# SOUTH AFRICAN TITANIUM: Techno-Economic Evaluation of Alternatives to the Kroll Process

by

Willem van Tonder

*Thesis presented in partial fulfillment of the requirements for the degree of*

MASTER OF SCIENCE IN ENGINEERING (MANAGEMENT)

*at*
*Stellenbosch University*

SUPERVISORS: Dimitri Dimitrov and Konrad von Leipzig

DEPARTMENT OF INDUSTRIAL ENGINEERING

March 2010

# DECLARATION

By submitting this dissertation electronically, I declare that the entirety of the work contained therin is my own, original work, that I am the owner of the copyright thereof (unless to the extent explicitly otherwise stated) and that I have not previously in its entirety or in part submitted it for obtaining any qualification.

DATE: March 2010

# ABSTRACT

Titanium has been identified by the South African government as a mineral resource with the potential to serve as a strategic economic driver for the country if a local processing and production industry could be successfully established. According to the US Geological Survey, conducted in January 2009, South Africa has approximately 14% of the world's reserves in ilmenite and rutile, the two most important titanium-containing minerals, but no metal producing abilities. The only role players, Exxaro and Richards Bay Minerals, have smelting operations and produce an enriched titania slag, but all the slag is exported.

The processing steps between titanium-containing minerals and the metal represent a significant portion of the total production costs and this study is chiefly concerned with recommending a more cost-effective alternative for these steps. The existing industrial process is archaic, cost and energy intensive, batch operated with unfavourable economics. A large number of internationally research initiatives are actively trying to address the problem of high production costs by searching for and developing alternative, more cost-effective, processes.

It was the purpose of this study to provide the decision making authorities with a ranking and evaluation of these alternatives to produce titanium metal. A 2-Phase Filtering System, based on both qualitative and quantitative techniques, was designed to assess, evaluate and formulate a final ranking. This evaluation was followed by a detailed sensitivity analysis of both local and global parameters.

A total of 26 process alternatives were selected to be evaluated in this techno-economic evaluation. The complete ranking is given in Table 8.8, and the four leading process alternatives, based on this evaluation and the findings of the sensitivity analysis, are as follows:

1. **CardQIT:** The Canadian affiliate of Rio Tinto, QIT, developed a high-temperature titanium extraction process based on an electrolysis reaction, where molten titania slag is the cathode.
2. **ArmITP:** The Armstrong process is a continuous process that produces titanium in a very similar fashion as with the Hunter process, by the reduction of $TiCl_4$ with

sodium. $TiCl_4$ vapour is injected into a stream of molten sodium to form titanium powder as the reaction product.

3. **Kroll:** This process was developed in the 1950s and the reduction step remains very much similar to the original process used by the USBM (United States Bureau of Mines). Two criteria played a big part in the unexpected high ranking of the Kroll process, and that were academic coverage, with almost 60 years of research, and the commercial readiness of an industrial process.
4. **FFC:** Solid pre-forms are pressed and sintered from pigment grade $TiO_2$, to be directly electrochemically reduced to metallic titanium in a molten electrolyte of $CaCl_2$.

For future work, it is recommended that an additional filtering stage, a detailed profitability analysis, be added to the decision model. The top 4 alternatives, as mentioned above, should be used to estimate the cost-reduction potential as well as the capital investment and production costs based on process, industrial and economic engineering fundamentals.

KEYWORDS: Titanium, South Africa, Kroll, Alternatives, Techno-Economic, Evaluation.

# OPSOMMING

Titaan is deur die Suid Afrikaanse regering geidentifiseer as 'n mineraalhulpbron met die potensiaal om te dien as 'n strategiese ekonomiese drywer, indien 'n plaaslike verwerking- en verwaardingsbedryf suksesvol op die been gebring kan word. Volgens die US Geological Survey, wat in Januarie 2009 gedoen is, het Suid Afrika ongeveer 14% van die wêreld se reserwes in ilmeniet en rutiel, die twee belangrikste titaanhoudende minerale. Suid Afrika het egter geen metaal-vervaardigingsaanlegte nie. Die enigste twee rolspelers, Exxaro en Richards Bay Minerals, het smelteraanlegte en vervaardig 'n verrykte titaandioksiedkonsentraat, wat alles uitgevoer word.

Die waardetoevoegingsaktiwiteite tussen die titaanhoudende minerale en die metaal verteenwoordig ‘n groot gedeelte van die produksiekoste van titaanmetaal en hierdie studie is hoofsaaklik daarmee gemoeid om ‘n meer koste-effektiewe aanbeveling te maak, m.b.t. dié stappe. Die bestaande bedryfsproses is argaïes, koste- en energieintensief, en is ontwerp as ‘n lot proses met ongunstige ekonomiese eienskappe. 'n Groot aantal internasionale navorsingsinstansies is aktief besig om oplossings te soek vir die probleem van hoë verwerking- en vervaardigingkostes, deur alternatiewe opsies te ondersoek en te ontwikkel.

Die doel van hierdie studie was om vir die besluitnemingsgesag 'n rangorde en vergelyking van die alternatiewe opsies om titaniummetaal te vervaardig, te gee. 'n Tweeledige Filter Stelsel, gebaseer op beide kwalitatiewe- en kwantitatiewe tegnieke, is ontwerp om die rangorde te vorm, te bereken en te formuleer. 'n Sensitiwiteitsanalise is gedoen om die besluitnemingsparameters se invloed op die finale rangorde en uitslag te toets.

'n Totaal van 26 prosesse is geidentifiseer en gekies om aan hierdie tegno-ekonomiese evaluasie, te onderwerp. Die volledige rangorde word in Table 8.8 getoon, en die vier leidende prosesalternatiewe, gebaseer op die uitkomste van dié evaluering en die bevindinge van die sensitiwiteitsanaliese, is as volg:

1. **CardQIT:** Die Kanadese filiaal van Rio Tinto, QIT, het ‘n hoë-temperatuur titaan ontginningsproses ontwikkel, gebaseer op ‘n elektrolitiese reaksie, waarin gesmelte titaandioksiedkonsentraat die katode vorm.

2. **ArmITP:** Die Armstrong proses is ‘n kontinue opsie wat titaan produseer op ‘n baie soortgelyke wyse as die Hunter proses, deur die reduksie van $TiCl_4$ met natrium, Na. $TiCl_4$ damp word in ‘n gesmelte stroom natrium ingespuit om titaanmetaalpoeier te vorm as die reaksie produk.
3. **Kroll:** Die proses is ontwikkel in die 1950s en die reduksie stap wat vandag gebruik word is steeds soortgelyk soos die oorspronklike proses, aan gebruik deur die USBM. Veral twee besluitnemingskriteria het ‘n belangrike rol gespeel om tot die onverwagte hoë plasing van die Kroll proses te lei. Eerstens, akademiese dekking en die feit dat omtrent 60 jaar se navorsing in hierdie opsie ingepomp is en tweedens, die kommersiële gereedheid van hierdie prosesalternatief as ‘n volskaalse bedryfsproses.
4. **FFC:** Gegoe vorms van pigmentgehalte $TiO_2$, word gepers en gesinter om die katodes te vorm wat dan direk elektrochemies gereduseer word tot titaanmetaal in ‘n gesmelte bad van $CaCl_2$, as die elektroliet.

Vir toekomstige werk word aanbeveel dat ‘n addisionele filtervlak, ‘n winsgewendheidsanalise, by die besluitnemingsmodel gevoeg word. Die vier prosesalternatiewe, soos hierbo genoem, kan gebruik word en vir elk moet die koste-besparingspotensiaal, die kapitaal insetkoste en die produksiekostes bereken word. Hierdie berekeninge kan gebaseer word op proses-, bedryfs- en ekonomiese ingenieurswese beginsels.

SLEUTELWOORDE: Titaan, Suid Afrika, Kroll, Alternatiewe, Tegno-Ekonomiese, Evaluasie.

# ACKNOWLEDGEMENTS

It is indeed a privilege to write the last section of this study. The time and energy invested in this endeavour resulted in much more than the mere completion of a research project, but rather involved the forging of friendships, the stimulation and exchange of ideas, together with the need to master a specific discipline. I would like to start this chapter of the study with the following quote, which stayed and inspired me for the duration of this research:

> "The new always happens against the overwhelming odds of statistically laws and their probability, which for all practical everyday purposes amounts to certainty; the new therefore always appears in the guise of a miracle."
>
> **HANNAH ARENDT**

A large number of people played an important, some even a critical role, in getting this study to this advanced stage.

- I would remember Mellet Moll as the one who originally recognized and identified the potential and selflessly searched for a suitable application thereof. The intellectual framework of this study was designed and cemented through several lengthy discussions. I would like to thank him as an academic and professional mentor for the support and guidance throughout and beyond the scope of this research.
- I am very grateful for the academic and financial support of Dimitri Dimitrov as one of my study leaders and project manager of the AMTS' titanium machining project. During the course of this study, it was necessary to visit the important role players within the South African titanium industry. I found myself in the fortunate position to have a sponsor in him for these excursions. Furthermore, I would like to extent my thanks for tediously working through my PICMET[1] article and aiding me in finalizing this document.
- I would like to thank James Bekker for assisting me in deciding on the appropriate analytic techniques. I required and tapped his expertise in simulation and modeling to design the framework of the techno-economic evaluation.

---

[1] PICMET: Portland International Center for Management of Engineering and Technology

- I am also very grateful for Konrad von Leipzig as my other study leader, who assisted in finalizing this document and helped me through the last administrative stages of this study.
- Several industrial experts played a critical role in helping me cross obstacles and technical difficulties. Without their assistance and knowledge, this study would not have been possible. Through these people, it was possible for me to experience the potential and possibilities of the South African titanium industry.
    a. **DST:** Nawaz Mahomed, Llanley Simpson and Umeesha Naidoo.
    b. **CSIR:** Dawie van Vuuren introduced and shared with me the wealth of titanium related research he has completed since he started his work at the CSIR in 2002. He was able to steer me in the correct direction in my search for cost-effective alternatives. He developed a comparative framework, as a summary of his work, which I incorporated into the first filtering stage of my evaluation. For his wisdom and guidance, I am very grateful.
    c. **Exxaro:** As one of the most important players in the South African mineral sands industry, mining both ilmenite and rutile. For the executives who scheduled me into their busy programmes, to share their vision and perspective of the titanium industry, I am extremely thankful. My visit to the Namakwa Sands mining complex and meeting David Southey was both interesting and insightful. I would like to extent my thanks to Brian Day, Hanno Olinger and Willem van Niekerk.
    d. **Mintek:** Peter Craven and Mike Freeman, who conducted a similar evaluation of the promising alternatives to produce titanium metal, a couple of years ago.
    e. **Anglo American:** Doug Alexander.
    f. **CSIRO:** Alan Manzoori and Terri Norgate.
- I would like to thank Ekkehard Friedrich, Denzil Kennon and Hendrik Snyman, my three colleagues. Together we transformed the office into an industrious and professional environment. We created something special; for wisdom and

laughter, creativity and true geniality lurked behind those walls. It was indeed a privilege to have been part of this foursome.

- Lastly, it will be impossible not to make use of this opportunity to thank my beloved ones. Without their love, enduring support, understanding, words of advice and courage, thoughts, patience and perspective, this study would never have reached the final stages. A sincere and hearty thank you, strangely feels vastly inadequate.

Kind regards. Salut.

WILLEM VAN TONDER

# TABLE OF CONTENTS

# LIST OF FIGURES

# LIST OF TABLES

# GLOSSARY AND ABBREVIATIONS

| | |
|---|---|
| **AHP** | Analytic hierarchy process is a structured technique for assisting with complex decisions, developed in the 1970s. It is used in this study to calculate the specific weights and priorities of all the decision criteria. |
| **AMI** | Advanced Metals Initiative. |
| **AMTS** | Advanced Manufacturing Technology Strategy. |
| **Conversion** | Conversion is a measure of the fraction of the reagent that reacts. To optimize reactor design and to minimize by-product formation, the conversion of a particular reagent is often less than 100% and is thus an important decision variable in chemical manufacturing processes. |
| **CSIR** | Council for Scientific and Industrial Research, a South African research council. |
| **DST** | The Department of Science and Technology of the South African government. |
| **EBSM** | Electron Beam Single Melt. |
| **HIP** | Hot Isostatic Pressing. |
| **Ilmenite** | It is a lustrous black to brownish titanium mineral ore, with a rhombohedral crystal structure and a composition of $FeTiO_3$. Ilmenite is the most abundant and important titanium mineral ore. Ilmenite is a common accessory grain in basic igneous rocks and the grains often become concentrated in sands resulting from rock destruction and weathering. |
| **ISM** | Induction Skull Melting. |
| **Kroll** | Refers to the existing industrial Kroll process used to produce titanium metal, which entails the reduction of $TiCl_4$ with Mg in a batch-like manner. |

| | |
|---|---|
| **LME** | London Metal Exchange. |
| **MCDA** | Multiple criteria decision analysis is a discipline aimed at supporting decision making authorities faced with numerous and conflicting evaluations. This discipline is studied in detail in chapter 4 with the aim to cement the fundamentals for deciding upon and recommending a technique to be used in this techno-economic evaluation. |
| **NECSA** | Nuclear Energy Corporation of South Africa. |
| **NNS** | Near-Net-Shape is an industrial manufacturing technique. As the name implies, the initial production of the item or product is very similar to the final shape, reducing the need for surface finishing. This is one of the main advantages of powder metallurgy, for it enables the use of NNS. |
| **Powder metallurgy** | The science of powdered metals, especially the production and utilization of metallic powders for fabricating dense materials and shaped objects. Significant cost reductions in the production of final titanium metal products could be achieved if the benefits of powder metallurgy are incorporated into the value chain. |
| **Rastering** | A scanning pattern of parallel lines that is traced by a beam to maintain even heating and consistent melting over the entire hearth. |
| **Rutile** | It is a lustrous red, reddish brown or black mineral with the composition of $TiO_2$. Rutile crystals, equi-dimensional and compact, are often embedded in metamorphic aluminous rocks. Since it is also hard, heavy and a common accessory mineral of primary rocks, it occurs in alluvial concentration of heavy sands. |
| **Specific weights** | Often referred to as the priorities of the decision criteria. The specific weights of the criteria are the outputs of the AHP in this study and used to give preference to those criteria that, according to the decision making authority, bears the greatest importance and significance. |

| | |
|---|---|
| **Sponge** | It is a crude, solid and porous, intermediate product of both the Hunter and the Kroll processes. The further processing and machining steps to produce titanium metal, greatly adds to the high costs of the final product. |
| **$TiCl_4$** | It is a dense, colourless, toxic liquid soluble in water and is used to make titanium and the pigment titanium dioxide, for it is an important intermediate in the titanium metal and paint industry. The most noteworthy reaction of $TiCl_4$ is its easy hydrolysis, reaction with water, to form titanium oxides and the corrosive hydrogen chloride. |
| **$TiO_2$** | The main titanium bearing mineral component. Present in both, ilmenite, rutile and titania slag. In pure form, $TiO_2$ is widely used as a pigment in the paint and plastic industry. $TiO_2$ pigment is a fine white powder chemically inert, which resists fading in sunlight and is very opaque. It has a very high refractive index and an optical dispersion higher than diamond. |
| **Titania slag** | Mined and refined ilmenite products with a low $TiO_2$ content are upgraded to a titania slag with a high $TiO_2$ content, which is then converted in the titanium metal value chain to titanium tetrachloride, $TiCl_4$, as the standard precursor for use in the Kroll process. |
| **TOPSIS** | The technique for ordered preference by similarity to the ideal solution is based on the premise that the preferred alternative would be the option closest to the positive and furthest from the negative ideal solutions, in Euclidean distances. In this study, this technique is used to conduct the techno-economic evaluation with the output a final ranking of the process alternatives. |
| **Valence** | Also known as valency or valency number, it is a measure of the number of chemical bonds possible or available to the atoms of a given element. For example, $TiCl_4$ has a valence of 4 or $Ti^{4+}$, and this occurrence together with the other intermediate and relative stable valences of titanium ($Ti^{3+}$, $Ti^{2+}$), leads to significant difficulties in the extraction of metallic titanium. |

| | |
|---|---|
| **VAR** | Vacuum Arc Remelting. |
| **Yield** | Yield is a measure of the performance of a reactor or plant. With industrial reactors it is necessary to distinguish between reaction yield, which includes only chemical losses to side products and the overall yield which includes physical losses. |

chapter | one

# 1 INTRODUCTION

"History and societies do not crawl.  They make jumps.  They go from fracture to fracture, with few vibrations in between.  Yet we, and historians, like to believe in the predictable, small incremental progression."

**NASSIM NICHOLAS TALEB**

Two novel technologies to produce titanium metal are currently being researched and developed in South Africa, the Peruke process by Anglo American and the CSIR process.  If a local technology delivers the cost-reductive breakthrough awaited by titanium researchers and academics, it would result in a significant and important increase in momentum and bestow impetus to the development of a South African titanium industry.  Not only to the upstream processing section of the value chain, but to the complete industry, including all the downstream beneficiation activities.

Unfortunately, these two alternatives are only two of approximately 24 endeavours to find a way of producing titanium metal cost-effectively.  The concern, what if not one of the two South African options reaches the final objective of commercialization, should therefore be studied and remedied.  An alternative technology must then be selected, imported and integrated into the existing titanium framework, if South Africa wants to reap the full benefit of its very rich natural mineral reserves.  Titanium has been identified as a mineral resource with the potential to serve as a major economic driver for the country if a local processing and production industry could be successfully established.

## 1.1 Overview of study and research

This study would provide the decision making authorities with a ranking and evaluation of these mentioned emerging alternatives. Based on both qualitative and quantitative techniques, a 2-Phase Filtering System was designed to assess, evaluate and formulate a final ranking, together with a detailed sensitivity analysis of both local and global parameters.

### 1.1.1 Technology and innovation management

The principles of technology management are used to illustrate the relationship between the technological and economical factors affecting the technology implementation strategy within the titanium industry. In Figure 1.1, the technology management framework is showed with the appropriate management processes: Identification, Selection, Acquisition, Exploitation and Protection. Also shown on the same figure are the required business processes: Strategy, Innovation and Operations.

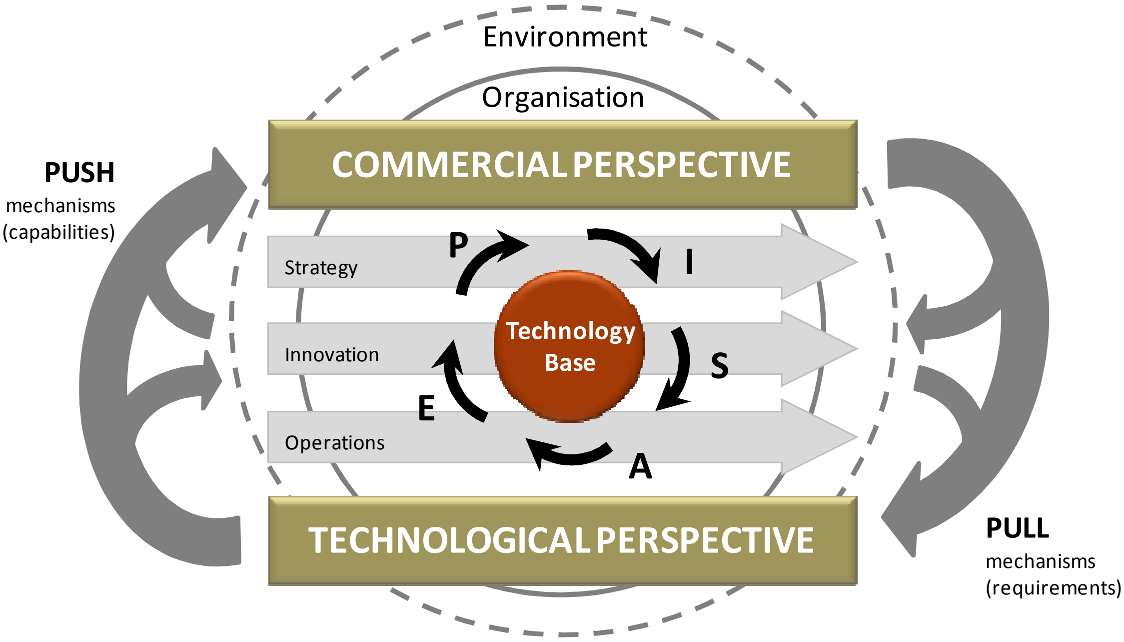


Figure 1.1: Schematic representation of the technology management framework (Garcia & Bray, 1997)

The figure highlights the dialogue required between the commercial and technological function in the business or industry to support effective technology management. With regards to the titanium technological scenario, the industry does experience a commercial pull for a more cost-effective metal producing technique, because the existing, the Kroll process, matured to such an extent that substantial improvement in performance has become impossible, owing to technical or economic constraints. A technology push is also noted, which can be interpreted as the academic, theoretical and practical progress of the titanium research community. These two forces together contribute to the urgency experienced by the global titanium industry.

