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Extraction of titanium from different titania precursors by the FFC Cambridge process

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Abstract

Cheap titania precursors including titania dust, metatitanic acid (solid) and titanium-rich slag were tested as the feeding materials in the FFC Cambridge process (laboratory scale). Porous pellets (\sim 20 mm in diameter, 2.0–3.0 mm in thickness) of the precursor were successfully reduced to titanium metal or alloy by constant voltage electrolysis (2.9–3.1 V) in molten calcium chloride (\sim 900 °C). The reduction was independent of the initial crystal structure of the precursor. More importantly, some metallic impurities in the titanium-rich slag, such as aluminium and manganese, were found to be partly or completely removed after electrolysis. The current efficiency decreased with electrolysis time, typically from 40% in the first 5 h to 20% in 12 h for the 2 mm thick TiO₂ pellets. The energy consumption of electrolysis was about 33 kWh/kg Ti when the oxygen level in the produced metal was reduced to below 3000 ppm. Analyses of the electrolysis data and of the phases and compositions in partially reduced oxide pellets suggested strong dependence of the electro-reduction on mass (ion) transfer in the pellet after metallisation of the pellet's surface. An earlier proposed "double-melt electrolysis" was compared with the electrolysis data, focusing on the origin and influence of background current. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

Commercial application of titanium is, to a great degree, restricted by the costly extraction method, e.g. the Kroll process, although titanium is the fourth richest element among all structural metals in the earth's crust and has many desirable engineering and functional properties. In 2000, Chen et al. reported a new process in which solid titania was directly electrochemically reduced to metallic titanium in molten CaCl₂ [1]. This new process, which is now called the FFC (Fray–Farthing–Chen) Cambridge process by the industry [2–5], is low in energy consumption, and simple and short (potentially continuous) in operation. The use of metal oxides as the feeding material is also advantageous over the current industrial choice of metal chlorides which are usually converted from the oxides. The FFC

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0925-8388/\$ - see front matter © 2005 Elsevier B.V. All rights reserved. doi:10.1016/j.jallcom.2005.10.048 Cambridge process is therefore considered to be able to significantly reduce titanium's production cost [6–9] and encourages academic interests [10–12] and ongoing pilot demonstration on larger scales in the industry [13]. It promises an economical and environmentally friendly alternative to the Kroll process which uses the toxic chlorine gas and expensive magnesium in the feeding materials, takes about 2 weeks for each batch production, and consumes a significant amount of energy: more than 50 kWh/kg Ti [14].

The cost of an industrial process can be from many origins, and a comprehensive cost analysis of the FFC Cambridge process goes beyond the scope of this paper. However, two of these cost-related factors deserve good scientific considerations: materials and energy. The commercial titanium sponge is usually priced on the market at about $\$8 \text{ kg}^{-1}$ Ti, which reflects well the energy, material and operation costs of the Kroll process. (Due to the relatively small production capacity and the very unstable demand around the world, Ti sponge has been very much over-priced recently at $\$20 \text{ kg}^{-1}$ Ti in high demanding regions. However, it had also been significantly under-priced in

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the past at \$ 5 kg⁻¹ Ti or lower, for example, when unexpected supply emerged from countries of the former Soviet Union.) Simple calculations show that, at a price of \$ 0.05 (kWh)⁻¹, the electricity cost in the FFC Cambridge process can vary from \$ 0.3 kg⁻¹ Ti to \$ $1.5 kg^{-1}$ Ti when the current efficiency changes from 100% to 20%. The titania market is however relatively more stable. The pigment grade TiO₂ (rutile) costs at about \$ $1.2 kg^{-1}$ TiO₂ (or \$ $2.0 kg^{-1}$ Ti) but the various precursors used to produce the TiO₂ pigment are much cheaper as discussed below. These numbers show clearly that the cost of titania, which is the feeding material, can be a major financial factor affecting the industrial application of the FFC Cambridge process. This fundamental understanding forms the basis of this work as one part of a grand ongoing research programme.

