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# A direct electrochemical route from oxides to Ti-Si intermetallics

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#### ARTICLE INFO

Article history: Received 7 January 2010 Received in revised form 8 April 2010 Accepted 8 April 2010 Available online 24 April 2010

 $\label{eq:keywords:} \begin{array}{l} \mbox{Keywords:} \\ \mbox{Ti-Si intermetallics} \\ \mbox{Ti}_5 \mbox{Si}_3 \\ \mbox{Electrochemical reduction} \\ \mbox{Oxides} \\ \mbox{SOM} \end{array}$ 

### ABSTRACT

The titanium silicide intermetallics have been directly prepared from the mixture of titanium oxide (TiO<sub>2</sub>) and silicon oxide (SiO<sub>2</sub>) powder by using the solid-oxygen-ion-conducting membrane (SOM) electrolysis process. The electrochemical process was carried out in a molten flux CaCl<sub>2</sub> at 950 °C with a potential of 3.5–4.0 V. The effects of the stoichiometry of the initial mixture on the electrolysis characteristics and the final product compositions were investigated. It has been found that the molar ratio of TiO<sub>2</sub>:SiO<sub>2</sub> dominates the composition of final products. A single-phase silicide Ti<sub>5</sub>Si<sub>3</sub> intermetallic was obtained when the TiO<sub>2</sub>:SiO<sub>2</sub> molar ratio is 5:3; the TiSi was identified as the dominant phase with a minor amount of TiSi<sub>2</sub> at TiO<sub>2</sub>:SiO<sub>2</sub> molar ratio 1:1; three silicide phases, Ti<sub>5</sub>Si<sub>3</sub> and TiSi, were found coexisting in the final product produced from TiO<sub>2</sub>–SiO<sub>2</sub> mixture of molar ratio 5:4; the product of electrolysis consisted of the compound Ti<sub>5</sub>Si<sub>3</sub> and the pure metal Ti as TiO<sub>2</sub>:SiO<sub>2</sub> molar ratio as 1:1; and two silicide phases, TiSi and TiSi<sub>2</sub>, are formed as TiO<sub>2</sub>:SiO<sub>2</sub> molar ratio equals to 1:2. The preliminary experimental results suggest that the electro-deoxidization process is fast and the current efficiency reached 75%.

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#### 1. Introduction

Transition metal silicides of the titanium-silicon system like Ti<sub>5</sub>Si<sub>3</sub> and TiSi<sub>2</sub> has attracted interest from researchers in recent years [1-3], due to their special physical and chemical properties. According to the phase diagram of the Ti-Si system (shown in Fig. 1 [1]), there are five silicide compounds: Ti<sub>3</sub>Si, Ti<sub>5</sub>Si<sub>3</sub>, Ti<sub>5</sub>Si<sub>4</sub>, TiSi, and TiSi<sub>2</sub>. Among them, Ti<sub>5</sub>Si<sub>3</sub> has the highest melting point  $(2130 \degree C)$  and the lowest density  $(4.32 \text{ g/cm}^3)$ , and also exhibits excellent creep resistance, good strength at elevated temperature, and high oxidation resistance [4]. The disilicide TiSi<sub>2</sub> is widely applied as ohmic-contacts, Schottky barriers, gates and interconnects in very large scale integrated (VLSI) circuits, etc., in its thin film forms in microelectronics. This primarily attributes to its large silicon content, remarkably low electrical resistivity (about 13–16  $\Omega$ /cm), high-temperature stability, and excellent property of corrosion resistance [2]. Recently the investigation of titanium silicides, especially the compound Ti<sub>5</sub>Si<sub>3</sub>, has attracted many interests of researchers [5–7]. As reviewed by Stoloff [8], metal silicides can be produced by a variety of powder techniques, i.e., hot pressing, hot isostatic pressing, reactive sintering, mechanical alloying, and thermal or plasma spraying, two or more of which are often used in combination. These conventional methods are costly, because most of them involve arc melting of the ultrapure elements Ti and Si. So far, pure Ti is mainly produced by the Kroll process [9], and Si is by carbothermic reduction method [10], with both processes involving extensive energy consumption. Our work aims at preparing titanium silicides (includingTi<sub>3</sub>Si, Ti<sub>5</sub>Si<sub>3</sub>, Ti<sub>5</sub>Si<sub>4</sub>, TiSi, and TiSi<sub>2</sub>) from titanium and silicon oxides by an alternative SOM process.

