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Electrochemical Deoxidation of Titanium Foam in Molten Calcium Chloride

PRABHAT K. TRIPATHY, MAXIME GAUTHIER, and DEREK J. FRAY

Titanium foam, prepared by using a patented powder-metallurgy-based process involving a powder blend that was molded, foamed, and sintered using a three-step thermal treatment, was deoxidized in a molten CaCl_2 bath. The polarization experiments were carried out by cathodically polarizing the foam (working electrode) against a counter (graphite) electrode. Under constant potential (polarization) mode, the dominant mechanism of deoxidation was the ionization of oxygen, present in the foam, and its subsequent discharge, as CO_2/CO , at the anode surface. More than ~85 pct oxygen could be effectively removed by carrying out the electrodeoxidation experiments in fresh and pre-electrolyzed melt(s) at an electrolyte temperature of 950 °C. Scanning electron microscopy-energy dispersive X-ray (SEM-EDX) detection of the deoxidized foams did not show a presence of any inclusion(s) or secondary phase(s).

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I. INTRODUCTION

METALLIC foams (also known as cellular metals), because of the presence of a high-volume fraction of interconnected network of voids/pores, are increasingly being used for a variety of purposes such as (1) load/sound absorbing material, (2) sandwich material in the construction industry, (3) heat-transfer media (fluid filters), (4) flame retardants, (5) catalytic supports, and (6) bio-medical implants.^[1-3] Although in many cases these materials look like typical polymer foams, they differ from them in metallic characteristics such as ductility, electrical conductivity, and weldability.^[4] Aluminum and nickel foams are being routinely used for a variety of applications, such as “crash protection,” electrodes, and current collectors;^[5] steel and titanium foams, on the other hand, have emerged as potentially new materials for many commercial applications. Steel foams are being developed as suitable materials for civil building and construction projects.^[6] Alternately, titanium foams, which have been found to be better efficient materials over solid titanium^[6] in many applications (especially as a bio-mimetic material), offer promising applications both as a construction material and in the field of bio-medical/bone-implant engineering.

Titanium foams, because of the combination of a series of attractive properties such as (1) low density as well as stiffness, (2) high porosity and permeability, (3)

good mechanical strength, (4) low modulus, (5) excellent corrosion resistance, and (6) superior bio-compatibility, are classified under “high performance” materials.^[6] A relatively higher working temperature, comparable specific strength (as that of aluminum foams), superior fracture toughness, and better energy absorbing ability (than that of aluminum foams) favor the potential use of these foams in rocket construction and in military and aerospace applications.^[6] Furthermore, it is predicted that these materials can offer effective gains in the ship-building industry (luxury boat hulls), car industry (car body as well as its interior), and armor.^[6] From a medical application perspective, titanium foams, in the form of porous scaffolds (that can mimic the human bone), have recently emerged as excellent bio-mimetic materials.^[7] These foams provide the necessary support to cells to proliferate and maintain their differential functions, and thus, eventually help shape the ultimate bone shape/structure.^[8] Although some polymeric/ceramic materials, such as hydroxyapatite (HA), poly(-hydroxyesters), and polymers (collagen and chitin),^[9,10] are being routinely used, because of their inherent weak mechanical properties, these materials are prone to fracture failure during the healing process when under sudden impact. Because of their superior mechanical stability and better interfacial stability, titanium foams can prove to be ideal substitutes for bone-replacement, tissue attachment, or dental implants in the jaw.^[7,8,11]

Common fabrication processes of different metallic foams can be classified under four broad categories: (1) gas-injection into the liquid metal/alloy; (2) *in-situ* gas release by incorporation of a blowing agent into the molten metal/alloy; (3) evolution of dissolved gas(es) in the liquid; and (4) solid-state sintering/powder metallurgy of a mixture, comprised of the metal powder and a polymeric vehicle. The powder metallurgy route is a preferred process for fabricating high-melting-point metallic foams, such as titanium

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foams. Also, this route is preferred for bio-mimetic foams, where one of the desirable properties in the resultant foam is to have small pores, preferably in the range 200 to 500 μm .^[8,12]

The objective of the present investigation was to deoxidize titanium foams produced using a process patented by the researchers at the Industrial Materials Institute of the National Research Council Canada (IMI-NRC).^[13,14] Such foams are intended for use as porous orthopaedic or dental implants.^[15-17] The samples were deliberately fabricated so that they picked up significant quantities of oxygen (up to ~1 wt pct) during the fabrication stage. These oxidized foam samples were then directly treated in a molten salt bath to remove the oxygen. The deoxidation experiments were carried out using a new and novel molten salt electrochemical approach, known as the Fray-Farthing-Chen (FFC) Cambridge process,^[18] where the sintered foam pieces were cathodically polarized in a pool of molten calcium chloride against a (graphite) counter electrode. Under potentiostatic conditions, oxygen present in the foam ionized into oxygen ions. The oxygen ions dissolved in molten CaCl_2 and subsequently discharged as CO/CO_2 on the graphite anode. This article describes the detailed experimental work pertaining to the deoxidation of the sintered titanium (foam) bodies.

