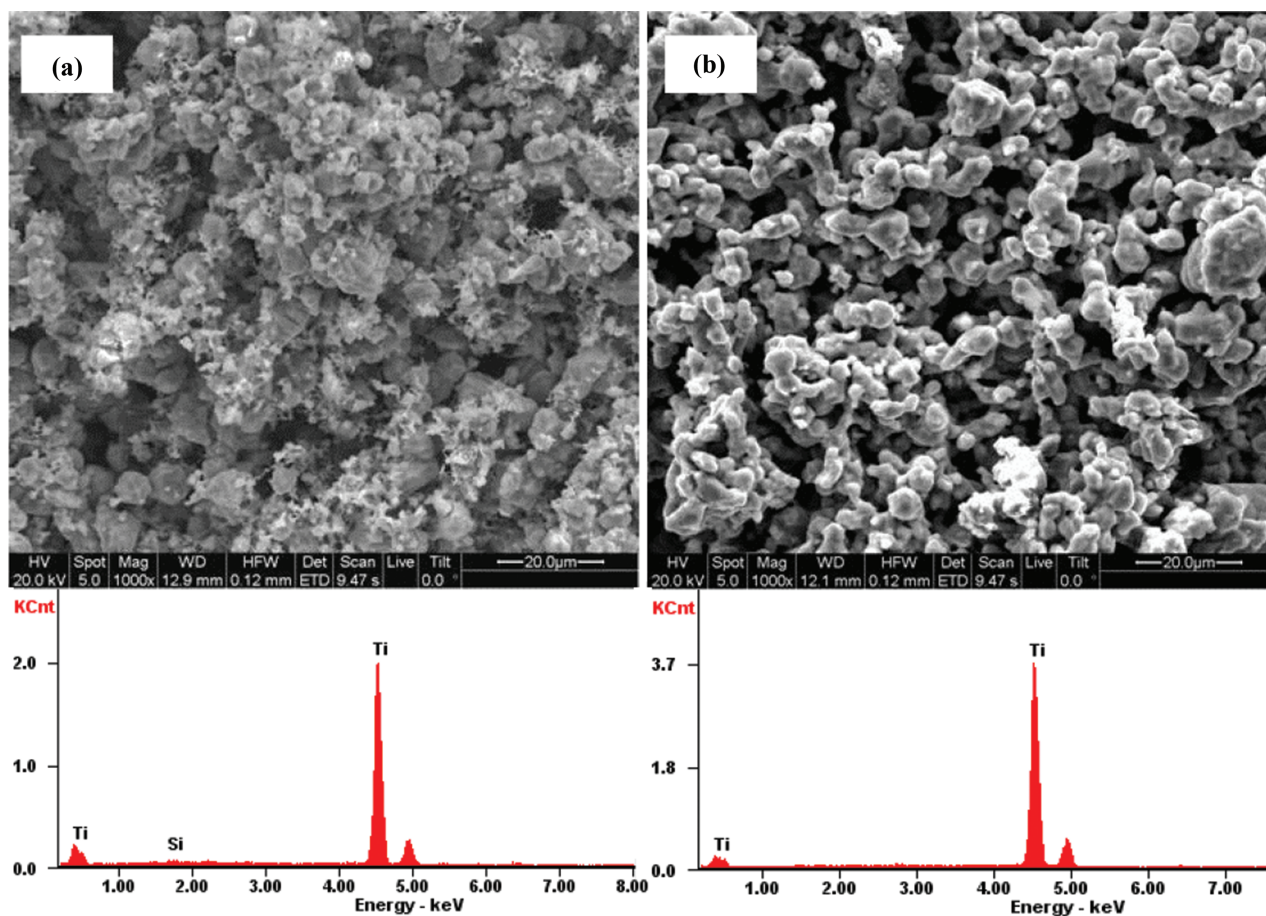


Figure 6: SEM images and EDX spectra of the electrolytic products at 1,100°C for different times (a) 4 h and (b) 6 h. The pellets were pressed under 3 MPa.

