

Reduction of Tantalum Pentoxide Using Graphite and Tin-Oxide-Based Anodes *via* the FFC-Cambridge Process

ROGER BARNETT, KAMAL TRIPURANENI KILBY, and DEREK J. FRAY

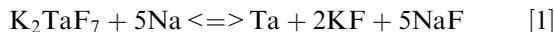
An investigation into the electrochemical reduction of tantalum pentoxide (Ta_2O_5) to tantalum metal in molten calcium chloride was performed. The oxide was made the cathode, and either graphite or tin oxide rods were selected as the anodes. The experiments were terminated after 8 hours of potentiostatic electrolysis using a two-electrode setup, with the current and anodic potential recorded. The cathode products were analyzed by means of X-ray diffraction, scanning electron microscopy (SEM), and inert-gas fusion analysis. The key result is that tantalum can be produced using either anode, but the tin oxide anode leads to greater current efficiency and a cleaner melt with no significant differences in the product microstructure.

DOI: 10.1007/s11663-008-9219-6

© The Minerals, Metals & Materials Society and ASM International 2009

I. INTRODUCTION

TANTALUM metal has a wide variety of applications in electronics, engineering, and metallurgy due to its remarkable properties. These include being extremely durable, being highly resistant to corrosion, and having a very high melting point (3017 °C). Currently, 60 pct of the world consumption of tantalum is used for the formation of capacitors, in the form of a fine powder.^[1] Presently, most tantalum metal is commercially produced by a series of complex procedures, which involves a particularly expensive step—the sodiothermic reduction of small crystals of K_2TaF_7 to tantalum powder in a molten fluoride salt bath.^[2,3]

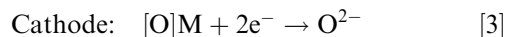
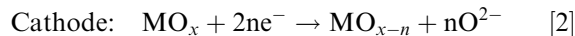


The use of fluorides raises environmental and safety concerns, and the electrochemical production of sodium is expensive in itself. Other nonfluorinated tantalum compounds may be produced from the same mineral stock, such as TaCl_5 or Ta_2O_5 , and a method of reducing the said compounds to tantalum metal would be desirable from both an economic and environmental point of view.^[1]

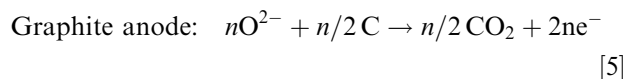
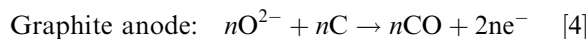
The novel FFC-Cambridge Process was discovered in 1997, by Derek J. Fray, Tom W. Farthing, and George Z. Chen at the University of Cambridge.^[4,5] They found

that by making a metal-oxide a cathode and a graphite rod an anode, in an electrolytic cell containing molten calcium chloride, the metal oxide was reduced to its metal. A significant amount of work has since been concentrated on the electrolytic production of numerous metals and alloys directly from their metal oxides (including but not limited to Cr_2O_3 , Nb_2O_5 , SiO_2 , and TiO_2), using other alkali-metal halide melts.^[6-9] The FFC-Cambridge Process may be applied to produce tantalum directly from its oxide, and may have certain advantages over current processes including being fluoride-free, being more energy efficient, and not requiring the use of sodium.

The inventors of the FFC-Cambridge Process have termed the ionization of oxygen at the metal-oxide (MO_x) as electro-deoxidation, and cell reactions have been derived to explain the mechanism. When a sufficiently high voltage is applied between the metal-oxide cathode and the anode, the oxygen found within the metal-oxide, or the metal-oxygen solid solution $[\text{O}]\text{M}$, becomes ionized. This is shown in Reactions [2] and [3], respectively.



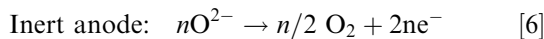
The oxygen anion then passes through the molten salt electrolyte by diffusional, convective, and migrational forces, before being discharged as carbon oxides on a graphite anode, or oxygen gas on an inert anode. The relevant half-reactions for the anodes are as follows.



ROGER BARNETT, formerly, Esquire, with the Department of Materials Science and Metallurgy, University of Cambridge, is Doctor, with TWI, Cambridgeshire. KAMAL TRIPURANENI KILBY, formerly, Esquire, with Department of Materials Science and Metallurgy, University of Cambridge, is Doctor, with Touche LLP, Cambridge. DEREK J. FRAY, Professor, is with the Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge, CB21RL, United Kingdom. Contact e-mail: kt285@cam.ac.uk

Manuscript submitted November 16, 2007.

Article published online February 5, 2009.



An overall reaction can be made by combining one of the cathodic half-reactions with an anodic half-reaction. Therefore, adding Eqs. [2] and [6] with ($n = x$), the overall reaction for a metal-oxide that is fully reduced in a cell containing an inert anode is as follows.



Table I presents a series of standard reduction potentials for the cathode, under the conditions employed in the FFC process, using a Ca^{2+}/Ca reference point of zero, at 900 °C, and assuming that all reacting or produced species are at unit activity or at unit atmosphere partial pressure.^[10,11] The standard reduction potentials presented for the oxygen ionization reactions show the relative ease of reduction for selected metal oxides to their metals, and can be used to determine the minimum potential needed for a full cell reaction to take place. Thus, the electrochemical production of tantalum metal from tantalum pentoxide is thermodynamically viable at -1.589 V (if oxygen is considered to be evolved at the anode) and if overpotentials and ohmic losses are ignored. However, it should be noted that the actual potentials will be higher as the oxides react with the CaO in the melt to form calcium tantalates and these will require a higher potential for reduction.

