Development status of the CSIR-Ti Process

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Abstract. South Africa is endowed with significant titanium-bearing reserves, which are concentrated to produce slag and exported as a low-value commodity, meeting about 20% of the global demand for the production of titanium dioxide pigment. Compared with the well-established titanium pigment industry, the much smaller titanium metals industry holds significant growth potential. Titanium metal is however notoriously difficult to refine from its abundant ores, and machining titanium is known to be challenging. Titanium usage is thus limited to niche applications in aerospace, defence, medical and chemical industries. Titanium powder produced at low cost promises a paradigm shift in titanium market size. Titanium powder has not been produced directly at commercial scale from the precursor for both pigment and metal production, titanium tetrachloride ($TiCl_4$). The Titanium Centre of Competence (TiCOC) at the Council for Scientific and Industrial Research (CSIR) has as its aim the establishment of a titanium metals industry in South Africa. To this end research and development work is being conducted towards the commercialisation of the CSIR-Ti process, a potentially cost-effective method for titanium metal production. This article discusses the history of the CSIR-Ti process for titanium metal powder production, challenges addressed, current development status and the unique products achieved.

1. Introduction

The research and development discussed herein was completed under the auspices of the Titanium Centre of Competence (TiCOC), based at the Council for Scientific and Industrial Research (CSIR) in Pretoria, South Africa. The Titanium Centre of Competence is funded by the Advanced Metals Initiative (AMI) of the Department of Science and Technology (DST). Both the AMI and TiCOC are driving the establishment of a South African titanium metals industry.

Mined titanium mineral is a mixture of rutile (TiO_2), ilmenite ($FeO.TiO_2$) and leucoxene (weathered ilmenite with a lower iron content than ilmenite). Significant processing of the minerals is required to produce the two main commodities, titanium dioxide pigment and titanium metal. Titanium is the ninth most abundant element, comprising 0.6% of the Earth's crust. It is also the fourth most abundant structural material after aluminium (8.1%), iron (5.1%) and magnesium (2.1%) [1]. Recent data from the U.S. Geological Survey (2015) indicate that ilmenite accounts for about 92% of the world's consumption of titanium minerals. World resources of anatase, ilmenite and rutile total more than 2 billion tons. Titanium ore reserves are widely distributed, with the major rutile and ilmenite deposits located in China, Australia, India and South Africa. Currently, South Africa is a world-class supplier of titanium raw materials, but a minor supplier in the added-value pigment industry. South Africa is the second-largest single producer of titanium-bearing minerals in the world, but despite supplying nearly 20% of the raw materials, the country only realises about 5% of the approximately US$9 billion dollar pigment industry [2].

South Africa presently has no titanium metals manufacturing industry and limited capacity in titanium fabrication, for which all the material is imported. The market value of titanium increases dramatically as it is beneficiated. Ilmenite ore fetches about US$0.3/kg, while TiO_2 is worth some US$1/kg. Next up the scale is $TiCl_4$, which can be bought for around US$3.00/kg. Once titanium is in metal form, its price is significantly higher – titanium sponge fetches around US$12.00/kg, titanium ingots cost on average US$22.00/kg and mill product upwards of $40/kg [3]. Titanium and its alloys have been in industrial use for over 50 years. However, its applications have been restricted primarily to the aerospace industry where it is prized for its high strength and light weight, and the chemical industry, where its use is driven by its resistance to corrosion [4].

The high price of titanium metal combined with the high waste-to-final-part ratio, in aerospace termed the "buy-to-fly ratio" which is on average 8:1 by weight, constrains its use even in the aerospace sector [2,5].

Titanium's properties make it highly suitable for use in many applications, but widespread use is precluded by the relative cost when compared with competing materials [6]. Titanium is at present known to be expensive to refine, process and fabricate [1]. On the basis of its processing cost per cm^3, titanium is five times more expensive than aluminium to refine, and more than ten times as expensive as aluminium to form into ingots and to fabricate into finished products [7]. Kraft indicated that this discrepancy in pricing and production volume is primarily due to the high reactivity of titanium.

Titanium has a great affinity for oxygen, nitrogen, carbon and hydrogen. The Kroll process and subsequent purification operations used for the majority of titanium production is energy, material and capital intensive. The use of titanium is furthermore hindered by long lead times of up to 12–18 months for plate, and often only aerospace companies are willing to enter into long-term offtake contracts stemming from this excessive lead time. High costs sensitivity is illustrated by Katrak, Agarwal and Loreth [8] who proposed that titanium demand should follow a '1:10:100 rule', where a cost reduction of US$1/lbs. in titanium metal sponge, followed by a reduction in mill production cost of 10% would lead to a 100% increase in the demand for titanium in non-aerospace applications. The development ideal is then the establishment of South Africa as a significant player in the higher value-addition industries of titanium metal production and manufacturing.