The solid-oxide-oxygen-ion conducting membrane (SOM) process [11-14], is developed on the basis of FFC process [9]. In comparison with other molten salt electrolysis processes, the SOM process is advanced and more economical, environmental friendly, and energy-efficient [9–11]. The key feature of this process is, a tubular solid-oxygen-ion conducting (yttria-stabilized zirconia (YSZ)) membrane introduced to the electrolysis system, to segregate the anode from the molten electrolyte and pump oxygen continuously away from the oxide resources, only the oxygen ions are electro-migrated across the SOM and oxidize at the separated anode owe to the oxygen-ion selectivity of SOM. So, the given metallic oxides or complex oxides ore are reduced at the cathode by applying a suitable voltage. In particular, it eliminates the environmental concerns associated with anode products (CO), and the anode product is water if hydrogen is introduced at the anode to react with the separated oxygen ions in electrolysis. In conventional high-temperature molten salt electrolysis processes, it is hard to avoid producing halide gases and oxy-halide-hydrocarbon compounds [13,14].

This paper reports the success of applying the SOM process to the preparation of titanium-silicon compounds directly from

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<sup>0013-4686/\$ -</sup> see front matter © 2010 Elsevier Ltd. All rights reserved. doi:10.1016/j.electacta.2010.04.032





mixed TiO<sub>2</sub>-SiO<sub>2</sub> powders (TiO<sub>2</sub>:SiO<sub>2</sub> = 3:1; 5:3; 5:4; 1:1; 1:2) in molten CaCl<sub>2</sub> electrolyte. The effects of the stoichiometry of initial mixtures on the electrolysis characteristics and the final products composition are investigated. The products obtained from electrolysis under different conditions are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energydispersive X-ray (EDX) spectroscopy. A formation mechanism of Ti<sub>5</sub>Si<sub>3</sub> by SOM is proposed based on experimental evidence.



**Fig. 2.** (a) Scheme of the SOM process electrolytic cell; (b) fundamental configuration of the SOM process [13].



Fig. 3. XRD pattern of sintered mixture of  $TiO_2$  and  $SiO_2$  powders ( $TiO_2$ :SiO<sub>2</sub> = 5:3).

#### 2. Experimental

Commercially available powder of titanium oxide,  $TiO_2 (\geq 99.99\%)$  and silicon oxide,  $SiO_2 (\geq 99.99\%)$  were used as raw materials for cathode. The reagent grade oxide powders were mixed at given stoichiometric ratios and ball-milled with anhydrous alcohol for 5 h, and then about 1.0 g of the mixture was pressed to form a cylindrical pellet (15 mm in diameter and 2 mm in thickness) under pressure load of 10 MPa. The pellet was then sintered in air at 1150 °C for 2 h. The sintered oxide pellet was wrapped with Mo wire mesh, and then attached to a Mo wire to form a cathode. The anode consisted of a solid-oxygen-ion conducting (yttria-stabilized zirconia (YSZ)) membrane tube filled with carbon-saturated liquid tin, and a Mo wire screwed graphite rod inserted into the tube. Liquid tin is used as a medium to transport oxygen from the YSZ/tin interface to graphite where it is oxidized.

The assembled cathode and anode were placed in a graphite crucible which contained anhydrous  $CaCl_2$  (purity,  $\ge 98\%$ ) flux as electrolyte. A schematic of the electrolytic cell is given in Fig. 2(a), and the fundamental configuration of the SOM process is given in Fig. 2(b) [13]. The experiments were performed under argon further purified from commercially available pure argon. The argon gas was sequentially passed through heated copper scrap (600 °C) to remove oxygen, and then passed through anhydrous CaCl<sub>2</sub>, silica gel and P<sub>2</sub>O<sub>5</sub> to remove moisture. When the temperature reached 950 °C, pre-electrolysis was performed at the low potential of 2.5 V



**Fig. 4.** The current–time curves of the electrolysis for different time,  $TiO_2$ :SiO<sub>2</sub> = 5:3, the insert is the initial part of the current–time curve.



