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ABSTRACT

The titanium market has a long history of seeking a low cost titanium production route in combination with low cost direct consolidation or PM component production routes. Metalysis has developed a new generation, electrochemical cell for producing titanium and its alloys utilising the FFC Cambridge process principles. The new plant is at a scale that will provide titanium for comprehensive development programs into the production of low cost titanium parts. The pilot plant is also at a scale that is commercially viable for the production of tantalum.

The current status of the development program will be discussed along with R&D developments in the use of the FFC Cambridge process for the production of CP-Ti and Ti-6Al-4V. This will include an overview of the new pilot plant design, future process equipment and recent results in terms of chemistry, structure and properties of powders.

Finally Metalysis’ scale up plans for titanium and its alloys will be presented.

INTRODUCTION

The FFC process is a patented technology capable of reducing a broad range of metal oxides to metals and mixtures of metal oxides to alloys in a solid state process using electrolysis (figures 10-16). In essence the technology involves immersing the oxide(s) to be reduced in a bath of electrolyte, typically molten calcium chloride at a temperature between 800°C and 1000°C and applying a cathodic potential to the oxide via a suitable immersed anode (figure 3).

The oxide is normally pressed or extruded and then sintered into a suitable preform shape (figure 6, 8, 14, 15) prior to attachment to the cathode or cathode tray and immersion in the electrolyte. When a voltage of around 3 volts is applied between the electrodes, oxygen is stripped from the metal oxide and transported through the electrolyte as an anion which discharges at the anode to form oxygen. Normally, the anode is made of carbon and therefore the oxygen reacts with the carbon to form a mixture of carbon dioxide and carbon monoxide which are evolved and the CO may be combusted to provide energy. The reduced metal is subsequently washed to remove salt and
carbides, dried and further post processed as required. A simple schematic of the process is shown in figure 1.

Whilst the process is capable of reducing this broad range of metals it is particularly suitable for difficult to reduce metals, for example, tantalum and titanium amongst others. The current incumbent technologies for the production of such metals are typically the Kroll or modified Hunter processes. These have been utilised for the last 60 years or more and are complex, multi-stage, capital intensive and expensive processes with significant environmental impact (Figure 2).

In contrast the FFC process is a much simpler, single stage process that has been calculated to have both lower environmental impact and capital investment cost. The single most striking feature of the FFC process for visitors when they are shown around the facility at Metalysis Limited is its simplicity.

However, in the early years of the discovery of the process many overoptimistic predictions for its future were made. This unrealistic approach to possible commercialisation resulted in eager anticipation followed by disappointment when the predictions were not realised. The current philosophy is to take a much more rigorous and measured approach, recognising the strengths (as well as weaknesses) of the current Kroll process (figure 2). As part of this approach Metalysis has undertaken a rigorous development program at both R&D and pilot scale to develop a new generation technology known as the O2M Process, which is not only clean and efficient but commercially viable at scale. A demonstration plant is under construction to prove the technology and is due to be commissioned in the 4th quarter of this year. The scale of plant is 10 tonnes per year for titanium and with the addition of another cell the plant will become commercially viable for the production of tantalum and hence Metalysis first production facility.

It is considered that penetration of the titanium market by the O2M process will be progressive with early adoption being for processes where there are significant cost or technical advantages. Such areas are considered to be the powder and resulting near net shape markets. As the technology and scale of manufacture grow it is expected that other areas of the titanium market will progressively open up to the technology.

CURRENT FACILITIES

Metalysis Ltd currently has a number of facilities for the FFC process and is nearing completion of the construction phase for the novel cell design which is capable of semi-continuous operation known as the O2M Cell. The existing equipment operates in a batch mode. There are 12 laboratory scale cells upon which a mixture of fundamental science and scaled down development experiments are conducted (Figure 4). The equipment has elaborate control, data logging and monitoring systems including a mass spectrometer for measuring the composition of the process off gases. Whilst these cells reduce only gram quantities of material per run they turn around quickly and operate flexibly and hence are able to generate quantities of scientific data relatively quickly.
The second design of equipment is capable of reducing multi-kilogram quantities of oxide per cycle. There are two of these cells; one is dedicated to tantalum and the other to titanium (figure 5). These cells function both to provide development data and quantities of O2M reduced product for testing, post processing and customer evaluation. However, like the smaller R&D cells they operate on a batch process basis and their design is such as to make them unsuitable for commercial production quantities. The cells have been modified to replicate O2M reduction theory (figures 6-9) and have proven the process design philosophy. The cells have provided important design and operational data that has been fundamental and underpinned the detailed engineering and construction of the new plant. The design has also been evaluated and refined by small and full scale physical modelling using alternative electrochemical systems and current pilot cells. The novel O2M Cell design is the subject of significant new intellectual property including patent applications.