Except for a brief mention [1], all previous work [1,10–12,15] has used the commercial pigment or reagent grade TiO₂ powder as the feeding material in the electro-reduction process, but these TiO₂ products are not sufficiently economical to meet with the mass demand on an industrial scale. The well-crystallised TiO₂ (rutile and anatase), which has been widely used as pigment and additives in industry, is mainly manufactured by two methods: the chloride and sulfate processes [16]. In these processes, the titanium concentrate (titanium enriched ilmenite, titanium-rich slag or rutile) is first reacted with chlorine gas or sulfuric acid to form TiCl₄ or TiOSO₄. The TiCl₄ is subsequently converted to TiO₂ at 1300–1800 °C, and the TiOSO₄ is hydrolyzed to form the metatitanic acid which is then washed, filtered, dehydrated and calcined in a rotary kiln (900–1250 $^\circ C)$ to form anatase or rutile TiO₂ depending on the operation conditions. The obtained TiO₂ is further treated to obtain some special physical properties, including dispersibility, wettability, brightness and opacity for pigment and other applications. Obviously, further cost reduction in the FFC Cambridge process for titanium extraction is expected by using one of the intermediate products from the above processes as the feeding material, instead of the pigment titania. (It should be mentioned that the sulfate route and its intermediate products are not preferred for the Kroll process in which the titania precursors must be first converted into TiCl₄ by carbochlorination.)

This paper reports our investigation on using three titania precursors, all collected from the industry in western China where over 0.9 billion tonnes of titanium mineral are stored, as the feeding material to produce titanium metal or alloy via the FFC Cambridge process (laboratory scale). The results reveal that titanium metal or alloy can be directly extracted from different TiO₂ precursors, namely titania dust, metatitanic acid and titanium-rich slag, disregarding the starting morphology and crystal structure of the precursor. The oxygen and other impurity concentrations in the obtained metals were analysed. Of particular importance is the finding that some metallic impurities in the titanium-rich slag, namely manganese and aluminium, were present at much lower levels in the electrolytic product. Typical electrolysis current-time curves are presented and used for calculations of the current efficiency and energy consumption, which provides the basis for in-depth discussion in terms of an earlier proposal for improving the electrolysis efficiency.

Table 1

EDX determined contents of metallic elements in the original titanium-rich slag and in the electro-reduction product at 3.1 V and 900 $^{\circ}$ C for 12 h in molten CaCl₂

Elements	Fe	Ti	Si	Mn	Al	Ca
Original sample (wt.%)	8.59	65.80	9.46	5.38	10.47	а
Reduced sample (wt.%)	8.68	80.94	9.08	1.30	а	а

^a The element was not detected in the sample by EDX.

2. Experimental

2.1. Materials and reagents

Metatitanic acid was collected from the vacuum dehydration stage of the sulfate process in the Titania Plant of Panzhihua Iron and Steel Group Corporation. The titania dust, a non-classified by-product from anatase production, was collected from the floor near the rotary kiln in the same plant. The as-received metatitanic acid and titania dust were labelled by the supplier to contain only Ti, H and O, and the particle size was of sub-micrometers. The titanium-rich slag, provided by Zunyi titanium plant, was manufactured by reaction between ilmenite and coal in a closed electric arc furnace. The composition of the slag was analysed by EDX and the results are given in Table 1. The slag was milled for 4 h at a rotation rate of 250 r/min in a planet ball-mill. The particle size of the obtained powder was around 1 μ m. Anhydrous CaCl₂ (AR grade) was purchased from Shanghai Chemical Regent Company.

2.2. Pellet preparation

The titania precursor powder was manually pressed into small pellets (20 mm in diameter and 2.0–3.0 mm in thickness). The titania dust and titanium-rich slag pellets were sintered at 900 °C for 2 h and gained sufficient strength for handling. The porosity was 40–50%. In the same sintering process, however, the metatitanic acid pellet cracked into small pieces, possibly due to rapid dehydration (decomposition). However, when the sintering temperature was raised slowly in a suitable programme, sufficiently strong pellets were prepared from the metatitanic acid. A typical programme used in this work was as follow: (1) room temperature to 300 °C in 1 h and holding for 4 h (to allow slow and complete dehydration), (2) 300–900 °C in 2 h and holding for 2 h. After sintering, the pellet lost weight and shrank. For example, after sintering, the mass of a 1.50 g metatitanic acid pellet decreased to 1.14 g, the diameter from 20 to 17 mm, and the thickness from 3.1 to 2.7 mm. The porosity was ~60%.

