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Extrusion Based Processing of Ti Alloys: Feasibility Study

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Introduction

This project was a feasibility study to explore the viability of using metal honeycomb technology developed at Georgia Tech as an economical alternative to processing titanium structures of relevance to aerospace applications. In the first part of this program, honeycombs with square prismatic cells were fabricated by extrusion of titanium oxide powder and experiments were conducted to convert the sintered honeycomb to metallic titanium through electrolytic reduction. This approach was pursued to explore extension of the FFC process[1] to electrolysis of thin wall (~ 300 μm) TiO_2 structures as the reduction stage of our proposed process. These tests focused on kinetics of titania reduction because high specific surface area oxide preforms can be fabricated using technology developed by the lightweight structures group at Georgia Tech[2-4] via extrusion of thin walled, small cell size, honeycomb structures from powders/binder mixtures. During the honeycomb reduction studies, dendritic electrodeposition of titanium was observed to be occurring on the cathode performs and it appeared that a titanium electro-refining process was occurring similar to the Hall process for aluminum. Thus, a series of tests were conducted to determine if high purity titanium could be electrodeposited from a molten salt saturated with titanium ore. Our conclusion was that this process is occurring and because this approach has potential for being of significant economic value, a provisional patent application has been filed.

Background

To build a background for electrolytic reduction of titania in calcium chloride, a visit was paid to the laboratories of the experts in the FFC process. Joe Cochran traveled to the UK and met with Derek Fray at Cambridge University and Richard Dashwood, Harvey Flower, and Kevin Dring at Imperial College in June 2003. The daylong meetings at both universities were very informative, both groups were very helpful in presenting their processes and viewing of their laboratories to learn state-of-the-art processing in this area. The visits enabled us to design and construct/assemble an equivalent electrolytic reduction apparatus in a time efficient manner.

Based on discussions from both universities, we came to the conclusion that for this feasibility study we would limit our investigations to reduction of pure titania and exclude alloying elements. Apparently, when a mixture of oxides designed to produce an

alloy is reduced, the reduction process becomes more electrochemically complex and kinetic studies to determine rate-limiting processes may be difficult to separate into clearly defined mechanisms.

The thrust of our effort is to determine if, and by how much, the total reduction time can be shortened starting with a thin-walled preform. From studies to date, the idea was expressed that starting with dense impervious titania, reduction occurs on the surface and kinetic are limited by oxygen diffusion through the bulk titania. If a porous preform is used, then the electrolyte penetrates to the interior. Thus, reduction is limited through oxygen ion transported through electrolyte filled capillaries. In either case, the kinetics of reduction should be enhanced by reducing the perform thickness using extruded honeycomb structures.

In addition to limiting the cathode composition, design objectives of cleanliness and simplification throughout the system were instituted. Crucibles were fabricated from cp titanium and the decision was made to use the crucible as the anode for most studies. For some investigations, a graphite liner inside the Ti crucible was used as the anode.

Experimental Procedures and Preforms

Preform Fabrication and Sintering of Titania – Two grades of electronic titania powder were obtained from the Tam Division of Ferro, Type A, 99.2% with particle size of 1-5 μm, and Type B, 98% with particle size of 3.5 μm. The Type A titania was extruded into 3mm diameter rods and 4x4 square cell honeycomb with 2.5 mm cell size and 0.3 mm wall thickness. The rods were sintered for six hours at various temperatures to develop a sintering profile, Figure 1. Stage 1 sintering initiates at ~1100°C and ends at ~1300°C. Based on comments from Cambridge University and Imperial College, both impervious and highly porous titania honeycomb were fabricated for electroreduction. In preparation for this, quantities of both were prepared by air sintering at 1100°C for the porous samples and 1350°C for the impervious samples, Figure 2. Both the porous and dense air sintered honeycombs were characterized for porosity and density and results agreed with the densities presented in Figure 1.

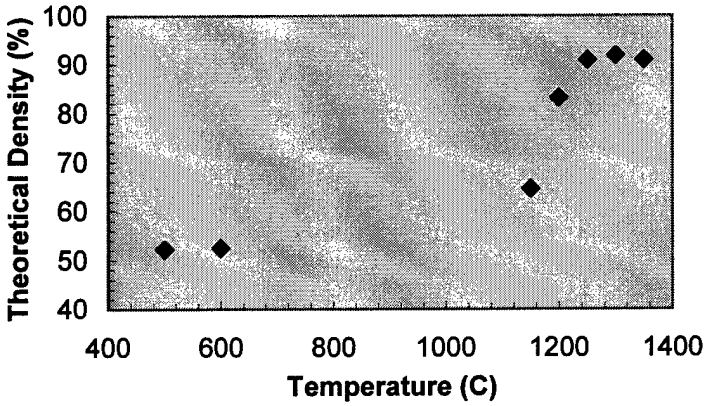


Figure 1. Density of TiO_2 sintered in air for six hours.

In addition to varying density as a parameter for controlling electroreduction of titania, several forms of thermochemical reduction (e.g., carbonthermic and hydrogen reduction) were evaluated as perform pretreatments prior to electrochemical processing.. The driving rational was that if oxygen contents in the titania could be reduced easily and cheaply in the preform, then the oxygen quantities to be removed in electroreduction are reduced and oxygen partial pressures the gas phase can be reduced with ultimately should provide lower oxygen content titanium. To support this, several ways of reducing titania were explored. In the first case, a mixture of titania with 20 weight % carbon was extruded and sintered in a 4% hydrogen atmosphere at 1280 °C. This sample converted mostly to Ti_2O_3 as determined by XRD, Figure 3. In addition, extruded titania rods were sintering in 4% hydrogen, also at 1280 °C. Certainly some level of reduction occurred because the XRD pattern is no longer the starting rutile but the pattern has not been matched to know phases. Weight reduction from the hydrogen reduction was investigated further because it has been reported that Ti_3O_5 can result from hydrogen reduction of TiO_2. Samples both of the air sintered honeycombs, Figure 2 were reduced in 100% hydrogen and weight loss indicated a Ti to O ratio of 1.7-1.8 assuming the weight loss was due to only loss of oxygen. XRD results were inconclusive.