### 1.1.2 Theoretical background

Before any techno-economic evaluation could be conducted, a multitude of disciplines, academic topics and theoretical fundamentals must be studied. To name a few: a) An understanding of the technical and economic nature of the decision environment, namely the titanium industry, its complete value chain and the South African perspective. b) To aid the design of the decision framework and evaluation by understanding the alternative processes being evaluated. c) Theoretical fundamentals, such as decision theory and MCDA[2], technology roadmapping and economic evaluation principles.

Once these disciplines, topics and fundamentals have been studied, the evaluation process could be started. The evaluation itself is a mixture of two completely different approaches, qualitative and quantitative analysis. The theoretical background behind the design of the evaluation framework will be briefly introduced in the paragraphs to follow:

- Qualitative analysis refers to a different approach in solving problems and making decisions, used especially within an environment where the scenario is too complex to be successfully modeled and simulated by quantitative methods and differential equations. It is argued that most real-life situations and scenarios are in fact too complicated to develop a rational model on which accurate and difficult decisions could be based. With regard to the research problem of evaluating titanium production processes, which have not yet been industrially and commercially proven, the solution and the investment decision framework become an increasingly complex matter. Also, the numerous technical difficulties for which process engineering solutions still need to be found, amplify the precarious nature of the predicament. It is for this reason, that the principles of qualitative analysis

---

[2] MCDA: Multiple Criteria Decision Analysis

would be applied to some of the decision criteria of this techno-economic evaluation.

- Quantitative analysis, on the other hand, deals with a specific mathematical approach, which together with measurable techniques such as differential equations, provides valuable insight and information to modeling a given real-life scenario. The model could then in turn be used to simulate the alternative titanium production processes in order to obtain an evaluation framework based on quantitative data. Within the domain of qualitative analysis it is extremely difficult to deal comprehensibly with risk management and probabilities. It is often necessary to make use of certain techniques to quantify and account for known and unknown uncertainties involved with the problem definition as well as the probable decision alternatives and outcomes.

### 1.1.3 Overview of decision framework: 2-Phase Filtering System

A techno-economic evaluation of several of the most promising titanium production processes is conducted in this study. Before any alternatives could be evaluated, the decision framework was designed and formulated, which, based on both qualitative and quantitative techniques, is a 2-Phase Filtering System. The initial step of the evaluation was to complete a preliminary screening and filtering stage, where all of the research and development programmes were assessed and a selection of 10 alternatives was made. Together with the two existing options, these 12 process alternatives were entered into the designed second phase of the techno-economic evaluation. The output of this evaluation was then subjected to a sensitivity analysis to test for disturbances in both local and global parameters.

### 1.1.4 Evaluation criteria of the framework

The evaluation criteria are based on technological fundamentals, as well as economics and financial feasibilities, briefly introduced below:

- **Academic and innovation activity.** This criterion represents the amount of research, in time and monetary terms, invested into the respective process alternatives and manifested as both academic articles and filed patents.

- **Commercial readiness.** Commercial readiness is a criterion to establish the status of development for each respective alternative. The maturity of the research and development programmes is measured and, based on the current production volumes, a comparative estimate of the commercial and industrial readiness is made.
- **Complexity of process.** To evaluate the complexity of the investigated processes the comments and remarks, made by industrial experts related to the concerns and issues they have with the fundamentals and scalability of these technologies, were used. A scorecard model based on 10 variables, each with specific weight calculated using AHP[3], was designed to formulate a complexity index, comparing all of the process alternatives.
- **Mode of operation.** The mode of operation plays an important role in the overall feasibility and cost-effectiveness of a proposed alternative. The Kroll process is a batch process and the dynamics and timeframe associated with producing a single batch significantly contribute to the cost and labour intensity of this batch process. The alternatives are thus categorized accordingly: batch, semi-batch or continuous operation.
- **Economics of raw material.** From an economic perspective, it is always advisable to start with an inexpensive as possible feedstock for any process, but if the complete upstream value chain of titanium is investigated the natural resources are always either ilmenite or rutile. Each process alternative that uses a different feedstock therefore faces a completely different set of difficulties, balanced by the potential cost-reduction.
- **Type of product.** Most research agrees that titanium sponge, as an intermediate reduction product, should be eliminated. The type and the format of the final product of the process alternatives are therefore an effective evaluation criterion.

---

[3] AHP: The Analytic Hierarchy Process, but for a detailed overview refer to section 4.2.3.

## 1.2 Strategic process to establish local titanium industry

In July 2007, the South African government approved the Department of Science and Technology's (DST) plan, *Innovation towards a Knowledge-Based Economy*, from 2008 to 2020. The aim of this ten-year strategy is to help to drive the transformation process towards an economy in which the production and application of knowledge leads to economic welfare and benefits all fields of human endeavour. Manufacturing and the processing of raw materials, stimulates and enhances many of the other sectors in a modern economy. The traditional South African industries have been primarily resource-based, in particular the mining and mineral industry. Most minerals are exported as ore or as enriched minerals, with the exception of steel industry. This prevents South Africa from reaping the full benefit of its very rich natural mineral reserves.

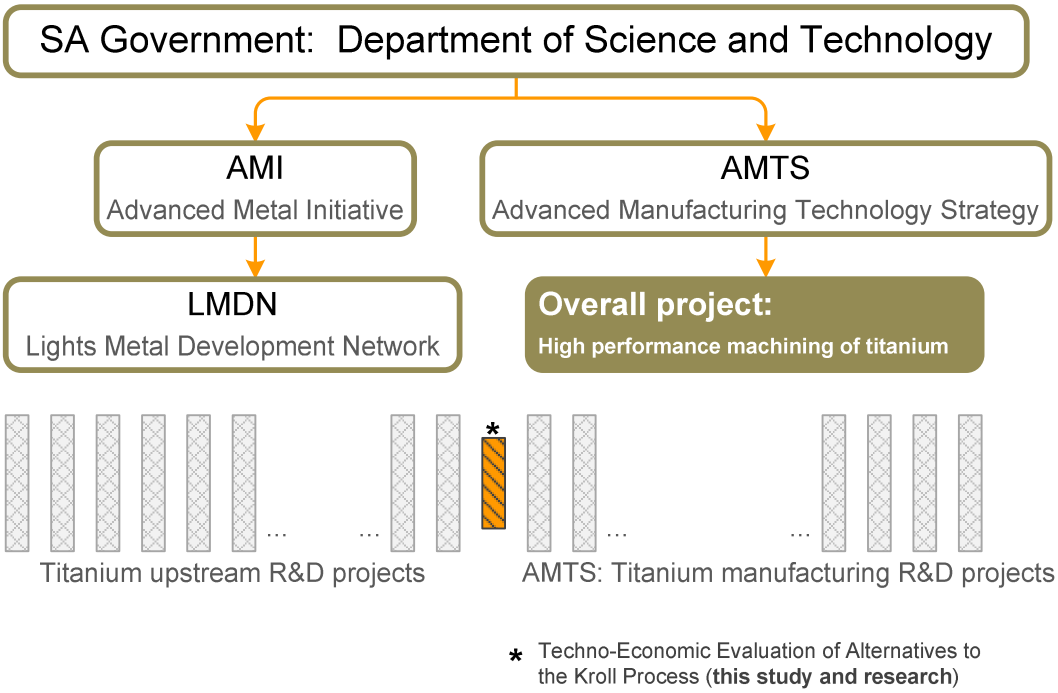


Figure 1.2: Hierarchical overview of the South Africa's titanium related initiatives and strategies

Titanium has been identified as a mineral resource with the potential to serve as a strategic economic driver for the country if a local processing and production industry could be successfully established. As seen in Figure 1.2, The DST formulated the Advanced Metals

Initiative (AMI[4]) and the Advanced Manufacturing Technology Strategy (AMTS[5]) to cater for these needs and to ensure the realization of this titanium metal industry. A major part of the AMI is the Light Metals Development Network (LMDN) with funding earmarked for titanium research and the AMTS has recently launched a project involving high performance titanium machining, with the operational head at the University of Stellenbosch.

Besides the above mentioned initiatives and programmes, the DST also formulated a strategic process for the development of a South African titanium metal industry with the vision to establish an internationally competitive titanium industry that will comprise both a primary metal production and downstream fabrication enterprises. This would enable South Africa to capture the benefits of an emerging light metals industry.

## 1.3 Significance of research

In defining the significance of this research project, the differentiation between local and global impacts must be made. This distinction is important, because the South African titanium industry and the world titanium industry differ greatly with respect to development strategies, technology implementation, value chain maturity and matters of magnitude.

The local significance of this research could be summarized as follows:

- Africa is richly endowed with natural resources and the Southern parts, including South Africa, has an almost unrivaled treasure of mineral reserves. Titanium, amongst the abundant mineral reserves, has been identified as a resource with the potential to serve as an economic driver as mentioned previously. Research initiatives are therefore necessary and important in order to create a thorough knowledge base with regards to related topics within the titanium industry. This study would provide a detailed overview, from a South African perspective, of the

---

[4] AMI: Advanced Metals Initiative was established by the DST in 2003 to facilitate research, development and innovation across the advanced metals value chain. The AMI's goal is to develop technological competencies and achieve optimal sustainable local manufacturing of value-added products, generating significant export income and new industries for South Africa by the 2020s, while reducing environmental impact.

[5] AMTS: Advanced Manufacturing Technology Strategy is a national implementation strategy managed by the CSIR (Council for Scientific and Industrial Research) and funded by the DST. The Light Materials Flagship Programme (LMFP) is one of the set of the objectives which seeks to increase competency and capacity in South Africa in the R&D of composites and light metals. The projects focus on the identification of existing technologies and the development of new materials and manufacturing processes.

titanium value chain, with special emphasis on the mining, primary and secondary processing steps, known as the upstream value chain.

- The DST, because titanium has been identified as a strategic economic driver, therefore developed a strategic process to develop such an industry. This research project, the techno-economic evaluation of titanium production processes, would assist in the understanding and representation of the competitive metal technologies. It is the objective of this study to focus on promising alternatives to produce and refine titanium metal cost-effectively and would thus provide a detailed study of the numerous differences, costs and benefits associated with these alternatives.

Globally, the titanium industry is relatively well-established, but because of the very competitive nature and the probability of a revolutionary technological breakthrough with significant cost-reduction potential, the technical information available and the knowledge transfer is very limited. Such a breakthrough would transform the titanium industry and market, which increase the secrecy involved with titanium related research because of the associated financial benefits. The following three matters could be considered as globally significant to justify this research project:

- The last 5 to 10 years have seen an increasing activity in titanium-related research, including technological improvements to the existing processes. This, partnered with the latest economic movements within the titanium markets (see Figure 3.3) created and sparked worldwide enthusiasm among mining and metal researchers, willing to be part of this transformation. This research project is part of this global research venture to further the application of titanium technologies.
- The experts and researchers involved with the titanium industry tend to be biased whenever it comes to calculating and estimating what the likely titanium future would look like. Their predictions are often coloured and infused by the inherent optimism, although and mostly unaware, related to the industry in which they practice and exercise their knowledge. For this, reason, an unbiased qualitative and more importantly a systematic quantitative assessment of the technological progress, especially a detailed evaluation of the emerging metal producing processes are required. This research project aims to address this specific need.

- Lastly, all academic research related to the beneficiation of titanium as a structural metal, could be seen as an attempt to assist in sustainable development. A feasible definition for sustainable development would be given with the words of the chairperson, Gro Harlem Brundtland, at the 1987 World Commission on Environment and Development WCED: "Economic and social development that meets the needs of the current generation without undermining the ability of future generations to meet their respective needs." The automotive and transport industry is the probable cause for a large variety of environmental issues and in recent years, there has been an increasing focus and intensity in developing more cost-effective alternatives to produce a structural material, like titanium, with the mechanical properties to reduce the weight of vehicles, both in the aerospace and the automotive industry, but retain the strength of the traditional options, such as stainless steel and aluminium. Even though this research project, in scope and definition, is an academic contribution to the understanding and progress of the titanium industry, it also adds to the mentioned aims of sustainable development.

## 1.4 Scope and limitation of this study

The scope and limitations of a research project are submitted to a series of iterations. It shows the progress and the increasing knowledge of a specific topic and discipline. Originally, the problem statement for this research was loosely defined and through these iterations the problem became more focused. The main driver of this iteration process is the need of mastering a specific discipline and the outcome or conclusion of the literature review should reveal that this mentioned topic has been covered in detail and thoroughly studied. The formulation of the literature review and defining the scope could thus be divided into three phases, each time moving closer to the core of the chosen discipline:

a) The first phase was a rough draft of possible topics involved with the research field and roughly related to the then impression of the problem statement. This phase involved redundant topics such as supply chain management, forecasting methodologies with scenario planning and building, and also separation process principles. The last topic was added and studied to investigate the possibility of designing an analogous separation process to screen the just created scenarios. At the time, the research problem was seen as the existing and prevalent gap in the

South African titanium value chain and the obvious solution was to attempt to fill this gap by designing a strategy. Part of this strategy would have been to discover the political, social, economic and technical reasons why it has been decided not to produce titanium metal locally. Once the reasons have been understood and comprehended, the remaining portion of the strategy would involve selecting the appropriate technology; continue to devise an implementation plan to complete the value chain and to establish a South African titanium industry. Instead of designing one strategy or scenario, it was thought wise to build a scenario generator which could run through a complete set of parameters, options and possible realities in the nearby future.

Importantly however, during this phase the various technical processes involved with the titanium value chain had been studied. The multitude of South African mining activities, performed by the major titanium role players, Exxaro and RBM, were investigated and explored. The existing and the only proven economically feasible method, the Kroll process, to produce titanium metal was researched, together with the appropriate history of its implementation and improvements through the years. Globally, there is an increased intensity with which titanium related topics are being researched and investigated. Thus, besides the Kroll process, several of the most promising cost-effective alternative processes were identified to be studied. These mentioned processes were investigated and summarized with the objective of developing a preliminary framework for comparison purposes. This latter activity resulted in the realization that the primary objective of the problem statement should migrate towards a techno-economic evaluation, with the possibility of a secondary objective being the design of an implementation strategy. The results of this phase of the literature review, together with the first elementary rating and ranking of the just mentioned processes, were drafted and formulated in article format, to be published in the PICMET[6] conference proceedings.

b) During the second phase, the scope of not only the problem statement, but also that of the literature study was narrowed to allow a more detailed and in depth

---

[6] PICMET: Portland International Center for Management of Engineering and Technology.

approach to selected literature subjects. Following the above first phase, it was concluded that by considering both political and social issues, this research project would be moved into a domain beyond the required and attainable scope. A valued and important overview of the South African situation with regard to titanium was however obtained in the previous phase. Although South Africa has vast reserves of titanium mineral ores, ilmenite and rutile, several important economic conclusions, such as the minuscule market for titanium metal in South Africa, together with the geographical position of the country, could possibly be drawn, which gave insight into the decision making considerations of those in political positions in the period when the titanium mining facilities were built. The economic considerations alone were valid enough to decide against the construction of the complete value chain.

Part of the motivation for this research covers the fact that several titanium experts agree with the reality that the global titanium market is expected to increase gradually, but with the distinct added possibility that a breakthrough, more cost-effective alternative, in titanium production technologies, could result in an rapid expansion of titanium demand in the nearby future. These two compelling arguments alone, gave weight to the required need to develop a professional titanium knowledge base, technical expertise and possible infrastructure within the boundaries of South Africa. Because of our endowed richness in titanium ore the DST thus understandably commenced with a detailed strategy and initiative to position South Africa accordingly.

The updated list of topics to be studied was:

- strategic management,
- decision philosophies and support systems,
- techno-economic evaluation fundamentals,
- technology implementing and roadmapping,
- risk analysis, and lastly,
- financial forecasting techniques.

All of these topics offer a vast amount of techniques, principles and insights into the problem statement, but it would be impossible to cover each of these topics in sufficient depth. Only elements thereof would be identified and studied to shed a valuable light onto the techno-economic evaluation.

c) The last phase of the literature review and study is, compared to both the above phases, the most important with regard to mastering a specific discipline. It is true that the previous phases led to this conclusion, and were vital, but during this phase, the philosophy of decision making would be investigated and studied.

chapter | two

# 2 LITERATURE REVIEW OF TITANIUM INDUSTRY

In this chapter the complete value chain of titanium metal will be investigated, from the mining and mineral processing steps, the extraction and refinement of the metal to the processing steps to obtain the final product. A detailed understanding of the global and local titanium industry is needed to design and conduct the techno-economic evaluation of the process alternatives.

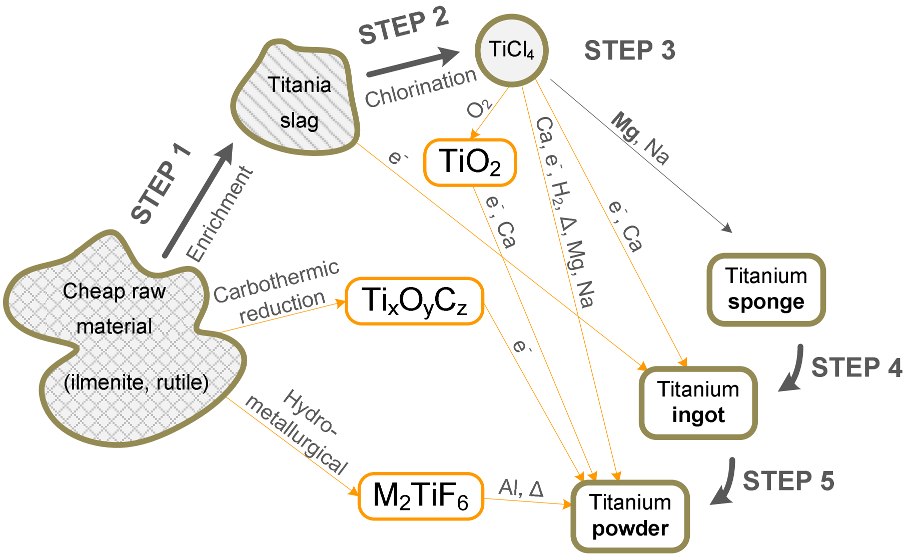


Figure 2.1: Illustrative overview of the upstream value chain of titanium metal

The details within the above figure will be discussed in later chapters, but it serves as an illustrative overview of the part of the titanium value chain that is investigated and evaluated within the scope of this study.

## 2.1 Introduction

However, it is necessary to pause for a while at the very properties of titanium, in its mineral and metal form, before exploring the means of extracting the metal and the further downstream activities. In the following paragraphs, not only the properties, but also the mechanical possibilities, of this metal will be introduced. Thereafter, the discussion will move to the South African mining perspective, the principle reasons why titanium metal has been identified as a strategic economic driver and later a brief overview of the existing local titanium related activities.

The introduction of this literature review will then give a brief overview of the following two topics: a) The history of titanium metal and b) The natural occurrence and mineral reserves of titanium ores.

### 2.1.1 Properties of titanium and the possibilities

Titanium is the 9th most abundant element in the earth's crust and is the fourth most abundant structural metal after aluminum, iron and magnesium. Most titanium is not consumed in its metal form, but as titanium dioxide ($TiO_2$), which is a white pigment used in the paint, paper and plastic industries. Currently only approximately 4.5% of the total titanium ore mined is used to produce metal.

With better specific strength than steel and with excellent corrosion resistance, the future of titanium as a structural metal was almost certain. Titanium has a low density of 4500 $kg/m^3$, compared to that of steel's 8000 to 9000 $kg/m^3$. Its strength-to-weight ratio that far surpasses the competing structural metals, a very high corrosion resistance and good high-temperature qualities make titanium almost the ideal structural metal. In Figure 2.2 the respective strengths of various structural alloys are given and the superior mechanical properties of titanium can be noted.

If titanium could be produced at cost comparable to say steel, or even aluminum, the performance standards would be much higher than we are used to today; supersonic jetliners would be common, the fuel efficiency of the automotive industry higher and structures much safer, because of the increase in strength per weight usage.

Most experts agree that the current production capacity of titanium metal is much too small given the outstanding combination of favourable properties and it is estimated by some that the current production is 1/20th of the global potential volume (Hurless & Froes, 2002).