By considering Table II, the carbon oxide gases and oxygen have noticeably lower standard reduction potentials when compared to chlorine. Therefore, the generation of carbon oxide gases and molecular oxygen will be preferred to chlorine gas evolution if the applied voltage is below that for salt decomposition to take place (3.214 V). However, it should be noted that even

Table I. Standard Reduction Potentials E° for Selected Cathodic Reactions, Calculated from Thermodynamic Data ($E_{\text{Ca}} = 0$) at 900 °C

Half-cell reactions	E° (V)
$\text{O}_2 + 4e^- = 2\text{O}^{2-}$	2.657
$2/3\text{Fe}_2\text{O}_3 + 4e^- = 2\text{O}^{2-} + 4/3\text{Fe}$	1.763
$2/5\text{Ta}_2\text{O}_5 + 4e^- = 2\text{O}^{2-} + 4/5\text{Ta}$	1.068
$\text{SiO}_2 + 4e^- = 2\text{O}^{2-} + \text{Si}$	0.843
$\text{TiO}_2 + 4e^- = 2\text{O}^{2-} + \text{Ti}$	0.761
$2/3\text{Al}_2\text{O}_3 + 4e^- = 2\text{O}^{2-} + 4/3\text{Al}$	0.407
$\text{ZrO}_2 + 4e^- = 2\text{O}^{2-} + \text{Zr}$	0.387
$\text{Ca}^{2+} + 4e^- = \text{Ca}$	0.000

Table II. Standard Reduction Potentials E° for Selected Reactions, Calculated from Thermodynamic Data ($E_{\text{Ca}} = 0$) at 900 °C

Half-cell reactions	E° (V)
$\text{Cl}_2 + 2e^- = 2\text{Cl}^-$	3.214
$\text{O}_2 + 4e^- = 2\text{O}^{2-}$	2.657
$\text{CO}_2 + 4e^- = \text{C} + 2\text{O}^{2-}$	1.631
$2\text{CO} + 4e^- = 2\text{C} + 2\text{O}^{2-}$	1.541

below this decomposition voltage, it is still theoretically possible to generate small amounts of chlorine gas at low partial pressures. Furthermore, it is evident that by employing a carbon oxide gas evolving graphite anode, it is theoretically possible to employ a potential 1V lower than for an oxygen-evolving inert anode. However, this thermodynamic advantage for the graphite anode may be partially offset by higher anode overpotentials when compared to an inert anode. Indeed, work performed by Popescu *et al.* established that the overpotential for a tin oxide (SnO_2)-based anode with Sb_2O_3 and CuO additions was only 0.6 V lower than for a graphite anode (at 0.5 A/cm^2 in a cryolite melt), partially offsetting this thermodynamic advantage.^[12]

These SnO_2 -based materials have received significant attention from gas sensor manufacturers, the glass industry, and from the aluminum electrolysis field.^[13] The SnO_2 -based anodes commonly used have combined additions of antimony oxide (Sb_2O_3) and copper oxide (CuO) to improve electrical conductivity and enhance densification, respectively. Typically, 1 to 2 wt pct Sb_2O_3 and <1 pct CuO are used.^[14] Such SnO_2 -based electrodes have been tested as inert anodes in cryolite melt.^[15] Its low solubility in such an electrolyte, and its relatively high melting point and conductivity, makes it a candidate anode material for the analogous FFC-Cambridge Process. Other factors that must be considered for the anodized tin oxide material for the FFC-Cambridge Process include the following: its resistance to attack by the molten salt, oxygen ions, and oxygen gas; its resistance to thermal shock; its robustness; its electrochemical stability; and its ease of deployment.^[16]

Previous work has shown that after electrolytic reduction of a metal oxide in calcium chloride with a graphite anode, the melt becomes heavily contaminated with carbon residue preventing reuse of the salt. The formed carbon residue has been attributed to parasitic reactions between calcium and carbon dioxide gases in the melt and the direct reduction of carbonate ions by Suzuki *et al.* By using a SnO_2 -based anode, it should be ensured that such reactions do not take place. This may ultimately lead to benefits for the FFC-Cambridge Process, such as improved current efficiency, increased melt cleanliness (allowing for reuse), less cathodic product contamination, and less cell downtime for anode replacement.^[17-19]

II. EXPERIMENTAL

A commercially available tantalum pentoxide (Ta_2O_5) powder was selected as the starting material (PI-KEM, 30279-P) for the preparation of an oxide precursor. Although specified as tantalum pentoxide of 99.995 pct purity with an average particle size of $2 \mu\text{m}$, analysis of the powder under scanning electron microscopy (SEM) revealed aggregation of the particles and the true particle size to be approximately $0.2 \mu\text{m}$. Uniaxially pressing the as-received powder into pellets resulted in significant flaking and layering, due to friction from the die. Thus, the tantalum pentoxide was mixed with 5 wt pct of a bis-stearamide wax lubricant (Abril,

Abrilube 84, Mid Glamorgan, UK) that would be completely combusted during sintering. The Ta₂O₅-Abrilube 84 mixture was uniaxially pressed at 125 to 135 MPa into pellets. Following the results of a pre-investigation, sintering was carried out at 1200 °C for 3 hours in air. The sintered pellets possessed sufficient integrity and mechanical strength for handling, with a mass of 1.9 g, a diameter of 17.0 mm, and a thickness of 1.7 mm. A relative density of 55 to 60 pct was calculated, and an open porosity of 26 to 30 pct was determined by a water saturation method.