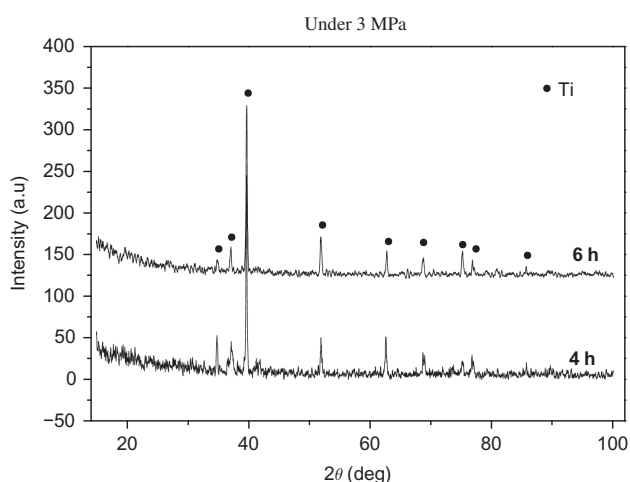


Figure 7: XRD spectra of the electrolyzed products at 1,100°C for 4 and 6 h; the pellets were pressed under 3 MPa.

deposited at the cathode from oxide impurity during electrochemical reduction can dissolve partly in the molten CaCl_2 [16]. Furthermore, the molten CaCl_2 without

drying and pre-electrolysis is prone to hydrolysis and produce HCl , which will react with those deposited metals to form chlorides by dissolving or volatilizing. Especially the electrolysis temperature was around 1,100°C, and the reaction will result in the formation of Mg vapor and spilling out the reactor. Therefore, further work is still ongoing for a better understanding of the causes to the observed losses of Al , Mn , Mg , Fe and Si , focusing on composition analyses of the molten salt after electrolysis and the gas phase products when volatile chlorides (e.g. MgCl_2 , AlCl_3 and SiCl_4) may form. In addition, Ti metal and Ti alloy will also be prepared from other titania dust by SOM process and the loss of the impurities will be analyzed.

Conclusion

- (1) Ti-Fe alloy and pure Ti metal can be prepared directly from Fe-Ti residue and titanium-rich residue by SOM

process, respectively. Porous cathode at a smaller forming pressure is more advantageous to remove the impurities. This also offers a flexibility process to exploit and utilize some complex ores directly.

- (2) For Fe–Ti residue, the nonferrous metal elements (Mg and Al) have not been found in products. The contents of Ti and Fe increase with the electrolysis time, and the morphology structure present as graininess.
- (3) For titanium-rich residue, the pellet pressed under 6 MPa demands 6 h to reduce fully. However, when the formation pressure decreased to 3 MPa, 4 h is enough for completely reducing, and obtaining pure Ti metal calls for 6 h electrolysis.

Funding: This project was supported by the National Natural Science Foundation of China (nos 51264006, 51474079 and 51464008) and The Basic Research Program of Guizhou Provincial Education Department (no. 20120002).

References

- [1] W.J. Kroll, *Trans. Am. Electrochem. Soc.*, 78 (1940) 35–35.
- [2] W. Mo, G.Z. Deng and F.C. Luo, *Titanium Metallurgy* (in Chinese), Metallurgical Industry Press, Beijing (1998).
- [3] D.Q. Yu, *Titanium Ind. Prog.* (in Chinese), 1 (2002) 42–46.
- [4] S.J. Gao and W.L. Zhang, *Shandong Ceramics* (in Chinese), 29 (2006) 29–31.
- [5] H.Y. Zheng and T.H. Okabe, *J Alloy. Compd.*, 461 (2008) 461–459.
- [6] M. Ma, D.H. Wang, W.G. Wang, X.H. Hu, X.B. Jin and G.Z. Chen, *J Alloy. Compd.*, 420 (2006) 37–45.
- [7] U.B. Pal, D.E. Woolley and G.B. Kenney, *JOM*, 53 (2001) 32–35.
- [8] C.Y. Chen, X.G. Lu and H.W. Cheng, et al., *Rare Metal* (in Chinese), 31 (2007) 306–310.
- [9] C.Y. Chen and X.G. Lu, *Acta Metall. Sin.* (in Chinese), 44 (2008) 145–149.
- [10] C. Schwandt and D.J. Fray, *Electrochim. Acta*, 51 (2005) 66–76.
- [11] X.F. Hu and Q. Xu, *Acta Metall. Sin.* (in Chinese), 42 (2006) 285–289.
- [12] E. Gordo, G.Z. Chen and D.J. Fray, *Electrochim. Acta*, 49 (2004) 2195–2208.
- [13] M.F. Liu, Z.C. Guo and W.C. Lu, *Miner. Process Extr. Metall.*, 114 (2005) 87–94.
- [14] P.G. Mrutyunjay, I.K. Atsushi and S.B. Etsuro, *J. Alloy. Compd.*, 550 (2013) 545–552.
- [15] X. Jin, P. Gao, D.H. Wang and G.Z. Chen, *Angew. Chem.*, 116 (2004) 751–754.
- [16] X.Y. Liu, M.L. Hu and C.G. Bai, *Funct. Mater.*, 42 (2011) 2042–2046.