Opportunities in the Electrowinning of Molten Titanium from Titanium Dioxide

D.S. van Vuuren, A.D. Engelbrecht, and T.D. Hadley

The value chain of titanium products shows that the difference between the cost of titanium ingot and titanium dioxide is about $9/kg titanium. In contrast, the price of aluminum, which is produced in a similar way, is only about $1.7/kg. Electrowinning of molten titanium from titanium dioxide is therefore believed to have significant potential to reduce the cost of titanium products. The process is hampered by the high operating temperatures and sophisticated materials of construction required; the high affinity of titanium for carbon, oxygen, and nitrogen; and physical and chemical properties of the different titanium oxide species when reducing titanium from Ti^{4+} to metallic titanium.

INTRODUCTION

Numerous attempts have been undertaken in the last 60 years to reduce the cost of producing titanium. Excellent reviews (e.g., Hartman et al.[1] and Turner et al.[2]) are available on past developments, and a comprehensive survey of current work was recently undertaken by EHK Technologies[3,4] on behalf of the Department of Energy and Oak Ridge National Laboratories.

Primary titanium can be produced from a number of feed materials using different reductants. Depending on the process, many physical forms of titanium can be produced. If an impure feed material were used, contamination of the titanium product would normally result, which may be acceptable for producing titanium alloys.

The different feed materials that can be used include slag or rutile (potentially acceptable for producing ferro-titanium alloys); high-purity TiO_2; high-purity $TiCl_4$; TiI_4; and Na_2TiF_6. The different reductants or driving forces used to convert the feed into metallic titanium are sodium, magnesium, calcium, calcium hydride, aluminum, hydrogen, electricity, and high temperature. Depending on the process used, the following forms of titanium are produced: titanium sponge, sintered electrode sponge, powder, molten titanium, electroplated titanium, hydride powder, and vapor-phase deposited titanium.

Comparing the economics of alternative process routes is difficult since the value of the final product is highly dependent on the form and quality of the titanium produced. For example, it has been reported that titanium powder from various parts of the world cost $18/kg to $440/kg[5] depending on quality and composition. This large variation in potential value becomes overriding in any techno-economic analysis of alternative routes. However, the value chain of producing titanium provides some perspective. The cost build-up for producing titanium via the Kroll process is approximately as follows: ilmenite ($0.27/kg titanium sponge); titanium slag ($0.75/kg titanium sponge); $TiCl_4$ ($3.09/kg titanium sponge); titanium sponge raw materials costs ($5.50/kg titanium sponge); total titanium sponge cost ($9–$11/kg titanium sponge); and titanium ingot ($15–$17/kg titanium).

Considering the cost build-up, it is clear that significant potential exists (in excess of $9/kg) to reduce costs if molten (or castable) titanium could be produced directly from $TiCl_4$. Electrowinning of molten titanium from $TiCl_4$—the development route selected by Ginatta—is a possible way to realize this potential.[6]

Whereas pure TiO_2 costs about the same as $TiCl_4$, the same margin exists to reduce the cost of titanium when using TiO_2 as feedstock. Electrowinning of molten titanium from TiO_2 or even titanium slag has been attempted,[7–10] but there are still some problems to resolve. A number of those issues are highlighted in this paper.

PROCESS DESCRIPTION

The process of electrowinning molten titanium from titanium dioxide is conceptually the same as the Hall-Héroult process to produce aluminum from alumina. The oxide is dissolved in a molten salt electrolyte at a sufficiently high temperature so that when it is reduced, molten metal settles out of the electrolyte. The feed is introduced continuously and the product is recovered periodically from the cell or pot.

If carbon is used as an electrode, the following simplified overall reactions occur at the anode and cathode, respectively: $2O^{2-} + 2C = 2CO(g) + 4e^-$ and $Ti^{4+} + 4e^- = Ti(l)$. The overall reaction is $TiO_2 + 2C = Ti(l) + 2CO(g)$. If an inert electrode is used, oxygen instead of carbon monoxide is produced.

Salt that can be used as electrolyte for electrowinning molten titanium must meet at least the following criteria: it must be liquid at the cell operating temperature and preferably have a low vapor pressure; it must have a lower density than molten titanium; it must have a low oxygen potential in order not to contaminate the product; and it must not react with titanium.