2.3. Electrolysis procedure

The sintered pellet was wrapped tightly with molybdenum mesh and wires. This assembly was used as the cathode in constant voltage electrolysis with a graphite rod anode (20 mm diameter, 200 mm length) in a graphite crucible (100 mm inner diameter and 230 mm height) containing 500 g anhydrous $CaCl_2$ granules. The electrolytic cell was placed at the bottom of a sealable stainless steel tube reactor in a vertical tube furnace. The electrolysis bath was heated and kept at \sim 330 °C in air for 24 h to remove moisture. Subsequently, high-purity argon was admitted into the sealed reactor continuously and the temperature was increased to and kept at a prescribed electrolysis temperature (850-950 °C). Pre-electrolysis was performed at ~2.6 V between an iron wire cathode and the graphite anode for 4-5 h to further remove residual moisture, metallic and other redox active impurities in the molten salt. Afterwards, the iron wire was replaced by the titania cathode and electrolysis proceeded at 2.9-3.1 V. The electrolysis was controlled by a computer, which also recorded simultaneously the current-time curve. When the electrolysis was terminated, the cathode was lifted from the molten salt, cooled in the argon stream, removed from the reactor, washed in distilled water and dried in air. The morphology, structure and composition of the electrolytic products were analysed by SEM, EDX (HITACHI x-650), XRD (SHIMADZU X-ray 6000), and Inert Gas Fusion Oxygen Analysis (LECO RO416-DR).



Fig. 1. SEM images of the interior of the titania dust pellet (a) before and (b, c) after electrolysis at 3 V for 10 h in molten $CaCl_2$ at 900 °C, and (d) the electrolysis product from a reagent TiO₂ pellet under the same conditions. The insert between a and b is the photograph of the titania dust pellet before (top) and after (bottom) electrolysis.

3. Results and discussion

3.1. Titania dust

The photo of a sintered titania dust pellet and the SEM image of its interior are shown in Fig. 1a. The sintered sample had particles of 0.1–0.3 µm in size, similar to the commercial TiO₂ pigment (0.2–0.3 μ m). Crystal structure conversion from anatase to rutile (Fig. 2a and b) occurred after sintering at 900 °C for 2 h. After electro-reduction in molten CaCl₂ by applying a constant voltage of 2.9-3.1 V between the pellet cathode and the graphite anode for 12 h, a grey pellet of the same shape as the precursor pellet was obtained (see the insert of Fig. 1b). XRD (Fig. 2c) and EDX analyses proved the electrolysed pellet was pure titanium metal. The particle size in the metallised pellet was $5-10 \,\mu\text{m}$ (Fig. 1b and c), which was much larger than that in the titania dust pellet. Due to the removal of oxygen and sintering of the metallic particles, the electrolysed pellet shrank slightly. These observations agree with the report by Chen et al. on the electrolysis of reagent titania [1]. For comparison, Fig. 1d presents an SEM image of the reduction product from a reagent titania pellet obtained in this work under the same condi-



Fig. 2. XRD patterns of (a) as received titania dust, (b) sintered titania dust pellet, and (c) the titanium metal prepared from the dust by electrolysis at 3 V for 10 h in molten CaCl₂ at 900 $^{\circ}$ C.