The O2M product is essentially in the form of a powder which, in the case of titanium, is partially sintered together as a result of the reduction temperature being a significant proportion of its melting temperature ($T_m = 1668^\circ C$). By way of contrast, tantalum with its significantly higher melting point ($T_m = 3017^\circ C$) does not sinter significantly and remains a powder.

The chemistry achieved to date is shown in table 1. This chemistry was obtained from two batches of material produced in the pilot simulation of the O2M cell, at multi-kilogram scale with current post process best practice to remove the carbides and salt by washing and mechanical cleaning. It should be noted that there are still significant improvements that have been engineered into the demonstration plant, such as a salt management system and changes to the materials of construction that should result in product chemistry optimisation when commissioning of the new O2M plant is complete.

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Typical reduced product forms are shown in figures 7, 8, 9 and 16.

In addition to the Metalysis’ CP-Ti product the company has started a research and development program into the production of Ti-6Al-4V using FFC fundamental principles. The key to the process is in the preparation of the Ti-6Al-4V preform (figures 14 and 15). The process uses the correct quantities of TiO$_2$, Al$_2$O$_3$ and V$_2$O$_5$ (figures 10-12) which are mixed and pressed to produce a homogenous preform in its green state. The preforms (figures 13-15) are then sintered to produce the Ti-6Al-4V feedstock.
Ti-6Al-4V has been successfully reduced at both R&D and pilot scale using O2M principles (figure 16) and has produced a homogeneous alloy. The development program is due to continue to optimise the process parameters and product required.

O2M PROCESS PLANT

Metalysis has developed and designed a new generation of semi continuous plant using the O2M process, the plant layout can be seen in figure 17. The plant construction is nearing completion and will move into the commissioning phase in the 4th quarter of this year with titanium anticipated to be produce in the 1st quarter of 2011, prior to the plant becoming a production facility for tantalum. The new plant and cell design incorporates a hot salt management system to maintain optimum temperature and chemistry throughout the reduction process (figures 20 and 21). This technology removes the need for heat up and cool down cycles and therefore dramatically improves the energy and heat balance efficiencies of the process, as well as removing contaminatees from the system and hence the product. The cell (figures 18 and 19) uses cathode trays and anodes. The cathode trays contain the product during electrolysis and after electrolysis the product is removed for cleaning.

The demonstration plant is not at a scale that would be commercially viable for titanium the design however is capable of being scaled up to larger units for commercial production and is modular in design so that additional reduction cells can be readily added as demand for the product increases.

There are a number of options for the conversion of this product into useful components and these are currently under investigation. A full development program will be conducted using the O2M product made in 2011.

One option is to consolidate the product of the O2M process directly to, for example, sheet by roll consolidation. The other possible consolidation routes are via conventional powder processes. Powders can be produced from O2M titanium directly by grinding, by hydriding-grinding-dehydriding and by fusion and gas atomisation. Figures 23, 24 and 22 respectively show the structures of O2M Titanium processed in these ways.

By adopting processing routes using near net shape production, either using powder or direct consolidation of O2M reduced titanium it is considered that significant cost benefits may be achieved compared to conventional Kroll sponge-ingot metallurgy-mill product type routes. In addition the anticipated much lower capital cost and modular nature of an O2M titanium facility compared to a Kroll plant adds further benefits.

CONCLUSIONS

1. It is considered that the early adoption of the O2M process will be for near net shape manufacture, in particular powder metallurgy products.
2. Titanium dioxide can be successfully reduced using O2M principles.
3. O2M titanium can be readily converted to powder by a variety of techniques, the choice of which is dependent on the end application.
4. The process is considered to be able to provide a low capital and production through cost alternative to the Kroll process for powder route products. It also has the benefit of being scalable to meet demand.
5. Ti-6Al-4V can be successfully produced using the O2M technology.

FUTURE WORK

The following future work is planned for the FFC process:

1. O2M commissioning and optimisation of 100T/Y Module.
2. Scale up and demonstration of O2M 250 T/Y Module.
3. End process route definition including O2M consolidation and mechanical properties.
4. Scale the development of Ti alloys, in particular Ti-6Al-4V by direct reduction in the O2M cell.
5. Commercialisation by engagement with customers and titanium related industry.
Figure 1: Schematic of the FFC Cambridge Process

Figure 2: Schematic of the Kroll Process – indicative of its complexity
Figure 3: Schematic of a Research and Development FFC reduction cell

Figure 4: 12 Research and Development scale FFC reduction facilities
Figure 5: Kilogram scale FFC reduction facility for titanium.