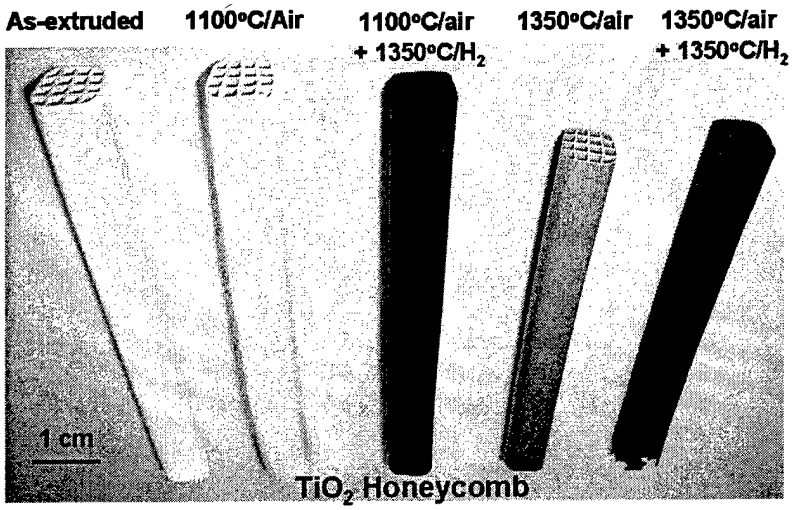


Figure 2. Titania honeycomb as-extruded and after sintering in air and hydrogen

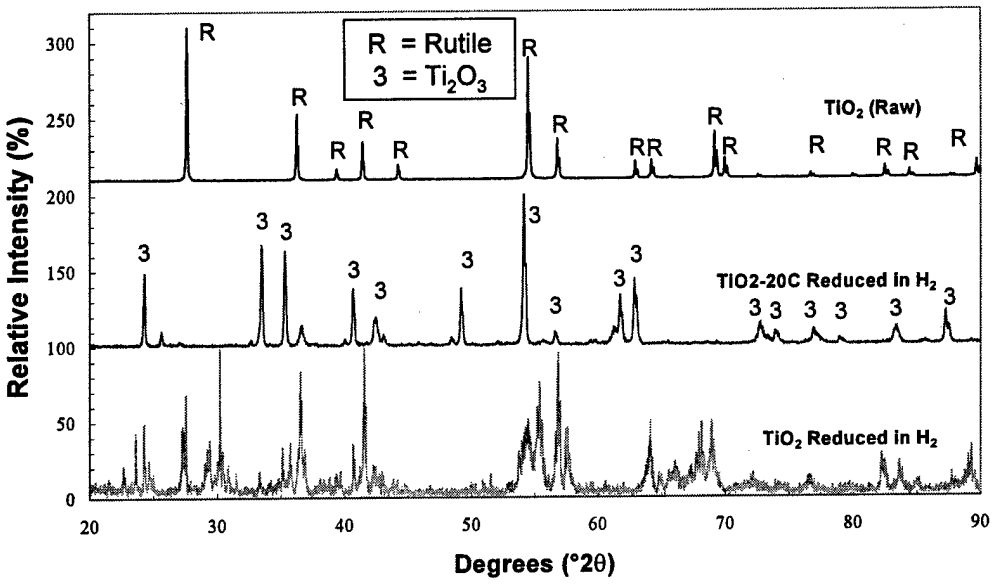


Figure 3. XRD patterns of Electronic grade titania powder as-received and extruded titania and titania-20% carbon reduced in H_2 at 1280°C.

Georgia Tech Electrolytic Reduction Cell (ERC) Design – Approximately three months were spent designing he reaction cell, procuring supplies, fabricating components and setting up an electroreduction facility. The decision was made to use un-alloyed titanium crucibles and if possible in a disposable manner so that they could be replaced on a frequent basis. Crucibles were fabricated from 8.9 cm (3.5 inch) diameter Ti tubing with 1.3 mm wall thickness and a welded Ti bottom. To date six 30.5 cm (12 inch) tall crucibles were fabricated but sufficient supplies are on hand to fabricate 24 more if needed. If all 30 crucibles are fabricated, cost per crucible will be ~$110.

The electroreduction furnace was assembled using a horizontal Inconel retort furnace manufactured by Electroxxxx of Pittsburgh, PA. The furnace was converted from horizontal to vertical by the addition of legs and retort door plug was positioned for easy vertical motion by a counter weight system. The furnace has an interior cavity cross-section of 7 x 11.5 inches by 26 inches deep (7.8 x 29.2 x 66 cm). The top 20 cm (8 inches) is filled with an Inconel door plug for insulation. A crucible support cage was designed, Figure 4, that will hold five crucibles so that multiple runs can be made simultaneously to make data collection efficient considering the long reduction time reported by others. The furnace modification to vertical operation was delivered the last week in September without the crucible cage. Due to timing and expense, the decision was made not complete the crucible cage but this would make the experimental process much more efficient. Reduction experiments were run with single crucibles and considering the experimental set-up, heating and cooling time, experimental electroreduction, sample cleaning at the end, run duration required approximately a week time period.

Electrolytic reduction cell construction is shown in Figure 5 and consists of:

1. Heating and atmosphere control was provided with a modified retort furnace for a constant isothermal and inert environment.
2. The electrolytic cell consisted of a Ti crucible, which served as the anode and a cathode assembly with vertical linear motion to permit insertion and removal of the sample from the melt. Insertion of carbon sheets (graphoil) can be used for chemical isolation of the titanium crucible.
3. Data acquisition consisted of PC based software and a PCI interface (8 channels: cell temperatures, cell voltage, cell amperage, and provisions for reference electrodes, effluent gas analysis, etc.)
4. A multiple crucible design to provide independent simultaneous experiments to be conducted side-by-side. To be utilized in the future if appropriate.
5. Modular cathode assembly for insertion and withdrawal independent of neighbor cells.

Design guidelines were directed to a totally clean system, which included:

1. A titanium crucible system with no carbon, aluminum, iron, or vanadium in contact with the molten $CaCl_2$. However, for several experiments, the titanium crucible was isolated form the system via a carbon liner.
2. For even better cleanliness, $CaCl_2$ was pre-dehydrated, and the system was continuously purged with Ar to flush out any oxygen generated.
3. A system designed to be washed and rinsed without major effort between runs.

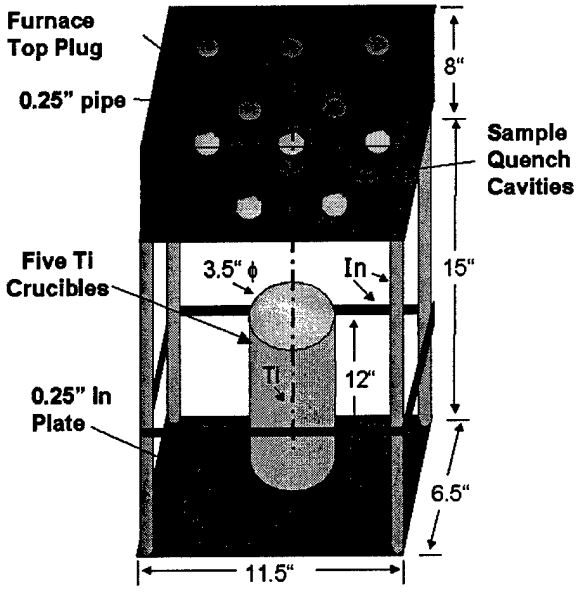


Figure 4. Furnace plug and crucible cage designed for multiple electroreduction cells.