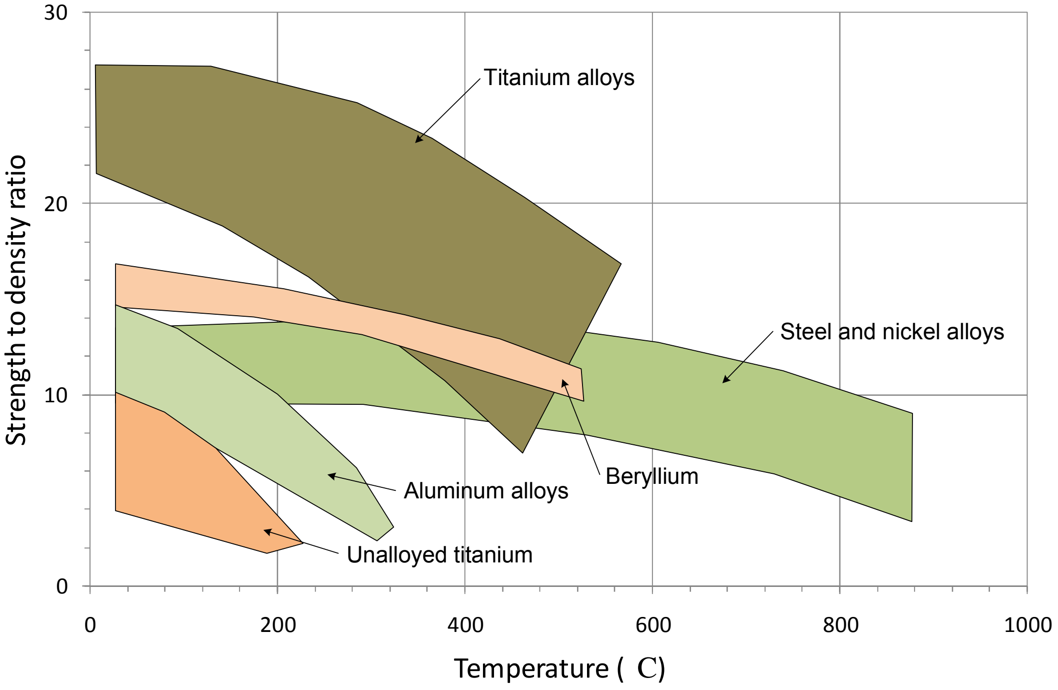


Figure 2.2: Representation of the strength-to-density ratios of various alloys plotted as a function of temperature (Askeland & Phulé, 2003)

However, titanium is difficult to extract from its ore, difficult to process and difficult to fabricate. Accounting only for the extraction and processing costs involved in producing ingot, titanium is approximately 30 times more expensive per tonne than steel and 6 times that of aluminum, as seen in Table 2.1. The higher cost of titanium places it more in a specialty material category in which sales are based on specific performance, unlike steel and aluminum which are commodity materials for which specific cost is the primary determiner of selection. It is expensive even in comparison with other specialty metals like nickel and cobalt.

Titanium, therefore, should have been used in significantly larger quantities when compared to aluminum, iron and magnesium. Instead, titanium markets experienced fifty years of instability during which the potential of titanium to expand to the chemical processing industry was primarily blocked by its high price. As a result of the high cost, production values for titanium are very low compared to commodity materials. To successfully compete, the cost of production must be reduced.

Table 2.1: Comparison of the various costs during the production stages of steel, aluminum and titanium, in volumes and per tonne.

**Comparison between:**

| **Production stage:** | Units | Steel | Aluminum | | Titanium | | |
|---|---|---|---|---|---|---|---|
| | | | | Factor to steel | | Factor to steel | Factor to aluminum |
| Ore extraction | $/tonne | 9.07 | 45.36 | **5** | 136.08 | **15** | **3** |
| | | | | | | | |
| Metal refining | $/tonne | 45.36 | 308.44 | **7** | 907.18 | **20** | **3** |
| | $/m$^3$ | 1708.67 | 4027.58 | **2** | 20137.91 | **12** | **5** |
| Ingot formation | $/tonne | 68.04 | 317.51 | **5** | 2041.17 | **30** | **6** |
| | $/m$^3$ | 2624.03 | 4149.63 | **2** | 44547.51 | **17** | **11** |
| Sheet formation | $/tonne | 204.12 | 1360.78 | **7** | 14741.75 | **72** | **11** |
| | $/m$^3$ | 7780.56 | 17941.05 | **2** | 322816.87 | **42** | **18** |

Efforts to reduce the cost of titanium products have continued practically uninterrupted since the beginning of the industry. Progress has been made in improving the efficiency of the conventional process route and also in developing some process alternatives. None of these efforts have provided pricing approaching that of the competing materials. Some academics therefore argue that the lack of progress over the last 60 years should be interpreted that an economic solution does not exist.

### 2.1.2 South African mining economy: Titanium as strategic driver

It could be argued that mining is the foundation of the South African economy as it is upon the mining industry that the economy of South Africa was and is built. These are the words with which the annual report of 2008 for the Chamber of Mines for South Africa opened (CoMSA, 2008). According to this same report, the mining sector accounted for 17.5% of the GDP (Gross Domestic Product), directly together with indirectly. In 2007 the South African mining sector has resulted in $20.67 billion merchandise exports and if the downstream semi-manufactured goods are taken into account, then the figure moves up to $34.62 billion (CoMSA, 2008).

Because titanium has been identified with the potential to serve as an economic driver the country must first successfully establish a local processing and production industry. It is the objective of any economic sector and business to continually grow and remain competitive and thus also the case for the South African mining industry. South Africa has the following competitive factors:

- The low-cost energy supply is consistent to energy-intensive users, even though South Africa experience disruptions in the last couple of years. Although the electricity prices are expected to increase at rates higher than the inflation rate, but is estimated to be still lower than elsewhere.
- Potential cost-reductive titanium metal production processes are currently being researched by South African based researchers. Well-established research centres, such as the CSIR, Mintek[7] and NECSA could assist in the supporting technology and establishing a knowledge infrastructure.
- Extensive proven natural mineral reserves, both ilmenite and rutile. As can be seen in Figure 2.3, it is estimated that South Africa has 14% of the global titanium mineral reserves. South Africa and Australia provide the bulk of feedstock to both the titanium metal and pigment industry, but both countries lack the capabilities to further the value chain by producing metal as product.

It could therefore be concluded that South Africa’s future growth and prosperity are closely linked to the mining and metallurgy industry, but continuous improvement and upgrading of the process technologies are required to stay ahead of the global competitors. The South African economy, in particular the mineral industry, has been resource-based with most of the minerals exported as ore or as enriched minerals.

The establishment of a South African titanium industry would enable South Africa to capture the benefits of this emerging international titanium market.

### 2.1.3 History of titanium metal

Titanium was discovered in 1790 by Reverend William Gregor, but it was another 86 years before Berzelius reduced potassium fluorotitanate with potassium to produce relatively pure titanium. In 1910, Hunter introduced sodium reduction of $TiCl_4$. However, the metal was still brittle due to impurities, primarily oxygen. Then, in 1925, Van Arkel produced pure ductile titanium by disproportionating $TiI_4$ (Habashi, 1997). During the 1930s, Kroll began

---

[7] Mintek is South Africa’s national mineral research organization. It is one of Africa’s leading technology organizations specializing in mineral processing, extractive metallurgy and related areas.

experiments that culminated in a 1940 patent for alkaline earth reduction of $TiCl_4$. In 1938, the United States Bureau of Mines (USBM) began a research program to find a method to produce commercial and economic quantities of titanium. By 1941, the USBM was using a small Kroll reactor to produce 100g quantities of titanium. By 1948, the USBM was making 91kg batches at a small pilot plant in Boulder City, Navada (NMAB, 1983).

The first uses of titanium were for military applications, which exploited and made use of the excellent mechanical characteristics of titanium. Governmental support and sufficient financial backing made it possible for the titanium production to grow rapidly in the 1950s. By the mid 1950s, several companies were producing titanium and more were considering entering the market. In 1957, the demand for titanium was on the rise and mill production was 5 130 tonne, so the plan to build a 5 000 tonne per annum titanium plant was announced using a new continuous process (Stamper, 1957). By 1960, there were only three titanium metal producers: Titanium Metals Corporation (TIMET), RMI[8] Titanium Co. and E.I. du Pont de Nemours and Co. In 1962, DuPont discontinued production of titanium metal and at the end of 1960s the interest for industrial applications, power generation and desalination plants, became the driving force of titanium usage.

The early 1970s marked a stage where the growth in demand declined, primarily due to the conclusion of the Vietnam War, and in addition, the hopes for a titanium intensive civil supersonic transport aircraft ended when the government-sponsored program was cancelled. During the mid 1970s, the energy crisis resulted in a sudden decrease in the aircraft orders from commercial airlines and the titanium consumption consequently dropped.

The early 1980s were characterized by a peak in consumption and a subsequent collapse due to an overestimation of aircraft orders that did not materialize or were later cancelled as the aircraft market deteriorated (NMAB, 1983). From 1985 through 1989, titanium metal consumption increased, reflecting renewed strength in the commercial and other industrial markets. The early 1990s marked the end of the Cold War era and globally, defense spending decreased significantly. In 1996, production of titanium mill products hit a peak of 62 000 tonne. In 1999 there were only 11 plants in the world that produced

---

[8] RMI: RMI Titanium manufactures titanium alloys and specialty metals in various extruded shapes and millings. RMI Titanium is a subsidiary of RTI International Metals and forms a part of the Titanium Group business segment, of RTI International Metals.

titanium sponge, with all of these in China, Japan, Kazakhstan, Russia and the United States of America. Globally, however, there are currently approximately double the amount of ingot producers, usually integrated with mill processing operations.

### 2.1.4 Occurrence and resources

Titanium mineral deposits are exploited primarily to produce raw materials for the production of titanium dioxide pigment. Approximately 93% of titanium mineral production is used for this purpose. The proportion used in the production of titanium metal increased from 3% in 2003 to 4.5% in 2006 (Roskill, 2007). The most common titanium-bearing minerals are ilmenite ($FeTiO_3$), rutile ($TiO_2$), anatase ($TiO_2$), arizonite ($Fe_2TiO_5$), perovskite ($CaTiO_2$), leucoxene (altered ilmenite) and sphene ($CaTiSiO_3$) or titanite. Of these, only ilmenite, leucoxene and rutile have significant commercial importance (Gambogi & Gerdemann, 1999).

On a stoichiometric basis, ilmenite contains 53% $TiO_2$ and is by far the most abundant mineral. Unweathered ilmenite often contains less $TiO_2$ than its stoichiometric value due to the presence of intergrown iron dioxide. However, weathering leaches iron from ilmenite resulting in higher $TiO_2$ content. Thus, the $TiO_2$ content of ilmenite varies considerably, usually between 50% and 70%. Above 70% $TiO_2$, altered ilmenite is referred to as leucoxene. Rutile is essentially crystalline $TiO_2$, with approximately 95% $TiO_2$ (Lynd & Lefond, 1983).

Economic deposits of titanium minerals occur in primary magnetic or secondary placer deposits, which could be any of the following (Roskill, 2007):

- Shoreline deposits upgraded by wind and wave action. Major commercial deposits of ilmenite, rutile and leucoxene occur in sand deposits, mostly near continental margins, where erosion of granite and metamorphic rocks containing ilmenite and rutile has led to the accumulation of these minerals in coastal plains sediments. The action of waves has led to various degrees of sand sorting and concentration, resulting in elevated concentrations of ilmenite, rutile and other heavy minerals. These shoreline deposits are by far the largest commercial source of titanium minerals.

- Inland basin deposits formed in fossil shallow marine basins or gulfs. In recent years, with the depletion of the more coastal sources of heavy minerals, exploration is focusing increasingly on geologically older marine deposits, which are often located at great distances from the present day coastline.
- Alluvial and eluvial deposits of ilmenite and rutile occur in existing and former river beds and flood plains, formed by the erosion and concentration of minerals originating from nearby source rocks.

Mineral reserves are classified as deposits capable of yielding economic concentrated under current economic condition with present technology (USBM, 1980). Titanium ore reserves are widely distributed throughout the world, with major rutile and ilmenite deposits in China (550 000kt), Australia (333 000kt), India (322 400kt) and Southern Africa (315 300kt) (USGS, 2009). In the figure below, the mineral reserve distribution can be observed.

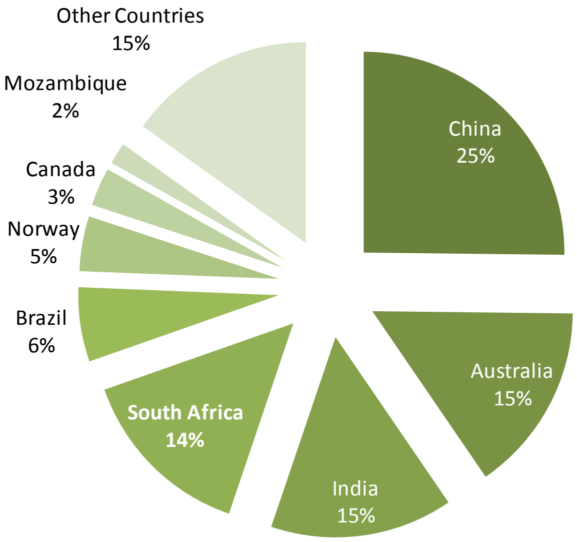


Figure 2.3: Comparison of the global titanium mineral reserves, both ilmenite and rutile (USGS, 2009)

Approximate minimum requirements for an economic sand deposit containing titanium minerals include reserves of 300 000 tonnes to 1 million tonnes of $TiO_2$ content in rutile or ilmenite, and heavy mineral content of between 1% to 5%, depending on the respective mixture of minerals (Gambogi & Gerdemann, 1999).

### 2.1.5 Overview of existing SA titanium value chain

In South Africa the economic titanium minerals, ilmenite and rutile, are produced from the extensive beach deposits along the eastern, southern and north-eastern coasts with some smaller deposits along the west coast, north of Cape Town. Titanium minerals are recovered at three major mines namely Richards Bay Minerals' Tisand and Exxaro's Hillendale and Namakwa Sands mines. Dredged and dry-mining techniques are used for the recovery of heavy-mineral sand deposits. Gravity spirals are used to separate the heavier minerals from the slurry, while magnetic and high-tension separation circuits are then used to separate the constituents.

A summary of the South African industrial activities, within the titanium value chain:

**Richards Bay Minerals:** Richards Bay Minerals (RBM), situated along the Indian Ocean coastline in northern KwaZulu-Natal, is a leading producer of titania slag, high purity pig iron and rutile in South Africa. RBM is the trading name for two registered companies, Tisand and Richards Bay Iron and Titanium (RBIT). Tisand is responsible for the dune mining and mineral separation operations, and RBIT the smelting and beneficiation process. The company is jointly owned by Rio Tinto and BHP Billiton, and is one of the largest single mining operations in South Africa, and the biggest titania slag producer in the world with annual production of about 1Mt (Williams & Steenkamp, 2006).

Tisand mines heavy mineral sands by means of dredging and the concentrate is road-hauled to the RBIT plant, 7km inland, for separation of the heavy minerals into ilmenite, rutile and zircon fractions (Macpherson, 1982).

The ilmenite, as mined, has a high $Cr_2O_3$ content and is not suitable for direct smelting to titania slag. An additional roasting step needs to be implemented because the magnetic characteristics of the ilmenite and the $Cr_2O_3$ are similar and makes separation difficult. The roasting process is carried out in two three-stage fluidized bed roasters operated in the temperature range of 730°C to 800°C (Lee & Poggi, 1978). After the roasting the chromium fraction is more magnetic and could thus be removed (Macpherson, 1982).

The grade of ilmenite produced at RBM is of too low grade to be used directly as a pre-cursor for the production of pigment or synthetic rutile. The $TiO_2$ content is increased by smelting the ilmenite with anthracite to produce a slag containing approximately 85%

titanium dioxide and a high-purity, low manganese content, pig iron as a by-product (Cowey, 1994). The smelting technology used at RBM was originally developed and proven at Quebec Iron and Titanium (QIT) in Sorel, Canada, where coarse ilmenite is smelted to produce a high-$TiO_2$ content slag and pig iron in similar furnaces. The technology was adapted for RBM to process the fine ilmenite concentrate mined on the north coast of KwaZulu-Natal (Williams & Steenkamp, 2006).

**Exxaro (Namakwa Sands and Hillendale):** Namakwa Sands, formerly owned by Anglo American Operations, but acquired by Exxaro in 2007, is another major player in the production of titania slag. The mine is situated at Brand se Baai, 385km north of Cape Town, and is divided into an east and west section where open-cast strip-mining activities occur, together with primary and secondary concentration of heavy mineral sands containing zircon, rutile and ilmenite (Gous, 2006). The non-magnetic zircon and rutile, and magnetic ilmenite concentrates are transported separately to the separation plant, approximately 60km south of the mine, near Koekenaap. The mine and Saldanha Bay smelter facility produce about 250kt of titania slag per annum.

Another Exxaro subsidiary KZN Minerals operates the Hillendale mine and smelter near the town of Empangeni in Kwazulu-Natal. Hydraulic mining is used at the Hillendale mine, 20km south-west of Richards Bay, to produce the slurry used in the primary wet plant. Further processing, including smelting of ilmenite to produce titanium dioxide slag then takes place at the central processing plant at Empangeni.

## 2.2 Mining and mineral processing

In the following paragraphs, the first few steps of the titanium value chain will be introduced. As explained above in section 2.1.4, titanium minerals occur in either primary magnetic or secondary placer deposits. The techniques used to remove the minerals from these deposits and the subsequent processing steps, are discussed below.

### 2.2.1 Mining and concentration of mineral ore

Mining of titanium minerals is usually performed using surface methods. Underground methods are sometimes used for the recovery of some hard rock deposits, but are uncommon. The mining process is fairly simple – the sands are either strip-mined or dredged and then transported to a mineral separation plant. Usually, a dredge (bucket-wheel or cutter head suction) is used for the recovery of titanium mineral placer deposits (Gambogi & Gerdemann, 1999). Wet gravity separation techniques, using spirals, Reichert cones and sluices concentrate the heavy minerals from the mined sand. The final concentrate is dried, normally in a rotary kiln, before the next treatment stage. There are numerous configurations used to separate the constituents of the heavy mineral suite using magnetic and high-tension separation circuits. As conductors, rutile and ilmenite usually are removed together by electrostatic separation. The conductor fraction of the dried concentrate then is subjected to high-intensity magnetic separation, yielding ilmenite product. The rutile fraction is further cleaned by screening and additional magnetic separation. Zircon and monazite by-products are recovered from the non-conductor fraction of the dried concentrate by a combination of gravity, electrostatic and high-intensity magnetic separation. The Recovery rate for titanium minerals from placer deposits is generally about 90% (Lynd & Lefond, 1983).

### 2.2.2 Production of titania slag

In the industry ilmenite products with lower $TiO_2$ contents are upgraded to the high $TiO_2$ products of titania slag or synthetic rutile. These products can then be converted to titanium tetrachloride for use in the production of titanium sponge. Natural rutile can be used directly for the production of titanium tetrachloride (Roskill, 2007). The beneficiation of ilmenite is accomplished by the removal of iron and other impurities in the mineral. Although numerous technologies are used, nearly all are based on either selective leaching or thermal reduction. These processes involve the oxidation, reduction and leaching of iron oxide contained in ilmenite. Two significant issues these processes face are that they often require higher grades of ilmenite and that they generate iron-base waste, which could be converted into a possible by-product (Gambogi & Gerdemann, 1999). The next section will deal with the production of synthetic rutile.

Production of titania slag involves smelting ilmenite in an electric furnace under reducing condition. Typically, anthracite is added as the reductant. During the process, all of the $Fe_2O_3$ and FeO can be reduced to metallic iron, which is recovered from the bottom of the furnace as high purity pig iron, and the slag containing the bulk of the $TiO_2$ and other impurities is tapped off the top of the furnace. The corrosive nature of titania slag necessitates limiting the reaction to create a protective frozen layer of slag. Since the reduction of iron is not taken to completion, trace elements such as manganese and magnesium usually remain in the slag (Doan, 1992). These impurities then pass into the slag product and are removed by further chemical processing (Roskill, 2007). The final quality of the titania slag is therefore highly dependent on the original impurity content of the ilmenite fed to the smelter.

The smelting reaction is given below:

Equation 1:

$$FeTiO_3 + C \rightarrow TiO_{2(l)} + Fe_{(l)} + CO_{(g)}$$

The produced slag is highly aggressive towards the furnace refractories and it is for this reason that the temperature inside the furnaces must be controlled and monitored very carefully. At optimum operation, a protective frozen layer of material is formed along the walls of the furnace. Undercharging would result in the melting of this freeze lining and exposing the refractory wall to the slag. Overcharging, however, would cause the furnace to freeze and froth over (Williams & Steenkamp, 2006).

The furnace products are further upgraded in subsequent processes. The slag is milled and classified into two product sizes suitable as a pre-cursor for both the sulphate and chloride pigment production processes (Williams & Steenkamp, 2006). QIT in Canada upgrades its standard 78% to 80% $TiO_2$ slag to approximately 95% by grinding, followed by heat treatment and chemical leaching to remove magnesium oxide (MgO), calcium oxide (CaO) and iron (Roskill, 2007). QIT calls the final product from this process upgraded slag or UGS, which has been used as a precursor for metal production as would be discussed in the appropriate chapter dealing with the emerging technologies.

### 2.2.3 Production of synthetic rutile

With regard to titanium South Africa and Australia are in very much in the same position. Both countries have vast reserves of titanium mineral ores, rutile and ilmenite, with extensive mining activity but no metal producing abilities. However, Australia is the world leader with regard to the production of synthetic rutile and by 2006 all commercial production was by either the Becher process, used in Australia, or the Benilite process. A number of other processes, some of which are simply modifications of the Becher or

Benilite processes, have been developed, but none are in commercial use (Roskill, 2007). The Becher process is the most widely used route for the production of synthetic rutile with product purity exceeding 95% $TiO_2$.

