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FFC CAMBRIDGE PROCESS AND REMOVAL OF OXYGEN FROM METAL-OXYGEN SYSTEMS BY MOLTEN SALT ELECTROLYSIS: AN OVERVIEW

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ABSTRACT

The FFC Cambridge process for the reduction of metal oxides was discovered in 1997 by observing that it was possible to reduce solid oxide films on titanium foil by making the foil cathodic in a bath of molten calcium chloride. This observation led to experiments, which demonstrated that it was possible to reduce solid titanium oxide pellets. Since the late nineties these results have been reproduced at laboratories across the world, not only for titanium dioxide but other metal oxides as well. Mixtures of oxides have also been reduced to form alloys and intermetallic compounds. This review discusses the process, the mechanism of reduction, its development and future prospects.

1. INTRODUCTION

Many metals are produced by reduction of the respective oxides. The reduction can be achieved by different methods and the method selected depends upon the relative stability of the metal oxides and the oxides of impurities[1]. Relatively unstable oxides can be reduced by heating to their decomposition temperature (eg. HgO). Slightly more stable oxides can be reduced by hydrogen (NiO). But by far the most common reductant is carbon, either as elemental carbon or as carbon monoxide (FeO). Though carbon can theoretically reduce all metal oxides, very high temperatures are necessary for achieving reduction and this often leads to problems like difficulty in stopping the back reaction (MgO) or the formation of stable carbides (TiO_2). In such cases the metal oxide is usually reduced by an element, which forms a more stable oxide than the one to be reduced (aluminothermic reduction of Cr_2O_3). The reduction can also be achieved by electrolysis of aqueous or molten salt solution in which the metal oxide is dissolved. For those elements whose compounds are very stable, fused salt electrolysis is found to be the best possible route (Al_2O_3). However, the method is satisfactory only for those metals that are deposited in the liquid state, i.e. the melting point of the metal is less than the reduction temperature of its oxide (Al). If the metal is high-melting (Ti), it is practically difficult to carry out molten salt electrolysis and the option is limited to electrowin the metal in the solid state at a lower temperature. But this results in dendritic deposit, which is prone to oxidation. In the case of titanium, there have been some attempts to produce the metal by direct electrolysis of titanium dioxide[2-5], but was not very successful as the product was always contaminated with substantial amount of oxygen due to the equilibrium between the metal and the oxide melt. This problem exists irrespective of whether the titanium product is solid or liquid.

Recently, researchers at the Materials Science & Metallurgy department of the Cambridge university, UK have reported a novel process for production of metals and alloys from their solid oxides directly by molten salt electrolysis[6]. The process called 'FFC (Fray-Farthing-Chen) Cambridge process' was discovered in 1997 by observing that it was possible to reduce solid oxide films on titanium foil by making the foil cathode in a bath of molten calcium chloride.

Subsequently, it was demonstrated that it was possible to reduce solid titanium oxide pellets. The feasibility of electro deoxidation of many metal oxides was established in laboratory experiments and the process was globally patented in 1998[7]. The process is reportedly more suitable for electro reduction of the high-melting transition metal oxides and actinides. It is claimed that titanium metal can be produced cost-effectively and in a more environmentally friendly way by the FFC process. The high demand for titanium metal and its high cost of production by the current Kroll process[8] has therefore generated a lot of interest in the new process worldwide. The process is being discussed as one with immense potential to change the entire scenario of extractive metallurgy.

The electro-deoxidation in the FFC Cambridge process has many similarities to the cathodic refining technique employed for purification of reactive metals from oxygen dissolved in them (deoxygenation). An analysis of both the techniques suggests that the electro-deoxidation in the FFC process is a natural extension of the cathodic refining of metal-oxygen solid solutions, even as the former retains its status as an important discovery in its own right. In view of the similarities of both the techniques, a brief discussion on the molten salt cathodic refining technique has been given as a prelude to the FFC Cambridge process. An introduction to the metal-oxygen systems, the thermodynamics of oxygen removal and the role of molten salt medium in the electro-deoxidation processes are also given below. The FFC Cambridge process and its development, especially with regard to the extraction of titanium metal from titanium oxide, have been presented in the subsequent sections.

2. METAL-OXYGEN SYSTEMS AND THERMODYNAMICS OF OXYGEN REMOVAL

Oxygen is present in metal-oxygen systems in two forms, one chemically bound as oxide and the other dissolved as atoms in the solid solution. Calcium metal has very strong affinity for oxygen and hence is used as a very effective reductant (de-oxidant) for removal of oxygen in a metal-oxygen system.[9] Okabe et al have given a detailed account of the various techniques developed for removal of oxygen from reactive metal-oxygen solid solutions and the thermodynamics of such reactions.[10] The present discussion is restricted to solid state electrochemical deoxidation methods, which are carried out in the molten salt medium and which have a direct relevance to the FFC Cambridge process.

In the deoxidation reactions, removal of oxygen is achieved by providing the metal/oxide with an environment whose oxygen potential is less than that in the metal/oxide. There are many ways to achieve this condition, the most common method being 'external gettering', i.e. chemical reaction of the oxygen present in the metal/oxide with a reductant,

$$M\ (O) + R = RO + M \qquad (2.1)$$

where M(O) is the metal M with oxygen dissolved in it, R the reductant and RO the product oxide. For a typical reaction

$$Ti(O) + Ca = CaO + Ti \qquad (2.2)$$

the equilibrium oxygen concentration in the metal is thermodynamically defined by the equation

$$[O] = (a_{CaO}/a_{Ca})\ (1/\gamma_o)\ \exp\ (\Delta G^o/RT) \qquad (2.3)$$

where ΔG^o is the standard free energy change of the reaction of eq. (2.2), a_{CaO} and a_{Ca} are the activities of calcium oxide and calcium respectively, and γ_o is the activity coefficient of oxygen in the metal. It is clear from eq. (2.3) that the minimum oxygen concentration achievable in a metal, at a particular temperature, is fixed by the ratio of the activities of calcium oxide and calcium (a_{CaO}/a_{Ca}) at the reaction interface. The lower the value of this ratio, the more efficient the deoxidation process is. In the case of external gettering, the CaO formed, at unit activity, makes a thick coating around the metal surface, which hinders further access of the reductant to the metal so that a_{CaO}/a_{Ca} ratio becomes very high ($a_{CaO}/a_{Ca} \gg 1$). Under this condition, the oxygen concentration predicted thermodynamically may not be realisable. For example, in the case of calciothermic reduction of TiO_2, the kinetic factor limits the oxygen purity to a few thousand ppm as against ~500 ppm predicted thermodynamically at 1000°C.[11,12] It becomes clear from the above discussion that the efficiency of any calcium deoxidation technique strongly depends on its ability to achieve a minimum

value of a_{CaO}/a_{Ca} at the reaction interface. Obviously a non-equilibrium processs, which simultaneously reduces the activity of CaO and ensures supply of calcium at close to unit activity at the reaction front, is necessary to achieve this condition.