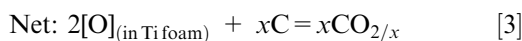
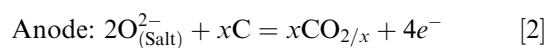
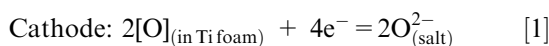
II. THEORETICAL CONCEPT

In the FFC process,^[18] it has been postulated that when a metal oxide/impure metal containing significant quantities of oxygen is cathodically polarized in an electrochemical cell, oxygen (from the cathode) gets ionized. The O^{2-} ions then travel through the electrolyte and eventually get discharged in the form of CO/CO_2 at anode surface, if a carbon rod is used as the anode material.

In a typical FFC cell that employs calcium chloride as the electrolyte, and foam and graphite as the cathode and anode materials, respectively, the overall anodic and cathodic reactions can be described as follows:



Reactions:



where the value of x , depending on the nature of the evolved (anode) gas, can be either 1, in the case of carbon dioxide (CO_2), or 2, if the gaseous species is CO .

The deoxidation, depending on the experimental conditions, can take place *via* two routes. According to the Ono-Suzuki process,^[19] calcium oxide, present in CaCl_2 , first undergoes decomposition to form metallic

calcium, which, in turn, reacts with the oxygen present in the cathode to form CaO . The oxygen, from CaO , subsequently gets discharged at the anode in the form of CO/CO_2 . Thus, according to this process, *in-situ* formation of calcium metal, prior to deoxidation, is an essential prerequisite condition. In the FFC process, on the other hand, experimental conditions can be tailored to avoid the formation of calcium metal and facilitate the ionization of oxygen. The ionized oxygen, because of its significantly high solubility in molten calcium chloride,^[19] is transported by the electrolyte from the vicinity of the cathode to the anode surface, where it gets discharged as the oxides of carbon. Thus, it is not necessary to invoke the role of calcium metal in order to carry out deoxidation. Although it is extremely difficult to prepare calcium oxide-free-calcium chloride, it has been observed that the presence of very little dissolved calcium oxide helps the deoxidation process. The detailed kinetics of the deoxidation process has been described elsewhere.^[20,21]

The extent of deoxygenation in the titanium-metal/titanium-oxygen solid solution in the CaCl_2 melt depends on various parameters, such as chemical purity of CaCl_2 , applied voltage, electrolyte temperature, nature of the cathode material, and CaO content in CaCl_2 . Also, during deoxidation, the cathode undergoes continuous composition and microstructural changes^[20,22] and makes the overall deoxidation process a complex one.

III. EXPERIMENTAL

A. Preparation of Titanium Foam

Titanium powder, a solid polymeric binder, and a foaming agent were intimately dry-mixed and then molded into the desired shape. The molded powder was then heat treated in a three-step cycle, which essentially consisted of three unit operations: foaming, debinding, and sintering. The structure, density, and pore size distribution (in the foam) could be controlled by adjusting the powder formulation and processing parameters. The final foam samples were cylindrical in nature, with an open porosity in the range of 71.4 to 74.7 pct and weight in the range of 2.35 to 3.43 g. The diameter and height of the samples were ~1.5 and ~1.2 cm, respectively.

B. Preparation of the Electrolyte

Nominally anhydrous CaCl_2 (Fluka, granular variety, > 97 pct CaCl_2) was subjected to vacuo-thermal treatment in order to remove the moisture content prior to melting. The salt was given a programmed and slow heating, starting from a temperature of ~60 °C to a maximum temperature of 210 °C for a duration of ~50 hours, in order to prevent the hydrolysis of CaCl_2 . The heating/drying of the salt was carried out under dynamic (rotary pump) vacuum throughout the entire duration. The vacuum-dried salt was carefully stored in airtight containers for subsequent use.

C. Experimental Setup

Deoxidation experiments were performed in a recrystallized alumina crucible (96-mm outer diameter, 90-mm inner diameter, 82-mm height, and 3-mm thickness) that contained molten CaCl_2 . The crucible was kept in a cylindrical INCONEL* 600 reactor (105-mm inner

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

diameter) that was placed in a vertical tubular furnace (Figure 1). A stainless steel lid with provisions for placing the electrodes and a thermocouple from the top was used to close the reactor. The reactor was made gas-tight with the help of suitable metallic clamps. The titanium foam and standard graphite bar (9-mm diameter, Tokai Carbon, United Kingdom) were used as working (cathode) and counter (anode) electrodes, respectively. High-purity nickel wire (>99 pct pure, 2-mm diameter) was used as the current collector for both the anode and cathode.