2. Titanium Powder

In the field of titanium, the work towards cost reduction and material savings of final products focuses on powder metallurgy, which is defined as the production, processing and consolidation of fine particles to make solid metal products. Much of the overall cost of titanium in the final application lies in machining to final configuration. Waste ratios are often very high for aerospace applications where the mill product may cost US$10/kg, but comparing material losses to the final weight of the part, the cost can be over US$500/kg [5]. According to Barnes, Peter and Blue [9] aluminium was considered to be as precious as platinum until the Bayer Process brought prices down from US$1200/kg to US$0.60/kg. Peter and Yamamoto [5] express a similar hope for titanium when they state: "The production of low cost titanium products from alternative titanium powders/sponge has the potential to enable a paradigm shift in the production and application of titanium, similar to the transformational effect of the Hall-Héroult process which enabled widespread industrial use of aluminium".

At present, powder metallurgy is based on powder from standard industrial titanium sponge. However, Sachdev, Kulkarni, Fang, Yang and Girshov [10] foresee the industrialisation of a process capable of producing titanium powder directly by a novel route that promises high-grade titanium powder at projections of US$8/kg. This cost reduction is expected to be achieved primarily through a melt-less route and smaller, low capital costs and more efficient plants. Titanium powder is prohibitively costly for most applications as it is commercially produced by crushing sponge via the extensive hydride/dehydride (HDH) process shown in Figure 1, or via melting ingots e.g. via the plasma rotating anode process.

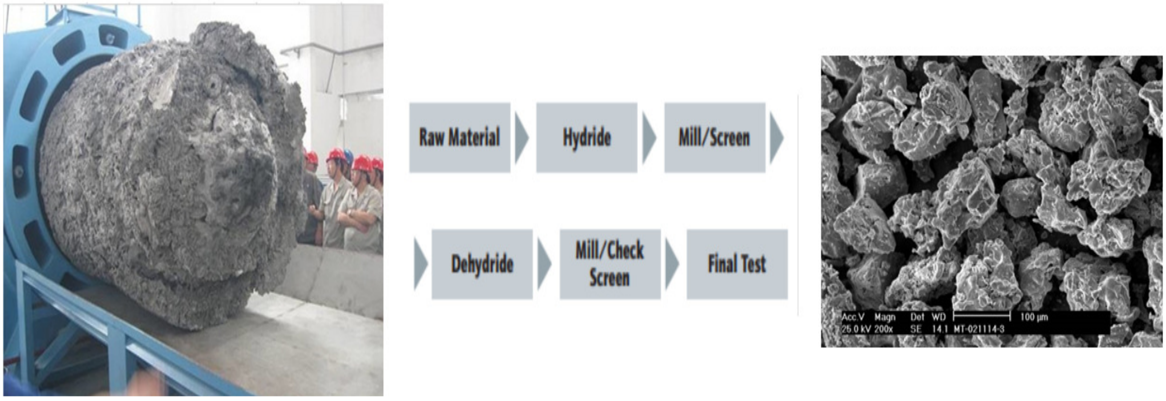


Figure 1. Steps to convert Titanium Sponge (LHS) to HDH powder.

Applications that are set to be unlocked by the availability of low-cost titanium are: automotive, heat exchangers, chemical processing, nuclear industry, condenser tubes, desalination, offshore petroleum, paper and pulp processing, additional defence applications, naval applications, liquid natural gas processing, biomedical supplies, sporting equipment and construction [5,10,11].

3. Titanium Centre of Competence (TiCOC)

A Centre of Competence (COC) is defined as a collaborative technology development consortium comprising science councils, academic institutions and industry [12]. It is guided by national priorities and relies on harnessing the resources, capabilities and synergies of all consortium partners, with clear research objectives in pursuit of products and services with commercial or public-good potential in response to market opportunity and socioeconomic challenges [12].