Considering oxides, chlorides, and fluorides, no single metal oxide is suitable and no chloride salt is suitable. The only fluorides that meet these criteria are CaF_2, SrF_2, BaF_2, and YF_3. Of these, CaF_2 has the advantage that it has the lowest vapor pressure at the operating temperature. BaF_2, on the other hand, has the highest density, which offers the advantage that, if any carbon particles would break off from the anode, they would float on top of the electrolyte and

EXPERIMENTAL PROCEDURES

A series of batch TiO_2 electrolysis experiments were conducted. The apparatus consisted of a graphite tube furnace used to heat an electrolysis cell to the desired temperature. Temperatures up to 1,800°C were used. The apparatus used is illustrated in Figure A. The electrolysis cell consisted of a graphite crucible, lined with molybdenum sheeting along the bottom and side of the cell. A close-fitting graphite lid was used to close the cell and a graphite anode protruded through a graphite tube inserted into the lid into the cell. The anode was electrically isolated from the graphite tube and, hence, the cell. The direct current used for electrolyzing the cell contents was supplied via electrical connections to the graphite anode and the graphite cell that formed the cathode via the molybdenum lining.

The internal dimensions of the cell were a diameter of 80 mm and a height of 120 mm. In all the experiments, CaF_2 was used as electrolyte. The electrolyte height was approximately 30 mm in all experiments.

The following experimental parameters were varied: temperature—1,750°C to 1,800°C; TiO_2 concentration—6% to 20%; current densities—10 kA/m² to 60 kA/m² at the anode and 2.5 kA/m² to 5 kA/m² at the cathode; anode diameter—25 mm to 40 mm; start-up and shut-down procedures; and anode-to-cathode voltage—1.1 V to 3 V (up to the time of the so-called anode effect). The experimental procedure was loading the cell, flushing it with argon, heating the system to the desired operating temperature over a period of about 6 h, and then lowering the anode until it made electrical contact with the molten electrolyte.

The system was in most cases run at a fixed current. During the experiments the voltage gradually increased as the TiO_2 concentration in the electrolyte decreased and as the anode became consumed. The anode was therefore lowered from time to time to compensate for its consumption. After a couple of hours, the measured voltage became unstable and jumped to 5V (the maximum set).

This effect is known in the aluminum industry as the anode effect. It is ascribed to the depletion of alumina in the electrolyte and the formation at the anode of CF_4 that increases the resistance between the anode and the electrolyte. In some of the experiments, the electrolysis was continued for several hours after observing the anode effect. In these experiments, the power supply operation was then changed to a fixed-voltage mode rather than a fixed-current mode.

At the end of each run, the cell temperature was reduced at ±5°C/min. while maintaining the applied voltage between the anode and the cathode. Once the temperature dropped to below about 1,600°C, the anode was lifted above the electrolyte surface and the system cooled to room temperature. Once cooled, the contents of the cell were removed, examined, and analyzed by x-ray diffraction, chemical analysis, and scanning electron microscopy analyses. The following key results were found:

- In all the experiments, the titanium product produced was in the form of small, almost spherical particles that settled to and concentrated in the bottom of the cell. Little evidence of coalescence or sintering was found.
- X-ray diffraction analysis showed in all cases that the bulk of the titanium product was Hongquiite, or TiO.
- The product layer of titanium-containing particles contained unacceptably high amounts of carbon. In most cases the titanium-to-carbon molar ratio was about 2, which translates to a carbon content in the titanium of about 10% by mass.
- Conclusive evidence of gas formation at the cathode was found. This was ascribed to gaseous calcium formation.
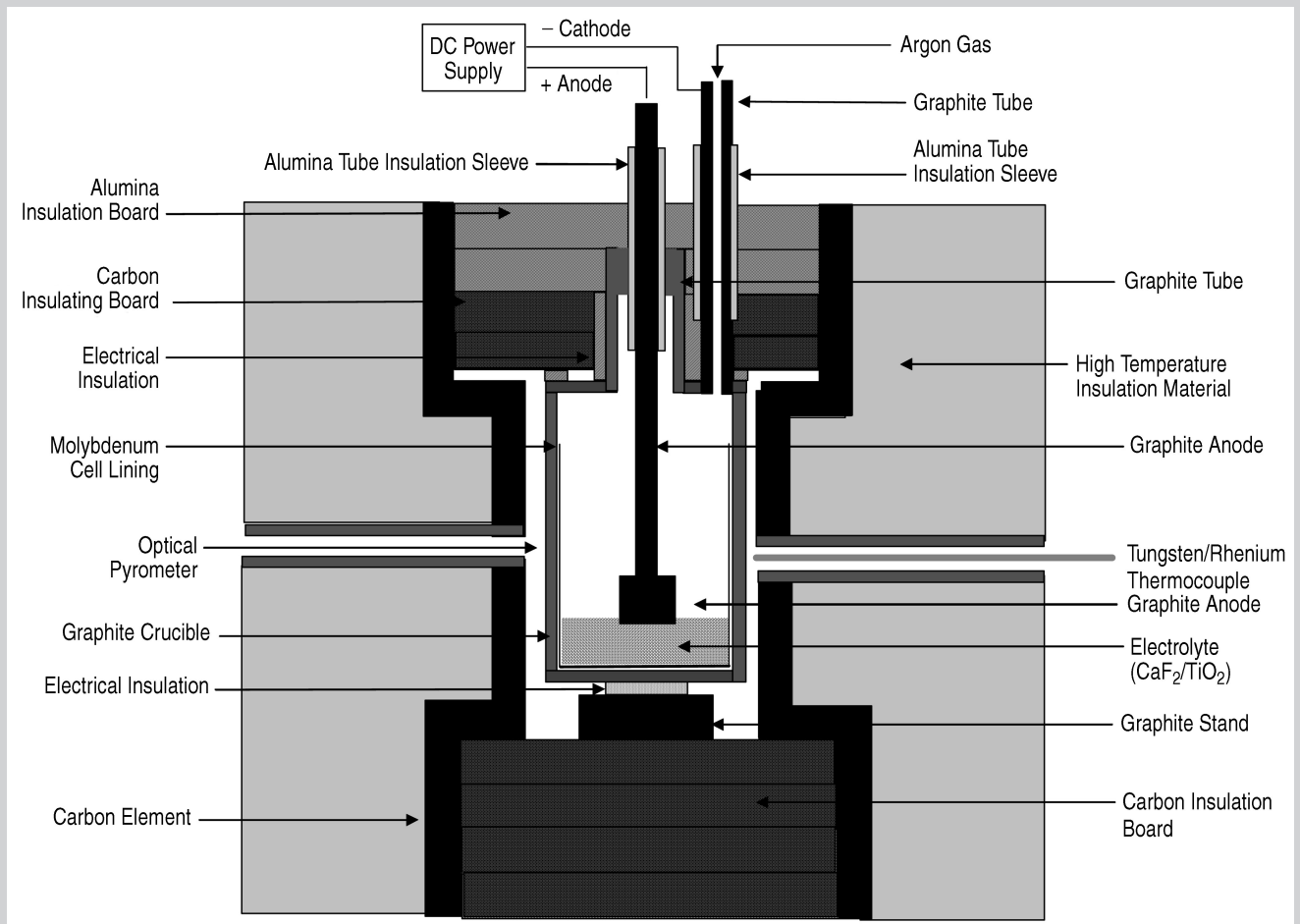

Figure A. Experimental apparatus.

not make direct contact with reduced titanium species. Although other salts do not meet the minimum criteria, it may be advantageous to use relatively small quantities in the electrolyte to influence the electrical and physical properties of the electrolyte.

The main differences between electrowinning titanium vs. aluminum, giving rise to more complex problems, are:

- Aluminum is produced at about 900°C, while molten titanium must be produced at above about 1,700°C.
- In the case of titanium, the electrolyte has a significantly lower melting point than the metal. This gives rise to problems in designing suitable pots in which to do the reduction since it becomes more difficult to form a freeze lining of the electrolyte to protect the pot.
- Titanium has a high affinity for carbon and nitrogen. Carbon can therefore not be used as construction material in places where the carbon can be in contact with the molten titanium. It is also unlikely that any carbide or nitride will be suitable in direct contact with molten titanium.
- Titanium has multiple oxidation states (Ti^{4+}, Ti^{3+}, Ti^{2+}, and possibly even Ti^{+}). Apart from decreasing the current efficiency of the cell, the different titanium oxides that can form have different physical and chemical properties.

ADVANTAGES OF ELECTROWINNING TITANIUM FROM TiO_2

An electrochemical process producing molten titanium directly from TiO_2 has the following advantages: fewer process steps; continuous operation; de-linking titanium production from $TiCl_4$ and magnesium or sodium production; nonhazardous feed material that is easily transported and stored (TiO_2 vs. $TiCl_4$); and alternative feed supply (TiO_2 from either the chloride or sulfate routes). These advantages all translate into potential cost savings. Direct electrowinning of molten titanium from TiO_2 would therefore be significantly more cost effective than the Kroll process, provided the inherent problems related to

the process are resolved. See the sidebar for experimental procedures.