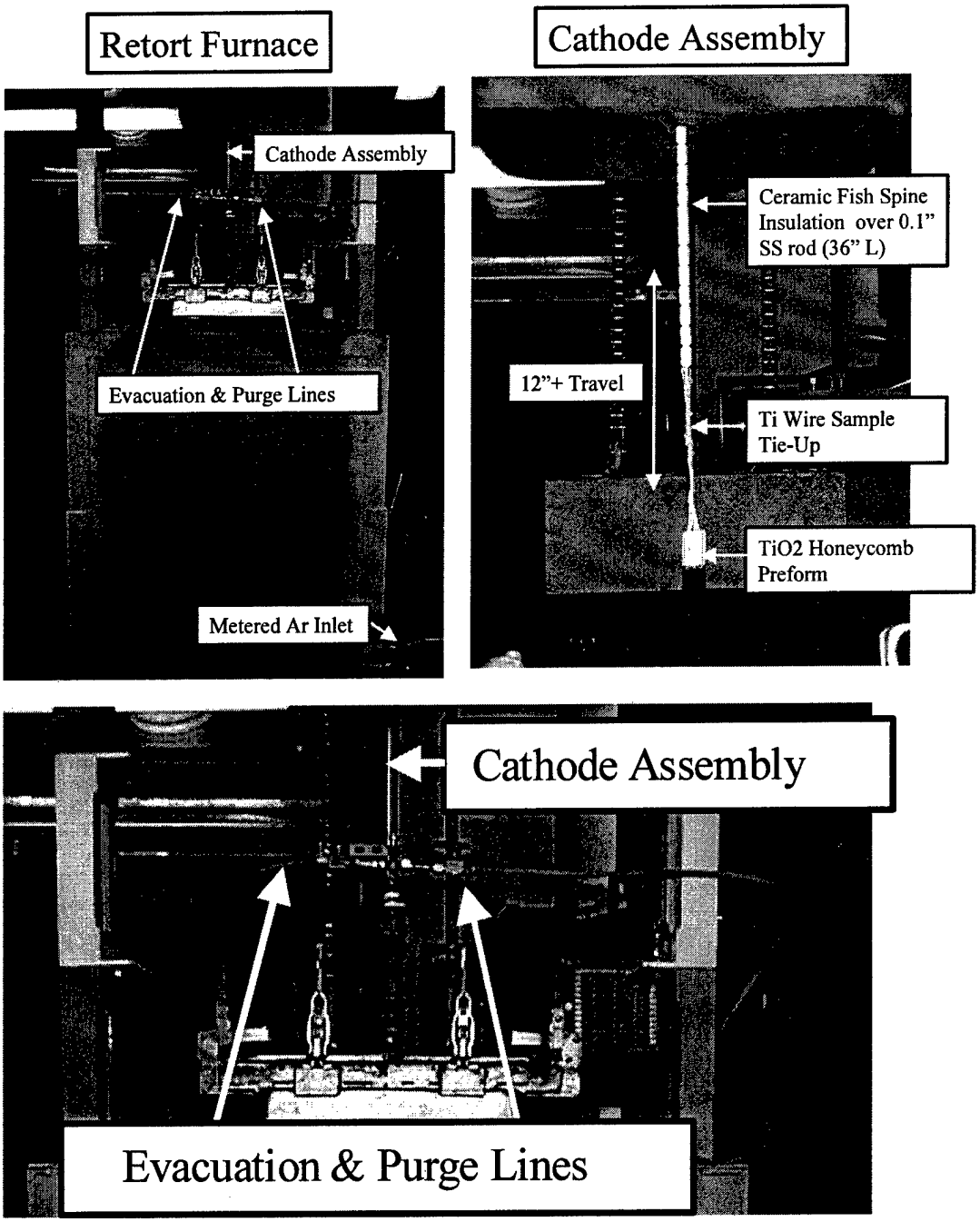


Figure 5. Georgia Tech Electrolytic Reduction Cell (ERC) Design

Experimental Procedure, Results, and Discussion

Electrochemical Reduction of TiO_2 Honeycomb, Run #1 - Honeycombs with square prismatic cells were fabricated by extrusion of titanium dioxide powder and sintering in air at 1350°C to densify the walls to an impervious state, Figure 1. A 2.5 cm long sample was converted to titanium sub-oxide through electrolytic reduction in $CaCl_2$ after the FFC process. The sample was reduced in $CaCl_2$ at 950°C for 6 hours at 3V and ~ 4 A. The anode was the titanium crucible and the cathode was supported in the molten salt with 0.63 mm diameter cp titanium wire. The current remained constant through most the experiment and increased approximately 10% near the end. (From later experiments, it was concluded that the background current was ~2A so that the reduction current was ~ 2A.)

A section through the center of the sample showed that the honeycomb was reduced throughout the interior, Figure 1. Demonstrating that honeycomb samples would effectively reduce internally was one of the objectives of this feasibility study and this sample appears to accomplish that goal. Also, it was proposed that kinetics of reduction should be accelerated because the titania honeycomb walls are thin, ~280 μm thick, and reduction should reach the center of the webs quickly. For this sample, the six hour reduction time provided a cumulative electron exposure of ~12 A.hr and it weighed ~ 1.8 g. Note that if the reduction process were completely efficient, TiO_2 would reduce to titanium after 1.38 A.hr/g exposure. This sample was exposed to five times the A.hr needed for reduction and if the process were perfectly efficient, the sample would have been reduced in under an hour. Thus, the source of excess current needs to be identified.

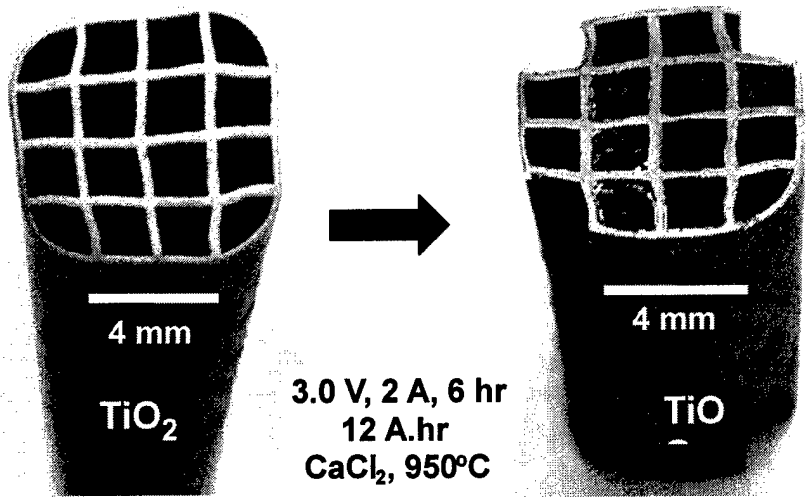


Figure 6. Conversion of TiO_2 honeycomb to TiO by electrochemical reduction in $CaCl_2$.