D. Procedure

Typically, between 250 and 300 g of CaCl_2 was held in the alumina crucible that was placed in the INCONEL 600 reactor. The reactor was set up as follows: through the top flange, (1) two graphite bars,

each connected to threaded SS cups, which in turn were attached to nickel wires, (2) one Ti foam, threaded to the nickel wire, and (3) one sheathed (with alumina) thermocouple (K type) were positioned, just above the (solid) salt level, with the help of the silicon rubber bungs. The top flange was tightened with the help of metallic clamps. The entire assembly was slowly heated with a programmed heating pattern to the desired temperature under continuous dry argon flow. A typical heating procedure involved initial heating to 500 °C at a rate of 50 °C/h. The temperature was then held for ~12 hours and raised to the final temperature (900 °C/950 °C) at the rate of 100 °C/h. The salt was kept at the maximum temperature for ~1 hour in order to allow the melt to become homogenized. The electrodes were then lowered into the homogenized melt, and experiments were carried out under continuous argon flow by varying the process conditions. A DC power supply (Thurlby Thander PL154, with 15 V and 4 A capacity), capable of carrying out the polarization experiments both under constant potential and current modes, was used for the experiments. The deoxidation current was recorded by monitoring the potential drop across a 1 Ω resistor that was in series between the power supply and the electrolytic cell. The configuration with the measured cell voltage included the potential drop that existed across the measurement resistor.

The deoxidized samples were then taken out of the furnace and washed/cleaned thoroughly, first with

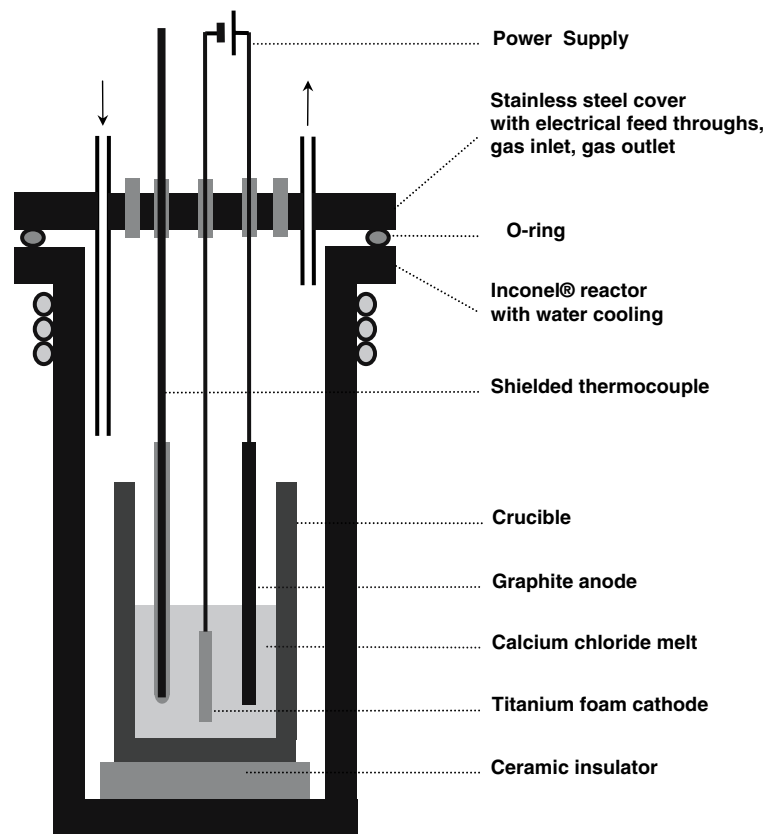


Fig. 1—Schematic representation of the electro-deoxidation experimental assembly.

distilled water and then by ultrasonic treatment. The samples were treated successively with dilute acetic acid, 1 N hydrochloric, ethyl alcohol, and acetone before drying them under mild vacuum at a temperature of $\sim 60^\circ\text{C}$. The cleaned samples were evaluated and characterized by techniques such as (1) scanning electron microscopy–energy dispersive X-ray detection (SEM-EDX), (2) porosity measurement, and (3) residual oxygen analysis.

IV. RESULTS AND DISCUSSION

The deoxygenation experiments were carried out by varying the (1) applied voltage, (2) electrolyte temperature, (3) duration of polarization, and (4) nature of the melt (with/without pre-electrolysis).