The development of a complete titanium value chain (production of titanium pigment, metal and downstream fabrication) has been identified as a key growth area for South Africa. This is further based on increasing world-wide demand, particularly with respect to titanium metal powder [13]. The CSIR is managing the South African Titanium Centre of Competence (TiCOC) which has as its objective the establishment of both an upstream titanium metal production industry and a downstream titanium fabrication industry [13,14]. A major goal of the TiCOC is the development and commercialisation of a novel, cost-effective and internationally competitive process for producing primary titanium metal powder in South Africa [2]. A process meeting AMI/TiCOC requirements was developed in the period 2010-12. The so-called CSIR-Ti powder process was operated initially in batch and semi-batch configuration, and a “continuous” 2kg/h pilot plant was operated in 2014-17.

4. Titanium Powder

The potential impact of a new, low-cost titanium-based industry in South Africa has been reported as follows [15]:

a) A titanium metal powder industry is estimated to have the potential to generate R3 billion to R5 billion a year, which could increase to between R10 billion and R30 billion a year once a downstream industry has been established.

b) The job creation potential of a local titanium industry includes 450 workers, engineers and technologists (on the metal production side), with about 2 000 workers, engineers and technicians in downstream component manufacturing.

c) There would also be a spillover of technologies and skills to other industries and enterprise creation opportunities in terms of inputs into the titanium value chain through the provision of goods and services. This translates into job opportunities and economic growth owing to the new businesses that will be created – all based on the beneficiation of titanium, the local production of titanium powder and metal, and the local production of high-strength components for application in advanced industries such as the aerospace, automotive and medical industries.

5. Development status of the CSIR-Ti Process

5.1. Intellectual Property and Technology Package

The Intellectual Property (IP) pertaining to the CSIR-Ti process comprises of a substantial body of know-how and trade secrets, but IP has also been secured internationally via three patents, the initial two patents having been granted at least 18 times across various territories. These patents cover the following aspects of the proprietary process:

a) Titanium powder production process: U.S. Patent No. 8,790,441 (2011)
b) Process for the production of crystalline titanium powder: WO 2013185153 A3 (2013)
c) Electroless titanium process: UK Patent office 1716024.3 (application submitted 2017).

The CSIR-Ti process (Figure 2) utilises alkali and alkali-earth metals as reductants to produce titanium metal powder from the same commodity that is used to produce white paint pigment, titanium tetrachloride ($TiCl_4$). The by-product chloride salt is separated from the metal powder and electrolysed to recover both chlorine gas for production of $TiCl_4$, and the reductant alkali/alkali earth metal. Key aspects of process (specifically related to equipment) have been filed with the CSIR Technology Development Office as technology demonstrators. Development of technology packages relating to both 500 and 10 000 tonne per annum scale plant plants has been partially completed.

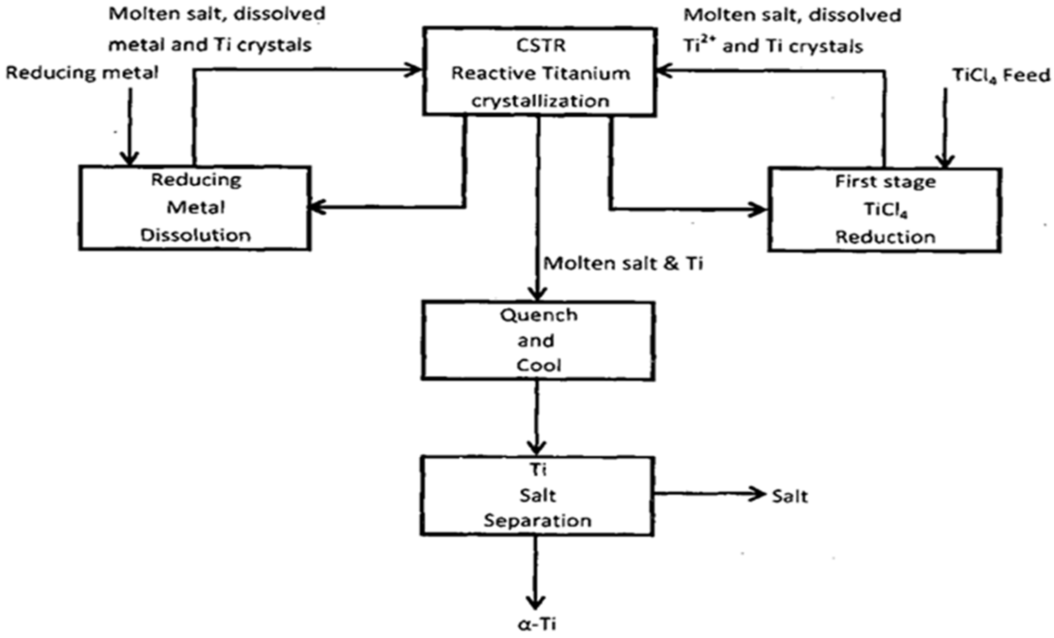


Figure 2. Block flow diagram of CSIR-Ti process.