**Becher process:** The Becher process involves roasting highly altered ilmenite with finely ground coal and char in a rotary kiln at approximately 1 100°C, reducing the iron in the ilmenite to its metallic state. Iron sulphate or sulphur may be added to remove the manganese (MnO), but essentially the Becher process is only for the removal of iron from ilmenite and no other impurities.

The reduced ilmenite is taken from the kiln, cooled and separated from the unreacted reductant and waste-fines using screens and magnetic separation. It is then added to a mixture of water and ammonium chloride, acting as a catalyst, through which air is bubbled to convert the iron to fine oxide particles (Mackey, 1994). Classifiers and hydrocyclones separate these particles from the synthetic rutile. Finally, the product is leached with sulphuric acid to remove residual iron and MnO and improve the final quality of the product. The Becher process, however, requires ilmenite containing 57% to 63% $TiO_2$ to operate at highest efficiency (Roskill, 2007).

**Benilite process:** The Benilite Corporation of America developed the Benilite process for synthetic rutile production in the 1960s. It involves partial reduction of iron to the ferrous state using a fuel oil reductant, followed by leaching with hydrochloric acid at elevated temperature and pressure. The reduction reaction converts iron present in the ferric form ($Fe_2O_3$) in ilmenite to FeO, which is soluble in hydrochloric acid. The leaching process converts the FeO to ferrous chloride and dissolves a number of the other impurities in the ilmenite, such as manganese, magnesium, calcium and chromium (Roskill, 2007). The Benilite process is slightly more costly than the Becher process, but treats a wider variety of ilmenite feeds.

## 2.3 Secondary processing and metal production

In virtually all commercial operations, titanium metal is recovered from natural and synthetic rutile or titania slag, with titanium sponge as the intermediate product. In the section to follow, the secondary processing and the metal, as titanium sponge, production steps will be introduced. Enriched titanium minerals are chlorinated to form titanium tetrachloride, which is in the international titanium industry the generally accepted feedstock for metal producers. Alternatively, the feedstock is purified by means of the sulfate process to produce titanium dioxide pigment, but this option is gradually being replaced by the chloride process. The metal production steps follow either the Kroll process or the less popular Hunter process, with titanium sponge as the final product, which can be shipped to the titanium mills for downstream refinement and treatment.

### 2.3.1 Chlorination of titania slag

Titanium tetrachloride ($TiCl_4$) is widely used as the pre-cursor for the final step in producing titanium metal. The chlorination reaction takes place in a fluidized bed reactor, where rutile or titania slag ($TiO_2$) reacts with chlorine and carbon at 1 000°C, according to the following reaction:

Equation 2:

$$TiO_2 + 2Cl_2 + C \rightarrow TiCl_4 + CO_{2(g)}$$

The reaction is fast and exothermic, and thus provides enough energy to be self-sustaining and a conversion rate of over 95% can be achieved (Turner, Hartman, Hansen, & Gerdemann, 2001). The temperature should be carefully controlled to prevent the silica and zircon content from being chlorinated and thus to keep them within the chlorinator residue. Unfortunately, some of the other impurities chlorinate and need to be removed at a later stage.

The $TiCl_4$ leaving the fluidized bed is spray-condensed with previously formed and cooled $TiCl_4$ and then proceeds to the purification step as liquid containing normally 94% $TiCl_4$, 4% solids and 2% soluble metal chlorides. As already mentioned, some impurities, such as calcium, manganese, sodium and magnesium, remain in the chlorinator and only need to be purged occasionally. The solids, carbon, rutile, insoluble metal chlorides and oxychlorides in the liquid stream are allowed to settle out. The liquid $TiCl_4$ is fed to a fractional distillation column to split the contents into the low-boiling-point chlorides and the higher-boiling components (Hansen & Gerdemann, 1998).

### 2.3.2 Sulfate process to produce pigment

The alternative to the chloride process is the sulfate process. The sulfate process is gradually being replaced by the chloride process and in the last 20 years, the chloride route has actually been the preferred route by pigment producers across the world (Van Vuuren, 2008). In the sulfate pigment process ilmenite or titania slag are reacted with sulfuric acid. An exothermic reaction occurs yielding the soluble salts, titanyl and both iron sulfates, $Fe^{2+}$ and $Fe^{3+}$. After passing through a settling tank, the liquid fraction is passed through a crystallization tank, followed by a centrifuge where the crystals of $FeSO_4.H_2O$ are removed. Titanium hydroxide is precipitated by hydrolysis, filtered and calcined (Gambogi & Gerdemann, 1999).

### 2.3.3 Brief overview of existing metal production processes

Only two processes to produce titanium metal reached commercialization, namely the Hunter and Kroll processes. These extraction processes coexisted since the early 1950s, but lately the advances in the Kroll process caused this process to become the primary industrial choice in the titanium value chain.

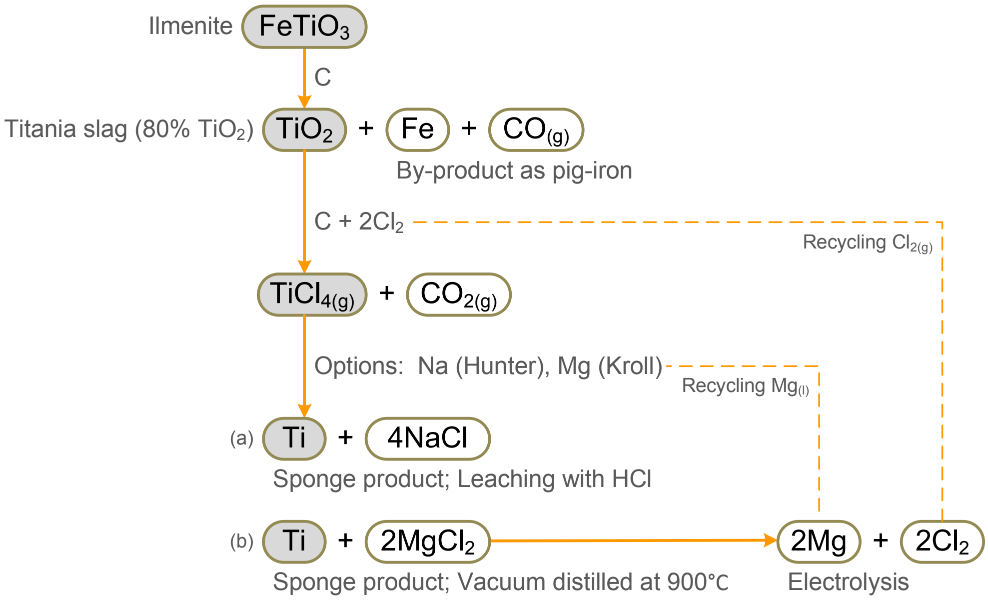


Figure 2.4: Chemical pathways, with reactions and respective products, of the two existing processes to produce titanium metal: (a) the Hunter and (b) Kroll processes

In Figure 2.4, the respective chemical pathways of both the Hunter and the Kroll processes are illustrated.

When $TiCl_4$ is mixed with metallic magnesium or sodium, highly exothermic reactions occur resulting in a crude product called titanium sponge, which is only an intermediate in the process of producing titanium metal. The sponge typically contains the metal, as well as mixed impurities, those that were present in the initial feedstock, and by-products, such as magnesium or sodium chloride, titanium subchlorides. The titanium sponge is refined, as discussed in section 2.4, in subsequent steps to produce titanium ingots for manufacturing and further downstream beneficiation.

Even though the Kroll process has been improved since its first industrial introduction, several drawbacks have remained and are to blame for the high costs of producing titanium metal. They are listed below:

1. It is performed under strictly batch conditions, leading to expensive downtimes.
2. The inefficient contact between reactants results in very slow reaction kinetics.
3. It requires the preparation, the purification and the use of the volatile and corrosive $TiCl_4$ as the preferred feedstock with its associated health and safety risks.
4. The process can only accept expensive natural or synthetic rutile or upgraded titania slag as raw materials.
5. The magnesium and chlorine must be recovered from the reaction products by electrolysis in molten salts, accounting for approximately 6% of the final cost of the sponge.
6. The specifications of low residual oxygen and iron content of the final ingot require expensive and complex refining steps, such as vacuum distillation and acid leaching of the crude titanium sponge in order to remove entrapped inclusions resulting in about 30% of the final cost of the ingot.

### 2.3.4 Comparison between the Kroll and Hunter technologies

The Hunter process was developed to produce higher quality sponge suitable for aerospace usage, but improvements to the Kroll process, coupled with better melting techniques that have made the quality of the sponge less critical, rendered the Kroll sponge suitable for aerospace applications. All of the major producers now use the Kroll process, mainly because magnesium is easier to handle industrially than sodium. Some of the main differences between these two processes are given in Table 2.2.

Table 2.2: The differences (benefits and disadvantages) between the two existing titanium metal refinery processes, Kroll and Hunter

| No | Kroll | Hunter |
|---|---|---|
| 1 | Batch | Batch/Continuous followed by batch step |
| 2 | 15% to 50% excess magnesium | Small excess of $TiCl_4$ |
| 3 | Few fines | Up to 10% fines |
| 4 | Hard to grind | Easy to grind |
| 5 | Substantial iron contamination from retort walls | Little iron contamination from retort walls |
| 6 | Sponge leached or vacuum distilled | Sponge leached |
| 7 | Retort contains mostly titanium | Retort contains 4 moles of NaCl for every mole of titanium formed |
| 8 | 1/3 Less energy for magnesium as compared to sodium recovery | |

Furthermore, production costs for the Kroll process have been steadily reduced, as the equipment has been made larger and better. Most plants now use fluidized bed surfaces for the chlorination of titanium ore and larger reaction vessels for reduction to sponge. In the 1940s sponge was produced in 1 tonne batches compared to the 10 tonne batches of today. Modern plants also use diaphragm-free bipolar electrolysis cells for by-product recycling, which consume 50% less energy than older diaphragm cells. Compared to these improvements to the Kroll process, the Hunter process was changed to a one-stage process, but there were no significant equipment enlargement or other technological advances or improvements (Roskill, 2007).

## 2.4 Processing of titanium sponge

Titanium sponge is melted, normally with recycled scrap and the necessary alloying elements to produce titanium metal and titanium alloy ingots or cast slabs. Cold hearth furnaces, using electron beam (EB) and plasma arc heat sources have, to some degree, replaced the original double or triple vacuum arc remelting (VAR) processes (Roskill, 2007). In the following section several techniques, existing and currently being developed or researched, used to process titanium sponge, will be introduced and discussed.

### 2.4.1 Double and triple vacuum arc remelting processes

VAR melting has been the standard, high volume melting technique that has been used to make ingots since the 1950s. VAR alloyed ingots are used as the starting material for subsequent semi-finished forms such as bar, plate, forgings, sheet and extrusions.

This melting technique is a method of sponge or scrap consolidation that is performed in a water-cooled copper crucible to avoid refractory contamination and in a vacuum or inert atmosphere to remove any atmospheric contamination (Gambogi & Gerdemann, 1999). The electrode is made from one or more compacted blocks of the metal charge, which usually consists of sponge or scrap metal, blended with the alloying elements required. These blocks are assembled into an electrode by mechanical compaction and/or welding (Roskill, 2007). This electrode fabrication step presents a large cost component of the arc melting technique. After suitable preparation, the crucible is evacuated or filled with an inert gas before a direct current is struck between the electrode and the bottom of the crucible to start the melting. As the electrode melts, the current quickly increases to between 500A and 1000A for each 250mm in diameter; molten metal drops from the electrode to the bottom of the crucible and an ingot is formed from the bottom up. The ingot progressively solidifies as the molten metal pool under the arc advances upward from the bottom (Gambogi & Gerdemann, 1999).

Recently, the use of a non-consumable electrode vacuum arc melting process has become more widely used than in the past. The sponge, scrap and alloy elements are fed directly into a molten pool produced by an arc struck between the contents of the crucible and a rotating electrode. The advantage of this technique is that a considerably higher melting temperature, higher than the melting point of titanium, could be employed, which increases the refining effect of the first melt (Roskill, 2007).

The melting of the sponge-scrap-alloy electrode constitutes the first melt, which produces a new ingot, which is melted for a second time to increase homogeneity and reduce the gas content. This second melting step is referred to as double VAR melting and, if repeated again, called triple VAR melting (Roskill, 2007). Arc melting is a batch process that is made more efficient and economic by increasing the size of the ingot, but it remains a lengthy and laborious batch process that also contributes to the high cost of titanium metal.

### 2.4.2 Cold hearth melting processes

Cold hearth single melting, using either EB or plasma arc torches (PA) as the heat source, is widely used. The EB or PA provides point sources of heat, which move rapidly over the surface in a programmable pattern, called rastering, to maintain even heating and consistent melting over the entire hearth.

The feedstock, which can be either bar stock or loose feed, is melted and flows into a water-cooled copper hearth and forms a skull of metal. Usually, there can be a series of these hearths with the melt flowing from the one to the next, each time forming a skull first. The melt flows from the last skull into a water-cooled crucible, with retractable base, to form an ingot that can be remelted in a conventional VAR furnace. Although the power consumption is higher, cold hearth melting processes offer several advantages over VAR (Gambogi & Gerdemann, 1999):

1. The electrode fabrication step is eliminated.
2. Low- and high-density inclusions are removed to produce higher quality product. The fact that these inclusions can be effectively removed, allows greater usage of scrap metal.
3. Mixing and dilution in the hearth improve homogeneity.
4. Melting can be halted and resumed nearly at any given moment.
5. The ability of EBSM (the electron beam single melt process has been refined to produce direct cast slabs and ingots of titanium alloy) to produce slab and other cast shapes without going through the ingot phase, directly from sponge and scrap, provides significant cost-savings in process costs and metal losses (Roskill, 2007).

### 2.4.3 Induction skull melting

The high reactivity of molten titanium leads to numerous difficulties in the processing stages of this metal. In the above techniques to process titanium sponge, a water-cooled copper crucible has been normally used. Alternatively, the problem could be avoided by the use of induction skull melting (ISM). A ring-shaped heating element is placed in titanium powder and heated to melt the titanium, forming a skull-shaped container (Roskill, 2007). This technique then eliminates the problem faced by most containing vessels. ISM, however, is not widely used.

## 2.5 Titanium powder metallurgy

A majority of the emerging alternative metal producing processes, studied in section 7.3, are designed to produce a powder as the main product, which could then be used in the existing titanium powder metallurgy (PM) industry. This industry, however, represents only a small percentage of the overall industry and much more research and development has to be done to make full use of the advantages offered by titanium PM, but the potential is significant and in the following section the main issues, benefits and difficulties, are introduced.

PM allows the use of Near-Net-Shape (NNS) technology, which reduces waste and thus dramatically reduces the costs. In addition, the fine grain size possible with powder metallurgy enhances mechanical properties and often allows the formulation of alloys not possible with conventional ingot metallurgy. Titanium PM, however, has been limited by the high cost of powder of acceptable particle size and purity. Because more than half the cost of a titanium part is incurred during fabrication, NNS technologies could have a substantial impact on the cost of titanium parts (Turner, Hartman, Hansen, & Gerdemann, 2001). The NNS parts require little subsequent machining. Dimensions can be tightly controlled; part stability and reproducibility are excellent. Homogeneity is assured by fine powder dispersion and mechanical properties are generally non-directional (Turner, Hartman, Hansen, & Gerdemann, 2001).

PM is a process that can be highly automated. Fine powders are placed in a metallic mold and compacted to form an intermediate ‘green’ part. A small amount of organic binder, such as wax or polymer, is needed to hold the powder together in this temporary state. In a PM variation, a polymer/powder combination may be injected into a mold to further automate the process. Subsequent heating debinds the organic binder, sinters and densifies the powders in the part. Heat treatment may be done concurrently, but full density is seldom achievable and further densification operations such as hot isostatic pressing (HIP) must be executed to close the voids and achieve the desired mechanical properties (Gambogi & Gerdemann, 1999).

The factors that have limited more widespread applications of titanium PM include:

- High cost of quality powders currently available.
- Understanding of the PM processing technology.
- Sintering facilities not fully compatible with the needs of titanium PM.
- Binder systems that result in high interstitial content in finished parts.
- The high reactivity of titanium making it difficult to obtain unoxidised titanium powder for sufficient purity requirements.
- Metallic or non-metallic impurities, which act as crack propagation nuclei when the material is submitted to mechnanical stresses, are more difficult to avoid with PM.
- Titanium tends to erode the conventional moulds that are used in PM.

If the powder could be made continuously and directly from $TiCl_4$, rather than from the already cast ingot, there would be a reduction in cost and energy. The ways, in which titanium parts are produced from powders commercially, are outlined below. All of these processes are still costly and result in an expensive product, as mentioned. PM processes are well developed, but the protection of these titanium powders from oxidation at several stages is expensive, if not impossible (Gambogi & Gerdemann, 1999). The success of titanium PM, thus, depends on the availability of new, high quality, low cost powders, as is the main product of several of the alternative titanium production processes. A plentiful source of such powder can be expected to have a positive influence on the titanium PM industry, but the factors mentioned above would restrict the rate of growth, if not addressed.

### 2.5.1 Blended elemental technique

The Blended Elemental technique (BE) uses sponge fines with particles of an approximate size of 150µm, irregularly shaped, porous and with sponge-like morphology. The fines are blended with additional alloy powders, cold compacted into a green part at pressures of up to 415Mpa before being vacuum sintered at 1 260°C to produce a 99,5% dense product. The use of HIP can increase the density of the parts. While the PM parts are cheaper to fabricate than similar cast or wrought parts, the porosity, present in the material, degrades both fatigue and fracture properties (Roskill, 2007).

### 2.5.2 Pre-alloyed powder production

There are a number of techniques for producing pre-alloyed titanium powder:

In the **Hydride-Dehydride (HDH)** process feedstock such as solid scrap, billet or machined turnings are processed to remove contaminants, hydrogenated to produce brittle material and then ground under argon in a vibratory ball mill, typically at 400°C. The resulting particles are angular and measure between 50 and 300µm. Cold compaction after dehydrogenation of the powder, followed by either vacuum hot pressing or HIP and a final vacuum anneal produce powders with hydrogen levels below 125ppm. The possible presence of contaminants makes these powders unsuitable for critical aerospace applications (Roskill, 2007).

The feedstock for the **Plasma Rotating Electrode Process (PRED)** is in the form of a rotating bar, which is arced with gas plasma. The molten metal is centrifugally flung off the bar, cools down and is collected. The powders produced are spherical; between 100 and 300µm in size, with good packing and flowing characteristics. This powder is thus ideal for high quality near-net-shapes produced by HIP, such as aircraft parts and porous coatings on hip prostheses (Roskill, 2007).

In the **Gas Atomization process (TGA)**, titanium is vacuum induction skull melted in a water cooled copper crucible. The metal is tapped and the molten metal stream atomized with a stream of high pressure inert gas. The tiny droplets are spherical and measure between 50 and 300µm. This process can be used to produce either commercially pure (CP) or titanium alloys (Roskill, 2007).

### 2.5.3 Powder consolidation

PM represents only a few percent of the overall titanium industry and the reasons for this include the obvious high cost of the current quality powders, but also the lack of familiarity by designers, sintering facilities that are not fully compatible with the required needs of titanium PM and binder systems. The availability of new, high quality, low cost powders can be expected to have a positive influence on the titanium PM industry, but the above mentioned factors are likely to restrict the rate of growth if not addressed (Kraft, 2004).

According to Kraft (2004), little work has been done on method of using powder to develop alternative routes to products such as bar, wire, sheet, plate and forgings. New processes still need to be developed for consolidation and forming of powders into plate or sheet which can be rolled and heat-treated to the desired end product. Work in the 1950s and 1960s at Du Pont, to demonstrate the feasibility of producing titanium plate, sheet and bar from powder, was abandoned when complications arose with the welding of the final product (Dombrowski, 1961; Dombrowski, 1963; Wartel, Wasilewski, & Pollock, 1963; Buchhovecky & Patton, 1969; Patton, 1970).

It was concluded that in order for this set of processes to be viable, chloride levels in the powder should be below 50ppm, whereas available powders then had levels in the range of 100ppm to 500ppm (NMAB, 1983). Recent literature shows that chloride levels below 50ppm are readily achieved, but still a lot of work is required to develop titanium PM sufficiently enough to ensure integration with the titanium value chain.

chapter | three

# 3 ECONOMIC AND STRATEGIC CONSIDERATIONS

The economic and strategic environment plays a major part in the feasibility of process alternatives and significantly affects the existing titanium industry. In the following chapter, the application and uses of titanium metal are discussed, together with a brief overview of the titanium market and related trends. Foresight techniques are then used to estimate the medium future demand for titanium metal.