Fig. 5. SEM images of the cross-section of a mixed powder pellet (TiO<sub>2</sub>:SiO<sub>2</sub> = 5:3) electrolyzed for 3 h. (a) The whole pellet; (b) the inner part of the pellet; (c) the boundary of inner and outer parts; (d) the outer part. The inset plots in (b) and (d) are the EDX spectra measured over the image areas, respectively.

for 0.5 h, to remove moisture and impurities. The cathode pellet was then electrolyzed at 4.0 V for about 1–5 h until the current approached to zero. A high-current electrochemical work station HCP-803 was employed to record current curves during the electrolysis. After the electrolysis was finished, the cathode pellet was cooled to room temperature with the furnace, then taken out of crucible, washed thoroughly in flowing water and dried in vacuum. The morphology of the reduced pellet was examined by using a JSM-6700F cold field emission scanning electron microscope and the alloy constitution was micro analyzed by EDX spectroscopy. The pellet was then manually ground into powder with a pestle and a mortar and then crystal structural analysis was carried out using a D/Max-2550 X-ray diffractometer.

## 3. Results and discussion

#### 3.1. The influence of sintering and the current features

To affirm whether there were new compounds produced during the sintering, the XRD pattern of the mixed oxide pellets  $(TiO_2:SiO_2 = 5:3)$  sintered at  $1150 \degree C$  for 2 h is given in Fig. 3. It is apparent that it exhibited no peaks other than those of the starting oxides.

The typical current-time curves for the SOM process are depicted in Fig. 4. All the curves have similar shapes at the beginning part of the electrolysis process (see the insert of Fig. 4). The current declined with time at beginning, reaching minimum (around 700 mA, see the larger panel in Fig. 4) in the first few minutes, which may imply that it corresponds to the electrolytic cell to reach equilibrium; and then the current increases to about 900 mA, within 0.5 h, and this is in agreement with the reduction occurring at the dynamic metal/oxide/electrolyte three phase interlines (3PIs) [15,16]. When the oxide in contact with the Mo mesh was reduced to metal, new 3PIs formed amongst the newly formed metal/oxide/molten salt. With such processes continued, the 3PIs at each of the Mo mesh/oxide contacts expanded initially and until all the surface of the pellet was metallised, then the current reached maximum (around 1000 mA). With the 3PIs moving into the interior of the oxide pellet along the depth direction, the current declined to a constant about 0.2–0.4 A within 3–5 h, and this is the typical current curve of SOM process. It should be noted that the current features were affected by many complicated factors, such as cell temperature, electrolysis voltage, membrane–flux and cathode–flux interfacial areas, membrane stability, etc. And the lifetime of the membrane depends on the chosen flux system, temperature and stirring conditions employed, the details have been discussed in an earlier study [14].

#### 3.2. The influence of reaction time

Electrolysis of mixed powders ( $TiO_2:SiO_2 = 5:3$ ) was carried out at constant voltage 4.0 V for 1 h, 3 h, and 5 h, respectively. No unfavorable layered structures were found in the cathode pellets after incomplete electrolysis. Fig. 5 shows the SEM images of the crosssection of the pellet electrolyzed for 3 h. It is obvious that the electrolysis process was not completed, the pellet consists of two parts with different morphology, the outer part is porous and the inner part is compact.

It is shown in Fig. 5 that there are two phases with a boundary (3PIs) existing in the pellet, a completely electrolyzed outer part and a partial or non-electrolyzed inner part. Fig. 6 is the X-ray patterns of the cathode pellets after electrolysis of different times. The XRD spectrum of (a-1h) in Fig. 6 shows that there is elemental Si found in the product, but no metallic Ti phase



Fig. 6. XRD patterns of the mixed powders (TiO<sub>2</sub>:SiO<sub>2</sub> = 5:3) electrolyzed for different times. (a) 1 h; (b) 3 h; (c) 5 h.