3. MOLTEN SALTS AS A MEDIUM FOR OXYGEN REMOVAL

The a_{CaO}/a_{Ca} ratio can be maintained low by conducting the deoxidation reaction in a medium in which both CaO and Ca can dissolve. Molten salts find use in this context. Alkaline earth metal chlorides, especially $CaCl_2$ and $BaCl_2$, have substantial solubility for its respective metal oxides[13,14] and hence are a suitable molten salt medium for de-oxidation. Molten calcium chloride dissolves about 20 mol.% CaO[15-17] and 2-4 mol. % calcium[18-20] at 900°C. The very high thermodynamic stability of CaO is another factor in favour of the calcium chloride melt.[21] When the deoxidation reaction is conducted in this molten medium (flux), the CaO dissolves in the flux, which reduces its chemical activity at the reaction zone ($a_{CaO} < 1$) and is no longer a barrier for the access of calcium. As the reductant (Ca) is also dissolved in the flux, its accessibility and availability at the reaction zone becomes more facile. If the melt is saturated with calcium, then $a_{Ca}=1$. Under this condition, the a_{CaO}/a_{Ca} becomes < 1 and the deoxygenation becomes more efficient. This is depicted in Fig.1 with calciothermic reduction of TiO_2 as a typical example[22]. As the deoxidation is continued, calcium will be consumed with a corresponding increase of CaO in the melt. This sets the condition $a_{CaO}/a_{Ca} >> 1$ at the reaction zone. Obviously, the efficiency of calcium chloride flux deoxidation process decreases with time as the calcium activity decreases and the activity of calcium oxide increases in the flux.

The above limitation demanded a method, which simultaneously ensured a continuous removal of CaO from the melt and supply of calcium on to the metal so as to maintain the $a_{CaO}/a_{Ca} << 1$. This could be achieved by incorporating electrochemistry into the deoxidation process, which essentially involved electrolytic decomposition and recycling of the dissolved CaO. In electrochemical deoxidation, molten calcium chloride may also serve as a source of the reductant and/or as an electrolyte medium for conduction of O^{2-} ions. These aspects of the deoxidation process are discussed in some detail in the following sections. Suzuki et al have given a good account of the chemistry and electrochemistry of deoxygenation/deoxidation of titanium-oxygen system in molten calcium chloride medium.[22,23]

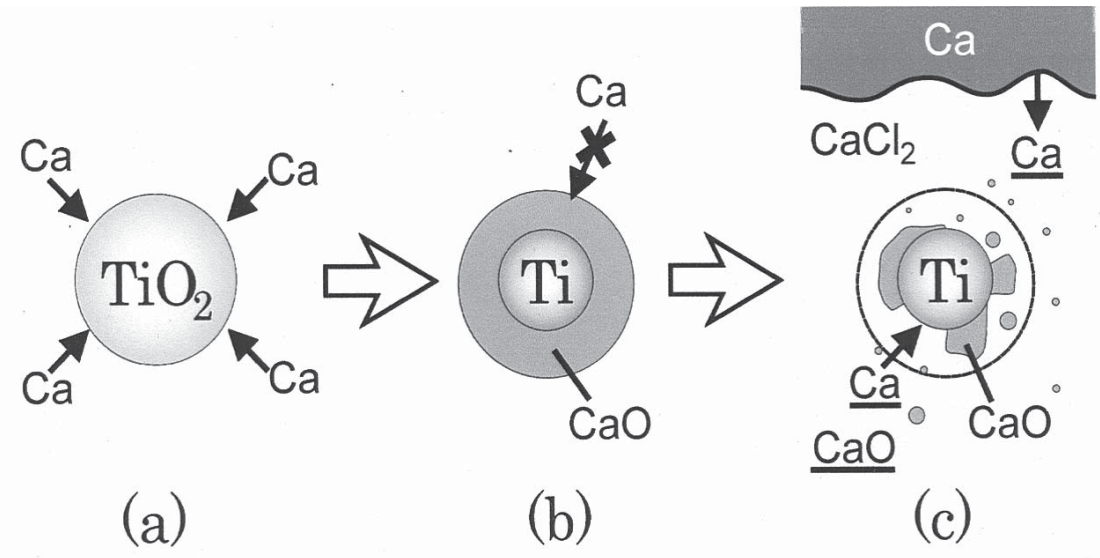

Fig. 1 : Mechanisms of calciothermic reduction of TiO_2. (a) depicts the direct reaction between Ca and TiO_2, resulting in the formation of CaO, which forms a coating around the metal and (b) hindering further deoxidation. (c) In calcium-saturated calcium chloride melt, the CaO gets dissolved with better accessibility for Ca to the Ti metal. The deoxidation is more effective in (c) as $a_{CaO}/a_{Ca} < 1$. Ca and CaO denote the dissolved state of the respective species in $CaCl_2$ melt. (Reproduced with permission from Ref. 22).

4. REMOVAL OF OXYGEN FROM METAL-OXYGEN SOLID SOLUTIONS

It was known for more than a century that a metal compound could be electrolysed from an aqueous or molten salt solution of the compound. During electrolysis the metal ion discharges at the cathode to produce the metal and the non-metallic component is produced at the anode, mostly as gaseous species. But Ward and Hoar[24] in 1960 had reported for the first time that non-metallic impurities such as oxygen can be expelled from a metal by the cathodic refining technique. They have successfully removed dissolved oxygen, sulphur, selenium and tellurium from molten copper by the electrochemical technique. Molten barium chloride was used as the electrolyte in the cell together with a carbon anode. A potential above the decomposition potential of $BaCl_2$ was applied to the cell to drive out oxygen and other non-metallic impurities from the cathode. A schematic of the cathodic refining process is given in Fig. 2. A chemical reaction between oxygen (also S, Se or Te) and barium metal, which deposited on the copper cathode at the applied potential, was assumed as the mechanism of oxygen removal. The overall cell reaction was assumed to be

$$Cu_2X + BaCl_2 = 2\ Cu + BaX + Cl_2 \qquad (4.1)$$

where X is O, S, Se or Te.