Fig. 3. SEM images of the interior of a metatitanic acid pellet (a) before and (b) after sintering at 900 °C for 2 h, and (c) after electrolysis at 3.1 V for 12 h in molten CaCl₂ at 900 °C.

tions. Obviously, the two products are microscopically identical although the feeding materials were significantly different in cost.

production of titania pigment and titanium sponge, and contains typically 60-90 wt.% TiO₂. The titanium-rich slag used in this work was produced by reducing the titanioferrite ore with coal in a closed electric arc furnace, following which most iron was sep-

3.2. Metatitanic acid

As confirmed by SEM (Fig. 3a) and XRD (Fig. 4a), the dried metatitanic acid sample had an amorphous structure. After sintering at 900 °C for 2 h, the amorphous TiO₂ was transferred into anatase (Figs. 3b and 4b). Upon electrolysis in molten CaCl₂ at 2.9–3.1 V for 12 h, metallic powder with particle size around 3–6 μ m was also obtained. Again, XRD (Fig. 4c) and EDX analyses confirmed that the product was pure titanium. The oxygen content in the electrolysed and washed sample was about 3000 ppm as measured by the LECO RO416 oxygen analyzer. These results reveal that disregarding the starting crystal structure of the titania precursor, pure metallic titanium can be produced by the FFC Cambridge process, which will be beneficial for reducing the cost of the feeding material in the new process.

3.3. Titanium-rich slag

The possibility of direct electrolysis of the titanium-rich slag was also investigated. Titanium-rich slag is the raw material for



Fig. 4. XRD patterns of metatitanic acid (a) before and (b) after sintering at 900 °C for 2 h and (c) after electrolysis at 3.1 V for 12 h in molten CaCl₂ at 900 °C.





Fig. 5. SEM images of the interior of a titanium-rich slag pellet (a) before and (b) after ball milling for 4 h, and (c) after electrolysis at 3.1 V for 12 h in molten CaCl₂ at 900 °C.

arated from the slag. The as-received slag was a coarse powder with the particle size being around $10 \,\mu m$ according to Fig. 5a. Its metallic elemental composition is shown in Table 1, with Fe, Si, Mn and Al being the main impurities. After ball-milling for 4 h in a zirconia container, the particle size was reduced to below a couple of micrometers (Fig. 5b). The milled slag powder was pressed into small pellets and sintered at 900 °C for 2 h to gain mechanical strength for the electrolysis operation. From Fig. 6a and b it can be seen that the structure of the titanium-rich slag was mainly rutile before and after sintering. This is understandable because the formation temperature of the slag was around 1150 °C, higher than the sintering temperature. After electrolysis at 3.1 V for 12 h in molten CaCl₂ at 900 °C, the slag pellet was fully metallised and could easily be ground into powder. Fig. 5c shows the SEM image of the product. The particle size of the nodular powder was in the range of $5-10 \,\mu\text{m}$, and the oxygen content was about 4500 ppm (this is an average of three parallel measurements of 3000-6000 ppm). However, the XRD pattern (Fig. 6c) differed from that of metallic titanium, and was close to that of titanium-iron alloys. This difference can be reasonably attributed to the metallic impurities in the slag. Interestingly, comparing the compositions (metallic elements only) between the slag and the electrolytic product reveals that most of iron and silicon remained in the product as alloying elements, but

manganese and aluminium were partly or completely removed during electrolysis.

While this unprecedented finding is scientifically interesting and commercially important, it warrants some comments.



Fig. 6. XRD patterns of titanium-rich slag (a) before and (b) after sintering at 900 °C for 2 h, and (c) after electrolysis at 3.1 V for 12 h in molten CaCl₂ at 900 °C.

Electrochemical reduction on a solid or liquid cathode of mixed elements in molten CaCl₂ has been known to be capable of removing some non-metallic elements [17] but alloying the metallic elements [1,18]. However, there has not yet been any formally published work on removal of metallic elements (excluding alkali and alkaline earth elements) during electroreduction, although loss of aluminium was observed in this and other laboratories when mixed TiO2 and Al2O3 (with or without other oxides) were electrolysed in molten CaCl₂. Losses of silicon, iron and manganese are unknown. The significance of the observed losses or removal of metallic elements during electro-reduction is at least two-fold: it can be negative for synthesis of various alloys with desired concentrations of these and potentially other metallic elements, but may also be positive for separation of metallic elements in a particular mineral. It should be mentioned of the previous successful synthesis of the Ni₂MnGa alloy by electro-reduction of a mixture of the respective oxides with the same composition of metallic elements [18]. Then, the observed losses of Mn from the Ti and Fe dominated oxide mixture suggests the interactions between different metal atoms be important factors affecting the final composition of an alloy to be synthesised by electro-reduction. However, our further work is still ongoing for a better understanding of the causes to the observed losses of Al, Mn, Fe and Si, focusing on composition analyses of the molten salt after electrolysis and of the gas phase products when volatile chlorides (e.g. AlCl₃ and SiCl₄) may form, and also on the behaviour of different oxide mixtures.