The electrochemical experiments were performed inside a 2-L vertical tubular INCONEL* reactor located

*INCONEL is a trademark of INCO Alloys International, Huntington, WV.

inside a programmable electrical furnace. A sufficiently constant heating zone was determined from measuring its temperature profile. The water-cooled upper end of the reactor was sealed with a stainless steel cover with silicone-sealed feed-throughs for a thermocouple, the electrode leads, and the gas inlet/outlet pipes. The cathode lead was connected to a stainless steel 316 mesh basket containing the tantalum oxide pellet and was formed from tying two sections of the mesh (25 × 25 mm) together. The corresponding anode lead was wrapped once around a 2-mm-wide groove of 1-mm depth cut around the chosen anode rod. Furthermore, the reactor was continually flushed through with argon (Air Products, Technical Grade, Cheshire, UK) dried over calcium sulfate granules.

A dense alumina crucible (Almath, CC69, Suffolk, UK) of 62-mm internal diameter and 105-mm height was placed inside the reaction vessel. This crucible contained 159.2 g of vacuum-dried CaCl₂ (at 200 °C) produced from calcium chloride dihydrate (Fisher, C/1500/65, Leicestershire, UK). It was calculated that 96.6 pct removal of the theoretical amount of water was achieved, with the condensate having a measured pH comparable to distilled water. Moreover, the alumina crucible contained 0.8 g of calcium oxide powder (Alfa Aesar, 10923, Lancashire, UK) of 99.95 wt pct purity, corresponding to approximately 1 pct mol of the total electrolyte composition. It should be noted that calcium oxide was added to the melt to inhibit chlorine evolution at low partial pressures by ensuring that the oxide activity in the electrolyte remains high. In order to remove residual moisture, the mixture was heated at 1 °C per minute to an operating temperature of 900 °C. Pre-electrolysis of the electrolyte, using a coiled nickel wire cathode with 20 cm² surface area in the melt, and a glassy carbon anode of 2 cm² surface area (HTW GmbH, Sigradur G, Thierhaupten, Germany) at 1.3 V constant voltage, showed that a stable current density of 3 mA/cm² could be attained within 5 minutes, suggesting that the melt was sufficiently dry and free of redox-active impurities. It should be noted that the applied potential used for pre-electrolysis was theoretically high enough to eliminate hydrogen present in water or its

derivatives but not high enough to decompose the electrolyte.

The actual reductions were carried out using the following procedure. A tantalum pentoxide pellet contained in the prepared mesh basket was made the cathode in a two-electrode setup. The anode used was either a 10-mm-diameter graphite rod (Tokai Carbon, HK-0, West Midlands, UK) or a 10-mm-diameter dense SnO₂-based rod (composed of ~1 wt pct Sb₂O₃ and ~0.5 wt pct CuO) (Glassworks Hounsell, Stannex E). The cathode mesh basket was completely submerged into the melt, while the anode was immersed to a depth of 15 mm into the salt. A constant voltage of 2.8 V was applied between the anode and the cathode with the corresponding current recorded, and the anode potential was measured by a glassy carbon quasi-reference electrode. This voltage is greater than the 1.589 V to reduce Ta₂O₅ when using an inert anode (calculated from Tables I and II). Therefore, this voltage was chosen as sufficient to produce either tantalum and CO/CO₂ or Ta and O₂ (using a graphite or a SnO₂-based anode, respectively) whilst still allowing for ohmic losses and overpotentials, and being sufficient to reduce CaO and carbon to calcium and carbon oxide gases. Also, it should be noted that the reaction with the least cathodic potential will occur first which will be the reduction of the metal oxide. However, it should be noted that this voltage is insufficient to decompose the CaCl₂ melt (3.214 V). After 8 hours, the run was terminated, and all of the electrodes were removed from the melt into the upper part of the reactor and the reactor allowed to cool. The conditions chosen were such that no continuous decomposition of calcium chloride could occur, similar to previous studies. Furthermore, it was calculated that this applied voltage should be thermodynamically sufficient to reduce tantalum pentoxide to tantalum metal. Electrical contact between the power supply (Instek, PSM-3004, South Ayrshire, UK) and the electrodes was made by 99.95 pct purity nickel wire of 2-mm diameter.

Upon removal of the cathode from the reactor, the pellets were still strong enough to handle, due to the presence of solidified calcium chloride both on the surface and within the pellet, but became extremely fragile upon washing. This necessitated a very gentle washing procedure. The pellets were placed in a cellulose cup within a Soxhlet extractor and washed for 18 hours with freshly distilled water at a temperature of 85 °C to 90 °C to remove all of the calcium chloride. This allowed extraction of pellets that remained intact long enough to collect samples from different parts of the pellet rather than a mixed powder. The anodes were washed under a vacuum using a 5-day washing procedure, involving water for the first day, 25 pct concentrated acetic acid for the second and third days, water again for the fourth day, and acetone for the final day. Such a vigorous drying procedure was necessary to remove the salt from the anode pores, to prevent subsequent fragmentation of the anode caused by hydration of the calcium chloride, and to ensure accurate weighing.