Chen and Fray[25] carried out a similar experiment with molten copper contaminated with oxygen, selenium and tellurium. The applied potential was below than that for the decomposition of $CaCl_2$ and $BaCl_2$, but still they could achieve the deoxygenation of the molten copper. Based on this observation and the electrode potential for deoxygenation deduced from voltammetric experiments with the oxygen contaminated copper working electrode, they have concluded that electrochemical production of Ca or Ba on the copper cathode and their chemical reaction

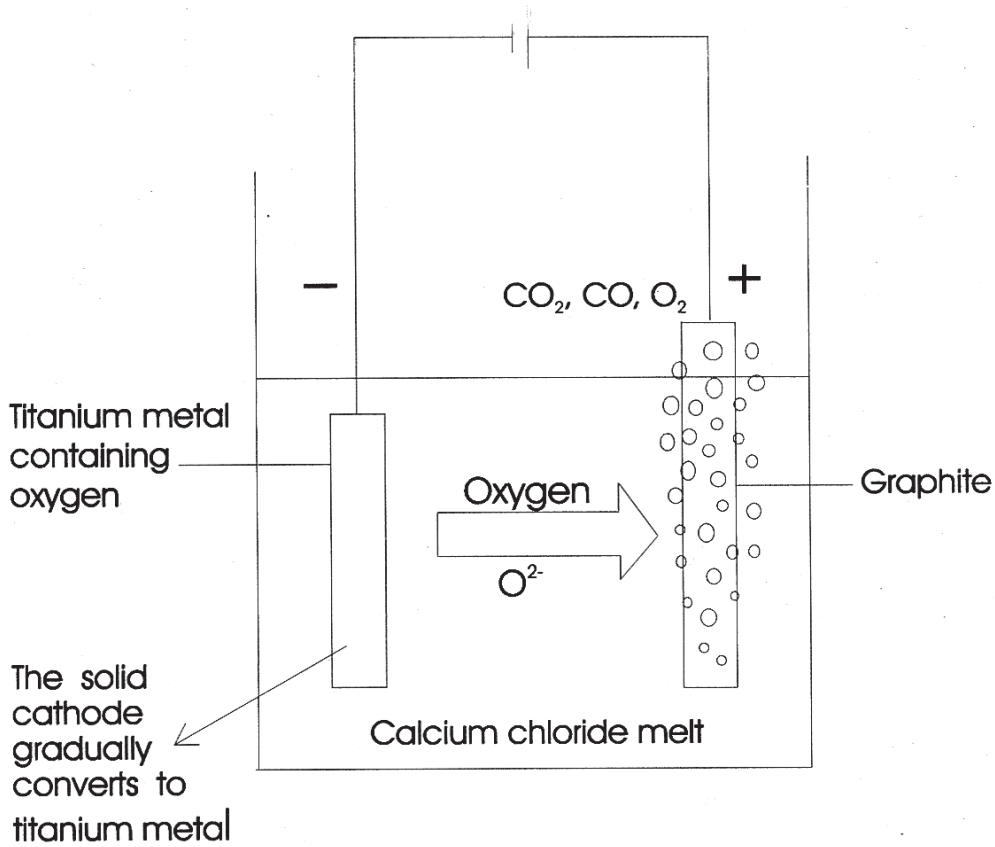

Fig. 2: Schematic of the deoxygenation of titanium-oxygen solid solution by cathodic refining technique. In the electro-deoxidation process (FFC Cambridge process), solid TiO_2 is used in place of the oxygen containing titanium metal in the above diagram.

with the oxygen are not necessary for the deoxygenation. They have demonstrated that the removal of the impurity element takes place via its cathodic ionisation and subsequent discharge at the anode. The reaction can be written as

$$X + 2e^- = X^{2-} \text{ (cathode reaction)} \quad (4.2)$$

$$X^{2-} = X + 2e^- \text{ (anode reaction)} \quad (4.3)$$

where X is O, S or Se.

High-purity metals are in demand for electronic applications, especially for high-performance information devices. For example, titanium produced by the Kroll process contains several hundred ppm of dissolved oxygen in it and hence it is necessary to thoroughly purify it for such applications. Purification of titanium to a very low level of oxygen is very difficult due to its strong affinity for oxygen. Okabe et al have developed many techniques for removal of oxygen from titanium[26-28] and titanium aluminides.[29] These techniques essentially involved the chemical reaction of oxygen with calcium in calcium saturated calcium chloride melt, in the temperature range 1000-1200 °C. They could succeed in producing titanium down to 20 mass ppm oxygen by the calcium halide flux deoxidation method.[27]

Okabe et al[30] have modified the calcium-halide flux deoxidation method by incorporating electrochemistry to it. In the electrochemical deoxidation method, the cell configuration is identical to that in the cathodic refining technique discussed above. The impure metal is the cathode, graphite is the anode and molten calcium chloride is the electrolyte. The deoxidant calcium metal is generated in-situ by electrolysis of the calcium chloride flux as is done in the cathodic refining of copper by Ward and Hoar.[24] The calcium metal thus produced at unit activity on the cathode reacts with the oxygen to give CaO. The CaO dissolves in the melt and subsequently is electrolysed to regenerate calcium metal for the deoxygenation reaction. Thus the reactive metal placed at the cathode is deoxygenated by the reaction with calcium produced on it electrochemically. By this method Okabe et al could achieve a purity level of ~10 mass ppm of oxygen in Ti. The reaction sequence in the electrochemical deoxidation process can be expressed as,

$$O(\text{in Ti}) + Ca\ (\text{in flux}) = O^{2-}(\text{in flux}) + Ca^{2+}(\text{in flux}) + Ti \quad (4.4)$$

$$Ca^{2+}\ (\text{in flux}) + 2\ e^- = Ca\ (\text{on Ti cathode: in flux}) \quad (4.5)$$

$$O\ (\text{in Ti}) + 2e^- = O^{2-}(\text{in flux}) + Ti\ (\text{overall cathode reaction}) \quad (4.6)$$

$$O^{2-}(\text{in flux}) + C\ (\text{anode}) = CO\ (\text{gas}) + 2e^-\ (\text{anode reaction}) \quad (4.7)$$

$$O\ (\text{in Ti}) + C\ (\text{anode}) = CO\ (\text{gas}) + Ti\ (\text{net reaction}) \quad (4.8)$$

The calcium halide flux electro-deoxidation method was effectively applied for oxygen removal from solid yttrium and rare earth metals. Yttrium metal containing more than 5700 mass ppm oxygen and rare earth metals (La, Pr, Nd, Gd, Tb, Dy, Er) containing more than 2000 ppm oxygen have been deoxygenated to below 100 ppm after a few hours of electrolysis.[31-34]

The method is reported to have many advantages over the calcium halide deoxidation method. First, the addition of metallic calcium as a deoxidant to the flux is not required. As CaO dissolves in the calcium chloride melt and undergoes electrolysis, its activity in the melt can be kept at a very low level and does not increase during the process. Third, as the calcium metal is in-situ generated by electrolysis, it will be free from impurities.