After reduction, the sample was washed in distilled water for a day, soaked in acetone for an hour and dried. The sample was examined in an SEM, Figure 7, and is seen to be relatively in tack. Few cracks are seen but a significant quantity of deposits can be observed on the wall. Based on results below, this is likely to be electro deposits of titanium but it was not analyzed for this sample. The chemistry of the honeycomb web was analyzed from an interior web, Figure 8, and found to be approximately $TiO_{1.1}$. There appeared to be a significant Mg peak but there is no explanation for the presence of Mg. The Ca and Cl contents were relatively low, < 1%, but it is unknown what level of $CaCl_2$ to expect in the sample at this point.

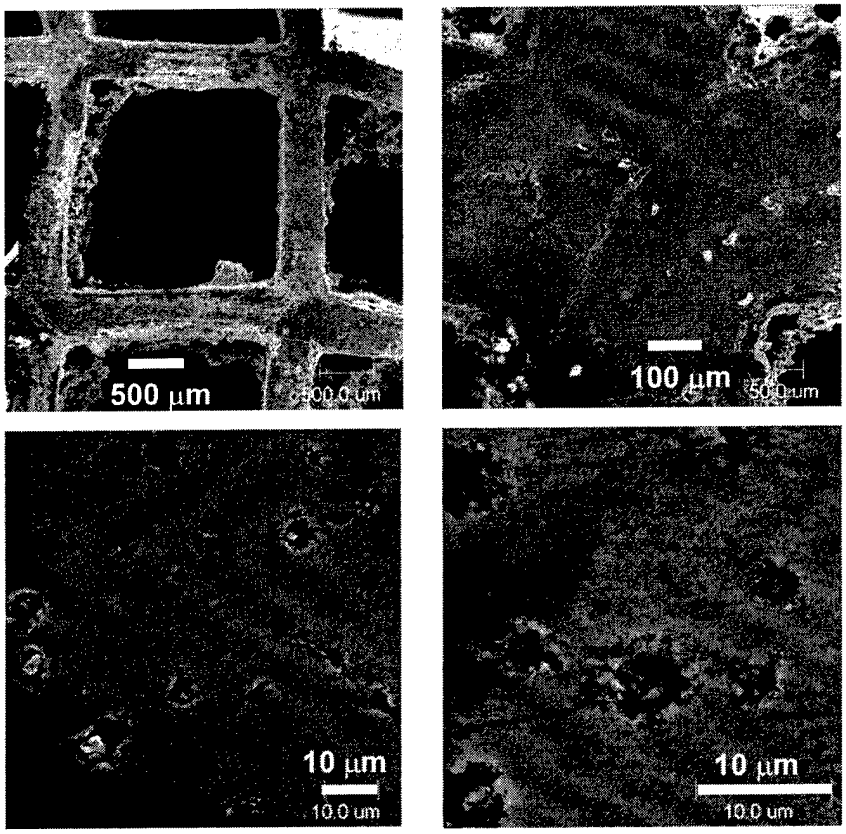


Figure 7. Micrographs of Ti honeycomb from electrochemical reduction of titanium dioxide honeycomb. Note the relative high density with a minimum of microcracking at this stage of the reduction process.

Element	Weight%	Atomic%
O K	24.82	47.12
Mg K	7.52	9.39
Si K	0.90	0.97
Cl K	0.49	0.42
Ca K	0.65	0.49
Ti K	65.63	41.61
Totals	100.00	

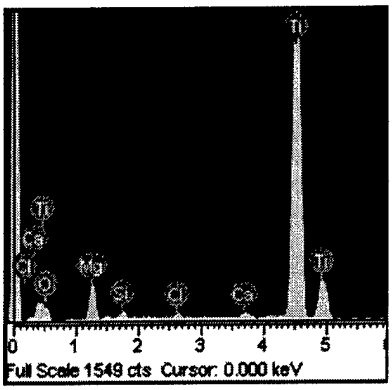


Figure 8. EDS chemical analysis from Reduction Run #1.

Electrochemical Reduction of TiO_2 Honeycomb, Run #2 – For the second run, a larger sample with an increased cell size was used, Figure 9. This sample was reduced at 950°C for 6 hours at 3.4 V and ~ 2 A. A larger cell size sample was used to ensure that reduction was uniform through out the interior. As can be seen, on exterior inspection the sample appeared to be converted to titanium and there were dendrites deposited in the corners of the sample plus on the titanium support wires. The sample was sectioned through the center perpendicular to the cell axis. As shown in Figure 9, the electrochemically reduced TiO2 wagon wheel appeared to have oxygen gradient from exterior to interior of the honeycomb webs. There was a titanium layer of uniform thickness on the exterior of all cell walls. The layer thickness was ~ 50 μm thick. This was presumed to be result of electrochemical reduction but the presence of dendrites on the titanium support wires suggests that the dendrites grew as a result of electrochemical deposition by transport of a titanium ion species through the chloride melt. These species could range from ions as simple as Ti^{+4} to TiO^{+2}, $TiCl^{+3}$, $TiCl_2^{+2}$ or more complex combinations. The overall morphology of the dendrites appear to be controlled by electric field lines radiating from curves wire supports and the corners of the honeycomb.

EDS chemical analysis of titanium dendrites from Run #2, Figure 12, indicates that the dendrites are pure titanium with no EDS detectable oxygen. The small carbon content is from carbon adhesive tape used for sample mounting. It is significant also that there was no detectable Ca or Cl. This suggests the possibility that the dendrites are dense titanium with no internal entrapment of CaCl2 as is common for the electrochemical reduction process. Obviously, if this were the feedstock for further titanium processing, a lack of contamination would reduce alloying cost significantly.