observed, which may imply that the SiO<sub>2</sub> mixed in the oxide powder was first deoxidized to Si following reaction (2). Part of SiO<sub>2</sub> converted into Ca<sub>3</sub>Si<sub>2</sub>O<sub>7</sub> following reaction (3) [17], and the TiO<sub>2</sub> compound was converted into CaTiO<sub>3</sub> following reaction (4) [18]. The foregoing studies on electroreduction of solid oxides, such as TiO<sub>2</sub> [19-22] and SiO<sub>2</sub> [20], show that the formation of the calcium-titanium and calcium-silicon intermediate compounds may be readily explained. The mechanism of formation of these intermediate products and their influence on the reduction process were studied [18,22], and reactions (3) and (4) refers to the interaction or reaction between solid TiO<sub>2</sub>/SiO<sub>2</sub> and calcium oxide or cation driven by chemical or electrochemical potentials [18,20]. The product after 3 h electrolysis consists of Ti<sub>5</sub>Si<sub>3</sub>, TiSi<sub>2</sub>, Ti, CaTiO<sub>3</sub>, and  $Ca_3Si_2O_7$  (shown in the spectrum (b-3h) in Fig. 6), which may suggest in reactions (1), (5) and (6), that the TiO<sub>2</sub> reduced to Ti and calcium-containing intermediate compounds (CaTiO<sub>3</sub>, Ca<sub>3</sub>Si<sub>2</sub>O<sub>7</sub>) reduced to Ti, Si and CaO, respectively. Then, CaO dissolves in molten CaCl<sub>2</sub> following reaction (7), and also titanium and silicon began to form TiSi<sub>2</sub> alloy (reaction (8)). With prolonging the electrolysis time, finally TiSi2 and Ti combined into a more stable Ti5Si3 phase (according to the spectrum (c-5h) in Fig. 6) following reactions (9)-(11), and this is consistent with previous studies [23,24]. Fig. 6 also shows that the inner part consists of two phases CaTiO<sub>3</sub> and Ca<sub>3</sub>Si<sub>2</sub>O<sub>7</sub>.

 $\mathrm{TiO}_2 + 4e^- \rightarrow \mathrm{Ti} + 20^{2-} \tag{1}$ 

$$\mathrm{SiO}_2 + 4\mathrm{e}^- \rightarrow \mathrm{Si} + 2\mathrm{O}^{2-} \tag{2}$$

$$2SiO_2 + 3Ca^{2+} + 3O^{2-} \to Ca_3Si_2O_7$$
(3)

$$\mathrm{TiO}_2 + \mathrm{Ca}^{2+} + \mathrm{O}^{2-} \to \mathrm{Ca}\mathrm{TiO}_3 \tag{4}$$

$$CaTiO_3 + 4e^- \rightarrow Ti + 2O^{2-} + CaO \tag{5}$$

$$Ca_3Si_2O_7 + 8e^- \rightarrow 2Si + 40^{2-} + 3CaO$$
 (6)

$$CaO \rightarrow Ca^{2+} + O^{2-}$$
 (7)

 $Ti + 2Si \rightarrow TiSi_2 \tag{8}$ 

 $TiSi_2 + Ti \rightarrow 2TiSi \tag{9}$ 

 $4\text{TiSi} + \text{Ti} \rightarrow \text{Ti}_5\text{Si}_4 \tag{10}$ 

 $3Ti_5Si_4 + 5Ti \rightarrow 4Ti_5Si_3 \tag{11}$ 

Table 1

SEM image and XRD spectrum with different starting stoichiometries.

TiO <sub>2</sub> /SiO <sub>2</sub> ratio	SEM image	XRD
3:1	Fig. 7(a)	Fig. 8(a)
5:3	Fig. 7(b)	Fig. 8(b)
5:4	Fig. 7(c)	Fig. 8(c)
1:1	Fig. 7(d)	Fig. 8(d)
1:2	Fig. 7(e)	Fig. 8(e)

#### 3.3. Synthesis of Ti<sub>x</sub>Si<sub>y</sub>

Electrolysis of pellets with different starting stoichiometries  $(TiO_2:SiO_2 = 3:1, TiO_2:SiO_2 = 5:3, TiO_2:SiO_2 = 5:4, TiO_2:SiO_2 = 1:1, TiO_2:SiO_2 = 1:2)$  were also carried out. The SEM images of the products completely electrolyzed (electrolyzed for 5 h) are shown in Fig. 7, and the XRD spectrum of products completely electrolyzed were shown in Fig. 8. The summary of the serial number of SEM image and XRD spectrum with different starting stoichiometries is listed in Table 1.