However, an analysis of the calcium halide electro-deoxidation method suggests that electrochemical formation of calcium on the titanium electrode and its chemical reaction with oxygen in titanium may not be necessary for the deoxygenation reaction. It may be noted that the overall cathodic reaction (eq. 4.6) does not show calcium as a reactant in the deoxidation process. Further, Okabe et al[30] have reported that the de-oxygenation could be achieved even at 2.5 V at 950 °C, which is about 720 mV less than the theoretical decomposition potential of calcium chloride at that temperature. It is explained that the deoxygenation in such cases is achieved, not by the calcium metal produced by the electrolysis of calcium chloride, but by the metal produced by electrolytic decomposition of CaO dissolved in the molten flux at a lower potential. The calcium metal dissolves in

the melt, which in turn effects the deoxygenation of the cathode. Chen and Fray[35] have also reported that the partial deoxygenation of an alpha case sample of titanium could be achieved in calcium chloride melt even at 2.5 V at 950 °C, including the IR drop in the cell. Chen and Fray have also made similar observations in the cathodic refining of molten copper contaminated with oxygen, sulphur and tellurium[25] and concluded that the removal of oxygen (or Se and Te) takes place via its cathodic ionization. So, it is possible that a similar mechanism is in operation in the case of deoxygenation of titanium metal in the calcium halide electro-deoxidation process too. The fact that eq. (3.8) shows cathodic ionization as the mechanism for oxygen removal also supports this observation. A very close similarity can be noticed between the deoxygenation of metal-oxygen solid solutions and the electrochemical reduction of TiO_2 reported by the FFC team, the only difference being the chemical state of oxygen present in both the cases.

As electrical potential is considered as the driving force for the oxygen removal in both the processes (a detailed discussion on the FFC process is given in section 5), the magnitude of the potentials necessary for these reactions can be obtained by considering the formation of a metal-oxygen solid solution, for eg. $Ti(O)_x$,

$$Ti + x/2\ O_2 = Ti(O)_x \qquad 4.9$$

$$E = E^o - RT/nF \ln [a_{Ti(O)x}/pO_2^{x/2}] \qquad 4.10$$

Where E is the formation potential of Ti(O), E^o the standard potential of the formation reaction, R the gas constant, T the temperature in Kelvin, $a_{Ti(O)}$ the activity of oxygen in Ti(O), pO_2 the equilibrium partial pressure of oxygen and n, the number of electrons taking part in the reaction.

It can be seen from eq. (4.10) that E increases as $a_{Ti(O)x}$ decreases. This would mean that the dissociation of $Ti(O)_x$ requires more energy with decrease in the oxygen activity. So, the reduction potential of oxygen in solid solution becomes more and more cathodic as the oxygen activity is decreased. Hence, more energy has to be expended for removing very low levels of oxygen from metal-oxygen solid solutions by the electro-deoxidation method. It becomes clear from the discussion that the ionisation of oxygen and hence the electro-deoxidation of TiO_2 will take place at a less cathodic potential than that of the solid solution, $Ti(O)_x$. The electro-deoxidation of titanium dioxide, under constant current, will take place through constant voltage steps due to the presence of sub oxides in the system. The electro-deoxygenation will take place over a range of potentials depending on the activity of oxygen in the metal.

5. THE FFC CAMBRIDGE PROCESS

The FFC Cambridge process[6] is a high-temperature molten salt electrolysis process. The patent[7] on the process claims that a host of metals/semi-metals such as Ti, Si, Ge, Zr, Hf, Sm, U, Al, Nd, Mo, Cr, Nb or their alloys can be produced with the starting material as oxide, sulphide, carbide or nitride. But almost all the work reported so far has been for solid oxides, especially titanium dioxide. Hence the electro-deoxidation of titanium dioxide to titanium metal is used as the typical example of the FFC Cambridge process in the following discussions.

Titanium dioxide is used as the solid cathode and graphite as the anode in the high-temperature (~950 °C) FFC cell in which molten calcium chloride (melting point 762°C) is used as the electrolyte. During electrolysis, the oxygen present in the solid TiO_2 abstracts electrons and gets converted to oxygen ions, the lower valence oxides and eventually to Ti metal. Under the influence of the applied electric potential and the high temperature of the melt, the oxygen ions leave the cathode and move towards the graphite anode through the molten electrolyte. These ions discharge at the graphite anode and liberate as carbon monoxide or carbon dioxide. A schematic of the electro-deoxidation process is given in Fig.2. The simplified electrode reactions can be written as follows

$$\text{Cathode: } TiO_2 + 4e^- \Leftrightarrow Ti + 2O^{2-} \qquad (5.1)$$

$$\text{Anode: } C + 2O^{2-} \Leftrightarrow CO_2 + 4e^- \qquad (5.2)$$

$$\text{Net reaction: } TiO_2 + C \Leftrightarrow Ti + CO_2 \qquad (5.3)$$

If an anode, inert to oxygen, is used, oxygen gas will be liberated on it so that the overall cell reaction will be

$$TiO_2 \Leftrightarrow Ti + O_2 \qquad (5.4)$$

Individual or mixed oxide powders of Al, B, Cr, Fe, V, Nd, Nb, Zr, U, Hf, Ce and Ni have already been reduced in laboratory experiments.[6,36-38] The extent of removal of oxygen in this process depends on the applied potential and duration of electrolysis. Even trace levels of oxygen can be removed by adjusting the electrolysis conditions. The alpha case on titanium metal was successfully deoxygenated by the electro-deoxygenation method.[35]