Phase composition of the reduced samples was determined through X-ray diffraction analysis (PW1050, PHILIPS**) with each scan running from

**PHILIPS is a trademark of Philips Electronic Instruments Corp., Mahwah, NJ.

10 to 90 deg. Microstructure and chemical composition of the samples were analyzed by SEM coupled with energy dispersive X-ray analysis (JSM-5800LV, JEOL[†]).

[†]JEOL is a trademark of Japan Electron Optics Ltd., Tokyo.

The acceleration voltage was 15 keV, and images were taken at 5000 times magnification using detected secondary electron emissions. All samples were analyzed with a gold sputter-coated layer. The oxygen content of the samples was determined by hot extraction and detection of evolved carbon dioxide (Eltra, ON-900, Neuss, Germany).^[20]

III. RESULTS

Figure 1(a) shows the current-time profile recorded during the 8 hours of electrolysis using a graphite anode at 2.8 V. Figure 1(b) shows the corresponding profile for the SnO₂-based anode under the same conditions. Both plots show a high initial current followed by a rapid drop, and this may be explained by capacitance discharge. This is followed by a peak that extends over 500 seconds, and then by a gradual decay of current. Afterward, there is a noticeable current shoulder that may be attributed to a phase change of the cathode material, and this precedes a small and time-independent current for the remainder of the run. The reduction performed with a SnO₂-based anode shows a lower initial slope and a lower final current, with the current shoulder being 2000 seconds later in the run. These features are all reasonably reproducible.

Figure 1(c) shows the anodic potentials for both anodes measured against a glassy carbon quasi-reference electrode. The anode potentials are relatively stable for both anode runs, but are noticeably higher for the SnO₂-based anode when compared to the graphite anode.

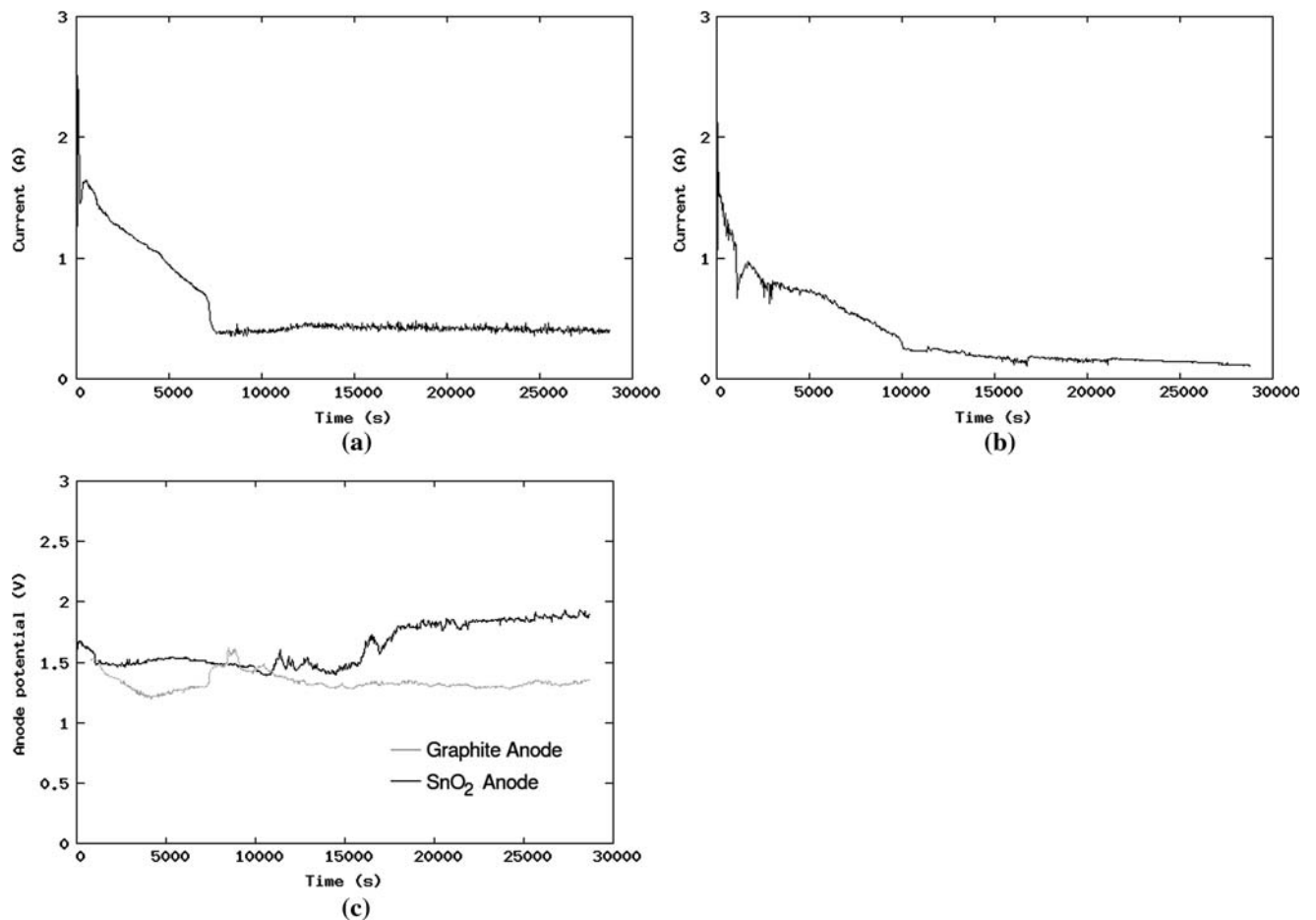


Fig. 1—(a) Current-time profile during reduction using a graphite anode. (b) Current-time profile during reduction using a SnO₂ anode. (c) Anodic potentials for graphite and SnO₂ measured vs a glassy carbon quasi-reference electrode during reduction.