A. General Observations

The distance between the electrodes, *i.e.*, between the cathode (foam) and anode (carbon bar), was maintained within 2 cm. At the start of both pre-electrolysis and deoxygenation experiments, bubbling (of gases) around the vicinity of the anode surface was observed because of the removal of residual gases, in the former case, and the evolution of anode gases, such as CO_2/CO , in the latter stage. During pre-electrolysis, when the applied voltage was in the range of 1.5 to 1.7 V, the molten salt surface appeared relatively calm, which perhaps indicated the very slow bubbling rate of the residual gases. The intensity of the bubbling activity was found to decline with time and, invariably after about an hour, no significant bubbling activity was observed. Also, the bubbling phenomenon was found to depend upon the applied voltage. At an applied voltage > 3.5 V during deoxygenation, the bubbling of gases was found to be vigorous. Such an intense bubbling activity could be partly ascribed to the decomposition of CaCl_2 (because the theoretical decomposition voltage of CaCl_2 is 3.25 V at a temperature of 950°C ^[23]) in addition to the bubbling of CO/CO_2 . Similar behavior was also reported by others.^[24] However, the present experiments were carried out by carefully controlling the experimental conditions, especially adjusting the applied voltage, so as to avoid the decomposition of the CaCl_2 electrolyte. Because of the considerable overpotential at the anode, the effective potential at the cathode got reduced, which is why the applied voltage was more than the required (theoretical) voltage.

B. Current vs Time Profile

The decline of current with time (Figure 2) during polarization under a constant applied voltage gave a measure of the deoxidation phenomenon. The current vs time profile was observed to critically affect the foam purity in terms of residual oxygen content. It has been reported by several authors^[25] that a relatively low background current (usually < 0.1 A) invariably resulted in lower oxygen content in the deoxidized/electro-reduced metal/alloy. Obviously, the longer the duration

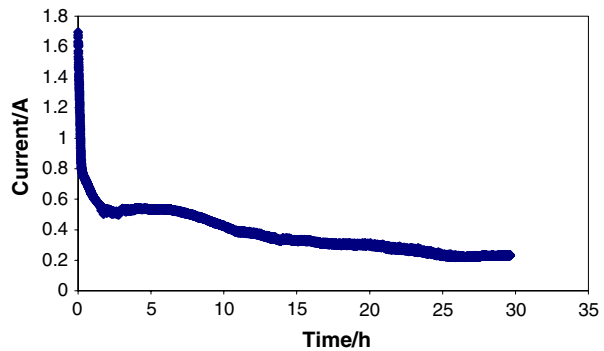


Fig. 2—Current vs time profile, obtained during the deoxygenation of a typical foam sample. Temperature of the electrolyte: 950°C ; applied voltage: 2.9 V; duration of the experiment: 30 h; and salt: fresh (vacuum-dried) CaCl_2 (Fluka, powdery).

of the polarization experiment, the lower the value of residual/background current, which resulted in relatively lower amounts of residual oxygen content (Figure 3).**

**The oxygen values were measured by using an ELTRA oxygen analyzer, which works on the principle of the conversion of oxygen, in the sample, to carbon monoxide and then quantifying the value (peak output) through the principle of thermal conductivity. Each value was an average value, obtained from two sets of samples, prepared under identical conditions. Also, the measurement was carried out by taking samples from different zones of the deoxygenated foam. Each measurement was carried out by taking ~ 100 mg sample.

It was also observed that very long hours of polarization resulted in an increase in the residual oxygen content (Figure 3). Such a phenomenon has also been reported to take place during the electro-reduction of Nb_2O_5 .^[26]

It was, therefore, required to identify an optimum value with respect to both the duration of the deoxygenation experiment and the background current, before terminating the experiment. The experimental data suggested that a duration in the range 24 to 30 hours was adequate to get an oxygen concentration of ~ 1500 mass ppm. The initial and final currents, in the present set of experiments, were found

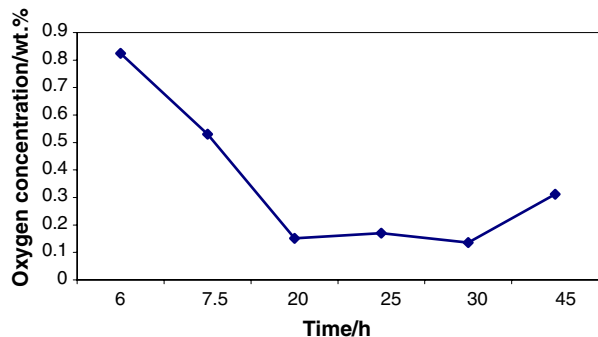


Fig. 3—Relationship between the deoxidation (reaction) time and residual oxygen content. It is seen from the figure that the residual oxygen content increased from ~ 0.1362 to 0.312 pct when the reaction time was increased from ~ 30 to 45 h.