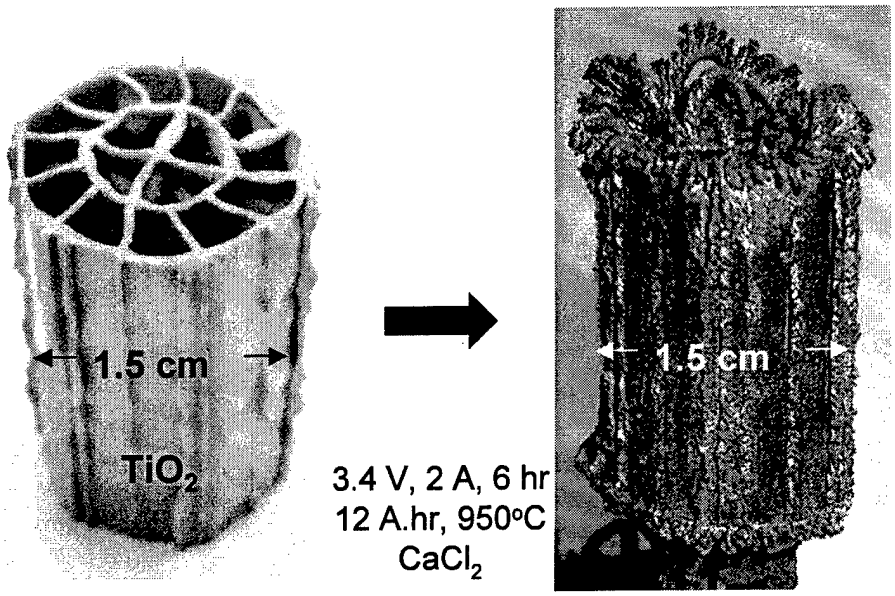


Figure 9. TiO_2 wagon wheel honeycomb with 3 mm cell size that was electrochemically, reduced in $CaCl_2$.

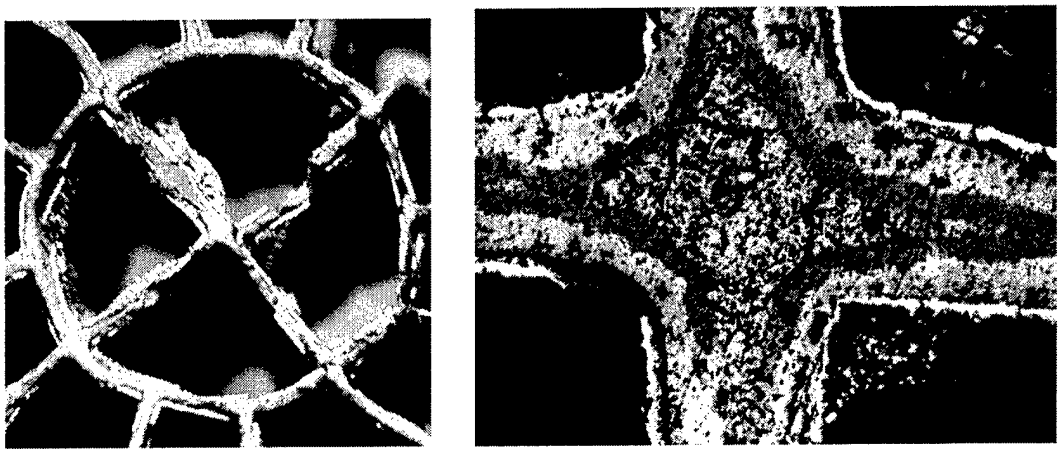


Figure 10. Electrochemically reduced TiO2 wagon wheel showing oxygen gradient from exterior to interior. Note the uniform thickness Ti layer on the exterior of cell walls. Layer thickness was ~ 50 μm thick.

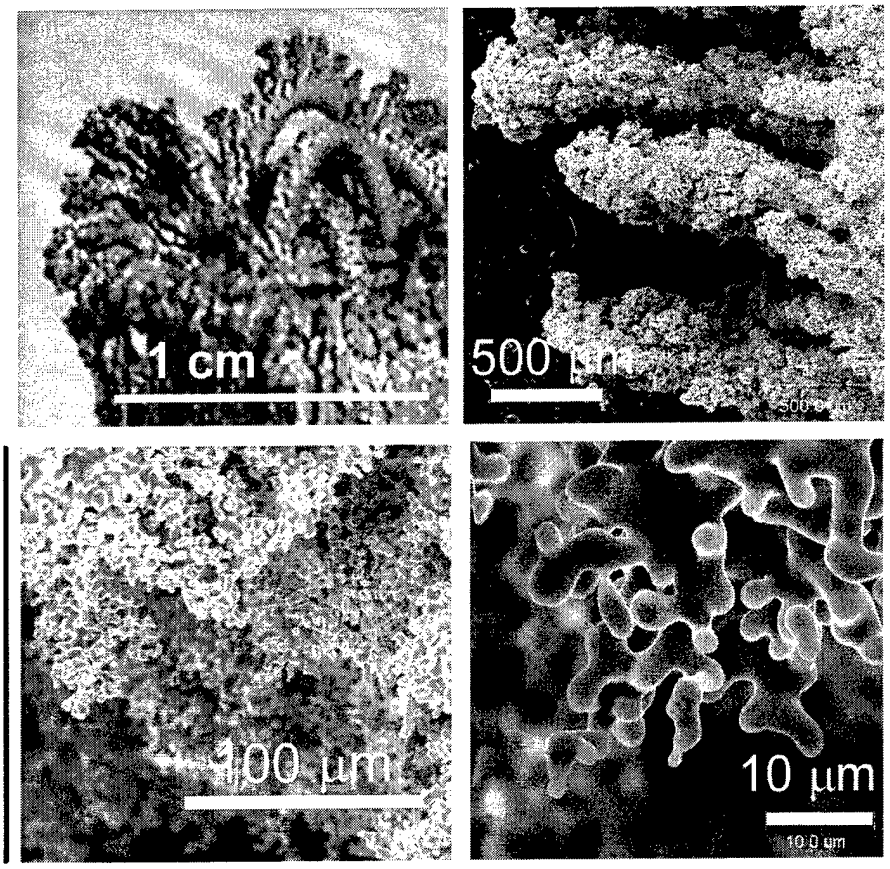


Figure 11. Titanium dendrites that were grown from electrodeposition of a titanium ion species from molten $CaCl_2$ at 950°C.

Spectrum	C	N	Ti	V	Total
Spectrum 1	1.27		98.73		100.00
Spectrum 2	1.77		97.51	0.72	100.00
Spectrum 3	1.53		97.34	1.12	100.00
Spectrum 4	4.51	3.81	91.02	0.66	100.00
Spectrum 5	2.06		97.94		100.00
Max.	4.51	3.81	98.73	1.12	
Min.	1.27	3.81	91.02	0.66	

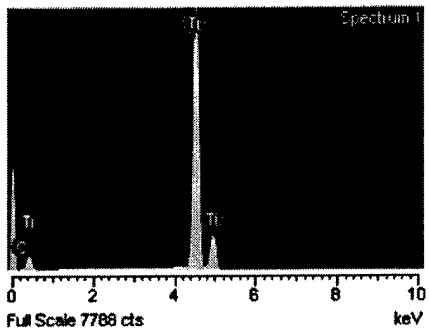


Figure 12. EDS chemical analysis of titanium dendrites from Run #2 that shows the dendrites to be pure titanium with no EDS detectable oxygen. The small carbon content is from carbon adhesive tape used for sample mounting.