## 3.1 Application and uses of titanium

Although aerospace applications still dominate the use of titanium metal products, titanium products are used in a variety of applications. In general titanium is used where there is need for reduced weight, higher strength, or improved corrosion resistance (Pawlek & Froes, 1999). The relatively costly processes associated with its extraction, manufacture and fabrication means that its use is largely restricted to advanced technological or high value applications.

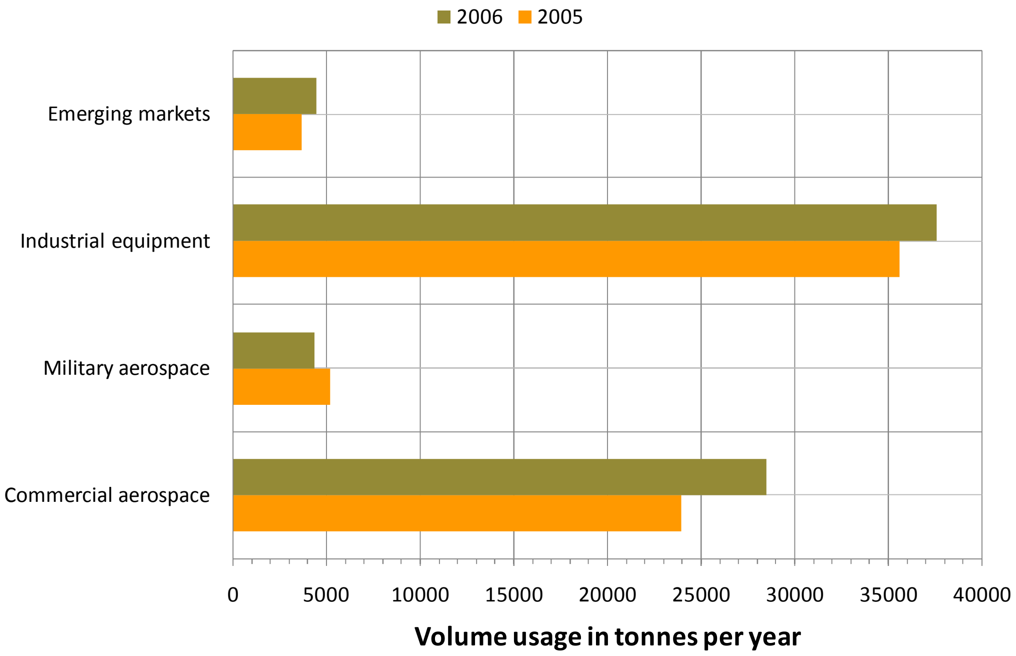


Figure 3.1: The global titanium metal market as divided into these four categories, with the volume usage shown and the growth experienced during the 2005-2006 period (Buch, 2006)

Globally, the aerospace industries of the USA and Europe account for almost 40% of the titanium market. The growth of industrial and consumer uses in China, Japan, South Korea and Taiwan have increased significantly in the last couple of years. The oil and gas, as well as the automotive industries, have received particular attention because of their respective potential to provide substantial and stable markets for titanium, in contrast to the very cyclic aerospace market (Roskill, 2007).

In the following paragraphs, the commercial applications of titanium are introduced with the objective to establish an understanding of the uses, the demand for titanium metal and to formulate the framework for estimating the potential growth of the titanium industry in the medium future.

### 3.1.1 Aerospace industry

Despite the volatility of the market and the development of other applications, aerospace remains the principal market for titanium, as mentioned above, roughly 40% or 31kt of mill products in 2005. Aerospace is thus by far the largest end use for titanium. Although titanium may cost approximately 8 times as much as steel, the performance advantage and weight reduction make it a material of choice for many aerospace applications. Most commercial and military aircraft have some percentage content of titanium. The driving forces for the use of titanium in aerospace are a focus on weight savings, high strength, volume savings and compatibility with composite materials. Most aircraft designers take advantage of titanium's high strength-to-weight ratio; when used as a direct substitute for steel, titanium may decrease the weight of a component by as much as 40%.

Also, as a substitute for aluminum, titanium may increase the possible operating temperature, reduce the volume and improve the compatibility with carbon fiber components. The material compatibility is an important characteristic, because other materials, such as aluminum and graphite can create a galvanic potential leading to serious corrosion problems (Gambogi & Gerdemann, 1999).

Europe and the USA have the largest aerospace industries in the world and about 65% of annual US titanium demand, and 50% of European titanium demand is accounted for by aerospace. By contrast, in the other principal markets, Japan, China, South Korea and Taiwan, the aerospace titanium demand is approximately 5%. The aerospace industry can be further divided into the following three categories:

- Commercial aerospace, comprising passenger and freight airliners, regional airliners and smaller business and general aviation, which probably accounts for about 70% to 80% of aerospace use.
- Military aerospace including missiles, small fighter and bomber aircraft and large transport planes, which account for an estimated 25% of aerospace use in the USA and about 10% in Europe.
- Space flight including commercial satellites and space exploration, accounting for about 5%.

The ratio of titanium use in airframes to that in engines has historically been about 1:1.1, but this is changing with the greater use of composites, which are compatible with titanium but not with aluminum, in the airframes of the new large passenger planes, such as the A380 and the B787.

### 3.1.2 Non-aerospace industry

In Figure 3.2, the titanium metal volume percentage used in each of the non-aerospace categories is shown. The use of titanium in heat exchangers in the chemical and petrochemical, power generation, desalination and other industries is the largest application.

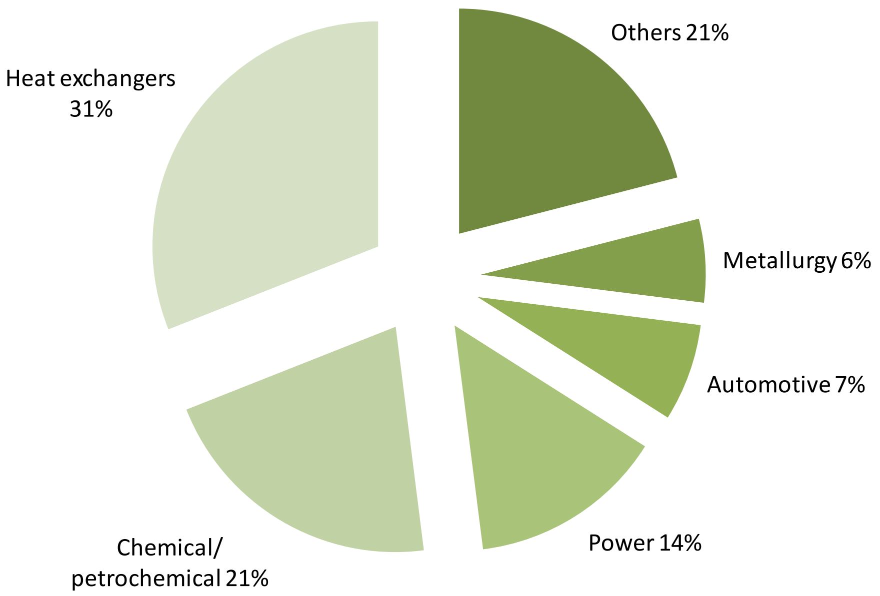


Figure 3.2: The volume percentage of titanium metal used in the non-aerospace applications (Gambogi & Gerdemann, 1999)

The use of titanium metal in heat exchangers will thus be dealt with separately in the following paragraphs.

- **Automotive.** Despite efforts by titanium producers to tap the colossal automotive industry, the use of titanium in cars has remained limited, primarily because of the high prices of titanium products and parts. Nevertheless, there has been a gradual increase from almost nothing in the 1990s, driven to a significant extent by the use of titanium silencers and exhaust systems within the motorcycle and car industry (Roskill, 2007).

  Although cost will prevent titanium from ever becoming a major material in vehicle construction, its use as standard in specialized components could create a substantial market. It is argued by several experts that the prospect of titanium components being used in the automotive industry is the principal driver behind the global research for a cost-effective process alternative to produce titanium metal.

- **Chemical and petrochemical.** The global market for titanium in chemical and petrochemical applications, other than in heat exchangers, is estimated to be about 9000 tonnes annually, approximately 21% of the total non-aerospace volume applications. Titanium forms an oxide film on its surface that is highly resistance to a large number of chemical compounds and thus a favourable choice of metal for process equipment. Especially in the chemical and food processing industry, where a high level of corrosion resistance is required, titanium is oftenly used. Vessels, tanks, agitators and piping systems manufactured from titanium metal or alloys, are used in the processing of aggressive compounds such as nitric acid, organic acids, chlorine dioxide, inhibited reducing acids and hydrogen sulphide (Roskill, 2007).
- **Power generation.** About 14% of non-aerospace consumption is used in thin-walled condenser tubes in steam turbine condensers and several other components, excluding heat exchangers, in power plants (Roskill, 2007). The demand for titanium to use in power plants is an important factor behind the rapid growth of the Chinese titanium market.
- **Heat exchangers.** Titanium is mostly used in plate heat exchangers, where the fluids are separated by a wall, as opposed to the mixing type of heat exchangers. Plate heat exchangers made of titanium are extensively used in chemical, power and desalination plants, refineries, pulp and paper plants, and also on offshore platforms, to name but a few. Large power plants have to use seawater for cooling purposes, but this practice leads to problems with biofouling and corrosion, which by using titanium metal greatly reduce or eliminate the problems altogether.
- **Metallurgy.** Titanium is also sometimes used as the starter cathode in highly corrosive environments to electrolytically refine specific metals and chemicals. The main market in this category is the electrolytic reduction of manganese oxide.

## 3.2 Titanium market and economic history

Since 2001, there have been significant developments in the global titanium industry. The real price of titanium sponge has risen by approximately 130% between 2001 and 2006, compared to the largest historical price increases (Hogan, McGinn, & Kendall, 2008). Also, the USA government has liquidated its strategic titanium metal stockpile that it had been holding since the 1950s. In the following paragraphs, several difficulties and risks inherent to the titanium market will be introduced.

### 3.2.1 Investment difficulties

The very risky nature and the uncertainties involved with the research and development initiatives within the titanium metal industry resulted in many investors adopting the wait-and-see approach. The lack of industrial commitment to the development process, together with the inherent skepticism surrounding the mentioned technological breakthrough, created a very difficult barrier to bridge.

If the titanium value chain is investigated, it should be noted that the upstream portion of the chain, the section dealing with mineral mining, primary and secondary processing, refining and procurement of titanium metal is fragmented into two distinct fractions. The major industrial role players involved in the upstream value chain tend to focus on their core business, which is either the mining and enriching of raw material up to titania slag or synthetic rutile, or the processing, refining and procurement of titanium metal. This well-established practice of focusing on a core business also contributes to the difficulty in bridging and smoothing the gap between these fractions. Especially, in economic troubled times, the growth and research departments of the respective role players are pressured to find ways to either add value to the final product or reduce the production and operating costs, but not to further or enlarge the value chain of their existing product.

The objectives of this research project are concerned with the production of titanium metal and the cost-reducing alternatives are thus investigated but the technology investment and adoption policies of the important titanium role players also need to be revised. If not, then this mentioned technological breakthrough would most probably be delayed a further decade or even longer. Both fractions of the upstream value chain have to take responsibility and ownership of the market potential unlocked by such a development.

### 3.2.2 Market size and associated risks

Unlike other metals markets, the titanium market is extremely small as seen in Figure 3.4. Given the small market size and highly concentrated buyers and suppliers, the titanium market is more exposed to turbulence caused by supply and demand shocks than are large raw material markets with well diversified buyers and suppliers.

### 3.2.3 Spot market vs. longer-term contracts

Titanium prices are based on both spot market transactions and longer-term contracts. Spot market transactions are basically agreements in which the purchaser pays on delivery the current price for titanium, as opposed to longer-term contracts where the titanium price is fixed beforehand for a pre-determined period of time. Titanium is not traded on a fully developed auction market such as the London Metal Exchange (LME). Contracts for less than three years are considered short-term contracts; contracts for three years or more are considered long-term. Major buyers of titanium often prefer five- to ten-year contracts. This coexistence of spot market prices and contract prices is a common characteristic of raw material markets and due to the two different price systems, there are multiple prices available in the same market at a given time. Spot market prices adjust quickly to economic forces and shocks, whereas long-term contract prices are a lot less flexible.

Compared to other raw materials, such as aluminum, steel, copper, and oil, titanium spot market transactions are less common and the titanium spot market has only recently become significant, but the exact size of this market is unknown. Industry experts estimate that it usually accounts for between 10% and 30% of all transactions. The relatively small volume of titanium spot market transactions is partly due to the limited size of the titanium market in general, the characteristics of downstream industries, and the nature of price shocks. Conversely, long-term contracts still dominate the titanium market, where the aerospace industry is the dominant downstream industry in which the major buyers are fixed and production lead time is significant. When demand shocks are more significant relative to supply shocks, it is more likely there will be greater contracting and price rigidity (Hubbard & Weiner, 1985). Long-term contracts usually stipulate conditions such as minimum annual quantity, minimum share of the customers’ titanium requirements, prices determined by an agreed-upon formula, and price adjustments for raw material and energy cost fluctuations. Long-term contracts reduce price volatility for the buyer while securing a base level of revenue for the supplier throughout the business cycle.

## 3.3 Medium-term future demand for titanium metal

It is a difficult task to predict and impossible to accurately predict what the future demand for titanium metal would be. The number of variables that greatly influenced this demand in the past is apparently changing and new ones are appearing as the titanium market itself undergoes a transformation. Before continuing and arguing what the likely titanium medium-term future would be, the following should be stated:

a) This section is based on a set of foresights, not predictions or forecasts. A foresight activity examines trends and indicators of possible future developments without predicting or describing a single stage or timeline and is thus distinct from a forecast or scenario development activity (Salo & Cuhls, 2003).

b) The experts and researchers involved with the titanium industry tend to be biased whenever it comes to calculating and estimating what the likely titanium future would look like. Their predictions are often coloured and infused by the inherent optimism, although mostly unintentionally, related to the industry in which they practice and exercise their knowledge.

c) The titanium metal and its associated mechanical properties, in itself possess the ability to convince even an uninformed person about the considerable potential hidden within the industry.

### 3.3.1 Titanium market trends

Several global trends are driving and governing the growth in the current and emerging titanium market and a brief summary of the most important and relevant ones is given below (Buch, 2006):

- Oil demand and stability of supply are driving planned oil explorations into more challenging environments. The weight, strength and modulus characteristics together with the corrosion resistance of titanium are closing the value gap with other metals, resulting in significant growth potential in the oil and petroleum industry.

- The need for performance, efficiency and environmental sustainability are moving the transportation industry towards titanium in a number of ways, especially in automotive parts and airframe structures. The weight, strength and temperature performance are opening up huge opportunities for titanium.
- The expectations around GDP[9] growth and continued expansion in China and India with other developing areas are drivers of power generation, desalination, chemical processing and transportation. Titanium plays an important part, an ever increasing part, in all of these industries, which implies the titanium market should continue to grow.
- While global tension and potential conflicts would in all likelihood depress the world economics and because aerospace continues to be an important driver for the industry, the overriding result in escalation would undoubtedly be negative. However, current and future military strategy leading to light armament and mobility, favours the use of titanium in most light weight and ballistic applications.

Jim Buch, of Timet USA, presented a paper at the annual International Titanium Association conference in 2006 on the challenge in meeting the titanium demand and he concluded that in each of the segments or industries mentioned above, the titanium demand is expected to double over a 10 year period (Buch, 2006).

### 3.3.2 Metal demand foresights

The primary barrier, rather a cul-de-sac, to achieving these possible foresights is the high costs of producing and refining titanium metal. The optimistic views rest firmly upon the belief and the assumption that a noteworthy breakthrough is bound to happen in the next decade, which would refresh and dramatically reduce the costs of the complete titanium value chain.

A large number of international research initiatives are actively trying to address this problem and to accomplish the mentioned breakthrough. It is also true that the last 5 or 10

---

[9] GDP: Gross Domestic Product is the most basic and often used measure of a country's economic performance and is the market value of all final goods and services made within the borders of the country in question, in a year.

years have seen an increasing activity in titanium-related research, including important technological improvements to the existing production methods. It is of interest to note the gradual increase and recent surge between 2002 and 2006 of the Producer Price Index for titanium mill products, as seen in Figure 3.3.

However, ever since the Kroll process was developed and designed on an industrial level, almost 60 years ago, the core of the process has not been altered. The costs of producing a given amount of refined titanium metal have thus not been dramatically reduced in any way since the first commercial steps of the titanium industry. It is with this in mind that the likely, more pessimistic, future demand for titanium is argued.

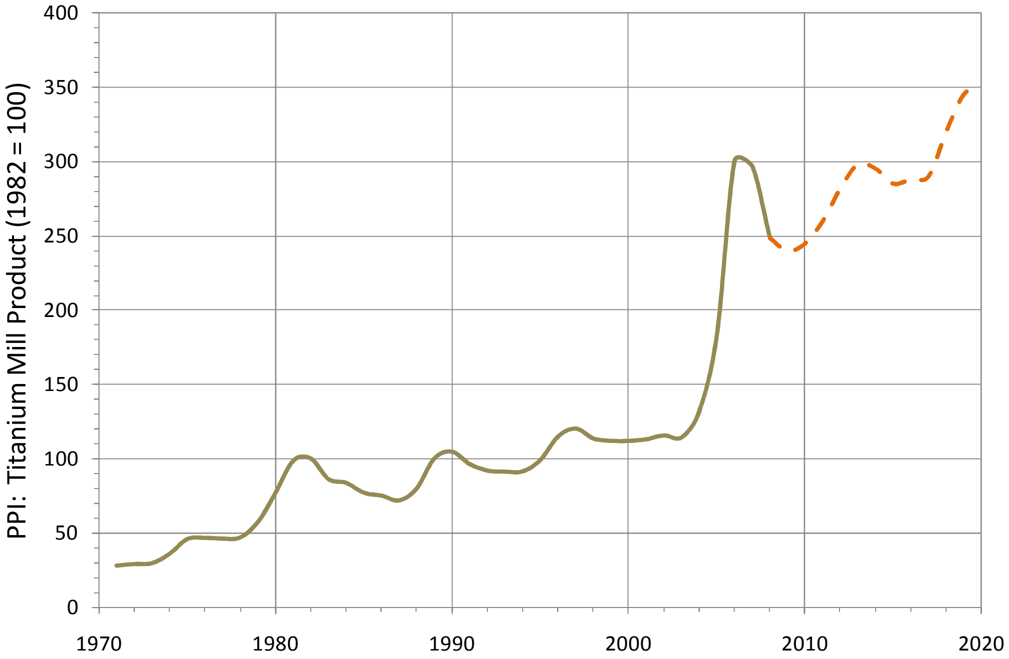


Figure 3.3: Producer Price Index for titanium mill products, 1971 to 2008, with estimated values up to the year 2020 (USBLS, 2008)

While the importance of titanium for the aerospace industry has increased, the importance of the aerospace industry has decreased for titanium. Besides this declining dependency, the aircraft manufacturing industry is still the largest user of titanium metal. In recent years, three main demand drivers within this industry could be identified, which together assisted the surge in titanium product prices:

- Commercial aircraft orders skyrocketed as both Boeing and Airbus received record levels of orders during 2005 and 2006.

- The average level of titanium content per aircraft rose significantly, which meant that the increase in aircraft orders in turn amplified the demand for titanium metal.
- Full-time production of the F-22A Raptor began in 2003, which caused the demand for titanium in military aircraft production to increase notably as well.

The estimated values given in Figure 3.3 for 2009 to 2020 are based on the decreasingly cyclic nature of the titanium industrial market, as the industrial demand is playing an increasingly larger role, stabilizing the overall cyclic effect. Also, it is argued that the PPI of titanium mill products would not return to the historic average, but would rather continue to grow gradually at a steady rate. The possibility of experiencing large jumps, as happened between 2004 and 2006, should not be completely ignored and would be briefly discussed in the following paragraph, explaining the relevance and the improbabilities.

These large jumps could correspond to the expected significant technological cost-reducing breakthroughs in the titanium value chain. It is argued, as mentioned earlier, that if the complete titanium value chain could be refreshed and the costs dramatically reduced, the industry would be transformed. If titanium metal can compete cost effectively with other structural metals, the superior mechanical properties would ensure that the titanium metal industry captures a large market volume share from the competing metals, see Figure 3.4.

Figure 3.4: The volume market comparison of structural metals in million tonnes, 2004

Stimulated by growth in industrial demand from power generation in China, and commercial aerospace in the USA and the EU, the global market for titanium mill products should increase by about 7% annually to about 124kt by 2011, compared to the 83kt in 2005 (Roskill, 2007).

In the event of a jump, as described in the above paragraph, the market demandfor titanium mill products could grow considerably faster than the estimated growth. The demand for sponge, however, would fall, if this breakthrough includes a process which eliminates the use of titanium sponge as an intermediate product in the complete value chain. This titanium metal demand will be driven largely by the growth in additional titanium applications throughout the industrial sector.