Figure 2(a) presents the X-ray diffraction spectrum of the tantalum oxide pellet after sintering, and Figures 2(b) and (c) present the X-ray diffraction spectra of the samples reduced with a carbon anode and a SnO₂-based anode, respectively. Both samples show that the oxide has been reduced to tantalum with no calcium tantalates above the detection limit, nor any other oxygen-containing phases. The sample reduced using a graphite anode was found to contain a small amount of tantalum carbide, while the sample reduced using a SnO₂-based anode contained a small amount of Ta₂Sn₃. Figure 2(d) shows an X-ray diffraction spectrum taken of the surface of the SnO₂-based anode that was immersed in the melt during reduction.

Figure 3(a) shows a micrograph of the compact sintered tantalum pentoxide pellet, as obtained after sintering in air for 3 hours at 1200 °C. Figure 3(b) shows a micrograph of the reduced sample, and Figure 3(c) presents the results obtained from energy dispersive X-ray analysis for the cathodic product when a graphite anode is used. The corresponding micrograph and the energy dispersive X-ray analysis for the reduced sample when a SnO₂-based anode is used are shown in Figures 3(d) and (e), respectively.

Finally, weighing the anodes before and after electrolysis revealed that the graphite anode was found to have lost 6.0 pct (0.39 g) of its original mass after electroreduction of the tantalum pentoxide. It was calculated that 0.34 g of oxygen was present in the original 1.9 g Ta₂O₅ pellet. If it is assumed that all of the oxygen within the Ta₂O₅ pellet reacts with the graphite anode, and then the amount of carbon that is removed from the anode *via* formation of CO/CO₂ may be determined. If CO were the sole product, then 0.26 g of carbon was consumed through oxidation, while if CO₂ were the only product, then only 0.13 g of carbon was consumed. The remainder of the lost carbon could be attributed to the black residue seen on the surface of the salt after electrolysis. The percentage mass loss for the graphite anode is significantly higher than the 1.5 pct mass loss for the SnO₂-based anode. The tested anodes after electrolysis are shown in Figure 4.

IV. DISCUSSION

First, the results in Section III show that the production of tantalum *via* the FFC-Cambridge process is viable not only using a graphite anode, but also with a SnO₂-based anode. In both cases, the tantalum is fully reduced to the metal, showing no oxide phases above 0.5 wt pct concentration. Oxygen has a small solubility in tantalum, and so the remaining oxygen is likely present either as dissolved oxygen or as a thin layer of surface oxide.^[21]

Figure 3(f) shows an example of long strands that occur very sparsely in the pellet reduced by the SnO₂-based anode. The EDX reveals the strands to contain calcium, tantalum, and oxygen, indicating incomplete reduction, but the concentration of these strands is sufficiently low as to be undetectable by XRD. The bulk concentration of oxygen in the sample is low, as

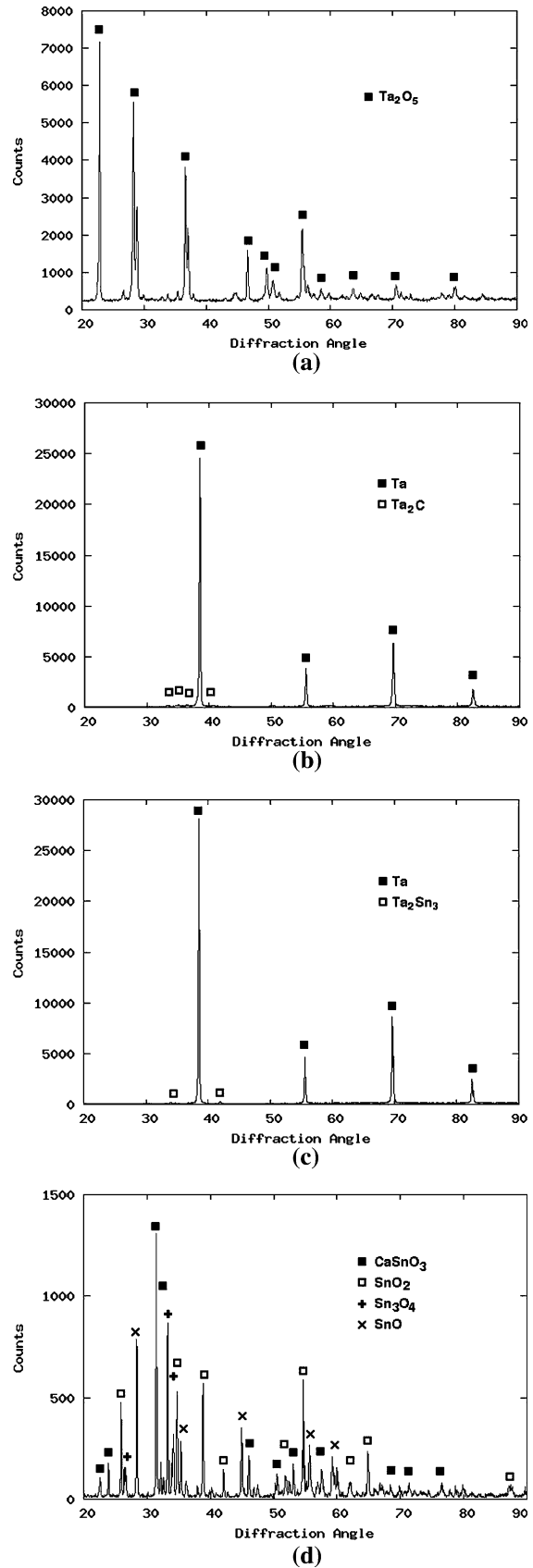


Fig. 2—X-ray diffraction spectra of (a) sintered unreduced Ta₂O₅ sample, (b) sample reduced using a graphite anode, (c) sample reduced using a SnO₂ anode, and (d) surface section of the SnO₂ anode after use.