3.4. Current and energy efficiency

Typical current-time curves recorded during constant voltage electrolysis of the three precursors are presented in Fig. 7a-c, respectively. It can be seen that all the three curves have similar shapes. The current increased with time at beginning, reached maximum (around 5 A, see the larger panel in each of Fig. 7a, b and c) in the first few minutes, and then declined, within 3-5 h, to a stable level, 0.5–0.7 A (see the inserted smaller panels in each of Fig. 7a-c). The observed initial current peak agrees with the reduction taking place at the dynamic *metal/oxide/electrolyte* three phase interlines (3PIs) [4,19]. As previously explained [4,19], the reduction began at the 3PIs of *cathode current collector* (Mo mesh)/*oxide* (titania)/*molten salt* (CaCl₂). When the titania in contact with the Mo mesh was reduced to Ti metal, new 3PIs formed amongst the newly formed Ti, the oxide and the molten salt. When such processes continued, the 3PIs at each of the many Momesh/oxide contacts expanded initially and overlapped with each other later (corresponding, respectively to the current increase and decrease before and after the current peak on the current-time curves) along the surface of the pellet until all the surface of the pellet was metallised. Afterwards, because the metallised surface layer was porous (see Figs. 1c, 3c and 5c and also the inserted SEM image in Fig. 7a), molten salt could access the interior of the pellet, and oxygen ions could move out through the molten salt contained in the pores of the metallised surface, the reduction continued, accompanied by the 3PIs moving along the depth direction into the interior of the oxide pellet.



Fig. 7. Current–time plots of electrolysis of (a) titania dust (1.5 g, 3.0 V), (b) metatitanic acid (1.5 g, 3.1 V) and (c) titanium rich slag (2 g, 3.1 V) in molten CaCl₂ at 900 °C. Note that the larger panels in each sub-figures are the enlarged portions of the respective inserted smaller panels in the larger panels. The inserted image in (a) is the SEM image of the cross section of a partially electroreduced TiO₂ pellet (3.1 V, 900 °C, ~5 h). The layers indicated were titanium (A, less oxygen), titanium + perovskite (B) and perovskite (C).

With reference to the inserted SEM image in Fig. 7a, the *Ti metal/titania/molten salt* 3PIs are located at the junction between the porous A and B layers, but also extend into layer B.

The electrolysis usually lasted for ~ 12 h to ensure reduction of the pellet to a sufficiently low level of oxygen (reaching, 2000 ppm). Using the current-time curve in the inserted small panel of Fig. 7a as an example, it can be calculated that the charge passed for reducing the 2 mm (1.5 g) TiO₂ was 5.08 Ah within 5 h, and 9.95 Ah within 12 h. The current efficiency changed

from 40% to 20%, as calculated from the ratio between the theoretical charge required to remove the amount of oxygen from the oxide pellet (or that from the reduced portion in a partially reduced pellet) and the measured total charge passed over the electrolysis time. The energy consumption after 12 h electrolysis was about 33 kWh/kg Ti.

It is worth noting that the current efficiency depended on a number of factors such as pellet thickness and porosity, and oxide particle size. Under similar conditions, thicker and denser pellets led to lower efficiency. Nevertheless, the efficiency values quoted above are much higher than that ($\sim 6\%$) recently reported by Liu et al. [15]. In their experiments, electronic conduction through the molten salt due to carbon contamination from the anode was considered as a key factor for the low current efficiency. Variations in current efficiency were also observed in the early stage of this program when graphite anodes of different sources were used. More importantly, it was found that strict control of the electrolysis procedures and conditions as described in this paper and also Chen's early report [1] is fatally important. For example, air leakage, even very small, into the reactor would cause a significant decrease in current efficiency.