For example, demand growth among emerging titanium buyers such as oil and gas installations, and the automotive and medical industries, has been particularly dramatic in recent years, showing a 50% growth between 2004 and 2006 (Seong, Younossi, & Goldsmith, 2009).

chapter | four

# 4 DECISION THEORY AND FUNDAMENTALS

Before continuing onwards to the design of the techno-economic evaluation, it is firstly required to study the theory of decision making and to understand the fundamentals thereof. This chapter will take a closer look at the underlying principles, the theoretical background and several techniques commonly used to assist decision making authorities.

Frederick Taylor could be regarded as the founder of scientific management and since 1911 this discipline has developed significantly, especially during World War II with the need and emphasis on operations research. Basically, scientific management could be defined as a means of providing managers with a quantitative basis for decisions regarding operations under their control (Morse & Kimball, 1952). The war was a turning point in the design of new systems, marking a level of complexity that required systems analysis, which resulted in researchers developing a game theory and decision analysis as well as technological forecasting tools. In this chapter the theory of decision analysis will be explored and introduced as scientific management techniques. With the theory of decision analysis discussed, it will be possible to conclude which areas of theory are applicable and feasible with regard to the nature of the problem statement. These mentioned areas will then be explored in more detail and depth in following sections.

## 4.1 Introduction

A problem may be said to have a multiple criteria nature when the analysis is not merely an optimization procedure where a particular quantity has to be maximized or minimized.

Instead, what is optimal depends on the different criteria and how they are weighted. It also therefore accommodates the subjective element of decision making. Multiple criteria decision analysis (MCDA) acknowledges the fact that the world is multi-dimensional and cannot be reduced to a single dimension. In dealing with actual problems, these dimensions may include several socio-economic, monetary, or performance measures (Drechsler, 2004).

MCDA involves making decisions when multiple conflicting criteria are present and is required when the following problem characteristics are of concern (Agrawal, Kohl, & Gupta, 1991).

- **Multiple attributes/objectives:** In the case of a selection problem where many attributes are to be considered, or in a design problem where many objectives are the case.
- **Conflict among criteria**: When multiple criteria are in conflict, where a particular option may score a high criterion value in one category but a low value for another criterion.
- **Incommensurable units:** Each criterion has different unit measurements, which complicates the direct comparison between criteria values.
- **Design/selection:** Solutions to these problems are either to design the best alternative, or to select the ‘best’ among a finite number of alternatives.

The above list of problem characteristics shows that conducting a techno-economic evaluation of the alternatives to the Kroll process is within the scope of multiple criteria decision analysis, because all four characteristics are present in the overall problem statement. For example, to assess the different processes a wide scope of evaluation criteria needs to be designed with diverse units and methods of measurement. The last characteristic, design and selection, is at the very core of the design problem: several emerging processes to produce titanium metal are critically evaluated with the objective to recommend the ideal solution among a finite number of alternatives.

Some applications of MCDA include areas such as evaluations of technology investments (Boucher, Luxhoj, Descovich, & Litman, 1993), which also borders on the nature of the problem statement of this research project.

## 4.2 Overview of MCDA methods

A brief discussion of the weighted sum method, weighted product method, analytical hierarchy process and several other MCDA methods is included in this section (Pohekar & Ramachandran, 2004). These methods are introduced to obtain an understanding of the variety of options available, but also to highlight the respective qualities of each mentioned method.

### 4.2.1 Weighted sum method (WSM)

This is the most commonly used approach, especially in single-dimensional problems and can be described as follows. If there are $M$ alternatives and $N$ criteria, the best one would be the one that satisfies the expression:

Equation 3:

$$A_{WSM}^{*} = \max_{i} \sum_{j}^{N} a_{ij} w_j \, ; \quad i = 1,2,3, \ldots , M$$

Here $A_{WSM}^{*}$ is the WSM score of the best alternative, $a_{ij}$ is the actual value of the $i^{th}$ alternative in terms of the $j^{th}$ criterion, and $w_j$ is the weight of importance of the $j^{th}$ criterion where $\sum w_j = 1, \; w_j \geq 0$. A difficulty with this method emerges when it is applied to multi-dimensional decision making problems. In combining different dimensions and units, the additive utility assumption is violated (Sones, 2003).

### 4.2.2 Weighted product method (WPM)

The WPM is very similar to the WSM with the main difference that, instead of addition in the model, there is multiplication. The alternatives are compared with each other by multiplying a number of ratios, one for each criterion. Each ratio is raised to the power of the relative weight of the corresponding criterion. According to the following, the ratios could be determined:

Equation 4:

$$R(A_K/A_L) = \sum_{j=1}^{N} \left( \frac{a_{Kj}}{a_{Lj}} \right)^{w_j}$$

In this case, $N$, similar to the previous method, is the number of criteria, $a_{ij}$ is the actual value of the $i^{th}$ alternative in terms of the $j^{th}$ criterion, and $w_j$ is the weight of importance of the $j^{th}$ criterion for $w_j \geq 0$. If $R(A_K/A_L)$ is greater than 1, then it means that the alternative $A_K$ is more desirable than $A_L$ (in the maximization case), and the best alternative is then the one that is better than or at least equal to all the other alternatives.

### 4.2.3 Analytical hierarchy process (AHP)

The essence of the AHP is the decomposition of a complex problem into a hierarchy with the objective at the top, criteria and sub-criteria at levels and sub-levels of the hierarchy, and decision alternatives at the bottom. Elements at given levels of the hierarchy are compared in pairs to assess their 'relative preference' in respect to each of the elements at the next higher level. The method compares and aggregates eigenvectors until the final vector for weight coefficients is obtained. The final vector then reflects the relative importance of each alternative with respect to the goal stated at the top hierarchy (Saaty, 1980).

This process could be decomposed into the following steps (Saaty, 2008):

a) Define the problem and determine the kind of knowledge sought.

b) Structure the decision hierarchy from the top with the goal of the decision, then the objectives from a broad perspective, through the intermediate levels (criteria on which subsequent elements depends) to the lowest level (which usually is a set of the alternatives).

c) Construct a set of pairwise comparison matrices. Each element in an upper level is used to compare the elements in the level immediately below with respect to it. The values in Table 4.1 are used to allocate an importance, or the intensity thereof, to each of the said criterion. The multiple pairwise comparison of the AHP, are based on this standardized scale of nine levels.

d) Use the priorities obtained from the comparisons to weigh the priorities in the level immediately below for every element. Then for each element in the level below, add its weighed values and obtain its overall or global priority. Continue this process of weighing and adding until the final priorities of the alternatives in the bottom most level are obtained.

Table 4.1: The fundamental scale of absolute numbers used in the AHP

| II* | Definition |
|---|---|
| 1 | Equal importance |
| 2 | Weak or slight |
| 3 | Moderate importance |
| 4 | Moderate plus |
| 5 | Strong importance |
| 6 | Strong plus |
| 7 | Very strong or demonstrate importance |
| 8 | Very, very strong |
| 9 | Extreme importance |

* Intensity of importance

### 4.2.4 Preference ranking organization method for enrichment evaluation

The PROMETHEE (Preference ranking organization method for enrichment evaluation) method uses the outranking principle in the ranking of alternatives (Pohekar & Ramachandran, 2004). It compares alternatives pairwise in order to rank them with respect to a number of criteria $J$. The method uses the preference function $P_j(a,b)$, which is a function of the difference $d_j$ between two alternatives $a$ and $b$ for a particular criterion $j$. There are an indifference threshold $q'$ and a preference threshold $p'$ which both depend on the type of criteria function. This implies that two alternatives may be different for criterion $j$ as long as $d_j$ does not exceed the indifference threshold, and if $d_j$ becomes greater than $p'$, there is a strict preference. A multi-criteria preference index $\pi(a,b)$, a weighted average of the preference functions $P_j(a,b)$ may be defined as follows:

Equation 5:

$$\pi(a,b) = \frac{\sum_{i=1}^{J} w_j P_j(a,b)}{\sum_{j=1}^{J} w_j}$$

The outranking index of $a$ is $\phi^{+}(a)$, and the outranked index of $a$ in the alternative set $A$ is $\phi^{-}(a)$, where $\phi(a)$ is the net ranking of $a$. These expressions are as follows:

$$\phi^{+}(a) = \sum\nolimits_{A} \pi(a,b)$$
$$\phi^{-}(a) = \sum\nolimits_{A} \pi(a,b)$$
$$\phi(a) = \phi^{+}(a) - \phi^{-}(a)$$

Here $w_j$ is the weight assigned to the criterion $j$. The maximum value of $\phi(a)$ is considered as the best. It can then be said that $a$ outranks $b$ if $\phi(a) > \phi(b)$, and $a$ is indifferent to $b$ if $\phi(a) = \phi(b)$.

### 4.2.5 Elimination and choice translation reality (ELECTRE)

This is a method which can accommodate both quantitative and qualitative discrete criteria, and provides compete ranking/ordering of alternatives (Pohekar & Ramachandran, 2004). The problem needs to be formulated so that it chooses alternatives which are preferred according to most of the criteria in order to prevent an unacceptable level of discontent. Concordance, discordance and threshold values are determined, evaluated and graphs are developed for the strong and weak relationships, based on the indices. The index of global concordance is given by the equation below, and it supports the concordance among all criteria, where $w_j$ is the weight associated with the $j^{th}$ of $m$ criteria:

Equation 6:

$$C_{ik} = \frac{\sum_{j=1}^{m} w_j c_j(A_i A_k)}{\sum_{j=1}^{m} w_j}$$

The ELECTRE method yields a whole system of binary outranking relations between the alternatives. Since this system is not necessarily complete, the ELECTRE method is sometimes unable to identify the most favoured alternative, but only provides a score of leading alternatives.

### 4.2.6 Technique for order preference by similarity to ideal solutions

TOPSIS is the technique for order preference by similarity to ideal solutions. This method was developed as an alternative to the ELECTRE method (Hwang & Yoon, 1981). The basic concept of this method is that the selected alternative should have the shortest distance to the ideal solution in a geometric sense, but this method is discussed in more detail in the section dealing with multi-attribute decision making.

### 4.2.7 Compromise programming (CP)

This method defines the best solution in the set of efficient solutions, where the best option is closest to the ideal point. The distance measure in this case is the family of $L_p$ metrics and is given as:

Equation 7:

$$L_p(a) = \sum_{j=1}^{j} w_j^p \left|f_j^* - f(a)\right| / \left|M_j - m_j\right|$$

$L_p(a)$ is the $L_p$ metric for alternative $a$, $f(a)$ is the value of the criterion $j$ for alternative $a$, $M_j$ is the maximum (ideal) value of criterion $j$ in set $A$, $m_j$ is the minimum (anti-deal), $w_j$ is the weight of criterion $j$, $p$ is the parameter reflecting the attribute of the decision maker with respect to the compensation between deviations, and $f_j^*$ is the ideal value of criterion $j$.

### 4.2.8 Multi-attribute utility theory (MAUT)

This theory takes into consideration the decision maker's preferences by defining a utility function over a set of attributes. The utility value may be determined by means of single attribute utility functions. The verification of preferential and utility independent condition s and the derivation of multi-attribute utility functions are also considered. The different utility functions can be additively or multiplicatively separable with respect to the single attribute utility. The multiplicative form of the utility equation is represented by the following:

Equation 8:

$$1 + ku(x_1, x_2, \dots, x_n) = \prod_{j=1}^{n} \left(1 + kk_j u_j(x_j)\right)$$

Where $j$ is the index of the attribute, $k$ is the overall scaling constant and $k \geq -1$, $k_j$ is the scaling constant for attribute $j$, $u(x_1, x_2, \dots, x_n)$ is the overall utility function operator and $u_j(x_j)$ is the utility function operator for each attribute $j$.

### 4.2.9 MADM vs. MODM

The class of MCDA methods can further be divided into multi-objective decision making (MODM) methods and multi-attribute decision making (MADM) methods. The difference between MODM and MADM is summarized in the following table (Agrawal, Kohl, & Gupta, 1991):

Table 4.2: A comparison between MADM and MODM

**Different multiple criteria decision analysis methods:**

| **Discriptions:** | | MADM | MODM |
|---|---|---|---|
| Criteria | 1 | Attributes | Objectives |
| Objectives | 2 | Implicit | Explicit |
| Attribute | 3 | Explicit | Implicit |
| Constraint | 4 | Interactive (Incorporated into attributes) | Active |
| Alternatives | 5 | Finite in number and discrete | Infinite in number and continuous (emerging) |
| Interactive with DM | 6 | Not so much | Mostly |
| Usage | 7 | Selection/evaluation | Design |

The MODM consists of a set of conflicting goals that cannot be achieved simultaneously, and it concentrates on continuous decisions. Mathematic programming techniques may often be of great help in solving MODM and it generally involves (Yang, Chen, & Hung, 2007):

1. Preference in accordance to the decision maker's (DM) objectives.
2. Relationships between objectives and attributes.

MADM deals with the problem of choosing among a set of alternatives that are characterized in terms of their attributes. It is a quantitative approach due to the existence of criteria subjectivity and requires information about the preferences of an attribute among a group of possibilities as well as preferences across the existing attributes (Yang, Chen, & Hung, 2007). MADM refers to a problem solving approach for problems involving selection from among a finite number of alternatives and is a procedure that specifies how attribute information is to be processed in order to arrive at a choice. It also supports decision making when multiple conflicting criteria are present.

## 4.3 Multiple attribute decision making

MADM refers to a problem solving approach for problems where the selection from among a finite number of alternatives is of concern and it is a procedure which specifies how attribute information is to be processed in order to arrive at a decision (Agrawal, Kohl, & Gupta, 1991). In a multiple criteria decision making (MCDM) problem, a decision maker has to rank and select alternatives associated with conflicting attributes. All MADM problems may be said to encompass the following three main characteristics (Hwang & Yoon, 1981):

- Each problem has multiple attributes and the decision maker must generate relevant attributes for the problem under consideration.
- Multiple criteria involved in the problem are usually conflicting in nature.
- Each attribute may have a different unit of measurement.

The main aspects of a MADM approach include: identifying the assessment hierarchy consisting of criteria and sub-criteria, determining the relative weights of the elements of hierarchy and comparing the various alternatives according to the identified criteria and ranking them in order of preference (Yang, Chen, & Hung, 2007). A problem can then also be classified into three categories according to the different forms of preference information given by the decision maker (Fan, Ma, & Zhang, 2002):

- Without preference information given by the decision maker.
- With information about the attributes.
- With information on the alternatives.

Current approaches for MADM problems with preference information on alternatives include the interactive simple additive weighting (SAW) method, the multi-dimensional scaling (MDS) with ideal point, and linear programming techniques for multi-dimensional analysis of preference (LINMAP).

### 4.3.1 MADM formulation

The MADM can be explained by the following notation (Fan, Ma, & Zhang, 2002):

- The alternatives are known: Let $S = S_1, S_2, \dots, S_m$ denote a discrete set of $m \geq 2$ possible alternatives.

- The attributes are known: Let $P = P_1, P, \dots, P_n$ denote a set of $n \geq 2$ attributes.
- The respective weights of attributes are known: Let $w = (w_1, w_2, \dots, w_n)^T$ be the vector of weights, where $\sum_{j=1}^{n} w_j = 1$, $w_j \geq 0$, $j = 1,2, \dots n$ and $w_j$ denotes the weight of attribute $P_j$.
- The decision matrix is known: Let $A = \left[a_{ij}\right]_{m\times n}$ denote the decision matrix where $a_{ij} \geq 0$ is the consequence with a numerical value for alternative $S_i$ with respect to attribute $P_j$, $(i = 1,2, \dots, m)$, $(j = 1,2, \dots, n)$.

### 4.3.2 Normalization of attributes

In the decision matrix $A$, every $a_{ij}$ is an objective value between 0 and 1 which allows each attribute to have the same measurement range. In order to achieve this, the elements in the matrix $A$ have to be normalized into a corresponding element in matrix $B = \left[b_{ij}\right]_{m\times n}$. The following method may be used (Ma, Fan, & Huang, 1999):

For benefit attributes:

Equation 9:

$$b_{ij} = \frac{a_{ij} - a_j^{min}}{a_j^{max} - a_j^{min}}; \quad i = 1,2, \dots, m; \quad j = 1,2, \dots, n$$

For cost attributes:

Equation 10:

$$b_{ij} = \frac{a_j^{max} - a_{ij}}{a_j^{max} - a_j^{min}}; \quad i = 1,2, \dots, m; \quad j = 1,2, \dots, n$$

Where $a_j^{max} = max\{a_{1j}, a_{j2}, \dots, a_{mj}\}$ and $a_j^{min} = min\{a_{1j}, a_{j2}, \dots, a_{mj}\}$. This method is applicable when the differences in performance measures are not significantly large. The decision maker can then choose $M < m$ most preferred alternatives $S^*$ from the set $S$, $S^* \subset S$ (Ma, Fan, & Huang, 1999).

An alternative normalization approach that is widely accepted is the vector normalization:

Equation 11:

$$b_{ij} = \frac{a_{ij}}{\sqrt{\sum_{i=1}^{m} a_{ij}^2}}; \quad i = 1,2, \dots, m; \quad j = 1,2, \dots, n$$

### 4.3.3 Selection of an alternative using the SAW method

The simple additive weighting method is one of the most commonly known and widely used MADM methods (Hwang & Yoon, 1981). The overall value of an alternative, according to the SAW method, can be expressed as (Ma, Fan, & Huang, 1999):

Equation 12:

$$\varphi(S_i) = \sum_{j=1}^{n} w_j\, b_{ij}; \quad i = 1,2, \dots, m$$

The chosen alternative, $S^*$ is then of such nature that $\varphi(S^*) \geq \varphi(S_i)$ for all $i$.

### 4.3.4 The TOPSIS method of selection

The technique for ordered preference by similarity to the ideal solution (TOPSIS) was developed by Hwang & Yoon (1981). This method is based on the concept that the chosen alternative should have the shortest distance from the positive ideal solution and the longest distance from the negative ideal solution. It forms part of the ELECTRE methods, relying on outranking relations to rank a set of alternatives (Wang & Triantaphyllou, 2008).

Three TOPSIS methods may be identified: the Manhattan distance, Euclidean distance and the Tchebycheff distance (Méndez, Galvan, Salazar, & Greiner, 2006). The Euclidean distance is found most relevant and is therefore discussed in more detail. The TOPSIS procedure may be explained according to the following series of steps (Jahanshahloo, Lotfi, & Izadikhah, 2006).

**Step 1**: Calculate the normalized rating for each element of the decision matrix.

Equation 13:

$$n_{ij} = \frac{x_{ij}}{\sqrt{\sum_{i=1}^{m} x_{ij}^2}}; \quad i = 1,2, \dots, m; \quad j = 1,2, \dots, n$$

In the above equation there are $m$ alternatives and $n$ different attributes. Here $x_{ij}$ is the element in row $i$ and column $j$.

**Step 2**: Calculate the weighted normalized ratings.

Equation 14:

$$v_{ij} = w_j n_{ij}; \quad i = 1,2, \dots, m; \quad j = 1,2, \dots, n$$

Where $w_j$ is the weight associated with the $j^{th}$ attribute or criterion and $\sum_{j=1}^{n} w_j = 1$ for $w_j \geq 0$.

**Step 3**: Identify positive ideal ($A^*$) and negative ideal ($A^-$) solutions. These solutions are defined in terms of the weighted normalized values as:

Equation 15 and 16:

$$A^* = \{v_1^*, v_2^*, \dots, v_n^*\} = \left\{\left(\max_i v_{ij} \,\middle|\, j \in I\right), \left(\min_i v_{ij} \,\middle|\, j \in I\right)\right\}$$
$$A^- = \{v_1^-, v_2^-, \dots, v_n^-\} = \left\{\left(\min_i v_{ij} \,\middle|\, j \in I\right), \left(\max_i v_{ij} \,\middle|\, j \in I\right)\right\}$$

Where $I$ is associated with benefit criteria and $J$ is associated with the cost criteria.

**Step 4**: Calculate the Euclidean distances as separation measures. The positive ideal is given by:

Equation 17:

$$d_i^* = \left\{\sum_{j=1}^{n} \left(v_{ij} - v_j^*\right)^2\right\}^{\frac{1}{2}}; \quad i = 1,2, \dots, m$$

The negative ideal is then given by:

Equation 18:

$$d_i^- = \left\{\sum_{j=1}^{n} \left(v_{ij} - v_j^-\right)^2\right\}^{\frac{1}{2}}; \quad i = 1,2, \dots, m$$

**Step 5**: Calculate the similarities to the ideal solution. With:

Equation 19:

$$R_i = \frac{d_i^-}{d_i^* + d_i^-}; \quad i = 1,2, \dots, m$$

**Step 6**: With this index, values and the associated alternatives can be ranked in decreasing order, with the best alternatives at the top of the list. The TOPSIS method then not only gives a solution which is closest to the hypothetically best option, but also the farthest from the hypothetically worst.