5.1 The mechanism of electro-deoxidation in the FFC Cambridge process

In order to understand the electrochemistry of the deoxidation process, Chen & Fray have carried out cyclic voltammetric experiments with an oxide-coated titanium foil as working electrode in molten calcium chloride at 800-900°C.[39] The oxide scales were earlier confirmed as consisting mainly of TiO_2. The voltammograms have shown that the ionisation of oxygen from the TiO_2 layer takes place at a much less cathodic potential than that of the calcium deposition. Fray and Chen have calculated the thermodynamic potentials for oxygen ionisation for various oxides in calcium chloride melt[37,40] and showed that the potential for calcium deposition ($Ca^{2+} + 2e = Ca$) is far more negative than that for oxygen ionisation ($O+2e = O^{2-}$) [Table 1]. The deoxidised titanium cathodes were subjected to chemical analysis, but no calcium metal could be detected on them. Similarly, no chlorine gas could be detected in the anodic gas.[6,35] The absence of calcium and chlorine suggested that decomposition of calcium chloride was not taking place in the cell. The applied potential of the cell, including the IR drop in electrodes and electrolytes, was 3.0 V, which is less than the

Table 1

ELECTRODE POTENTIALS IN FUSED CHLORIDES.
Vs ($E_{Na^+/Na} = 0$) AT 973 K

Electrode reaction	Potential (E^o) (V)
$O_2 + 4e = 2O^{2-}$	2.713
$2PbO + 4e^- = 2O^{2-} + 2Pb$	2.082
$SnO_2 + 4e^- = 2O^{2-} + Sn$	1.734
$MoO_2 + 4e^- = 2O^{2-} + Mo$	1.650
$2/5\ Nb_2O_5 + 4e^- = 2O^{2-} + Nb$	1.209
$2/3\ Cr_2O_3 + 4e^- = 2O^{2-} + 4/3\ Cr$	1.189
$2/5\ Ta_2O_5 + 4e^- = 2O^{2-} + 4/5\ Ta$	1.038
$TiO_2 + 4e^- = 2O^{2-} + Ti$	0.750
$ZrO2 + 4e^- = 2O^{2-} + Zr$	0.349
$2/3Al_2O_3 + 4e^- = 2O^{2-} + 4/3Al$	0.348
$2TiO + 4e^- = 2O^{2-} + Ti$	0.338
$UO_2 + 4e^- = 2O^{2-} + U$	0.337
$HfO_2 + 4e^- = 2O^{2-} + Hf$	0.211
$2MgO + 4e^- = 2O^{2-} + 2Mg$	0.143
$2Ca^{2+} + 4e^- = 2Ca$	-0.060

reversible decomposition potential of the $CaCl_2$ (3.2 V) at 900 °C. Based on these observations, Chen and Fray[25,35,39] have ruled out the possibility of formation of calcium metal on the oxide cathode and hence its role in the deoxidation process. The ionisation of oxygen, dissolution of the oxygen ions in calcium chloride electrolyte, its transport to the anode under the influence of the applied potential and discharge on the anode are assumed as the steps involved in the de-oxidation reaction in the FFC process.

However, notwithstanding the above arguments against the theory of cathodic calcium deposition, it may not be entirely correct to rule out the role of calcium in the deoxygenation, based on the decomposition potential of calcium chloride. This is so because the reversible electrochemical decomposition of a chemical compound requires that the cathodic and anodic reactions take place reversibly on the respective electrodes under standard conditions. In the case of pure calcium chloride, the decomposition to chlorine and calcium at unit activities can take place only if reversible (or inert) electrodes are used in the decomposition reaction. When either of the two electrodes or both the electrodes are reactive, as in the case of the deoxidation/deoxygenation experiments, the reversible decomposition of the electrolyte (here calcium chloride) to its elements is not possible and hence the reversible decomposition potential is no longer valid. The oxide cathode is electrochemically reactive in the calcium chloride melt and hence the metal deposition as per reaction $Ca^{2+} + 2e^- = Ca$ at its reversible potential cannot take place. But an electrochemical/chemical reaction between calcium and the oxide cathode can take place at potentials below than that for the deposition of calcium metal. This means that even as a mechanism involving the deposition of calcium metal on the cathode and its chemical reaction with oxygen, as assumed in the calcium halide electro-deoxidation method is unlikely, electrochemical formation of calcium oxide/calcium-oxygen-titanium ternary compounds at lower potentials below calcium deposition potential is possible.

It can be seen from eq. (5.3) that the overall cell reaction in the FFC process is $TiO_2 + C \Leftrightarrow Ti + CO_2$ ($\Delta_f G^o_{rean}$ = -326.5 kJ/mol. at 950°C) and hence the theoretical potential for the reaction is 0.85 V. Even with an inert anode in the place of graphite (eq. 5.4), the theoretical cell voltage will only be 1.87 V ($\Delta_f G^o_{TiO2}$ = -722 kJ/mol., at 950°C). But, as in the case of any electrolysis, the applied voltage has to be higher than the theoretical potential in order to overcome the IR drop in the electrodes and electrolyte and polarisation losses. The voltage applied, over and above the IR drop in the cell, may aid the diffusion of the oxygen ions from the bulk of the cathode to the electrode-electrolyte interface so as to make the deoxidation process faster.

Whatever be the applied cell voltage, ionisation of oxygen at the cathode, transport of oxygen ions through the melt and their discharge at the anode are necessary. It is possible to think of a transport mechanism in which the cathodically generated oxygen ions dissolve in the melt and are transported to the anode by exchange with the oxygen ions present as dissolved CaO in the melt. So, calcium chloride melt can be assumed to play the role of a medium for the dissolution and transport of oxygen ions. In this sense, the CaO formation, its thermodynamic stability vis-à-vis the metal oxide, its dissolution in calcium chloride melt etc., which are considered as important steps in the mechanism of deoxidation in calcium chloride melt, seem not to influence the de-oxidation process. This kind of a mechanism might probably fit into the cathodic oxygen ionisation theory of the electro-deoxidation process. However, in this mechanism, the oxygen ion current and hence the rate of deoxidation will be limited by the amount of dissolved oxygen ions present in the melt. This may mean that the efficiency of deoxidation with a melt with very low levels of dissolved oxygen, for eg. thoroughly pre-electrolysed melt, will be very low. Hence, in order to explain the higher currents observed in the deoxidation experiments, it may be required to invoke a different mechanism in which formation of CaO takes place cathodically, its dissolution in the melt and subsequent electrolysis. It is possible that some amount of chlorine could have been released in the beginning of the electrolysis so as to maintain the high current, though reportedly not detected in the experiments.[6,35] Suzuki et al[23,41] have suggested a certain role for calcium ions in the electrodeoxidation process and predicted the possibility of many parasitic reactions in the molten electrolyte medium. The low current efficiency of the FFC process (less than 50%) also indicates the possibility for parasitic reactions in the cell. Redox cycling and electronic conductivity of the melt might also be contributing to lower the

current efficiency of the process. Overall, the mechanism of the FFC process appears to be a more complex one.