Further, and more importantly, the CaO level in the molten salt should also be controlled to satisfy the transport of oxygen ion from the cathode to the anode. It was reported that the CaO level in a freshly prepared CaCl₂ melt by the combined thermal-electrochemical dehydration procedure should be well below 0.1 wt.% [11]. Higher CaO contents must be avoided, but this was not always practiced properly. If the CaCl₂ was inadequately thermally dried in air, hydrolysis could lead to CaO formation to a significant degree. Because the decomposition voltage of CaO is about 2.6 V at 900 °C, under the applied cell voltage (2.9–3.1 V), reduction of the Ca^{2+} cation to a low valence state, e.g. Ca(0) and Ca (I) species dissolved in molten CaCl₂, or calcium metal on the cathode is highly likely to occur in a molten CaCl₂ bath containing too much CaO. The use of a carbon anode further reduces the cell voltage for Ca²⁺ reduction by lowering the anodic discharging potential of the O^{2-} ion to form CO or CO₂. The occurence of Ca^{2+} reduction lowers the current efficiency not only as a side-reaction (if its product is not consumed by reaction with the oxide on the cathode), but also by increasing the electronic conductivity of the molten salt through the dissolved Ca (0) species, or through the electron hoping mechanism: $_{A}Ca(I) + _{B}Ca(II) \rightleftharpoons _{A}Ca(II) + _{B}Ca(I)$ [22] where the front-subscripts A and B denote the relative positions of the species in the melt. Note that theses species can be linked via disproportionation, i.e. Ca (I) + Ca (I) \rightleftharpoons Ca (0) + Ca (II). Also, once such electron conduction paths are established in the melt, all the Ca (0) and Ca (I) species formed at the cathode will be balanced by their consumption/oxidation at the anode. In other words, there will not be any "net" increase of Ca (0) or Ca (I) on the cathode and in the melt.

It may be argued that an "optimal CaO level" in the melt is needed to balance the need for current flow and for avoiding electronic conductivity via the cathodic generated Ca (0) and Ca (I) species. For information, based on the total amounts of titania (1.5–2.0 g) and CaCl₂ (\sim 500 g) used in this work, it can be estimated that the increase of the CaO level in the melt after electrolysis would not be higher than 0.3 wt.%. However, it must be pointed out that any theoretically or experimentally determined "optimal CaO level" will not be applicable universally because the initial current flow through the melt is strongly dependent on the total amount of oxide on the cathode and also on the design of the cell. Even for a given amount of oxide, the "optimal CaO level" will depend on the total amount of salt used. In our experience, the best way to control the CaO level is to let the electrolysis to generate a sufficient amount of CaO to maintain the current flow, although this means that an equivalent amount of Cl^- will be anodically discharged to chlorine gas.

We would like to emphasise again here that careful dehydration of the as-received $CaCl_2$ and pre-electrolysis of the molten salt bath (which removes redox active impurities, particularly those polyvalent transition metal ions) are crucially important to reduce the electronic conduction through the molten salt. However, these are not enough because, as it can be derived from Fig. 7, the energy wasted by the background current was still greater than 20 kWh/kg Ti. Further effort is greatly needed to avoid, reduce or eliminate the background current.

3.5. Further discussion

In fact, the influence of the background current on the electrolysis efficiency has long been recognised and some measures were proposed [20,21]. One of these is to use an oxidant, such as chlorine gas, to remove the accumulated CaO and Ca metal in the molten salt [21], but this approach is yet to be demonstrated. The other proposal involves electrolysis of the oxide cathode in two molten salt baths containing different levels of CaO, i.e. the "double-melt electrolysis" [20]. The high CaO concentration bath is to reduce the oxide to the metal phase with a high level of oxygen. Afterwards, the metallised cathode is transferred to, and electrolysed in the second bath of low CaO concentration with a smaller background current. The thought was that the removal of the last amount of oxygen from the metallised cathode involved oxygen diffusion in the solid metal, and hence was a slow process in comparison with the reduction of the oxide phase. If this slow process proceeds in a CaO free or low CaO concentration melt, the parallel current due to electronic conduction can be avoided or reduced and a higher current efficiency is expected. Preliminarily tests demonstrated the double-melt electrolysis for achieving low oxygen level in the metal [20], but no data of the current and energy efficiency were available. However, as discussed below, electro-reduction of TiO₂ is more complicated and there are other slow steps giving rise to a low reduction current (in comparison with the parallel background current due to electronic conduction) before full metallisation of the cathode. Consequently, it may be necessary to apply the second bath at an earlier stage of the electrolysis to avoid energy waste.