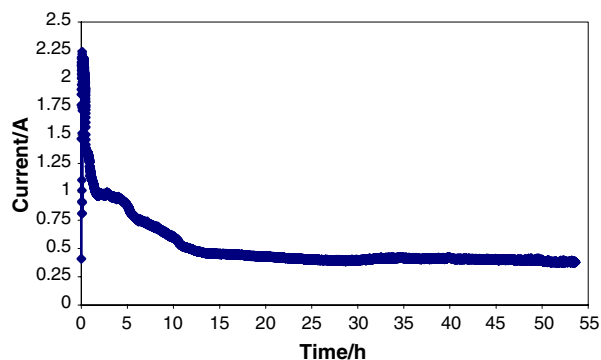


Fig. 4—Electro-reduction of TiO₂ (synthetic rutile), showing initial peaking (in current) behavior. Pellet dimensions: geometry, circular, and 2.5-cm diameter; thickness: 0.4 cm; temperature of the electrolyte: 950 °C; applied voltage: 2.9 V; duration of polarization: 53.5 h; and salt: vacuum-dried and pre-electrolyzed CaCl₂ (Fluka, granular) melt.

to be in the ranges 1.03 to 2.28 A and 0.19 to 0.397 A, respectively.

The initial (peak) current was also found to depend on the applied voltage. An initial higher applied voltage resulted in the higher (initial) current. A similar study has been carried out by Okabe *et al.*^[24] Contrary to the present findings, they could successfully deoxidize various titanium samples (mostly in the form of wires and small pieces) to very low levels of residual oxygen contents, starting from an initial value in the range of 140 to 1400 mass ppm to a final value in the range < 10 to ~770 mass ppm, within a duration of 6.0 to 7.5 hours. However, unlike in the present studies, they did carry out the experiments at higher voltages (> 3.0 V) to invoke the role of calcium metal, which was generated *in situ*, during deoxygenation.

The nature of the current vs time profile does depend on the nature of the cathode material and its characteristics, such as particle-size distribution, percentage-open porosity, geometry (shape and size), chemical composition, *etc.* For example, unlike in the case of the electro-reduction of rutile, TiO₂ (Figure 4),^[27] it was observed that the current during deoxygenation of the foam started declining sharply (and in a progressive manner) with time without attaining any peak value (Figure 2). Such a behavior could be explained on the basis of the difference in the nature of both cathode materials. In the case of rutile (Figure 4), a change in the nature of the electrode (from insulator-to-electronic conductor during polarization) together with the incorporation of Ca²⁺ into the structure/cathode did cause an initial rise in the current (from 0.41 to 2.24 A). However, because of the predominantly metallic nature of the foam, the current during deoxygenation started declining sharply (from 1.7 to 0.5 A within ~1 hour) without attaining any peak value.

C. Role of Pre-Electrolysis

Pre-electrolysis of the melt, prior to deoxidation, is an important step to purify the molten salt with respect to the presence of (traces of) redox species, such as the

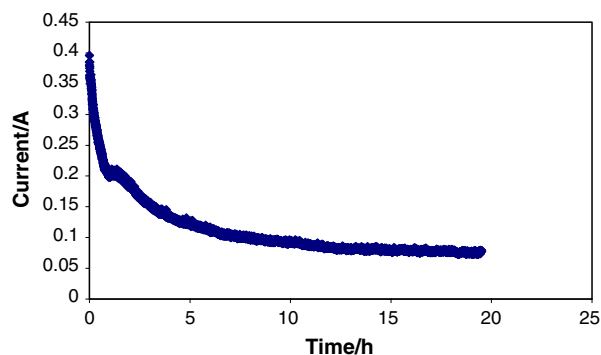
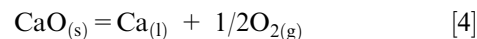


Fig. 5—Current vs time profile, obtained during the pre-electrolysis of (nominally) anhydrous and vacuum-dried CaCl₂ (Fluka, granular variety). Electrolyte temperature: 900 °C; applied voltage: 1.5 V; argon flow: 100 to 150 ccmin⁻¹; duration: 19.5 h; and quantity of salt: 300 g.

removal of residual water that could not be removed during vacuum drying. Pre-electrolysis was carried out using graphite as the anode and cathode, at an applied voltage of < 1.7 V. Such a voltage, although sufficient to remove the water, was insufficient to generate calcium metal in the melt. Figure 5, which illustrates the change in current with time during pre-electrolysis, shows the characteristic pattern of the sharp increase in current followed by its gradual (and slow) decline. Such a pattern has been ascribed to the evolution of hydrogen at room temperature.^[28] Moreover, careful measurements have also revealed that, most likely, the anode gas under these conditions would be CO/CO₂ rather than O₂.^[29] It was also observed that pre-electrolysis, prior to deoxidation, was necessary in achieving relatively lower levels of residual oxygen in the deoxidized foam.