The products of the electrolysis have porous morphology. The microstructure of the products from different starting stoichiometries has slight difference. As shown in Figs. 7 and 8, the (TiO<sub>2</sub>:SiO<sub>2</sub> = 5:3) sample was completely electrolyzed to a single-phase silicide Ti<sub>5</sub>Si<sub>3</sub>, and the SEM micrograph shows the particles have a similar morphology. The microstructure of the electrolytic products with the starting stoichiometries (TiO<sub>2</sub>:SiO<sub>2</sub> = 3:1, TiO<sub>2</sub>:SiO<sub>2</sub> = 5:4, TiO<sub>2</sub>:SiO<sub>2</sub> = 1:1, TiO<sub>2</sub>:SiO<sub>2</sub> = 1:2) exhibits different particle sizes, that is, the large particle size was about  $1-5 \,\mu$ m while the small particle size was less than  $1 \,\mu$ m. This is mainly due to the products containing two or three silicide phases, which Fig. 8 shows the XRD spectrum of the products electrolyzed completely.

The XRD spectrum of mixed powders completely electrolyzed for 5 h are shown in Fig. 8. When the  $TiO_2:SiO_2$  molar ratio is 3:1, the products of electrolysis consisted of the compound  $Ti_5Si_3$ and the pure metal Ti; a single-phase silicide  $Ti_5Si_3$  intermetallic was obtained when the  $TiO_2:SiO_2$  molar ratio is 5:3; three silicide phases,  $Ti_5Si_4$ ,  $Ti_5Si_3$  and TiSi, were found coexisting in the final product produced from  $TiO_2-SiO_2$  mixture of molar ratio 5:4; the silicide TiSi was identified as the dominant with a minor amount of  $TiSi_2$  at  $TiO_2:SiO_2$  molar ratio 1:1; and two silicide phases, TiS and disilicide  $TiSi_2$ , are formed as  $TiO_2:SiO_2$  molar ratio equals to 1:2. The summary of silicide phases formed in electrolysis products with different initial compositions is listed in Table 2.

### 3.4. Formation mechanisms

A mechanism for the formation of  $Ti_5Si_3$  by SOM process is suggested by the experimental work (shown in Fig. 9). During the electrolysis, the intermetallic  $Ti_5Si_3$  is formed following a multistep process: at the beginning of the electrolysis, it has been established that the origin of leakage current in the cell prior to the oxides dissociation is due to oxygen impurity in the cell

Table 2
Silicide phases formed in electrolysis products with different initial compositions

Reactants (TiO <sub>2</sub> :SiO <sub>2</sub> )	Electrolysis products			
	Dominant phase	Secondary phase	Trace phase	
3:1	Ti <sub>5</sub> Si <sub>3</sub> and Ti			
5:3	Ti <sub>5</sub> Si <sub>3</sub>			
5:4	Ti <sub>5</sub> Si <sub>4</sub>	Ti <sub>5</sub> Si <sub>3</sub>	TiSi	
1:1	TiSi	TiSi <sub>2</sub>		
1:2	TiSi <sub>2</sub>	TiSi		



**Fig. 7.** The SEM images of the products completely electrolyzed (electrolyzed for 5 h) with different starting stoichiometries: (a)  $TiO_2:SiO_2 = 3:1$ ; (b)  $TiO_2:SiO_2 = 5:3$ ; (c)  $TiO_2:SiO_2 = 5:4$ ; (d)  $TiO_2:SiO_2 = 1:1$ ; (e)  $TiO_2:SiO_2 = 1:2$ .

[13], however, when the applied voltage above the oxides dissociation potential, the SiO<sub>2</sub> was first deoxidized to Si because the SiO<sub>2</sub> had lowest theoretical decomposition voltage at 950 °C (SiO<sub>2</sub> - 1.80 V [25], TiO<sub>2</sub> - 1.90 V, CaTiO<sub>3</sub> - 2.03 V, Ca<sub>3</sub>Si<sub>2</sub>O<sub>7</sub> - 2.06 V, the theoretical decomposition voltages are calculated according to thermodynamic data [26]). The Ca<sub>3</sub>Si<sub>2</sub>O<sub>7</sub> and CaTiO<sub>3</sub> were formed in the cathode simultaneously by reactions (3) and (4), and this is supported by the result given in Fig. 6(a). A similar scenario was reported for the reduction of mixtures of TiO<sub>2</sub> and other oxides in which the formation of various perovskites was observed in the intermediate products [27]. Next, the CaTiO<sub>3</sub> and Ca<sub>3</sub>Si<sub>2</sub>O<sub>7</sub> reduced into Ti, Si and CaO following reactions (5) and (6), respectively, then Ti and Si were combined to form  $TiSi_2$ ,  $Ti_5Si_3$  following reactions (8)–(11). It is worth noting that there is a general trend that silicides such as TiSi<sub>2</sub> and TiSi form first during the electrolysis procedure, then they further react with the Ti to form the intermetallic  $\text{Ti}_5\text{Si}_3$  if there is enough Ti present.