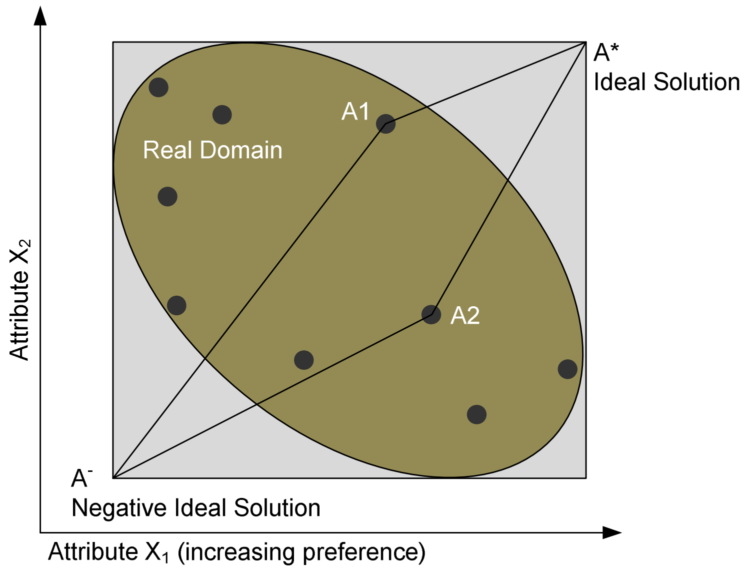


Figure 4.1: The TOPSIS method with two attributes considered

This is illustrated in Figure 4.1, where two attributes have been considered and plotted against each other. The black dots represent $R_i$ values. When comparing $A1$ to $A2$, $A1$ is better since the distance to the negative ideal, $A^-$, is longer and $A1$ is also closer to the positive ideal, $A^*$ (Agrawal, Kohl, & Gupta, 1991).

## 4.4 Ranking irregularities

Often, different multiple criteria methods may yield different answers to the same problem, which is a potential problem and drawback. The ELECTRE family of MCDA, strongly relying on outranking methods, may also provide different rankings (Wang & Triantaphyllou, 2008). There exist different evaluation techniques and comparisons to decide on the 'best' multi-criteria method. Three test criteria may be established to test the relative performance of various MCDA methods (Wang & Triantaphyllou, 2008). For the purpose of this study, these ranking techniques will not be discussed in detail, however, in concluding which of the above mentioned techniques would be most suitable to address the problem statement, they were considered.

## 4.5 The matter of weighting in MADM

The crucial problem in MADM is to assess the relative importance of attributes. Different criteria or performance measures in this case, are assigned weights in order to express preference/importance. The result of the multiple criteria decision analysis will most likely depend on the weighting (Du Plessis & Bekker, 2008). Weighting is done according to preference and is therefore subjective. If several decision makers are involved, it is most likely that there will be differences about the weights assigned to the criteria. However, by performing a sensitivity and robustness analysis (Drechsler, 2004) it is possible to reduce the subjectivity of the weight selections.

Subjective and objective approaches may be used. Subjective approaches select weights based on the preference information of attributes given by the decision maker. Objective approaches include principal element analysis, the entropy method and multiple objective programming. An integrated approach of both objective and subjective information is provided by Ma *et al*. (1999).

chapter | five

# 5 ECONOMIC EVALUATION PRINCIPLES

In this chapter the principles and the techniques to evaluate the economics of chemical processes, will be investigated and studied. Within this chapter, the term economics refers to the evaluation of capital costs and operating costs associated with the construction and operation of a processing plant. As an introduction to this chapter, some time will be spent on explaining the anatomy of a chemical manufacturing process, because an understanding of the various stages would form the platform of the economic evaluation.

## 5.1 Anatomy of a chemical manufacturing process

The basic components of a typical chemical process are shown in Figure 5.1, in which each block represents a stage in the overall process for producing the final product from the raw materials. This figure represents a generalized process, so not all of the stages might be needed for any particular process and the complexity of each stage will depend on the nature of the process. Chemical engineering design is concerned with the selection and arrangement of the various stages, the selection, specification and design of the equipment required to perform the stage functions (Sinnott, 2004).

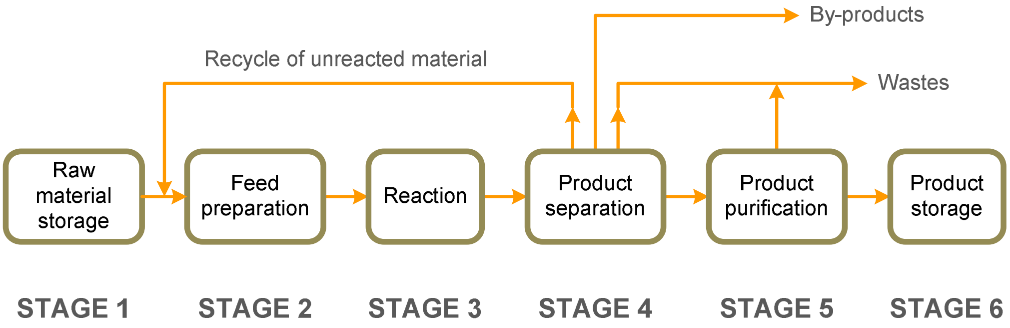


Figure 5.1: Anatomy of a chemical process with the six manufacturing stages

The various stages and their respective functions are introduced in the following paragraphs:

- **Stage 1:** Raw materials storage. Unless the raw materials are supplied as intermediate products from a neighbouring plant, some provision must be made to hold several days, or sometimes even weeks, storage to smooth out disturbances and interruptions in the supply. Even when the materials come from an adjacent plant, it is common practice to also install a buffering system with raw material storage capacity, to decouple the processes. The storage requirements will depend on the nature of the raw materials, the method of delivery and what assurance can be placed on the continuity of supply.
- **Stage 2:** Feed preparation. Some purification and preparation of the raw materials will usually be necessary before the raw material is sufficiently pure, or in the appropriate form and size, to be fed to the reaction stage. During this stage, several impurities might be removed, the feed could be milled to a specific required particle size distribution or a phase change needed and achieved.
- **Stage 3:** Reactor. The reaction stage is the heart of chemical manufacturing processes. In the reactor the prepared raw materials are allowed to react with each other under carefully designed and controlled conditions that promote the production of the desired product. Unwanted species are normally also formed during the reaction stage, which require further processing steps if it iis decided to

produce by-products, if economically viable, and environmentally friendly waste, if not[10].

- **Stage 4:** Product separation. In this first stage following the reactor, the products and by-products are separated from any unreacted material, which, if in sufficient quantity, can be recycled. This recycled unreacted material could either be returned directly to the reactor or to the feed preparation stage. The recycling of unreacted product is an important part of the overall plant design to ensure that the reaction conversion and the formation of product be financially attractive.
- **Stage 5:** Purification. Before the product can be shipped or transported to a point of sale, it usually needs a final purification stage to meet the required product specifications. As mentioned earlier, if the by-products are produced in economic quantities they would also be purified at this stage.
- **Stage 6:** Product storage. For a similar reason as the raw material storage, the final product is normally stored to match production with sales, depending on the nature of the product and the market. Provision of product packaging and transport will also be needed, depending on the nature of the product.

## 5.2 Understanding process conditions

It is not uncommon to investigate process economics based on assumed process performance. Stream specifications and process conditions are influenced by physical processes as well as economic consideration and are not chosen arbitrarily. The conditions used in a process most often represent an economic compromise between process performance and the capital and operational costs of the process equipment (Turton, Bailie, Whiting, & Shaeiwitz, 2003). In this section, process conditions are analyzed that require special considerations.

---

[10] Virtually all chemical processes produce waste streams and in these industrial times, with governmental and international focus on sustainable development, the environmental impact of a chemical manufacturing plant is an important consideration. The waste streams include gases, liquids and solids that must be treated prior to being discharged to the atmosphere or sequestered in landfills. The streams may contain unreacted materials, chemicals produced by side reactions, fugitive emissions, impurities coming in with the feedstock and the reaction products.

### 5.2.1 Pressure

There are economic advantages associated with operating equipment at above ambient pressure when gases are present. These result from the increase in gas density with increasing pressure. This means that the process equipment for the same fluid residence time need not be as large when the pressure is increased and everything else is kept constant.

Most chemical processing equipment can withstand pressures up to 10 bar without much additional capital investment. At pressures above 10 bar, thicker walled and generally more expensive equipment is required; similarly, operating in vacuum conditions tends to make equipment large and needs special construction techniques (Turton, Bailie, Whiting, & Shaeiwitz, 2003). Both options result in increasing the cost of equipment.

### 5.2.2 Temperature

There are several critical temperature limits that apply to chemical processes. At elevated temperatures, common construction materials suffer a significant drop in physical strength and must be replaced by more costly materials. For example, at operating temperatures of 550°C, carbon steel has a maximum allowable tensile strength of about 15% of its ambient characteristics and for stainless steel, about 33%. It is thus clear that, carbon steel is unacceptable and stainless steel severely limited as structural material at 550°C (Askeland & Phulé, 2003). For any options and alternatives, which require higher temperatures, more expensive alloys are needed and most equipment may have to be refractory lined.

Thus, if elevated temperatures are required, one must be able to justify the economic penalty associated with more complicated processing equipment. Also, at temperatures above 400°C and below a critical minimum, the availability of common utilities for heating and cooling a process stream becomes another problem. Generally, these two utility options are available (Turton, Bailie, Whiting, & Shaeiwitz, 2003):

- **Steam**: High pressure steam at 40 to 50 bar is commonly available and provides heat at 250 to 265°C at most industrial plants. Above these temperatures, additional costs are involved.

- **Water**: Water from a cooling tower is normally available at about 30°C. Again, for utilities below this temperature, costs increase because of refrigeration needs and as the temperature decreases, the costs increase dramatically. If cryogenic conditions are necessary, there may be an additional need for expensive materials of construction.

## 5.3 Estimation of capital costs

In the following section, the background and the recommended technique to use in the estimation of process capital costs are introduced.

### 5.3.1 Classification of capital cost estimates

Capital cost pertains to the costs associated with construction of a new plant or modification to an existing chemical manufacturing plant and in this section the fundamentals of estimating these costs will be discussed. There are generally five accepted classifications of capital cost estimates that are most likely to be encountered in the process industries (Peters & Timmerhaus, 1991):

1. **Ratio or Feasibility estimate:** This type of estimate typically relies on cost information for a complete process taken from previously built plants. This cost information is then adjusted using appropriate scaling factors, for capacity and for inflation, to provide the estimated capital cost.
2. **Major or Factor estimate:** This classification utilizes a list of the major equipment found in the process. This includes all pumps, compressors and turbines, columns and vessels, fired heaters and exchangers. Each piece of equipment is roughly sized and the approximate cost determined. The total cost of equipment is then factored to give the estimated capital cost.
3. **Scope estimate:** This type requires more accurate sizing of equipment than used in the factor estimate. In addition, an approximate layout of equipment is made along with estimates of piping, instrumentation and electrical requirements. Utilities are also estimated.

4. **Project Control estimate:** This is an estimation based on the preliminary specification for all the equipment, utilities, instrumentation, electrical and off-sites.
5. **Firm or Contractor's estimate:** This type of estimate requires complete engineering of the process and all related off-sites and utilities. Vendor quotes for all expensive items will have to be obtained. At the end of this detailed estimate, the plant is ready to go to the construction stage.

### 5.3.2 Estimation of purchased equipment costs

To calculate and determine an estimate of the capital cost of a chemical plant, the costs associated with the major plant equipment must be known. The equipment required can usually be divided into: 1) process equipment, 2) equipment for handling and storage of raw materials and 3) finished products handling and storage equipment. The most accurate estimate of the purchased cost of a piece of equipment is obviously provided by a current quotation from a suitable vendor, with the next best alternative, to use cost data on previously purchased equipment of the same type. Another technique, sufficiently accurate for major or factor cost estimates, utilizes summary graphs available for various types of common equipment (Turton, Bailie, Whiting, & Shaeiwitz, 2003).

The cost data must then be adjusted for any differences in unit capacity and also for any elapsed time since the cost data was generated. The most common simple relationship to account for attribute differences is given by:

Equation 20:

$$\frac{C_a}{C_b} = \left(\frac{A_a}{A_b}\right)^n$$

$A$ is the equipment cost attribute, $C$ the purchased cost and $n$ is the cost exponent which varies depending on the class of equipment being represented. The subscripts $a$ and $b$ refer to the equipment with the required and the base attribute respectively. According to Turton *et al.* (2003) the generalized version of the above equation, called the six-tenths-rule because of $n = 0.6$, should be used with care for a single piece of equipment . The use of this rule for a total chemical process is more reliable.

Lastly, before the methods used to estimate the total capital cost of a plant be introduced, the effect inflation has on the purchased cost should be discussed. All cost-estimating methods use historical data and are themselves forecasts of future costs. The method (Sinnott, 2004) usually used to update this data makes use of published cost indices. These indices relate present costs to past costs and are based on data for labour, material and energy costs published in governmental statistical journals. The most generally accepted are the Marshall and Swift Equipment Cost Index (MSECI) and the Chemical Engineering Plant Cost Index (CEPCI) as given in Figure 5.2.

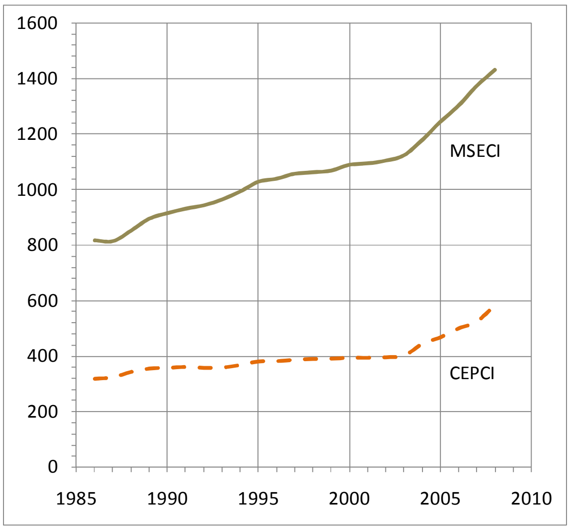


Figure 5.2: The Marshall and Swift Equipment Cost Index (MSECI) and the Chemical Engineering Plant Cost Index (CEPCI) from 1986 to 2008[11]

Within the context of this research, the CEPCI will be used to update the capital costs according to the following equation, with $C$ the purchased cost and $I$ the appropriate cost index value. The subscripts, 1 and 2, relate to the base time when the cost is known and the time when the cost is desired, respectively.

Equation 21:

$$C_2 = C_1\left(\frac{I_2}{I_1}\right)$$

All cost indices should be used with caution and judgement, because they do not necessarily relate the true make-up of costs for any particular piece of equipment or plant

---

[11] SOURCE: All index data obtained from the Chemical Engineering journal, www.che.com, August 2008.

and do not take into account the effect of supply and demand on prices. The longer the period over which the correlation is made the more unreliable the estimate (Sinnott, 2004).

## 5.4 Calculating total capital cost of a plant

Besides the purchased cost of the equipment, the total capital cost for a chemical plant must take into account many other costs. The following factors, with their respective symbols as used in the calculation, affect the costs associated with the total capital cost of a plant (Peters & Timmerhaus, 1991):

Direct project expenses:

a) $C_P$ is the purchased cost of equipment delivered at the manufacturer's site. Also known as the equipment FOB (free on board).

b) $C_M$ is the cost of materials required for installation. It includes all piping, insulation and fireproofing, foundations and structural supports, instrumentation and electrical, together with the painting associated with the process equipment.

c) $C_L$ refers to all labour cost associated with installing the equipment and material mentioned in (a) and (b).

Indirect project expenses:

a) $C_{FIT}$ includes all transportation costs for shipping equipment and materials to the plant site, all insurance on the items shipped and any purchase taxes that may be applicable.

b) $C_O$ is the cost associated with all fringe benefits such as vacation, sick leave retirement benefits etc. Labour burden such as social security and unemployment insurance, salaries and overhead for supervisory personnel.

c) $C_E$ refers to the contractor engineering expenses, which includes the salaries and overheads for the engineering, drafting and project management personnel on the project.

Contingency and fee:

a) $C_{Cont}$ is a factor to cover unforeseen circumstances. These may include loss of time due to storms and strikes, small changes in the design and unpredicted price increases.

b) $C_{Fee}$ varies depending on the type of plant and a variety of other factors.

Auxiliary facilities:

a) $C_{Site}$ includes the purchase of land; grading and excavation of the site and other preparations; installation of electrical, water and sewer systems; construction of all internal roads, walkways and parking lots.

b) $C_{Aux}$ is the costs involved in erecting administration offices, maintenance shop and control rooms, warehouses and service buildings.

c) $C_{Off}$ includes raw material and final product storage; raw material and final product loading/unloading facilities; all equipment necessary to supply required process utilities; central environmental control facilities, such as wastewater treatment, incinerators and flares; and fire protection system.

Two methods, Lang Factor Techniques and the Module Costing Technique, to calculate and estimate the total capital cost will now be introduced.

### 5.4.1 Lang Factor technique

This is a simple technique to estimate the capital cost of a chemical plant, formulated by Lang (Lang, 1947). The total cost is determined by multiplying the total purchased cost for all the major items of equipment, those shown in the process flow diagram, by a constant, which is called the Lang Factor. The capital cost calculation is determined using the following equation:

Equation 22:

$$C_{TM} = F_{Lang} \sum_{i=1}^{n} C_{p,i}$$

$C_{TM}$ is the total module capital cost of the plant, $C_{p,i}$ the purchased cost for the major equipment units and $n$ is the total number of individual units. The Lang Factor, takes on one of either three values, for fluid processing plants 4.74, solid-fluid processing plants 3.63 and for solid processing plants 3.10. One of the main disadvantages of this estimating technique is the fact that it is insensitive to changes in process configurations, especially between processes in the same broad categories (fluid, solid-fluid or solid). It also cannot account for common problems of special materials of construction and high-operating pressures.

### 5.4.2 Module Costing technique

The equipment module costing technique is commonly used to estimate the cost of a new chemical plant. According to Turton (2003), it is generally accepted as the best for making preliminary cost estimates and will thus be used extensively in this research project. Originally, developed by Guthrie (1969), it forms the basis of many of the equipment module techniques in use today (Guthrie, 1969).

This technique relates all costs back to the purchased cost of equipment evaluated for some base conditions and deviations from these base conditions are handled by using multiplying factors depending on the equipment type, the system pressure and the specific materials of construction. The following equation is applicable when using this technique:

Equation 23:

$$C_{BM} = C_p^o F_{BM} = C_p^o (B_1 - B_2 F_M F_P)$$

Here $C_{BM}$ is the bare module equipment cost, direct and indirect costs for each unit. $F_{BM}$ is the bare module cost factor, which is a multiplication factor to account for the factors (direct, indirect, contingency and auxiliary) as listed earlier, plus the specific materials of construction and operating pressure. $C_p^o$ is the purchased cost for base conditions, available in academic references (Turton, Bailie, Whiting, & Shaeiwitz, 2003). The values of the constants $B_1$ and $B_2$ can be found in relevant literature, with $F_M$ and $F_P$ the correctional factors to determine the bare module cost factor for nonbase case conditions.

chapter | six

# 6 DESIGN OF TECHNO-ECONOMIC EVALUATION

The theoretical platform has been cemented in chapters 4 and 5. The theory and fundamentals of decision making have been studied, together with the appropriate economic evaluation principles to form a theoretical basis for this framework. Also, the complete titanium value chain has been investigated, from the mining and mineral processing steps, the extraction and refinement of the metal to the processing steps to obtain the final product.

> “Take time to deliberate, but when the time for action has arrived, stop thinking and go in.”
>
> **NAPOLEON BONAPARTE**

In this chapter the techno-economic evaluation is designed and formulated, the filtering methodology is introduced and the details of the framework with all the decision criteria, explored.

## 6.1 Introduction and filtering methodology

The filtering methodology could be summarized into the following four steps, designed around a 2-Phase Filtering System, incorporating qualitative and a quantitative assessment, as well as an estimation of several economic indicators. Analytic data assessment techniques such as the AHP and TOPSIS, see section 4.2, were used to design the decision framework and formulate the specific weights or priorities.

a) **PROCESS FEED PREPARATION:** Investigate the existing processes, Kroll and Hunter, and summarize the emerging alternatives. This is the preparation of the feed, just before entering the filtering system. It involves the systematic research and documentation of relevant details related to the process alternatives.

b) **FILTERING STAGE A:** This is the qualitative assessment partially based on Van Vuuren's comparative framework pivoting around the costs or value of the feedstock, the reduction agent and the final product (Van Vuuren, 2008). The total number of alternatives to produce titanium metal is currently approximately 24 and if the two existing ones, the Kroll and Hunter processes, are included it brings the total to 26. On a qualitative basis, these processes are assessed and 12 options selected, again including the two existing ones, as can be followed in Figure 6.1.

c) **FILTERING STAGE B:** This stage is mostly a quantitative assessment, constructed on the hypothesis that the appropriate and carefully selected decision criteria be an accurate negotiation to bridge the research impossibility in deriving detailed values for a large population of process alternatives. Critical reviews of alternatives made by industrial experts were partially used to establish a systematic and completed scorecard to assess some of the evaluation criteria, such as the complexity of each process alternative. The output of this filtering stage is a final ranking of the selected 12 alternatives.

d) **SENSITIVITY ANALYSIS:** This 2-Phase Filtering System is followed by a sensitivity analysis on the key decision criteria, the local (Sensitivity Analysis A) and global (Sensitivity Analysis B) parameters. This analysis must be completed to observe the sensitivity and effect disturbances have on the intermediate products and the final recommendation.