It can be seen in Fig. 7 that the electrolysis current dropped to the background level within ~ 5 h. In this initial period, the total charge passed and the charge used for oxide reduction (excluding the background current contribution by estimation from the shaded area in Fig. 7b) were, respectively about 2.5 times and half of that needed to remove all the oxygen in the oxide pellet.

(The total charge passed in the same period was slightly less in Fig. 7a and c.) Inspection of the cross section of the pellet electrolysed in this period revealed typical layered structures similar to that shown by the inserted SEM image in Fig. 7a. EDX analyses confirmed that the outmost layer was titanium metal (A) and the interior layers were titanium with or without perovskite (B) and perovskite (C) phases with the oxygen level increasing inwardly. In addition to perovskite, more detailed XRD analyses of partially reduced TiO₂ pellets under similar conditions indicated the presence of TiO and Ti₂O₃ phases, both belonging to the Magnelli phases, i.e. Ti_nO_{2n-1} [1,12]. Apparently due to the combined effects of oxygen removal from the surface layer and calcium inclusion inside the pellet, the overall mass and thickness of the partially reduced pellets varied only slightly, even though the total charge passed was significantly increased.

Observations of the perovskite and Magnelli phases in electro-reduction of TiO₂ in molten CaCl₂ are well documented [10,11,20]. Detailed stoichiometric analyses of the perovskite and Magnelli phases and their formation mechanisms were recently reported [12]. However, it is worth pointing out that, as observed in this laboratory at 2.9-3.1 V and 850-950 °C, the phase change in the oxide cathode always progressed inwardly from the surface, and the pellet was never in a single phase before full metallisation. Table 2 presents the reduction depth (the thickness of the metallised surface layer) as a function of the time of electrolysis of the titanium-rich slag pellets. Whilst the observation of a distinct metallised surface layer becoming thicker with electrolysis time is in general accordance with the dynamic three phase interline model [4,19], the phases linked by the interlines in the electro-reduction of TiO₂ are expected to be quite different from that of SiO₂ [19]. Because the Magnelli and perovskite phases formed during electrolysis of TiO₂ [1,12] are semi-conductors to electrons, and they are formed progressively with time, different three phase interlines may form and co-exist in the cathode to allow electro-reduction at different locations and stages. Some of these interlines can be derived from the inserted image in Fig. 7a and from data reported in literature [12], including (1) titanium |Magnelli phase| molten salt at the junction between the porous Ti layer A and the underneath layer B, (2) Magnelli phase |perovskite| molten salt and (3) titanium *perovskite molten salt* within layer B in which both perovskite and Ti phases were detected. At these interlines, the molten salt assists supply or removal of ions (Ca²⁺and O²⁻) that accompa-



Fig. 8. Correlation between the reduction depth (thickness of metallised surface layer) and electrolysis time for the titanium-rich slag pellets in molten $CaCl_2$, 3.1 V and 950 °C.

nies the electro-reduction. However, it cannot be excluded that ion conduction may proceed in some solid phases, and electroreduction may occur at the interface between two solid phases or at the interline linking more than three phases [19].