5.2. Process Development

The process was launched as a pilot plant (Figure 3) adopting a Continuous Stirred Tank Reactor (CSTR) configuration as per original patents. The pilot plant was commissioned early in 2014 and operated over several campaigns until the end of 2017. The aggressive nature of the chemicals and elevated temperatures demanded by the process has provided a number of challenges [16,17]. These challenges were to a large extent overcome via sequential process developments. Numerous improvements were made to a range of systems such as electrical heating, agitation, molten salt-titanium powder slurry pumping, process control and instrumentation [17,18].

Figure 3. CSIR-Ti Pilot Plant (reduction section on right hand side).

The pilot plant met annual production targets, despite significant technical challenges which required the development of prototype equipment and novel solutions [16,17,18]. Given that several years of development effort has been expended on the process, an independent technical review of the development status was conducted in early 2018. The review panel, consisting of leading experts from industry saw merit in continuing development of the CSIR-Ti process, in both batch and continuous formats. A key outcome of the technical review was to further demonstrate the CSIR Ti-process in a scaled-up batch format as an accelerated means towards commercialization of the technology. It was also the opinion of the review panel that a batch design would attract potential investors more readily given the alignment with industry norm, given the inherent simplicity of batch processes.

Work on the continuous process is being taken forward in a new generation of reactors known as the TITAN High Flow Reactor (HFR), which targets higher production rates using a smaller reaction unit. The new reactor configuration also intends to achieve significantly better process control of parameters. Early stage powder samples have already been produced and analysed from the current TITAN V2.0 HFR.

The CSIR-Ti Pilot Plant has stimulated and intensified multi-disciplinary and inter-disciplinary research at the CSIR Pretoria campus. These disciplines include: Computer Flow Simulations and Process Modelling, Process Control and Electrical Engineering, Metallurgical Engineering and Corrosion, Mechanical and Thermodynamic Engineering and Design, Chemical and Process Engineering; and various support disciplines, such as Safety, Environmental, Risk and Project Management. The capacity developed at TiCOC can be accessed by research organisations and academic institutions by contacting the CSIR.

6. Challenges Addressed

Lower cost processes for the production of titanium metal have been a research and development goal for several decades [1,4,5,7,19], however the high temperatures and reactivity of the feed chemicals and titanium product has posed significant challenges. By developing solutions to these challenges, the CSIR has made significant progress in the demonstration of a process capable of continuously producing titanium metals powder [16,17,18]. One example is the CSIR developed molten salt slurry pump in conjunction with Lakeside Equipment, suppliers of Slurry-Busta® pumps [18]. These pumps, shown in Figure 4, were prototypes developed specifically for the high temperatures and inert gas atmosphere conditions of the CSIR-Ti process, thus requiring novel water cooled sealing systems on the rotating shafts.

The pumps operated with a single vane on the impeller as per manufacturer standard. It was found that at slurry densities approaching steady-state conditions, defined as when salt by-product and titanium powder are being produced in stoichiometric ratio, metal powder accumulation occurred behind the back plate of the impeller. Ti powder would become compacted behind the back plate of the single vane impeller of the centrifugal pump, shown in Figure 5, which decreased performance and could lead to stoppages through seizing of the vanes. A double vane impeller was then proposed for the original CSTR system. Nonetheless, the TITAN HFR utilises a design which may eliminate the need for vertical cantilever pumps.

Figure 4. Vertical cantilever molten salt slurry pumps (centre).

Figure 5. Single vane pump impeller with Ti metal powder visible behind the back plate.

7. Product morphology

Due to a range of chemical and electro-chemical reactions possible in the CSIR-Ti continuous system, improvements to process control have allowed increased opportunity to influence product morphology. A significant breakthrough was made in the development of electrochemical sensors capable of real time monitoring of reagent concentrations and activity in the molten salt medium.

Through adjustment of reagent concentrations and process parameters, it is possible to preferentially generate certain product morphologies, ranging from amorphous to a variety of crystalline structures, or a mix of these morphologies. Typical morphologies achieved in batch and continuous operations of the CSIR-Ti process up to end 2017 are shown in Figure 6, descriptors of the microstructures were generated by CSIR staff.