D. Mechanism of the Deoxygenation Reaction

According to Okabe *et al.*,^[24] dissolved CaO in CaCl₂ played a very important role in determining the course of the deoxidation pattern. Similarly, Okabe *et al.*^[30] deliberately generated calcium *in situ* by electrolyzing CaCl₂, which, in turn, reacted with the dissolved oxygen present in impure titanium. The presence of a sufficient quantity of CaO in CaCl₂ would generate calcium (Eq. [4]) *in situ*, if the applied voltage is ~2.0 V.^[31]



In the present set of experiments, the CaO content in CaCl₂ was very low (typically in the range of 0.1 mol pct). Because of the very low activity of CaO, Reaction [4] might have taken place at a higher voltage, possibly ~2.5 V,^[24,31] thereby significantly reducing the role of CaO in the overall deoxygenation process. Thus, the bulk removal of oxygen did take place by the electro-deoxidation (FFC process) alone.

E. Physical Nature of the Deoxidized Samples

After cleaning, the deoxygenated samples looked rather dull as compared with their initial luster,

Table I. Experimental Parameters and the Analysis of Oxygen Concentration before and after Deoxygenation

Serial Number	Nature of the Electrolyte and Operating Temperature (°C)	Pre-Electrolysis Parameters			Electro-Deoxygenation Parameters			Oxygen Concentration (Pct)		Sample Porosity (Open, Pct)	
		V*	I, A**	Duration, h	V*	I, A**	Duration, h	Before	After	Before	After
1	fresh CaCl ₂ /950	—	—	—	2.5 to 3.1	S: 1.6 [†] E: 0.19 [‡]	45	0.609	0.312	72.19	67.75
2	fresh/850	2.0	0.27	2	2.7 to 3.1	1.03/0.22	7.5	0.752	0.53	73.45	66.1
3	fresh/950	1.8	0.38	15	2.6 to 2.9	1.7/0.36	30	0.8272	0.1362	ND	ND
4	fresh/950	2.0	0.25	15	2.6 to 2.8	2.2/0.39	25	0.775	0.1702	78.12	70.31
5	fresh CaCl ₂ added to the used bath/900	2.0	0.7	2	2.7	1.8/0.26	6	0.9236	0.825	67.27	60.54
6	fresh/950	2.0	0.5	10	3.0	1.5/0.23	20	1.0427	0.151	65.22	ND

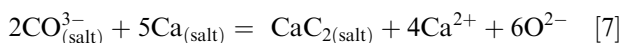
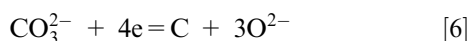
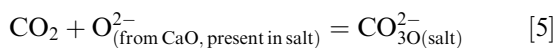
*V: applied voltage.
 **I: measured current.
 †S: current at the start of the experiment.
 ‡E: current just before the termination of the experiment.
 ND: not determined.

i.e., prior to deoxidation. Also, because of both increased metallicity and partial sintering, there was a slight decrease in the porosity (open) of the deoxidized samples (Table I), as compared with their original values. Some of the deoxidized samples became powdery depending on the experimental conditions. Table I summarizes the effect of various experimental conditions on the extent of removal of oxygen.

F. Carbon Contamination during Deoxygenation

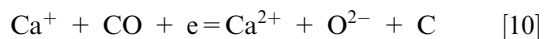
In line with the reported observations,^[24,27,32] in the present case, it was observed that both the electrolyte and foam were contaminated with carbon dust, which emerged as an undesired product (of parasitic/unwanted reactions) during the deoxidation reaction. The source of the carbon contamination could be ascribed to the occurrence of one or more reactions as follows.

(a) According to Kipouros *et al.*,^[32] the presence of CaCO₃ in CaCl₂ can result in the formation of carbon. This compound can either be present in CaCl₂ as an impurity or is generated during the reduction/deoxygenation by the following set of side reactions:



Mishra *et al.*^[33] also suggested that CO₂ generated at the anode as a result of deoxidation can be reduced at the cathode, because the CO₂ can dissolve in the melt, forming CO²⁻₃. Pistorius *et al.*^[31] have also corroborated the possibility of the occurrence of such a reaction during deoxidation.