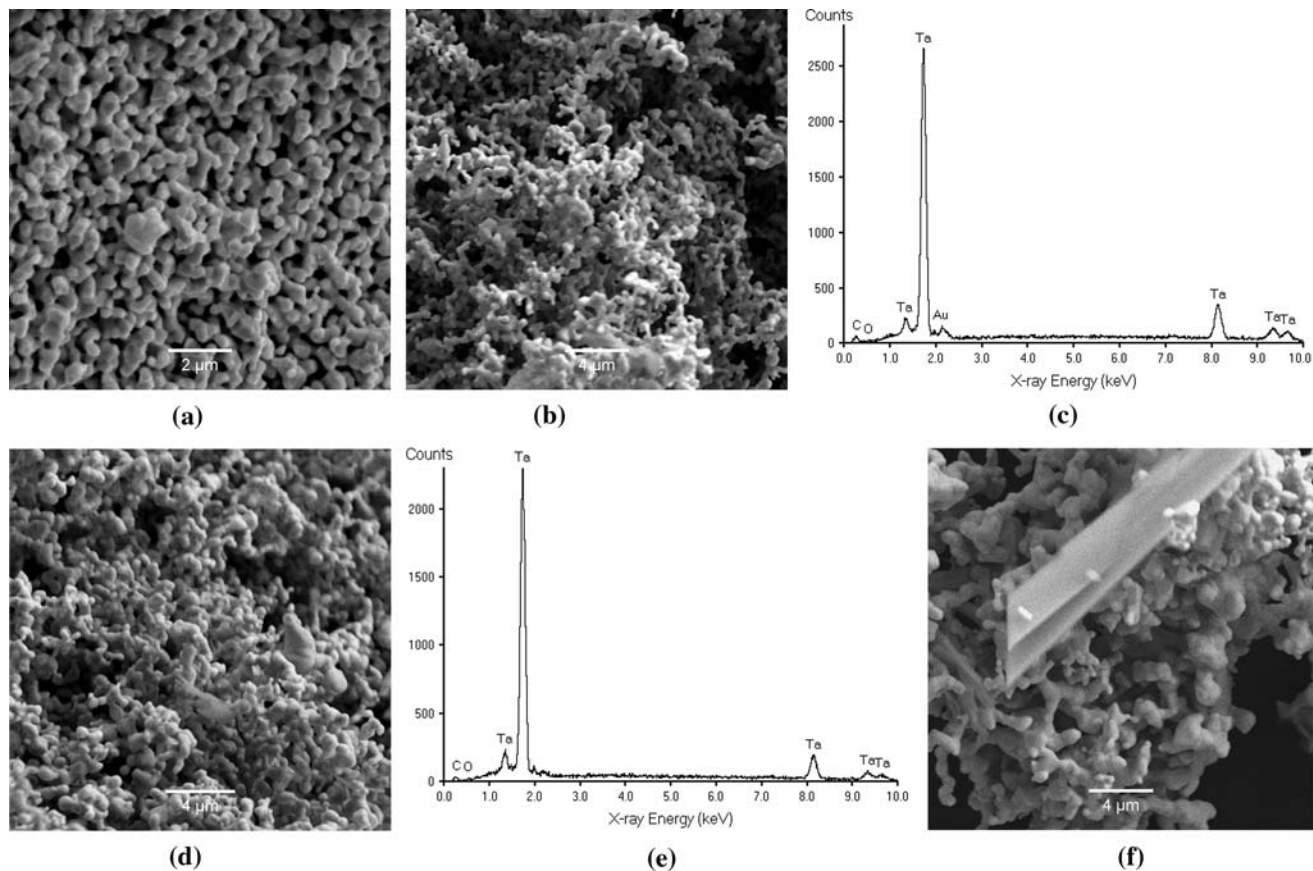


Fig. 3—(a) SEM image of the unreduced Ta_2O_5 sample. (b) SEM image of a sample reduced using a graphite anode. (c) Energy dispersive X-ray analysis on a sample reduced using a graphite anode. (d) SEM image of a sample reduced using a SnO_2 anode. (e) Energy dispersive X-ray analysis on a sample reduced using a SnO_2 anode. (f) SEM image of strands present in a sample reduced using a SnO_2 anode.