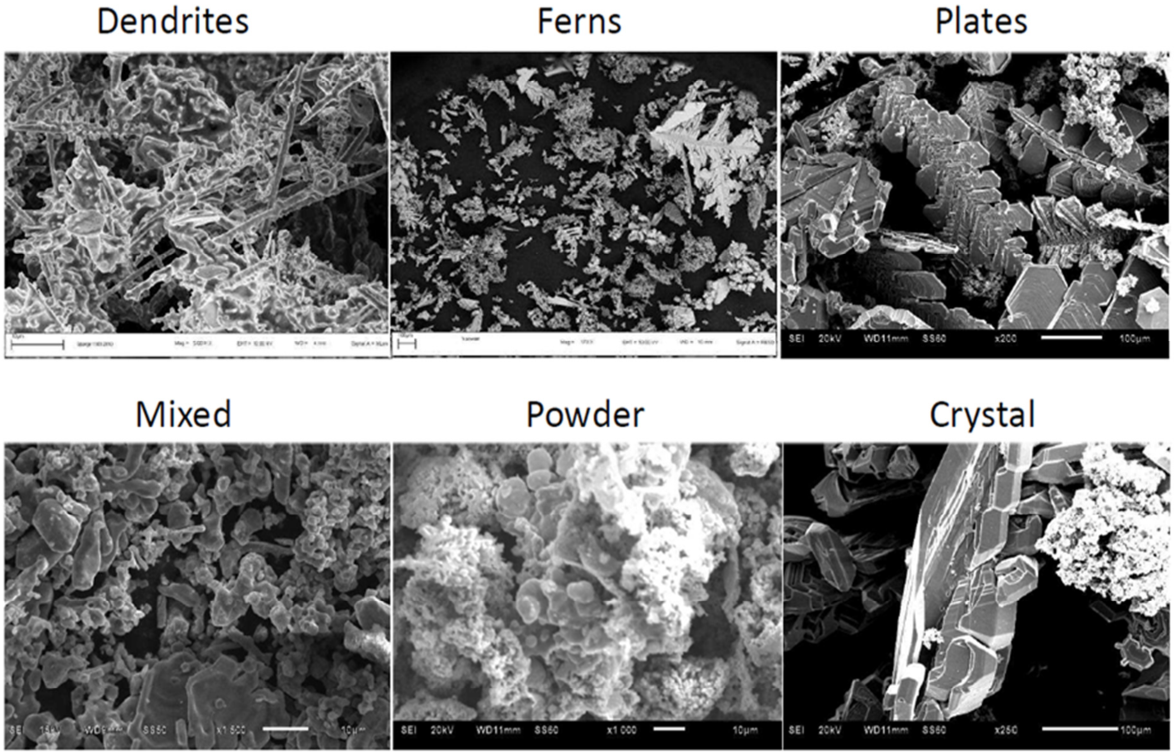
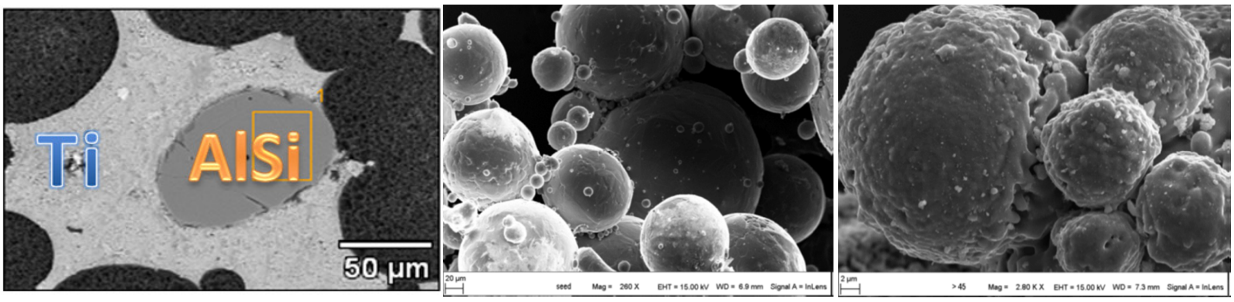


Figure 6. Microstructures of crystalline and amorphous CSIR-Ti powders produced to date.

8. Electroless Plating of Titanium

It was found that the process could be operated in a manner to grow, through contactless electrochemical plating, known in industry as electroless plating, a layer of titanium metal on particles present in the system. This was discovered when a particle of an impurity, most likely originally a particle of sand, was found to be coated with titanium metal, as shown in Figure 7a.