(b) During reduction, the generation of metallic calcium from CaO at the cathode could lead to the occurrence of the following parasitic reactions:^[19]



It has also been reported that applied voltage could play a significant role in the generation of carbon dust in the electrolyte during deoxidation. According to Okabe *et al.*,^[25] an applied voltage ≥3.0 V resulted in the significant carbon contamination of the titanium products. This observation also seemed to be valid in the present investigation. However, when the applied voltage during polarization was in the range of 2.6 to 2.8 V, a negligible amount of carbon was found to deposit on the foam (Figure 6).

Carbon contamination of the cathode can possibly take place at a low-calcium activity if the concentrations of both O²⁻ and CO²⁻₃ during polarization are high.^[24] However, it is presumed that under the present experimental conditions, the generation of these ions perhaps took place at a much slower rate. Relatively high contamination of the cathode by carbon can also occur because of the anode breakdown during deoxidation/reduction. In the present experiments, such a condition never took place and uniform erosion of the anode after deoxidation was observed.

From a purely experimental observation, it was further noticed that the position of the cathode (foam) in the molten salt also affected the degree of carbon contamination to some extent. Carbon contamination was found to be relatively higher when the foam was positioned just beneath the molten salt. On the other hand, carbon contamination was observed to be

negligible when the foam was positioned deep inside the molten salt (~1 cm below, from the top surface of the molten salt pool, in a bath height of ~2.5 cm). This can be explained on the basis of the fact that carbon dust generated during deoxidation (predominantly) became concentrated/distributed in the form of a thin layer around the surface of the molten salt, and deep inside the molten salt, the presence of carbon dust was a bare minimum. Experiments with very porous TiO₂ pellets (pore size ~100 μm) showed very little carbon contamination (only on the surface of the reduced pellets) when they were placed in the bottom of the reactor during deoxidation.^[34] Any carbon contamination was most likely caused by the pellet being withdrawn through the layer of carbon on the surface of the salt.



Fig. 6—Photograph of the foam before (left) and a section of the same sample after (right) deoxidation. The deoxidized sample is almost free from carbon contamination. Electrolyte: fresh (and pre-electrolyzed) CaCl₂ (Fluka, granular variety); electrolyte temperature: 950 °C; applied voltage: 2.8 V; duration of polarization: 25 h; and residual oxygen content: 0.1702 pct.

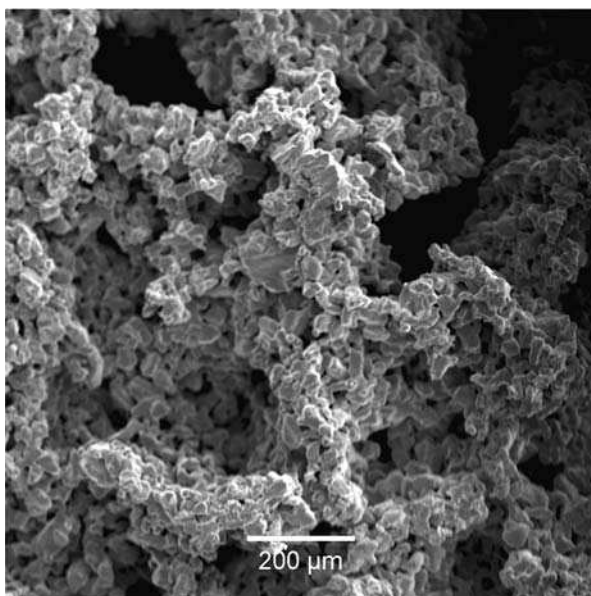


Fig. 7—SEM photograph of a foam sample, before deoxygenation (magnification 110 times), showing the interconnected pore structure.

G. SEM Photographs of the Samples

The SEM photograph of a typical foam sample before deoxidation (Figure 7) revealed its (desired) interconnected network structure with a considerable amount of porosity. The deoxidized samples were also found to