Most of the metal oxides are known to be non-conducting. It is therefore surprising that such a material is used as the cathode in an electrochemical cell! However, in the case of TiO_2, removal of a small amount of oxygen, resulted in the formation of magnelli phases (TiO_{2-x}), which are highly conducting.[42] It is possible that a small amount of oxygen close to the electronic conductor (current collector) is ionised under the influence of the applied potential and the Magnelli phases so formed in the oxide cathode make the entire specimen electronically conducting. In this case, the electrochemical reaction can be assumed to occur at the interface between the solid oxide and the molten salt and the electrons and oxygen move to the interface through the oxide.

$$TiO_x + 2xe^- \text{ (through oxide)} = Ti + xO^{2-} \quad (5.5)$$

$$O \text{ (in bulk } TiO_2) \rightarrow O \text{ (at the interface)} \quad (5.6)$$

Chen & Fray reported that even oxides like ZrO_2 and SiO_2, which cannot be made conducting like TiO_2, can also be deoxidised in the FFC method.[43,44] We have extracted zirconium metal from ZrO_2 by the electro-deoxidation method[45]. Recently Nohira et al have reported an interesting study of the electro-deoxidation of SiO_2 in molten $CaCl_2$ melt.[46] The mechanism of electro-deoxidation in this case, it is explained, involves a three-phase interface between the oxide, the conducting material and the molten salt. The oxide material in contact with the conductor (current collector) gets reduced to produce the metal. As the metal is being produced, it extends the point of contact to further oxide grains and the reduction process extends outwardly. The mechanism for reduction of SiO_2 may be expressed as

$$SiO_2 + 4e^- \text{ (through conductor or Si)} = Si + 2O^{2-} \quad (5.7)$$

The proposed mechanism indicates that electrical conductivity of the oxide is not an essential condition for electro-deoxidation. It may be a desirable feature and may probably make the electro-reduction process kinetically more favourable.

5.2 Salient features of the FFC process

From the above discussions it is clear that in the FFC process a metal is produced by driving out the non-metallic component of the metal compound by application of electrical potential. The metal compound and the extracted metal remain in the solid state during the processing. This is in sharp contrast to the conventional electrometallurgical processes wherein the metal compound remains dissolved in the electrolyte and is electrolysed subsequently to produce the metal. The novel approach to the metal production in the FFC process, therefore, obviates the need for many cumbersome operations, which are otherwise necessary for the conventional electrometallurgical processes. A paradigm shift in the traditional theory of metal electrowinning is quite evident in the FFC Cambridge process.[47]

As oxygen is driven out from the solid oxide to leave behind the metal in the process, it can be effectively used to prepare alloys from the respective oxides. For this the constituent metal oxides can be mixed together in the appropriate ratio and made the solid cathode in a FFC cell. As the metal phases start forming by deoxidation, they tend to combine to give the respective alloy. The uniqueness of the method is that the alloy formation takes place without melting of the constituent metals. This kind of alloy preparation has many advantages over the conventional methods. As it is not required to melt the metals, metals of very different melting points can be alloyed together. The problems such as oxidation and segregation, associated with the alloying of reactive metals in conventional methods, can be overcome by this method. The method is also suitable for preparation of alloys, which cannot be synthesised using the conventional techniques. Several alloys like Ti-Al, Ti-Al-V, Ti-Ni, Ti-Fe and Nb_3Sn have been prepared in the laboratory by employing the FFC technique.[40] Preparation of a ternary alloy by infiltration of a molten salt in a porous binary alloy matrix has been patented.[48] It has been claimed that most of the metal carbides can be prepared by the FFC technique.

The FFC cell product (metal powder or sponge) may be suitable for fabrication using powder metallurgical

techniques. This would eliminate casting, machining and other costly fabrication processes associated with conventional powder metallurgical techniques. Another application of the technique envisaged is the production of small near-net shaped objects directly from the electrolytic cell. It is predicted that the non-polluting and energy-efficient process may become generic for the production of many metals and alloys in future, especially those that are difficult and expensive to prepare or are highly reactive.

5.3 Experimental conditions for FFC process

As the FFC process is a high temperature molten salt process, special attention is required in the cell design, construction and operation. The molten electrolyte, calcium chloride, is moisture-sensitive and the product metal (eg. titanium) is reactive to oxygen. Hence it is necessary to carry out the electro-deoxidation process in a leak-tight electrolytic cell with a moisture-free inert gas (argon) blanket. Care should be taken in the selection of material for construction of the electrolytic cell and the crucibles, in which the molten electrolyte and solid oxides are to be contained.[35]

5.3.1 *Purification of calcium chloride*

Commercial calcium chloride invariably contains water in it and hence needs to be purified before use in the cell. Different dehydration procedures have been used with calcium chloride dihydrate ($CaCl_2.2H_2O$) or anhydrous calcium chloride as the starting chemical. Fray and Chen preferred $CaCl_2.2H_2O$ as the starting material to the anhydrous calcium chloride, as the dehydration of the latter is more difficult. A four stage heating procedure for dehydration of $CaCl_2.2H_2O$ is given.[39] Alternatively, pre-electrolysis of molten calcium chloride at a slightly lower potential than its decomposition potential is an effective method to eliminate the hydrolysis product (CaO) in the melt as well as to get rid of other easily reducible metallic impurities.[39] The melt purity can be confirmed by performing cyclic voltammetry of the melt using a tungsten or molybdenum working electrode. The absence of any irregularities between the cathodic (calcium deposition, 0 V vs Ca^{2+}/ Ca) and anodic (chlorine evolution, 3.2 V vs Ca^{2+}/Ca) peaks can be taken as an indication that the melt is free from any impurities.