Electrochemical Deposition of Titanium, Run #4 - As a result of the appearance of titanium electrodeposition from Run #2, an experiment was designed to amplify this deposition process. Again, using the titanium crucible as the anode, 50 grams of TiO2 powder (~1 μm diameter particle size) was added to 2 Kg of $CaCl_2$. The cathode consisted of a bundle of six strands of 0.63 mm diameter cp titanium wire approximately 4.5 cm long with a weight of 0.50 grams. The cell was operated at 3.4 volts, 4.0A, and 6 hours. Approximately 1.1 grams of titanium were deposited and the appearance was that of a sponge like deposit, Figure 13. The deposit morphology consisted of fibrous and nodular geometries, Figure 14. The fibers had short branches and the fiber diameter was 5-10 μm and lengths up to several μm. The nodules were approximately spherical with diameter in the 10-100 μm size range. Chemical analysis indicated the deposits to be essentially pure titanium with no detectable oxygen of chlorine. Minor elements identified by the automatic EDS software ware were at the limits of detection and thought to be random.

From these results, it certainly appears that when titanium dioxide powder is added to calcium chloride melt, the TiO_2 dissolves in the electrolyte and electro-deposits on the cathode as a titanium sponge in the form of dendrites and whiskers. Certainly some of the titanium deposit may be from the crucible but the dramatic increase in deposit quantity did not occur until TiO_2 powder was added to the melt. This process has happened in runs 2 and 4 and probably was operative in run 1 but dark looking deposits on the honeycomb were washed off and discarded not suspecting they could be Ti deposits. The economic implication is that this is similar to the Hall process for aluminum and costs could be comparable. The obvious difference is that the titanium is solid and in the form of dendritic type sponge and not as easy to separate as liquid aluminum but still there is no reason that this can not be a continuous process of adding titanium ore to the melt in one location and pulling a continuous Ti sponge out at another location. Titanium deposition requires ~1.4 A.hr/g and from the ratio of deposit weight to time integrated current for Run #4, the electrical efficiency of the process was in the 10% or high range.

To determine if this process has been observed before, a brief search was made for a similar titanium electrochemical processes[5-7]. In no case could we find where anyone had suggested that titanium could be electrodeposited as a result of dissolving TiO_2 in a molten salt. At this point this appears to be a unique observation. Certainly, from the limited information available at this point, the deposition process may involve some chemical interaction of the titanium crucible and the TiO_2 to assist in the solution process. This will obviously need to be explored in future efforts.

Basically there are several possible transport modes of Ti or titanium precursors to cathode for the deposits to grow. In the basic case that TiO_2 is used as the cathode, electrolytic reduction of Ti is *in-situ* and there is only accompanying electron transport and oxygen liberation, Figure 15a, which is essentially the Cambridge FFC process. When TiO_2 powder (or any other precursors) is added to the system as a suspension in the molten salt bath, there are two scenarios for the transport of Ti-bearing particles to cathode, Figure 15b. They can either move to the cathode electrophoretically or as dissolved species (e.g., forming chlorinated complex ions). Regardless of how they get on the cathode, complete reduction can be expected since the extremely low pO_2 ($<10^{-49}$ atm.) environment at the cathode. In the former case, the driving force is the electric

field. And for the latter case, the driving force is both electric field and concentration gradient. In our particular case where Ti is also used as the crucible material, an enhanced Ti sponge growth may be due the abundance of the conducting Magnéli phases of titanium Ti_NO_{2N-1} through the redox reaction of Ti-TiO_2, Figure 15c. For all the possible reactions prior to reduction, a higher transport flux of Ti-bearing species to the cathode should translate to high electrolysis efficiency.

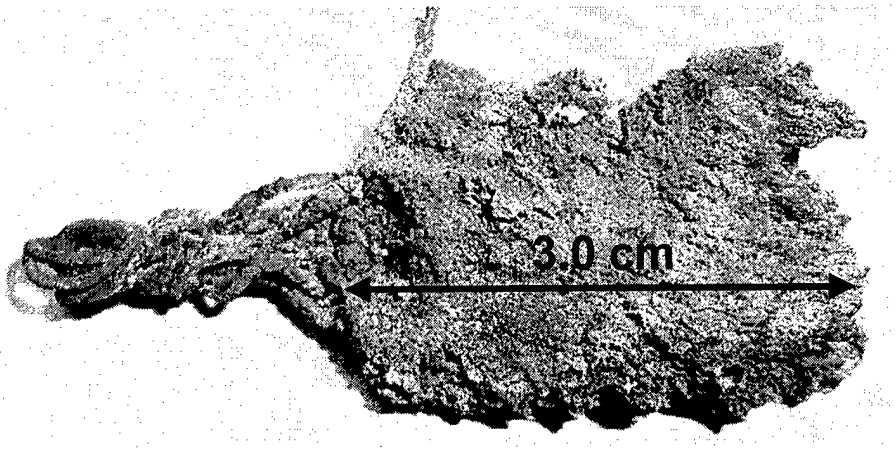


Figure 13. Electrodeposited titanium from molten $CaCl_2$ containing 2.5 % TiO_2 powder in a titanium crucible anode under 3.4 volts, 4.0A, and 6 hours. Approximately 1.1 grams of titanium were deposited.