(a) (b) (c)

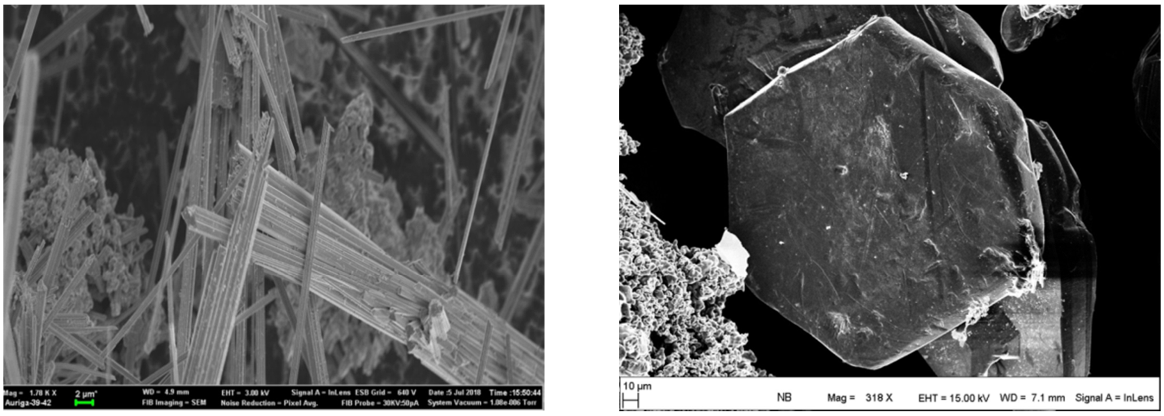
Figure 7. Micrographs showing electroless plating of titanium metal on particles.

The ability of the process to grow particles was further tested by feeding commercially purchased plasma spheriodised titanium powder as seed material to the process, and a scanning electron microscope (SEM) image of the seed material is shown in Figure 7b. The spherical titanium seed particles were circulated in the CSIR-Ti process, retrieved and again viewed by SEM. A new layer of titanium metal was found to have grown on the surfaces of the seed particles, shown in Figure 7c. This discovery implies the possibility of plating titanium metal on a variety of conductive and semi-conductive seed particles.

9. Titanium Crystal Production

Titanium metal sponge contains entrapped chloride salt which can cause micro and macro porosity if utilised directly, hence the industry requirement of purification through vacuum arc remelting or electron beam melting [20]. The CSIR-Ti process has shown potential for controlled growth of titanium crystals with little or no entrapped chloride. The new reactor configuration demonstrated in the TITAN HFR has delivered new product morphologies, and through altering process parameters titanium crystals were produced as fibres/rods, shown in Figure 8a, or as larger crystals with a hexagonal crystal structure, shown in Figure 8b.

Titanium's unique characteristics, such as the discovery of osseointegration of titanium implants which opened up a market for medical applications, have driven the creation and rapid growth of new niche markets [21]. It is the hope that electroless plating of titanium may similarly find new applications.



(a) (b)

Figure 8. (a). Crystalline titanium metal fibres; (b) Hexagonal titanium crystal.

10. Conclusions

TiCOC was established that South Africa, already in possession of a large titanium minerals resource base and established associated mining industry, may stand to benefit from expanding the titanium value chain. The size of the global titanium metals market is constricted by the relatively high cost of titanium metal production and downstream manufacturing, and titanium is then locked into a paradigm of being selected primarily for high-end applications such as aerospace or medical applications.

Research and development efforts at the CSIR aim to impact the titanium metals market by lowering metal production costs via a novel primary production process, including the utilisation of powder metallurgical processes to lower manufacturing costs of components.

The article presents non-confidential new knowledge generated in the development of the novel CSIR titanium production process, and learning gained from operation of the CSIR Ti-Powder Pilot Plant over a 3 year period (2014-2017). In this period numerous technical challenges were overcome and confidence in the process has grown significantly. The continuous CSIR-Ti process has shown the ability to produce promising new product morphologies, accelerated by the development of increasingly sensitive process control systems and a new reactor configuration. An exciting development was the demonstration of growing layers of titanium metal on seed material introduced to the CSIR-Ti continuous process, a discovery which has been added to the growing patent portfolio.

Acknowledgements

The authors would like to acknowledge the Department of Science and Technology for their continued support in the establishment of the TiCOC in South Africa. The authors also acknowledge staff at CSIR and NMISA who assisted in producing the micrographs, often at short notice, in order to help characterise products and guide the research.

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