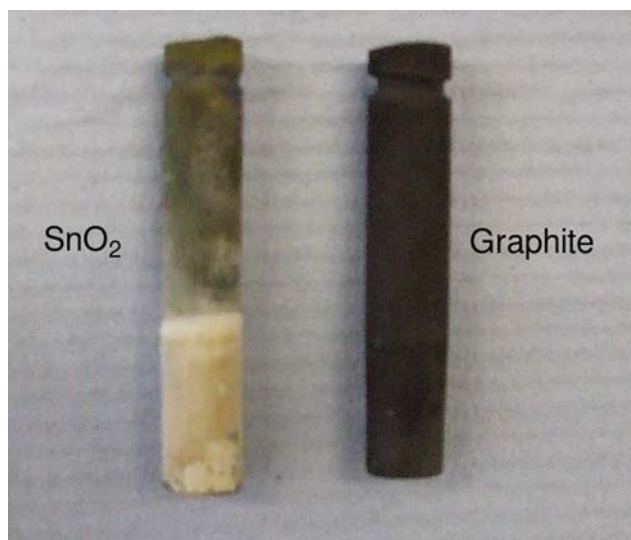


Fig. 4—Anodes after use.

determined by inert-gas fusion analysis. Other than the very occasional presence of these strands, there is no significant difference in microstructure between the products for the graphite and SnO_2 -based anode

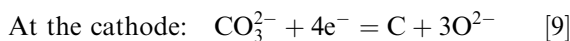
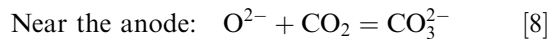
reductions, as can be seen from comparing Figures 3(b) and (c) with Figures 3(d) and (e).

Furthermore, both products show a decrease in particle size from the sintered perform after electroreduction, ranging from $2\ \mu\text{m}$ particles to $0.2\ \mu\text{m}$. Considering the small particle size, and thus the large surface area, the surface oxide may account for a considerable fraction of the remaining oxygen.

The reduction using a SnO_2 -based anode is marginally slower when compared to the graphite anode reduction, as can be seen in Figures 1(a) and (b). This may be due to the formation of an electrically resistive layer of calcium stannate (CaSnO_3) being formed on the surface of the SnO_2 -based anode (Figure 2(d)), which could inhibit electron transfer. All the features that appear with the graphite anode appear with the SnO_2 -based anode, but they appear later when the SnO_2 -based anode is used. In particular, the current shoulder at 7500 seconds for the graphite anode shown in Figure 1(a) appears at 10,000 seconds for the SnO_2 -based anode presented in Figure 1(b). This shoulder is hypothesized to correspond to the point at which all oxide phases have been reduced to tantalum metal (with remaining dissolved oxygen), with the subsequent steady background current corresponding to the slow removal of oxygen dissolved in the tantalum metal.

The anode potentials measured by the glassy carbon quasi-reference remain stable throughout electrolysis and within a range of 0.4 V. It can also be seen that the mean graphite anode potential of 1.3 V is lower than the measured mean value of 1.6 V for the SnO₂-based anode. As the electrolysis was conducted at a constant cell voltage, if the anode potentials are higher, then the cathode potentials must be lower, leading to a lower rate of deoxidation at the cathode. This may also contribute to the slower reaction speed when a SnO₂-based anode is used. It should be noted that prior cyclic voltammetry work conducted using either a graphite or SnO₂-based working electrode revealed that peaks assigned to carbon oxide gas evolution and oxygen evolution were at 0.4 and 1.4 V, respectively, vs a glassy carbon quasi-reference electrode.^[22] These results suggest that the anode potential is sufficiently high for carbon oxide gas evolution to take place using a graphite anode and for oxygen gas evolution to take place from a SnO₂-based anode. Furthermore, the higher anode potential on the SnO₂-based anode may be a reason for the slight delay in the SnO₂-based anode current profile, as there is a lower mean voltage of 0.3 V, when compared to the graphite anode, to drive the current.

The reduction using a SnO₂-based anode was also more current-efficient than the reduction using a graphite anode. The calculated charge required to reduce a 1.9 g tantalum oxide pellet is 4150C, but 10,300C were actually passed for the SnO₂-based anode during the 8 hours, giving an efficiency of 40 pct. This is compared to 17,100C being passed with a graphite anode, leading to an efficiency of only 24 pct. Thus, although a graphite anode may theoretically be used at a 1V lower voltage, it is actually the case that a SnO₂-based anode is significantly more efficient at the same voltage. It is believed that this is due to the lack of carbon contamination for electrolysis using a SnO₂-based anode. It is believed that for the graphite anode that the carbon residue floats to the surface, making a conductive path resulting in partial short circuiting. Furthermore, some of this residue may appear as a result of the graphite anode being eroded physically, but could also be a result of parasitic reactions between the carbon oxide gases produced at the anode and the formed carbonate ions being reduced at the cathode.

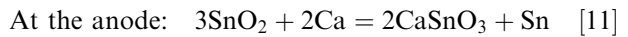


Reactions [8] and [9] clearly cannot occur if a SnO₂-based anode is used, hence providing an explanation for the improved current efficiency by using a SnO₂-based anode for tantalum pentoxide reduction by the FFC-Cambridge Process.

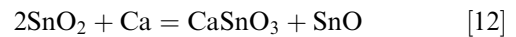
The carbon residue formed from Reactions [8] and [9] when using a graphite anode may also lead to contamination of the cathodic product. X-ray diffraction analysis revealed the presence of tantalum carbide (Ta₂C) in the final cathodic product, indicating that either the carbon residue reacts directly with the

tantalum during electrolysis or some dissolved species (such as CO₃²⁻) does. It may also be possible that the formed tantalum reacts with the carbon residue upon removal of the cathodic electrode from the melt.