5.3.2 *Electrolyte container crucibles*

The reaction vessel in which the electrolyte is contained can be made of graphite, titanium, stainless steel, alumina or magnesia. However, it is desirable to avoid oxygen containing ceramic material like alumina, especially when high purity metal is to be produced. Ti is an oxygen getter in the electrolyte and hence is the ideal material of choice for the crucible, especially when high-purity titanium metal is sought.

5.3.3 *Electrodes*

The solid oxide is the cathode in the process. Pellets of 5-10 mm diameter and 2-10mm thickness have been used in the laboratory experiments. Generally the oxide powder is pressed in a pellet press, dried and sintered at ~1000 °C for a few hours to give good quality pellets. The sample preforms can also be prepared by slip casting method. A porous cathode may be preferred to a compact one as the electrolyte can penetrate deep inside the bulk material and give electrochemical contact to a larger area. This can also reduce the diffusion path length of the bulk oxygen atoms to the electrode-electrolyte interface and hence effect a faster deoxidation.

Almost all the experiments reported on the process so far have used graphite rods as anode. However, as in electrolytic production of aluminium, graphite electrodes may become unacceptable in commercial FFC cells due to its potential for environmental pollution. An inert anode is an answer to this problem.[49]

5.3.4 *The demonstration experiments*

In the laboratory demonstration experiments[6], the solid TiO_2 cathodes in the form of pellets (5-10 mm dia., 2-10 mm thickness) were used. The pellets were prepared either by slip casting or by powder compaction method. These pellets were either placed at the bottom of the crucible in which the molten electrolyte was taken [Fig. 3a] or suspended from top of the cell with the help of Kanthal wires [Fig. 3b], which also served as the cathode current collector. Graphite rods (6-10 mm dia.) were used as the anode in the cell with molten calcium chloride maintained at ~ 950 °C. The experiments were performed in a sealed Inconel reactor, which was

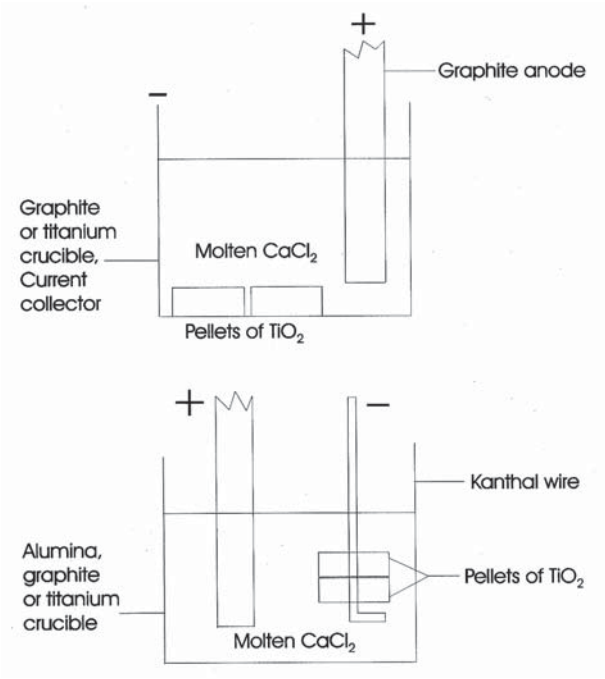

Fig. 3 : Fig. 3a & Fig 3b: Two different configurations of the electro-deoxidation experiment [6]

continuously purged with high-purity argon. Voltages in the range of 2.8V-3.2 V, including the IR drop in the cell, were applied to the cell. The duration of electrolysis ranged from 5-24 hours depending on the number and size of the pellets used. Upon electrolysis, the TiO_2 electrode with average particle size of 0.25 mm, was transformed into titanium metal particles of about 12mm size. The microstructure of the titanium metal produced [Fig. 4] resembled that of the Kroll titanium sponge.

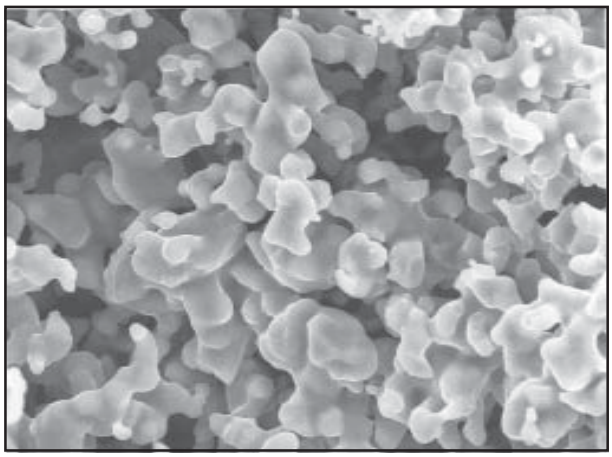

Fig. 4 : SEM image of the titanium metal obtained by electro-deoxidation of a TiO_2 pellet in molten $CaCl_2$ at 950 °C [6].

6. DEVELOPMENT OF FFC PROCESS FOR TITANIUM PRODUCTION

The FFC Cambridge process is projected as an alternative to the Kroll process[8] for titanium production. A schematic of the various stages involved in the production of titanium by the process is given in Fig. 5. As titanium is directly extracted from its dioxide, the conversion of the oxide to chloride as is done in the Kroll process can be avoided. This will help to reduce the energy consumption as well as the risk factor associated with the handling of volatile $TiCl_4$[50]. In the absence of carbothermic reduction, the FFC process can be expected to be far less polluting than the conventional pyrometallurgical process. Molten calcium chloride is a low toxic chemical to handle and hence the overall safety of the process will be good. Calcium chloride is water-soluble and hence can be easily washed and discarded. It is readily available at a low cost. Above all it has very high solubility for oxygen ions, which is necessary for the de-oxidation reaction.

A year after the discovery of the electro-deoxidation of titania by the FFC team, the process was evaluated at a small scale (1kg/day) by Defense Evaluation and Research Agency (DERA), UK. The experience with the pilot plant scale operation was described as very satisfactory[51]. Around this time a new company called BritishTitanium plc. was incorporated to further exploit the FFC invention. The company's new plant has reported production of the first batch of titanium metal in March 2003. More recently, DARPA (Defense Advanced Research Project Agency of US) has funded development of the FFC process for extraction of titanium metal and selected TIMET Ltd., a leader in titanium production in USA, for carrying out the work. A TIMET-led syndicate will be working on this ambitious project for the next four years. So, the next four to five years can be considered to be crucial to the FFC process, as its projected potential for commercial production of titanium will be put to the test during this period.