The point of the above discussion is to highlight the complexity of the electro-reduction of TiO₂ and to elaborate why and how the metallisation of the pellet proceeded non-uniformly, starting from the surface. It can be seen from Table 2 that the current efficiency decreased significantly with the metallised layer becoming thicker. Plotting the reduction depth against the electrolysis time led to either a logarithm or parabolic correlation, see Fig. 8. While the number of data points in Fig. 8 is insufficient for reliable discrimination between the two, they are however indicative of the influence of mass transfer. Because the pellets were far from being fully metallised, the mass transfer could only be associated with the ions moving out of the pellet through the molten salt contained in the pores of the porous metal layers. Because of the co-existence of different solid phases and threephase interlines in the pellet, it is challenging to identify which of these and the corresponding reaction(s) to be associated with the slow ion transfer. However, in terms of the application of the double-melt electrolysis, it is more important to recognize that the oxide reduction contribution to the total current becomes sig-

Table 2

Electrolysis data for the titanium-rich slag pellets at 3.1 V and 950 °C in molten CaCl₂ for different times

Oxide pellet thickness (mm)	Oxide pellet weight (g)	Electrolysis time (min)	Total charge passed $(Q)^a$	Reduction depth (mm) ^b	Oxygen in metallised layer (wt.%) ^c	Reduced portion (wt.%)	Current efficiency ^d
2.88	1.81	68.0	1.0	0.50	10.5-8.6	41.1	41.1
2.83	1.78	126.4	1.5	0.72	-	57.7	38.5
2.83	1.78	181.6	2.0	0.85	6.3–5.8	66.5	33.3
2.84	1.79	250.1	2.5	1.00	4.6-4.2	76.0	30.4
2.84	1.79	343.0	3.0	1.10	2.7-0.4	82.2	27.4

^a Q is the theoretical charge required to remove all the oxygen from the oxide pellet.

^b The thickness of the metallised surface layer on the electrolysed pellet.

^c Measured by EDX.

^d The current efficiency given here is lower mainly because of the use of thicker pellets.

nificantly smaller long before the full metallisation of the oxide cathode. In other words, after surface metallisation, the reduction of the pellet's interior contributed insignificantly to the total current in comparison with the background current which then became the main energy consumption factor.

In this laboratory, the background current was found to be much higher in a repeatedly used molten $CaCl_2$ bath than in a properly thermally dehydrated and pre-electrolysed fresh bath. Thus, the origin may be linked to the accumulated CaO and Ca metal in the melt as discussed afore. The other source might be the trace amount of electrolysis-generated low valence titanium species, such as TiO [10–12,23], that can dissolve in molten CaCl₂ and hence contribute to electronic conduction [22]. However, because large background currents were also observed in the electro-reduction of other oxides [4,24,25], the influence from the accumulated Ca and CaO must have prevailed.

Based on the above analyses and discussion, we propose to apply the second bath after the pellet was properly metallised on the surface, instead of waiting until full metallisation of the pellet. This change from the original proposal [20] should lead to avoidance of unnecessary energy consumption by the large background current in the first bath. In this work, the proper completion of surface metallisation coincided well with the current approaching the stable background current on the current-time curves. This feature actually agrees with the attribution of the background current to electronic conduction through the molten salt [17,22] and is to be used in our planned investigation of the double-melt electrolysis for avoiding or reducing the influence of the background current. Nevertheless, it should also be acknowledged that the use of two molten CaCl₂ baths means additional operation steps and devices, and may therefore face strong competition for industrial application from other emerging methods [21,26].

4. Conclusions

Porous pellets made from three titania precursors, namely titania dust, metatitanic acid and titanium-rich slag, were successfully electrochemically reduced to metallic titanium in molten CaCl₂ at 900 °C by applying a constant cell voltage around 3 V. The reduction was independent of the initial crystal structure of the titania precursor. Aluminium, manganese, iron and silicon, which were all present in the titanium-rich slag, were, respectively completely and partly removed from the electrolytic product. In comparison with the commercial pigment TiO₂, using these cheap titania precursors as the feeding material promises further reduction in cost, and is helpful to the industrial application of the FFC Cambridge process. Analyses of the elec-

trolysis data indicated the reduction of the oxide pellets strongly depended on the mass (ion) transfer after the metallisation of pellet's surface. Following this initial period, the background current became a major factor influencing the electrolysis efficiency, requesting further research on different measures, such as the earlier proposed "double-melt electrolysis", that are capable of avoiding or decreasing electronic conduction through the molten salt.

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