However, X-ray diffraction analysis also indicated the presence of a contaminant (Ta₃Sn₂) in the cathodic product when a SnO₂-based anode is used. It is believed that this contaminant is formed because of the SnO₂-based anode being reduced by decomposed calcium oxide under the electrolytic conditions used. The X-ray diffraction spectrum presented in Figure 2(d) of the off-white colored layer formed on the SnO₂-based anode after electrolysis verifies the presence of calcium stannate and reduced tin oxide compounds (SnO and Sn₃O₄). It is possible to suggest a mechanism for the formation of Ta₃Sn₂ based on the established compounds.



The tin formed at the anode by Reaction [11] could then anodically dissolve into the salt under the applied voltage used for these experiments, migrate to the cathode, and form an alloy with tantalum.^[23] The SnO and Sn₃O₄ phases may be explained by Reactions [12] and [13].



The formation of SnO is unexpected, as it is not a stable phase in the Sn-O phase diagram,^[23] but may be stable in this more complex system. Indeed, it can be calculated that ΔG° for Reaction [12] at 900 °C is -297.1 kJ, making it thermodynamically favorable.^[10] The reactions presented previously explain the formation of the predominant phases found from X-ray diffraction analysis, why no tin was detected on the anode surface, and also the feasible formation of a small amount of a tantalum-tin phase at the cathode. Furthermore, these reactions also explain the mass loss of the SnO₂-based anode.

V. CONCLUSIONS

Tantalum pentoxide has been reduced to tantalum metal, by both a graphite anode and a SnO₂-based anode, with low impurity concentrations and low oxygen concentrations in both sets of reduced samples. It was found that tantalum pentoxide electroreduction *via* the FFC-Cambridge Process was found to be significantly more current-efficient when a SnO₂-based anode was used rather than a conventional graphite anode. Furthermore, the salt cleanliness was much improved (allowing the possibility of reuse), while a smaller proportion of the anode mass was consumed. No apparent differences in microstructure can be seen when using an inert anode, indicating that the cathodic reaction is unchanged.

ACKNOWLEDGMENTS

The authors are grateful to EPSRC and MetalYSIS Ltd. for financial support and to the members of the Materials Chemistry Group (Department of Materials Science and Metallurgy) for valuable scientific discussions.

REFERENCES

1. T. Wu, X. Jin, W. Xiao, X. Hu, D. Wang, and G.Z. Chen: *Chem. Mater.*, 2007, vol. 19, pp. 153–60.
2. K. Gupta: *Int. Met. Rev.*, 1984, vol. 29, pp. 405–44.
3. W. Kock and P. Paschen: *J. Min. Met. Mater. Soc.*, 1989, vol. 41, pp. 33–39.
4. G.Z. Chen, D.J. Fray, and T.W. Farthing: Patent No. WO9964638, 1999.
5. G.Z. Chen, D.J. Fray, and T.W. Farthing: *Nature*, 2000, vol. 407, pp. 361–64.
6. G.Z. Chen, E. Gordo, and D.J. Fray: *Metall. Mater. Trans. B*, 2004, vol. 35B, pp. 223–33.
7. X.Y. Yan and D.J. Fray: *J. Mater. Res.*, 2003, vol. 18, pp. 346–56.
8. P.C. Pistorius and D.J. Fray: *J. S. Afr. Inst. Min. Met.*, 2006, vol. 106, pp. 31–41.
9. D.T.L. Alexander, C. Schwandt, and D.J. Fray: *Acta Mater.*, 2006, vol. 54, pp. 2933–44.
10. A. Roine: *HSC Chemistry Version 4.1*, Outokumpu Research Oy, Pori, Finland.
11. K.S. Mohandas and D.J. Fray: *Trans. Ind. Inst. Met.*, 2004, vol. 57, pp. 579–92.
12. A.M. Popescu, S. Zuca, and M. Gaune-Escard: *Int. Symp. on Ionic Liquids in Honour of Gaune-Escard*, Carry le Rouet, France, 2003, pp. 491–99.
13. J.H. Yang and J. Thonstad: *J. Appl. Electrochem.*, 1997, vol. 27, pp. 422–27.
14. S. Zuca, M. Terzi, M. Zaharescu, and K. Matiasovsky: *J. Mater. Sci.*, 1991, vol. 26, pp. 1673–76.
15. J. Yang and J. Thonstad: *J. Appl. Electrochem.*, 1997, vol. 27, pp. 422–27.
16. D.R. Sadoway: *JOM*, 2001, vol. 53, pp. 34–35.
17. R.O. Suzuki, K. Teranuma, and K. Ono: *Metall. Mater. Trans. B*, 2003, vol. 34B, pp. 287–95.
18. K. Dring, O.-A. Lorentson, E. Hagen, and C. Rosenkilde: in *Innovations in Titanium Symp.*, M.N. Gungor, M.A. Imam, and F.H. Froes, eds., TMS, Warrendale, PA, 2007, pp. 59–67.
19. K. McGregor, A.J. Urban, and E.J. Frazer: *ECS Trans.*, 2006, vol. 2, pp. 369–80.
20. C. Schwandt and D.J. Fray: *Electrochim. Acta*, 2005, vol. 51, pp. 66–76.
21. H. Jehn and E. Olzi: *J. Less Common Metall.*, 1972, vol. 27, pp. 297–98.
22. K. Tripuraneni Kilby and D.J. Fray: University of Cambridge, Cambridge, United Kingdom, unpublished research, 2007.
23. T.B. Massalski: *Binary Alloy Phase Diagrams*, 2nd ed., 1990, vol. 3, American Society for Metals, OH, pp. 2920–21.