The titanium silicide Ti<sub>3</sub>Si is not produced during electrolysis, even as a trace compound at an excess of titanium oxide in the starting mixture. The foregoing study [28] suggested that the free energy of the reaction Ti<sub>5</sub>Si<sub>3</sub>(s) + 4Ti(s)  $\Leftrightarrow$  3Ti<sub>3</sub>Si(s) is approximately equal to zero, and its entropy change should be very small, which lead to the formation of Ti<sub>3</sub>Si would be a very slow solidstate phase change process at the electrolytic temperature. Ti<sub>5</sub>Si<sub>3</sub> is the most thermodynamically stable of the titanium silicides at the electrolytic temperature [29], therefore, the SiO<sub>2</sub> is first deoxidized to Si and provided sufficient Si to form stable Ti<sub>5</sub>Si<sub>3</sub> phase, and the presence of the large primary phases of Ti<sub>5</sub>Si<sub>3</sub> contributed to a reduction in the kinetics of Ti<sub>3</sub>Si formation [6]. To obtain Ti<sub>3</sub>Si intermetallic must be held at an appropriate temperature for a long time heat-treatment.



**Fig. 8.** XRD patterns of the completely electrolyzed products (electrolyzed for 5h) with different starting stoichiometries: (a)  $TiO_2:SiO_2 = 3:1$ ; (b)  $TiO_2:SiO_2 = 5:3$ ; (c)  $TiO_2:SiO_2 = 5:4$ ; (d)  $TiO_2:SiO_2 = 1:1$ ; (e)  $TiO_2:SiO_2 = 1:2$ .



Fig. 9. Schematic of the formation mechanism of  $Ti_5Si_3$  in SOM process.

#### 4. Conclusions

The  $Ti_x Si_y$  intermetallic compounds were synthesized by direct electrochemical reduction of mixed TiO<sub>2</sub>-SiO<sub>2</sub> powders in molten CaCl<sub>2</sub>, the mechanism for the formation of Ti<sub>5</sub>Si<sub>3</sub> is a multi-step process. It was found that for the case of  $TiO_2$ :SiO<sub>2</sub> = 5:3, singlephase silicide Ti<sub>5</sub>Si<sub>3</sub> was obtained and the final product keeps the starting stoichiometry of raw materials. The silicide TiSi was found to be dominant phase (with a minor amount of TiSi<sub>2</sub>) in the product of 1:1 molar ratio oxide mixture; three silicide phases, Ti<sub>5</sub>Si<sub>4</sub>, Ti<sub>5</sub>Si<sub>3</sub> and TiSi, were discovered at 5:4 molar ratio; electrolysis products consisted of compound  $Ti_5Si_3$  and metal phase  $Ti as TiO_2:SiO_2 = 3:1$ ; two silicide phases, TiSi and TiSi<sub>2</sub>, were formed as  $TiO_2:SiO_2 = 1:2$ . A typical complete electrolysis of pellets of the mixed oxides  $(TiO_2:SiO_2 = 5:3, 1.0 \text{ g and } \sim 2 \text{ mm in thickness})$  at 4.0 V forming intermetallic compound Ti<sub>5</sub>Si<sub>3</sub> can be finished within 5 h. Current efficiency was calculated as the ratio of the charge required theoretically to achieve complete reduction and the charge passed in total throughout the course of the experiment. The total charge passed through the cell was 2.4 Ah in 5 h as measured from the current-time plot (Fig. 4), and the current efficiency was calculated to be 75%. This implies that the SOM process is a highly efficient and environment-friendly novel process to produce metals or alloys directly from their solid oxides, and it is promising for industrial application.

#### Acknowledgements

The authors gratefully thank the Ministry of Science and Technology of China, the Nature Science Foundation of China and Ministry of Education of China for their financial support under contract nos. 2007CB613606 (MOST), 50774052 (NSFC), NCET-06-0434 and IRT0739 (MOE).

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