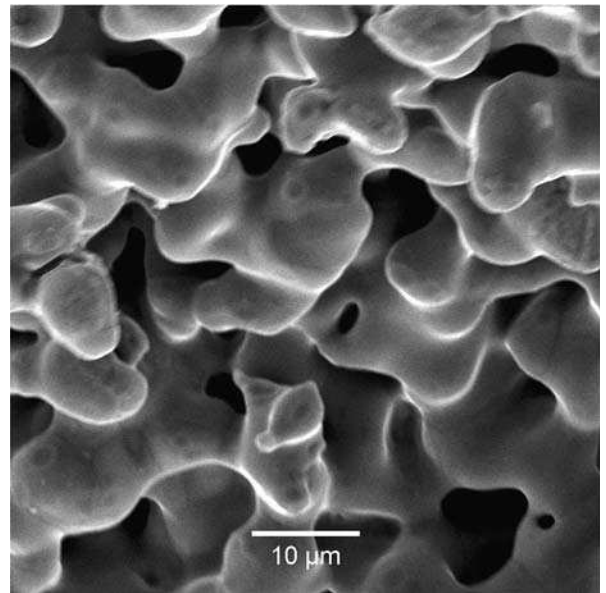


Fig. 8—SEM photograph of the deoxidized foam (magnification 2200 times). The preparation conditions were as follows: salt, vacuum-dried (nominally anhydrous, Fluka, flake-type) CaCl₂; amount, 300 g; pre-electrolysis parameters, electrolyte temperature, 900 °C; applied voltage, 1.5 V; argon flow, 100 to 150 ccmin⁻¹; duration, 19.5 h; deoxygenation parameters, electrolyte temperature, 900 °C; applied voltage, 2.8 V; duration, 25 h; oxygen values, before deoxygenation, 0.775 mass pct; and after deoxygenation, 0.1702 mass pct.

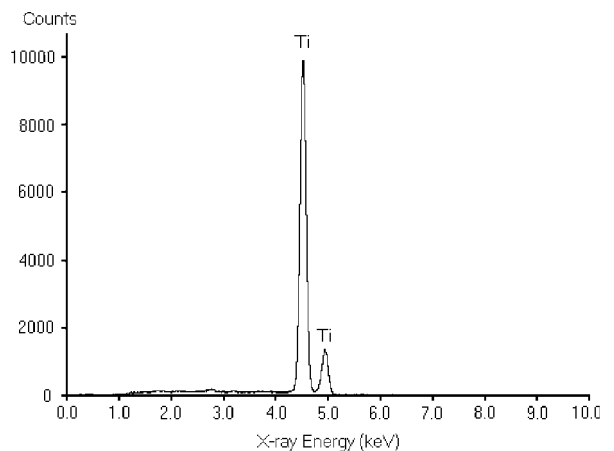


Fig. 9—SEM-EDX (bulk) analysis of the deoxidized foam. Preparation conditions were as follows: salt, vacuum-dried Fluka (nominally anhydrous, powdery-type) CaCl₂; amount, 317 g; pre-electrolysis parameters, electrolyte temperature, 950 °C; applied voltage, 1.7 V; argon flow, 70 to 80 ccmin⁻¹; duration, 15 h; deoxygenation parameters, electrolyte temperature, 950 °C; applied voltage, 2.9 V; duration, 30 h; oxygen values, before deoxygenation, 0.8272 mass pct; after deoxygenation, 0.1362 mass pct.

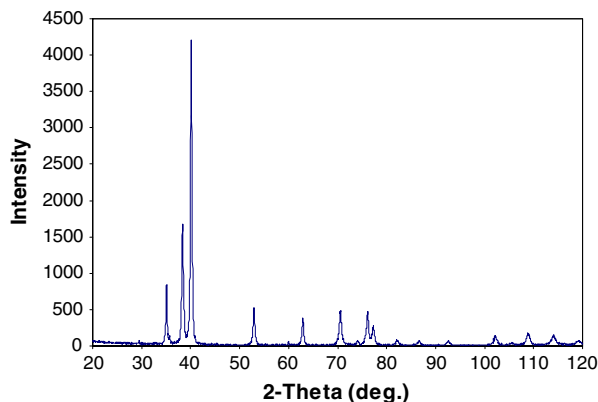


Fig. 10—Typical XRD pattern of the deoxidized foam (of the sample, whose EDX pattern is shown in Fig. 9), showing peaks of α -Ti only.

retain the similar interconnected structure with high (open) porosity (Figure 8) across the entire surface of the deoxidized sample. Moreover, the structure revealed identical microstructures at different points.

Also, SEM photographs did not reveal the presence of any other inclusions/precipitates/compounds across the reduced surface, which suggested that the deoxidized samples were phase-pure titanium. This fact was further substantiated by the EDX analysis of the deoxygenated samples (Figure 9), where the titanium content was 99.93 wt pct. Calcium was the only impurity (0.06 pct) and no chlorine could be detected.

H. XRD of the Deoxygenated Sample

As expected, the XRD of the carbon-contaminated deoxidized sample showed a mixture of both titanium carbide (TiC) and α -Ti, the latter being the predominant phase. However, the relatively carbon-free sample showed the lines of α -Ti only (Figure 10).

V. CONCLUSIONS

The feasibility of the removal of oxygen from titanium foam by the FFC Cambridge Process was conclusively established. Under potentiostatic conditions, it became possible to bring down the initial oxygen concentration from a value in the range of 6,000 to 10,000 mass ppm to a final value in the range of 1362 to 3120 mass ppm by directly (cathodically) polarizing the foam against a graphite counter electrode in a bath of molten calcium chloride.

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