Figure 6: O2M experimental reduction tray containing titanium honeycomb preforms.
Figure 7: O2M experimental reduction tray containing reduced titanium honeycomb.

Figure 8: Potential feedstock for O2M reduction cell
Figure 8: Potential O2M product form prior to cleaning.

Figure 9: Potential O2M product form after cleaning.
Figure 10: Structure of TiO₂ preform powder at 0.25μm.

Figure 11: Structure of V₂O₃ preform powder at 0.50μm.
Figure 12: Structure of Al₂O₃ preform powder at 0.50μm.

Figure 13: SEM of Ti 6-4 sintered preform.
Figure 14: Photograph of Ti 6-4 preform.

Figure 15: Experimental O2M reduction of Ti and Ti 6-4.
Figure 16: Reduced experimental O2M Ti 6-4.

Figure 17: O2M Plant layout.
Figure 18: Technical drawing of O2M reactor vessel.

Figure 19: Photograph O2M reactor vessel during installation.
Figure 20: Technical drawing of O2M salt management vessel.

Figure 21: Photograph O2M reactor vessel during installation.
Figure 22: Structure of FFC titanium powder produced by fusion and gas atomisation of the reduced product.

Figure 23: Structure of FFC titanium powder produced by direct grinding of the reduced product.
Figure 24: SEM of FFC hydride-grind-dehydride powder.
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Development of a New Generation Pilot Plant for Production of Low Cost Titanium and Titanium Powders Utilising FFC Cambridge Process Principles

Authors: Mark Bertolini, Lucy England, Lee Shaw, Kartik Rao, Peter Dudley, Allen Wright and Melchiorre Conti
Presentation Content

- Introduction
  - Brief description of the process
  - Current approach to commercialisation

- Current Facilities
  - Description of the current facilities at Metalysis Ltd.
  - Development of CP Titanium
  - Chemistry and structure of FFC titanium
  - Development of Ti 6-4

- O2M Production Plant
  - Novel Plant Design

- Future Work
Introduction
The FFC Process
Introduction
Incumbent Ti Production Process

- Most Ti is made by the Kroll process
  - 60 Years old
  - Produces a sponge product requiring melting before use
  - High capital cost - Highly capitalised
  - High environmental impact
  - Highly developed and optimised process
  - Complex and multi-stage
Introduction

FFC Advantages to Kroll

- Relatively simple process
- Lower expected capital cost
- Lower expected environmental impact
- Higher grade direct product
- However, not a mature technology
Current Facilities
R&D and Development

- 12 Reduction Cells used for:
  - Fundamental Investigations
  - Proof of principle
  - Small scale reductions

- 2 Development cells – Titanium (& Tantalum)
  - Producing multi-kilogram quantities of Ti
  - Experiments for pre-production scale plant
Current Facility
CP Development

- Scale up design
- Pilot experimental testing
- Design validation
Current Facilities
CP Direct Product Forms
Current Facilities
FFC CP Ti Product

- Chemistry of product direct from development cell
- Produced at multi-kilogram scale
- Product not post processed other than light cleaning
- Not an optimised product

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Current Facilities
Ti 6-4 Development

- Oxide powders.
  - TiO$_2$ 0.25µm
  - V$_2$O$_3$ ~ 0.500µm
  - Al$_2$O$_3$ ~ 0.10 µm

- SEM of Ti 6-4 sintered preform and photograph
Current Facilities
Ti 6-4 O2M Reduction

- Reduced 600g of alloyed TiO$_2$, Al$_2$O$_3$ and V$_2$O$_5$
- Material reduced along side CP Titanium precursor
O2M Process Plant
Novel Plant Design

- Novel design of cell developed
  - Eliminates current process limitations
  - Demonstration design for titanium scalable to larger size for commercialisation
  - Commercially viable throughput for Tantalum
  - Semi-continuous and modular so the design can be expanded as demand increases
- Under final construction
- Commissioning Q4 2010
O2M Process Plant
Plant Layout
O2M Process Plant
Electrolytic Reactor Vessel
O2M Process Plant
Salt Melting and Management Vessel
O2M Process Plant

Products

FFC Ti Product

- Beads for direct consolidation
- Wire/sheet
- Gas Atomisation
- Light Milling
- Hydride-dehydride

Powder Feedstock
Future Work

- O2M commissioning and optimisation of 100T/Y Module.
- Scale up and demonstration of O2M 250 T/Y Module.
- End process route definition including O2M consolidation and mechanical properties.
- Scale the development of Ti alloys, in particular Ti-6Al-4V by direct reduction in the O2M cell.
- Commercialisation by engagement with customers and titanium related industry.
Time to think about a Change?

Conventional Routes

FFC Process?
Thank you for your attention.