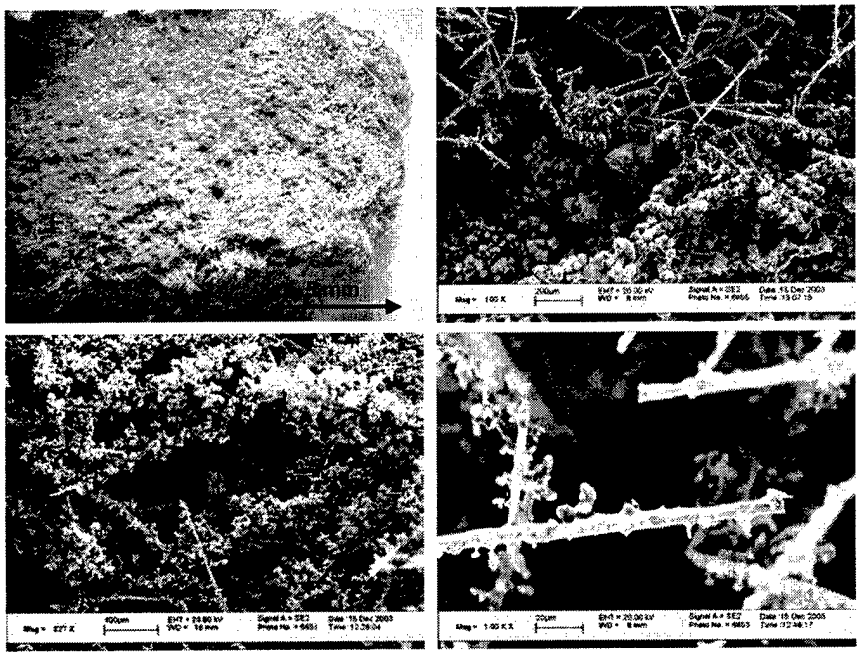
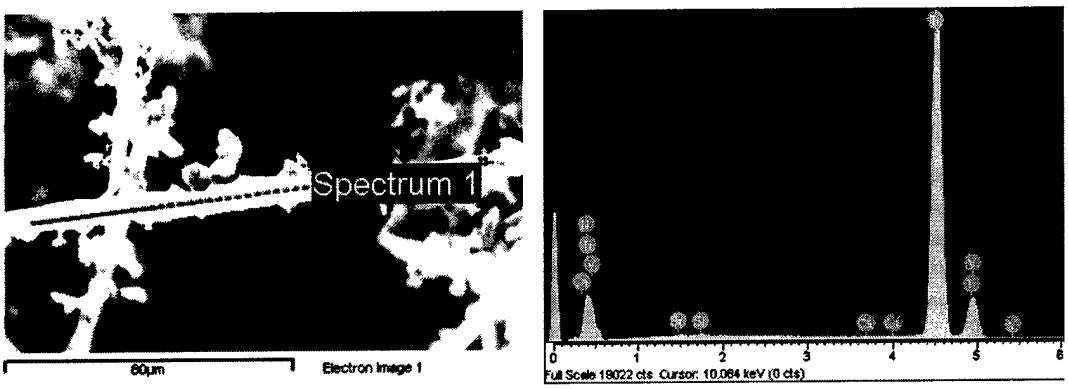
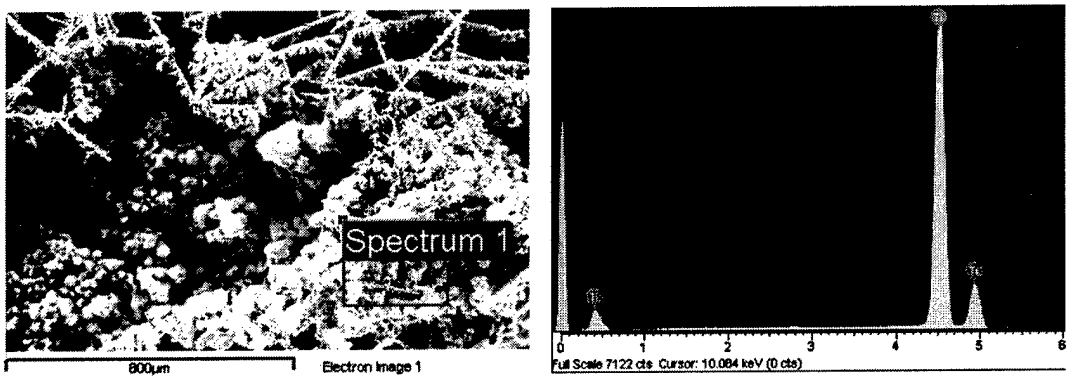


Figure 14. Morphology of titanium electrodeposits consisting of fibrous and nodular geometries.



Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
N K	1.91	0.5394	3.65	0.71	11.49
Si K	0.16	0.8492	0.19	0.05	0.30
Ca K	0.16	1.3942	0.12	0.04	0.13
Ti K	91.19	0.9902	95.04	0.72	87.39
V K	0.44	0.9747	0.46	0.14	0.40
Br L	0.33	0.6480	0.53	0.12	0.29
Totals			100.00		



Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
Ti K	109.22	1.0000	100.00	0.00	100.00
Totals			100.00		

Figure 14. EDS chemical analysis of titanium electrodeposits from Run #4 that shows the fibers and nodules to be pure titanium with no EDS detectable oxygen. The small carbon content is from carbon adhesive tape used for sample mounting.

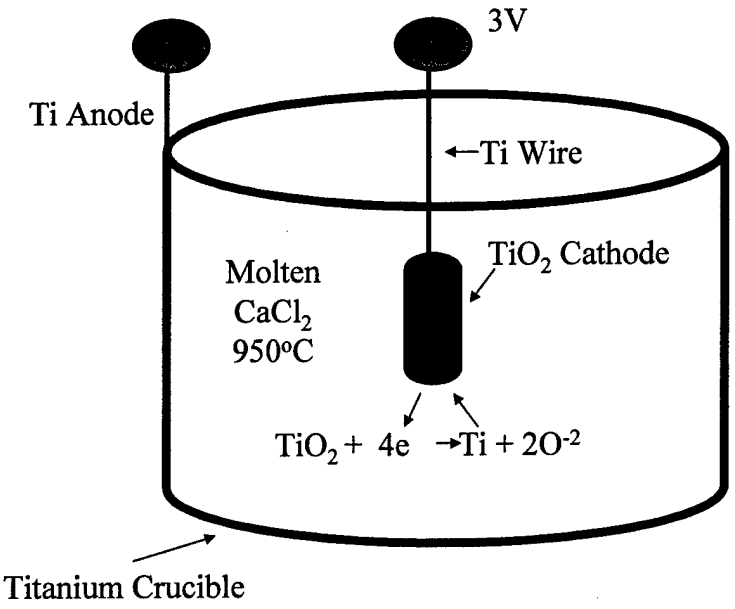


Figure 15a. Chemistry of electroreduction process.

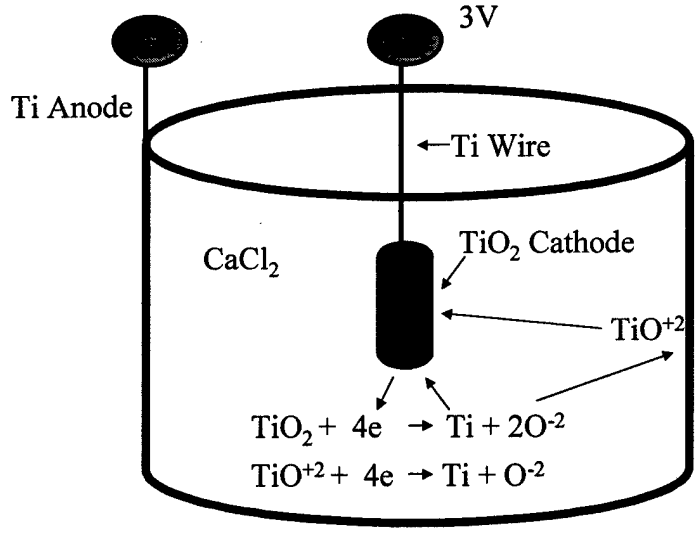


Figure 15b. Chemistry of combined electroreduction-electrodeposition process.