The FFC process is capable of extraction of many other metals from their respective oxides. In order to exploit the technology for production of metals other than titanium, Cambridge University has recently formed a company of its own called Metalysis Ltd..

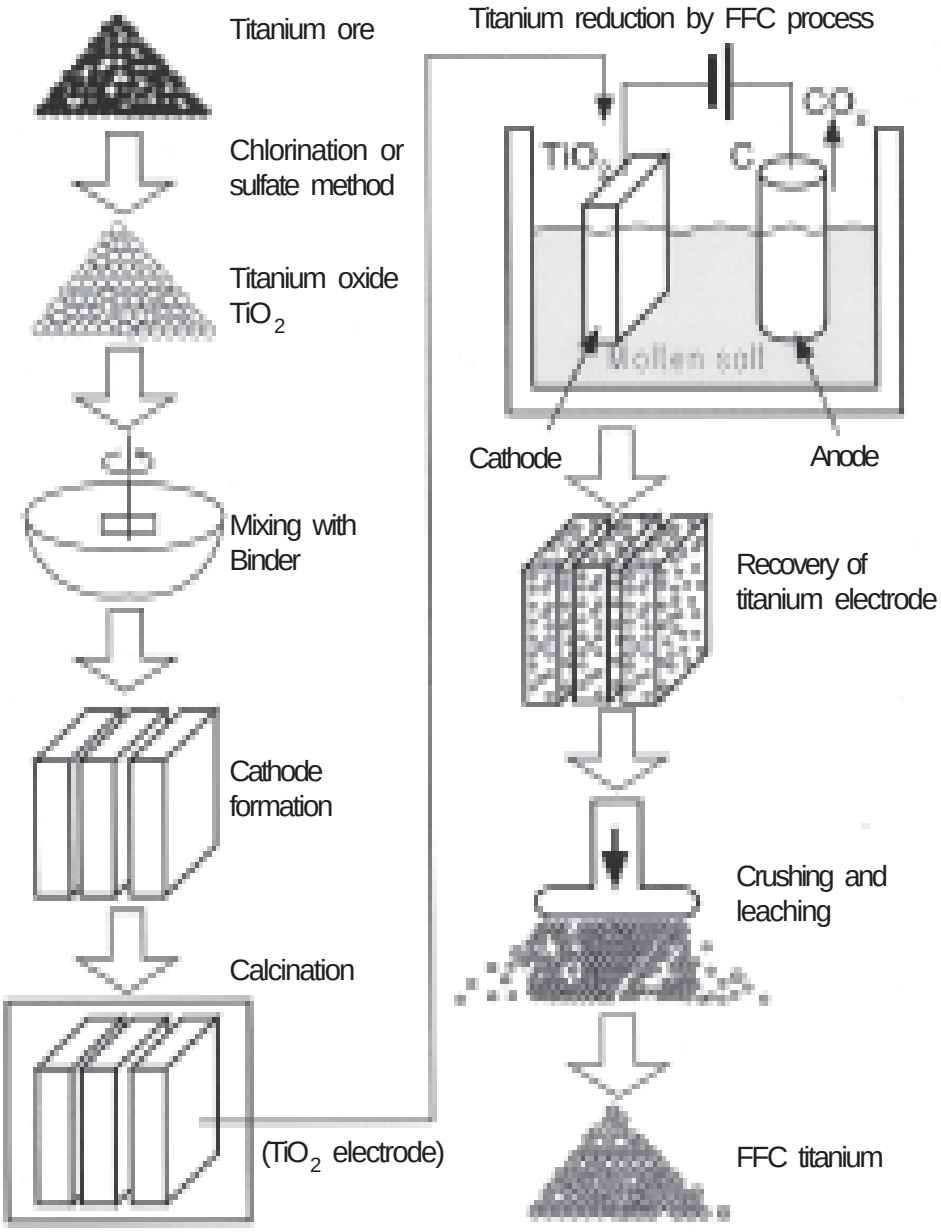

Fig. 5: Various stages in the titanium production by the FFC Cambridge process

Some important areas, as given below, can be identified for the successful industrial production of titanium by the FFC process.

1. The oxygen ionisation and hence deoxidation takes place at the solid oxide-molten electrolyte-metal interface and for this the oxygen ions from the bulk should diffuse to the interface. The rate-limiting step is likely to be the diffusion of oxygen in the solid-oxide. Industrial scale production of metal may require the use of bulky solid oxide preforms, which may increase the path length of diffusion of bulk oxygen and hence the duration of electrolysis. So, the design of the solid TiO_2 electrode will be an important factor.

2. As chlorination step is not involved in the FFC process, it may be necessary to purify the feed rutile by some other means. The solid oxide cathodes have to be prepared by powder compaction/slip casting method and these are to be sintered at about ~1000 °C for sufficient strength. Fine TiO_2 powder may have to be used

to obtain good quality electrodes. So, the cost of preparation of the solid oxide electrode can be an important factor, which decides the economics of titanium production.

3. The reactive metals extracted by the FFC process are in the form of porous or fine structure or powder. It is possible that the metal can get easily oxidised upon exposure to air, even at room temperature. So, collection of the metal product without it being oxidised, is an important aspect. The frozen electrolyte around the metal can protect it from contamination, but removal of the frozen mass with minimum contamination of the metal may be a challenging task in large–scale metal production.

4. The current efficiency of the process achieved in laboratory scale cells is about 50%. For a viable industrial process, the current efficiency has to be higher.

5. As in the case of aluminium production by Hall-Heroult process, environmental pollution by the FFC process by-product gases (CO, CO_2 and chlorocarbons) will be serious. So, inert anodes may have to be developed and used in FFC cells. But this will increase the cell voltage by more than 1 V.

7. CONCLUSION

Removal of oxygen from metal-oxygen systems has been an area of immense interest in the production and purification of reactive metals. The finding that the oxygen can be removed from a metal oxide/ metal-oxygen solid solution by molten salt electrolysis is hence a leap forward in the electrometallurgy of reactive metals. The discovery may lead to significant changes in the conventional metal production technologies. Apart from metal production, the new technology is adaptable to synthesis of new materials and alloys, some of which could not have been possible with the conventional methods. However, the commercial viability of the FFC Cambridge process for production of titanium and other reactive metals is yet to be established. The indications are that the efforts towards it have started in earnest. The next few years will be crucial to the FFC Cambridge process, as it will be known during this period whether the initial excitement over this novel process can be transformed to a commercial success.

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