INTERPRETATION AND CONCLUSIONS

The formation of particulate TiO/TiC agrees with the findings of Hashimoto et al.,[7] but contrasts with the claims of Cardarelli.[10] As the dissolved TiO_2 is reduced, it likely forms less soluble, liquid suboxides that come out of solution. As it is reduced further, its melting point increases until it solidifies so that no droplet coalescence can take place.

The so-called anode effect occurs when the dissolved oxide concentration becomes low, causing an increase in the electrical resistance of the electrolyte. This leads to an increase in voltage (at a fixed current supply), which in turns gives rise to the electrolysis of CaF_2 to form gaseous calcium and CF_4. The calcium gas forms at the bottom of the cell and tends to blanket the cathode, leading to a further increase in the anode-to-cathode resistance.

Carbon contamination of the product was reported by Hashimoto et al.,[7] whereas Takenaka et al.[9] reported that carbon contamination decreases substantially with increasing anode-to-cathode distance. Analysis of the possible mechanisms of carbon transfer to the product showed that it cannot be via carbon monoxide; the mass transfer rates are simply too low. It is also unlikely that in the described experiments it occurred via the formation of calcium carbide as postulated by Hashimoto et al.[7] The reason is that while the product was formed, the applied voltage was simply too low for calcium carbide formation and the analysis of the upper electrolyte layer showed a lower carbon-to-titanium ratio than the bottom product layer. Another possibility is direct reaction between the dissolved oxide and the carbon anode. This might have occurred due to thermal convection currents assisting contact between the dissolved titanium oxides and the carbon anode. Lastly, it is also possible that some carbon eroded from the anode and settled into the product. Inspection of the anodes after the experiments showed evidence of pitting.

FUTURE DEVELOPMENT

Apart from overcoming the problem of selecting suitable materials of con-

struction for the process, the fundamental problems to overcome before scaling up the process are the formation of TiO instead of molten titanium, and the prevention of carbon contamination.

Whereas Hashimoto et al.[7] used high temperature (>1,800°C) to increase the solubility of the reduced titanium oxide species, testing of various electrolyte formulations is planned. Techniques similar to that used by Suzuki and Ono[11] to reduce TiO_2 calciothermically in the solid state with in-situ electrochemical regeneration of CaO will be investigated. Approaches to overcome carbon contamination, such as increasing the anode-to-cathode distance, using different electrolytes, and using an inert anode will also be tested. Various material-of-construction tests have already been undertaken, showing some unexpected problems, but also leading to feasible design concepts. This work will be extended as progress is made on resolving the two described fundamental problems.

References

1. A.D. Hartman, S.J. Gerdeman, and J.S. Hansen, *JOM,* 50 (9) (1998), pp 16–19.
2. P.C. Turner et al., *EPD Congress 2001,* ed. Patrick R. Taylor (Warrendale, PA: TMS, 2001), pp. 43–65.
3. EHKTechnologies, "Opportunities for Low Cost Titanium in Reduced Fuel Consumption, Improved Emissions, and Enhanced Durability Heavy-Duty Vehicles," a study performed for the U.S. Department of Energy and Oak Ridge National Laboratory, Subcontract 4000013062 (2002).
4. EHKTechnologies, "Summary of Emerging Titanium Cost Reduction Technologies," a study for the U.S. Department of Energy and Oak Ridge National Laboratory, Subcontract 4000023694 (December 2003).
5. F.H. Froes, *JOM,* 50 (9) (1998), pp. 41–43.
6. M.V. Ginatta, "Process for the Electrolytic Production of Metals," U.S. patent 6,074,545 (2000).
7. Y. Hashimoto, K. Uriya, and R. Kono, *Denki Kagaku,* 39 (6) (1971), pp. 516–522.
8. H.R. Larson and T.W. Eager, *JOM,* 50 (9) (1998), pp. 56–57.
9. T. Takenaka et al., *Electrochemistry,* 67 (6) (1999), pp. 661–668.
10. F. Cardarelli, "A Method for Electrowinning of Titanium Metal or Alloy from Titanium Oxide Containing Compound in the Liquid State" (PCT Patent Application, 2003), Publication No. WO03046258.
11. K. Ono and R.O. Suzuki, *JOM,* 54 (2) (2002), pp. 59–61.

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