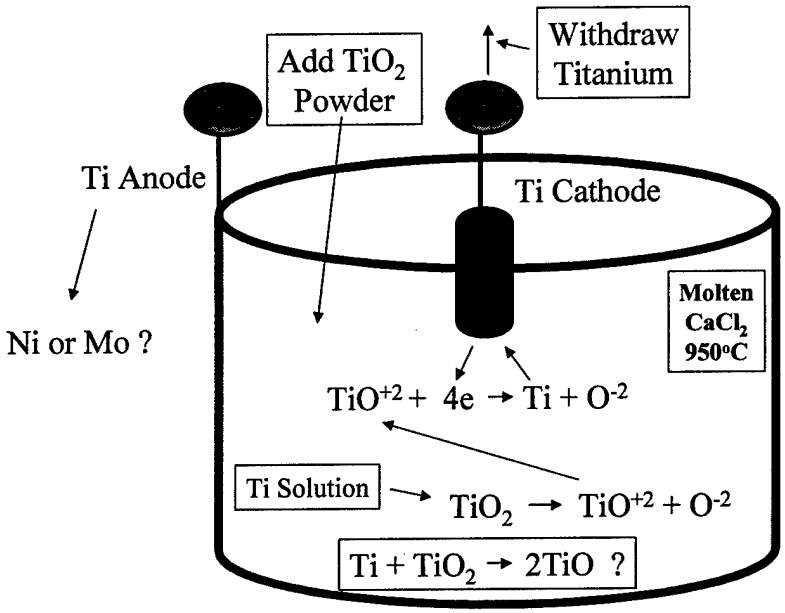


Figure 15c. Model of chemistry for electrodeposition process.

Future Efforts for Direct Electrolysis of TiO_2 for Ti Sponge Production

To make direct electrolysis of Ti from TiO_2 a viable production process, several critical quality issues must be investigated. This information would allow process economy be assessed subsequently. On quality issues, the main concern should be low oxygen content (as well as other interstitial contaminants such as N, C) and a sponge free of virtually trapped salt. When of these prerequisites are meet, the primary process parameters can then be defined and quantified. The parameters can be grouped in the following categories: construction materials (crucible, electrodes), salt chemistry, feed materials composition, and operating conditions. In the feasibility study stage, certain baseline conditions in each category were established (see above report). The objective of this short-term follow-up investigation is to optimize what has been demonstrated, i.e., Ti sponge from TiO_2 via electrolysis in fused $CaCl_2$.

To explore for higher process efficiency, the first strategy is to enhance Ti flux to cathode. Basically there are several possible transport modes for Ti or titanium precursors to the cathode to support electrodeposition as described above. When TiO_2 powder (or any other precursor) is added to the system suspending in molten salt bath, there are two scenarios for the transport of Ti-bearing particles to cathode. They can either move to the cathode electrophoretically or as dissolved species (e.g., forming chlorinated complex ions). Regardless of how they get on the cathode, complete reduction can be expected since the extremely low pO_2 ($\sim 10^{-45}$ to 10^{-49} atm) environment at the. In the formal case, the driving force is the electric field. And for the latter case, the driving force is both electric field and concentration gradient. In our particular case that Ti is also used as crucible material, an enhanced Ti sponge growth may be due the abundance of the conducting Magnéli phases of titanium Ti_NO_{2N-1}

through redox reaction of Ti-TiO_2. In all cases of the possible leading reactions prior to reduction, the higher the transport flux of Ti-bearing species to the cathode should translate to high electrolysis efficiency.

A second strategy is to identify possible reactions of TiO_2 with the fused salt that is beneficial. These reactions include partial reduction of TiO_2, solvation, chlorination, and formation of complex ions. With inert working electrodes and using certain dynamic electrochemical technique such as cyclic voltammetry, one can deduce the state or species of Ti that is most efficient in terms of electrodeposition. The feed material will then be steered in that particular direction to have quality attributes better suited for the process. These attributes include O/Ti ratio (by pre-reduction in hydrogen or pre-reacted product mixture of Ti-TiO_2) and raw material of various particle sizes.

In addition to process efficiency, the sponge or deposit morphology will be an important property to be characterized. Metals which are reduced electrolytically from melts at temperatures[8] below their melting point are known to form non-coherent solids and such deposits has a high tendency to break off and get swept into the electrolyte. Morphology will also be important for salt trapping or cleaning. Operating temperatures are known to have wide range implication on process efficiency, deposit morphology and metal purity, and of course process economy. Following literature guidance, certain eutectic mixtures of alkali chlorides not only allow lower temperature operation but also are stronger anion donors. These are salts which typically have a large cationic radii. Several systems will be tried.

Future Experimental Efforts

It is suggested that future TiO_2-Ti electrolysis experiments consist of:

1. Use anodes/crucibles of non-Ti materials (Ni, Mo, W) and cathodes with fixed surface area.

   Construction materials for crucible, anode, cathode, reference electrodes and any wetted parts will be refractory metals with low inter-diffusion with Ti and no reaction with chloride salts. To eliminate carbon activity and carbide formation, graphite parts will not be used in the system. A fixed geometry of cathode and anode will make it possible to control current density at both electrodes. This would allow control of the redox potential and transport driving force (electric field lines) at the cathode.

2. Operate with TiO_2 at various concentrations in the $CaCl_2$ bath.

   This parameter is related to the need to establish a concentration gradient in the electrolyte for the active species.

3. Produce and operate with Ti oxide feed stocks of various O/Ti ratios.

   Sub-stoichiometric (O/Ti <2.0) oxides are net charge carrier and their electrophoretic mobility should increase with decreasing O/Ti ratio. The different valence ions would also change the susceptibility of the ion to be solvated or chlorinated in the fused salt.

4. Operate with Ti oxide powder of various particle sizes.
   Particle size of powder translates to specific surface area that is known to have a strong effect on reaction kinetics.

Efforts are also required to keep TiO_2 dispersed and suspended uniformly in the bath by stirring or circulation. Other primary parameters that should be investigated are electrolysis temperature and salt bath composition. An inert reference electrode near the cathode should be used to document ionic activity of the electrolyte. Analyses of effluent gas for oxygen, carbon monoxide or water vapor will also be very useful in understanding the process in real time.

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