## 6.2 The 2-Phase Filtering System

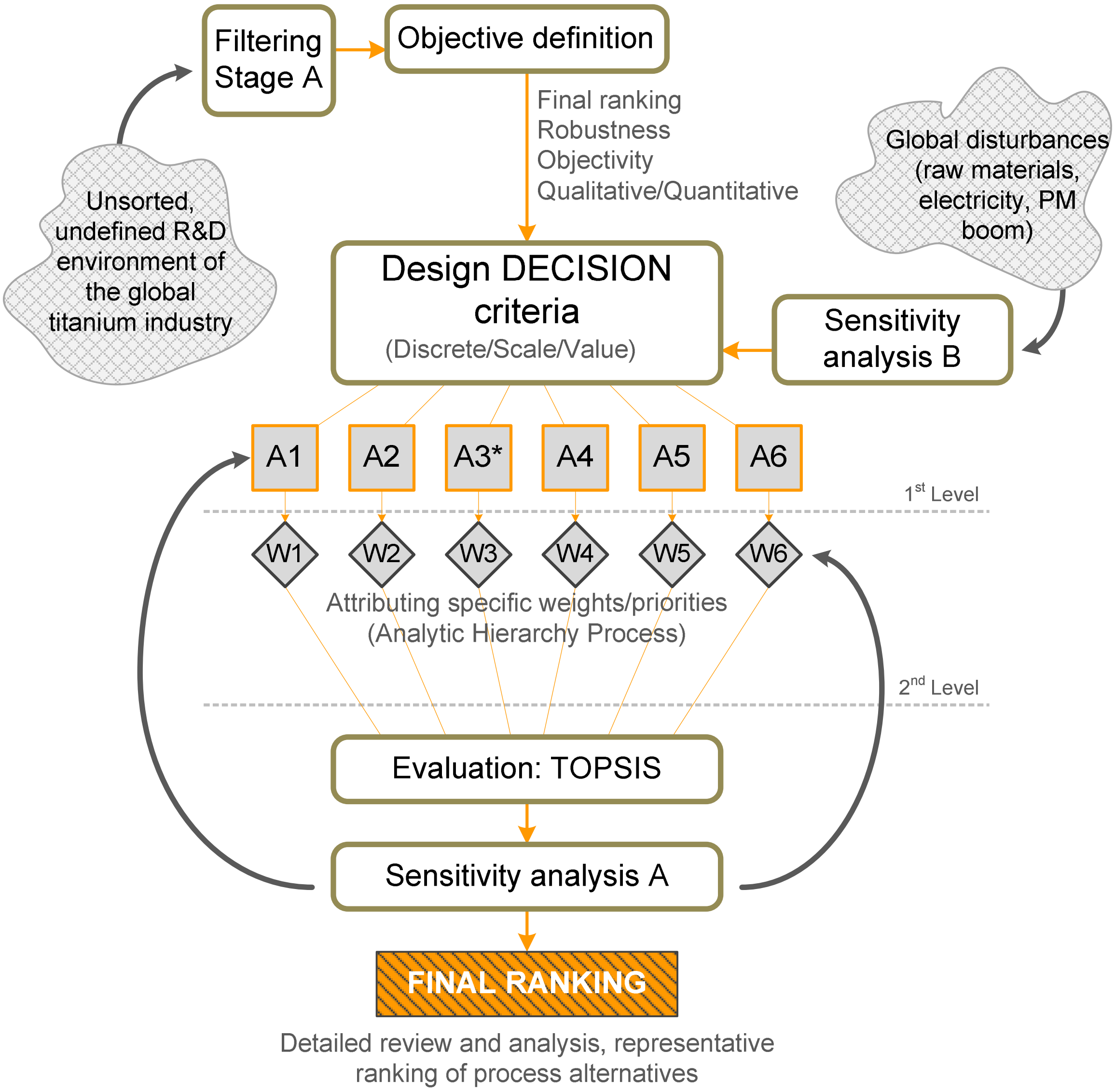


Figure 6.1: Schematic diagram of the decision framework: The 2-Phase Filtering System

Based on both qualitative and quantitative techniques, a 2-Phase Filtering System, as seen in Figure 6.1, was designed to assess, evaluate and formulate a final ranking, together with a detailed sensitivity analysis of both local and global parameters.

## 6.3 FILTERING STAGE A: Initial screening

Several different pathways are possible and most have been explored, encountered a variety of difficulties and are currently struggling to address these. The framework used as the Filtering Stage A is shown in Figure 6.2 with the selection of the processes to be further investigated, numbered. Currently the preferred and used industrial process is the Kroll process, as mentioned and discussed in section 7.2.1, that entails the reduction of $TiCl_4$ with Mg in a batch-like manner. Various precursors can be reduced using any one of a number of different reducing agents to produce a product that is either in sponge, powder or in a fully consolidated form, ingot.

### 6.3.1 Introduction and brief overview of framework

Van Vuuren (2008) developed a rational basis to evaluate some of the alternative processes, which was done by comparing the underlying fundamentals that ultimately determine the costs and benefits of the various proposed processes. Thus, before the techno-economic evaluation criteria are introduced, it would be sensible to explain and discuss this comparative framework, because it also functions as a solid foundation and rationale to work from.

The index for Figure 6.2: 1) Armstrong/ITP, 2) Cardarelli (QIT Fer et Titane), 3) FFC Cambridge, 4) Ginatta Process, 5) Idaho Titanium Technologies, 6) MER Corporation, 7) OS Process, 8) Peruke, 9) SRI International, 10) TiRO (CSIRO), 11) Kroll and 12) Hunter Process.

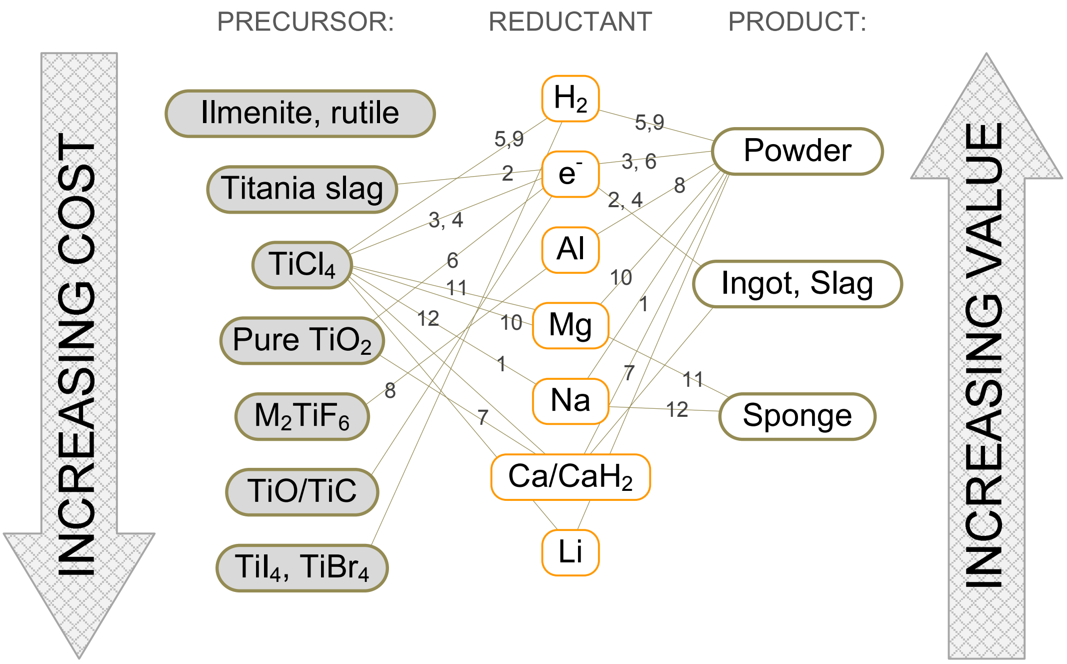


Figure 6.2: Schematic representation of the framework used as the Filtering Stage A (Van Vuuren, 2008)

The three main decision variables, according to Van Vuuren (2008), which influence the cost of production the most are as follows:

a) the cost of feedstock or precursor

b) the cost of reduction agent

c) the economic value of the primary metal product

Besides these three variables, there exist a number of different factors which all contribute in various degrees to either the capital or production costs involved, but these were mostly used within the Filtering Stage B. The original objective of this comparative framework was to develop a rational basis for selecting which route for the CSIR[12] to pursue in its own research in the field of primary titanium technology. Within the scope of this study, the comparative framework, as designed by Van Vuuren, was used to screen and filter the 26 alternatives to obtain a selection of 12 promising emerging technologies.

### 6.3.2 Screening variable 1: Precursor

The feedstock of all the titanium metal producing processes is not naturally mined mineral, but rather a precursor from which impurities in the mineral have been removed so that titanium, meeting the strict impurity specifications, can be produced. However, whereas $TiCl_4$ is the generally accepted precursor, titania slag, ilmenite and rutile have been included into the evaluation, because of the research done on these options, but all attempts to date have apparently failed (Van Vuuren, 2008). The current reality is therefore that it is essential to first produce a high-purity, intermediate titanium precursor, $TiCl_4$, $TiO_2$, fluorotitanate salts, titanium suboxide/carbide mixtures or heavier titanium tetrahalides, that can subsequently be reduced to commercially pure (CP) grade titanium.

### 6.3.3 Screening variable 2: Reductant

There are only a limited number of practical means to reduce any one of the titanium precursors. These are: electrolysis, in other words the reduction with electrons, metallothermic reduction using an alkali metal (lithium or sodium), an alkali earth metal

---

[12] DS van Vuuren is with the Materials Science and Manufacturing Department of the CSIR and has been involved with titanium related research since 2002 and has published several academic articles. The comparative framework, as introduced in this chapter, could be seen as a summary of his academic progress and endeavours.

(magnesium and calcium) or aluminum; and the reduction with hydrogen. All the possible metal options which can be used to reduce any of the titanium precursors are produced electrolytically. It is therefore argued by Van Vuuren that this pathway must also be the most economic for titanium metal.

Table 6.1: Approximate prices of the respective reducing agents (Van Vuuren, 2008)

| | **Reductants** | **Price** | | **Usage*** | | **Cost** |
|---|---|---|---|---|---|---|
| No | | | Units | Unit/kg Ti | | $/kg Ti |
| 1 | Electricity | 6.7 | c/kWh | 9 | kWh | 0.60 |
| 2 | Al | 2.5 | $/kg | 0.8 | kg | 2.00 |
| 3 | Mg | 3.1 | $/kg | 1 | kg | 3.10 |
| 4 | Na | 2.2 | $/kg | 1.9 | kg | 4.20 |
| 5 | Ca | 8.5 | $/kg | 1.7 | kg | 14.50 |
| 6 | Li | 95 | $/kg | 0.6 | kg | 57.00 |

* For electricity an energy efficiency of 40% was assumed to electrowin titanium from $TICl_4$ and for the metals the stoichiometric amounts of metal to reduce tetravalent titanium were used.

However, hydrogen, produced from natural gas or coal, might be a cheaper option, but no practical process has been developed to date. In Table 6.1 the prices of the possible reducing agents are approximated in absolute terms as well as in terms of equivalent cost per kilogram of titanium (Van Vuuren, 2008).

### 6.3.4 Screening variable 3: Product

The final product of these, to be discussed, processes could be either in the form of sponge, powder or ingot. Sponge is the form in which it is currently made on industrial level. However, significant downstream processing costs could be saved if ingots or powder be made directly and it is for this reason that many research initiatives focus on producing ingots or powder as final product. The industrial and potential value of powder as a final product is speculative, because of the immaturity of this particular industry. Currently titanium powder is either produced by the hydride-dehydride route or by spray atomization of molten titanium using argon. The possibilities and opportunities if titanium powder could be produced as final product cost-effectively, are remarkable, because this would then in turn lead to the implementation of several established powder metallurgy technologies, again, reducing the final product cost. Therefore, because of the high potential associated with titanium powder, it is seen as a more attractive option compared to ingots.

## 6.4 FILTERING STAGE B: Techno-economic evaluation

As mentioned during the initial screening stage and seen in Figure 6.2, several different pathways are possible to produce titanium metal. It is partially the objective of this second filtering stage, to add complexity and credibility to the selected process alternatives.

In the paragraphs to follow, the method used to determine the specific weights of the criteria is introduced. Also, in this section, a detailed overview of all the decision criteria is given, together with the arguments that lead to the selection of the respective criteria.

### 6.4.1 Determining the weights and priorities of decision criteria

As with every techno-economic evaluation, all criteria used do not influence the outcome of the final result or decision with the same intensity. It was therefore necessary to devise a system of respective weights to simulate the expected and predicted influence each evaluation criterion would have on the outcome and feasibility of the alternative methods.

The AHP, refer to 4.2.3, has been chosen as the method to determine the specific weights of the decision criteria in a systematic and unbiased manner.

### 6.4.2 Academic coverage and innovation activity

All of the processes investigated are actively and extensively being researched. A measureable indication of the amount of research, both time and money, which has been invested into a specific technology, could be noted by the number of research articles published. This is a fairly general assumption because it is quite possible that such a relationship simply does not exist. Research and development programmes could for a number of valid reasons such as a commercial implementation strategy or preventing opposition from obtaining a technological advantage, decide to keep their academic progress hidden. However, the following arguments make it clear that the amount of academic articles published and international patents registered is an indication of the amount of research invested:

- More academic articles relates to a greater number of research personnel involved with the development of such an emerging process. With a greater population of researchers, the rate of academic progress would naturally be higher, because various critical obstacles, sub-divisions and core-related issues could be investigated simultaneously.
- Not all the research associated with the specific technology would be about solving the difficulties directly in the way of commercialization, but some only to increase the understanding of the thermo-chemical nature of the said process. Others would experiment with a different range and specifications, such as particle size distributions, temperature, composition and/or quality of feed material, reaction properties. The basic assumption, however, still holds true that wherever there is an increased research activity, the likelihood of a technological breakthrough is enhanced.

To obtain a representative measure of the extent of academic coverage and the international patents filed, the following approach was used. A standardized academic search engine was employed to search the WIPO[13] database for relevant patent information of the studied processes. The search results were then sorted, processed, normalized and represented as a general value on the evaluation scorecard.

### 6.4.3 Commercial readiness

Each of the processes investigated in this techno-economic evaluation are at various stages of commercialization, ranging from the Kroll process, which has been used in the industry for approximately 60 years, to several of the most recent attempts which have not yet been tested any further than the laboratory.

This is a very important criterion, because of the overall technology implementation strategy and the fact that the commercial readiness is in a sense the culmination of all the research; the time and money invested into the development of the respective process. It is the final aim of any research endeavour to develop a commercially viable technique to add to, improve or replace aged technology. The fact that there are academics and

---

[13] WIPO: The World Intellectual Property Organization is a specialized agency of the United Nations and it is dedicated to develop a balanced, accessible international intellectual property (IP) system, which rewards creativity, stimulates innovation and contributes to economic development while safeguarding the public interest.

researchers who, convinced of the belief that their approach and technique promise the most cost-reduction and elegant process engineering, demonstrate the difficulty and uncertainty involved with measuring this factor. If it was possible to formulate a single and measurable way to determine the exact level of readiness, then a techno-economic evaluation would have been a relatively simple exercise.

To bridge this difficulty, it was decided to simplify and categorize this mentioned criterion into only four base options. These four options refer to the experimental, tried and tested application of the said process technologies and the scale of the production volume. These options are briefly be explained:

- **Lab**: This category represents all the novel technologies that enjoy various stages within the laboratory, but have not been successfully applied on any larger production scales. According to the OSHA Laboratory Standard[14], laboratory scale is "work with substances in which the containers used for reactions, transfers, and other handling of substances are designed to be easily and safely manipulated by one person". Relative small quantities of chemicals are used and the experiments are conducted mostly to test the scientific fundamentals of the proposed technologies.
- **Bench**: The up-scaled version of the laboratory experiments. Process equipment, which could fit on a laboratory bench, is normally designed and built to test the feasibility of the proposed technology on a small production scale. The fundamentals of process engineering, such as reactor design, heat transfer, fluid dynamics and separation principles, could be tested and the experimental equipment is designed with this in mind.
- **Pilot**: Whenever most of the fundamental process engineering difficulties have been addressed and understood, the decision is made to scale-up the proposed technology in order to start testing the commercial viability of the concept. A pilot plant is then commissioned, designed and constructed which is normally a close representation of what the planned industrial plant would look like. The idea is to experiment and test the technology within a simulated industrial environment, but

---

[14] OSHA Laboratory Standard: Officially titled the "Occupational Exposure to Hazardous Chemical in Laboratories". This standard was developed to address health hazards unique to laboratories, where a laboratory is a facility where the use of hazardous chemicals occurs and it is a workplace where relative small quantities are use on a non-production basis.

on a scale which could be easily and safely operated. It is thus possible to study the consequences and additional difficulties the scaling-up, from bench to pilot, has introduced to the novel technology. Some of the engineering fundamentals could be unscalable and therefore become an integral part of the final design specifications. At this production level it is possible to do thorough economic and feasibility planning in order to assess the overall profitability of the said technology.

- **Industry**: A novel technology that has survived the previous scaling stages and which promises an attractive return on investment would be earmarked for industrial production. A detailed environmental impact assessment together with a thorough economic evaluation of the proposed technology on an industrial scale would then be completed. Once finished, the plant would be designed, constructed and the commercial production of the final product would start, based on the freshly tested and tried technology.

Several industrial-scale electrolytic plants have been built in the past, the Dow Chemical and Howmet venture in the 1980s, a TIMET electrolytic process pilot with a molten NaCl bath in 1985 and RMI also built a $40 million pilot plant, based on the Ginatta process, in the early 1990s, but all three projects were compelled to be abandoned because of the periodic downturn of the titanium market (Turner, Hartman, Hansen, & Gerdemann, 2001). Given the wide publicity of these failures, any new attempts to revive electrolytic reduction in the near future would face serious difficulties.

It has been considered, but decided against, to include past commercial implementation failures, such as the events described above, or even the number of years a specific technology has been unable to progress further than a certain production stage. Such events do in fact relate to certain difficulties due to either the nature of the technology or the scalability thereof, but would be better represented in the other evaluation criteria. For example, the complexity of the process, the option of either having a continuous or batch type of operation or the quality and the ease of separation of the final product, all cater to represent the difficulties in the commercialization of the process. These factors would be dealt with specifically and separately.

To conclude, this evaluation criterion, namely the commercial readiness, will only aim to group the investigated technologies into the four categories as discussed above: lab, bench, pilot and industry. However these categories will be further sub-divided as discussed in section 8.1.2.

### 6.4.4 Complexity of the process alternative

Some very good and critical reviews of the emerging alternatives to the Kroll process have been made in the recent past, such as the study performed by EHK Technologies[15] in 2004, the Roskill's technical report[16] in 2007 and the academic articles and works of authors like Froes, Gambogi, Gerdemann, Kraft and Van Vuuren (Gambogi & Gerdemann, 1999; Hurless & Froes, 2002; Kraft, 2004; Roskill, 2007; Van Vuuren, 2008). To evaluate the complexity of the investigated processes, the comments and remarks, made by these industrial experts on the concerns and issues they have with the fundamentals and scalability of these technologies, were used.

In order to combine this wealth of information and expert commentary, an evaluation scorecard with its own criteria was developed as seen in Figure 6.3. The 10 criteria used in the scorecard model were partially based on the engineering economic principles and cost estimation techniques introduced in Turton *et al.* (Turton, Bailie, Whiting, & Shaeiwitz, 2003), and listed below:

- Big volume of chemicals
- Complex reactor
- Extended high temperatures
- Fluid processing plant
- Hazardous chemicals
- High/low pressures
- Issues with fundamentals
- Reaction efficiency
- Scalability

---

[15] "Summary of emerging titanium cost reduction technologies". A study performed for the US Department of Energy and Oak Ridge National Laboratory by EHK Technologies, in 2004.

[16] "The economics of titanium metal", 4th Edition, which is a detailed study of the global titanium industry, markets and technological progress as conducted by Roskill Information Services in 2007.

- Solid/fluid processing plant

All of these scorecard criteria were selected to each add a perspective on the nature of the complexities faced by the process alternatives. These complexity criteria and the associated specific weights, as seen in Table 6.2, formed the framework used to assess and calculate a qualitative representation of this criterion, referred to as the Complexity Index (CI) which is then re-integrate with the main framework.

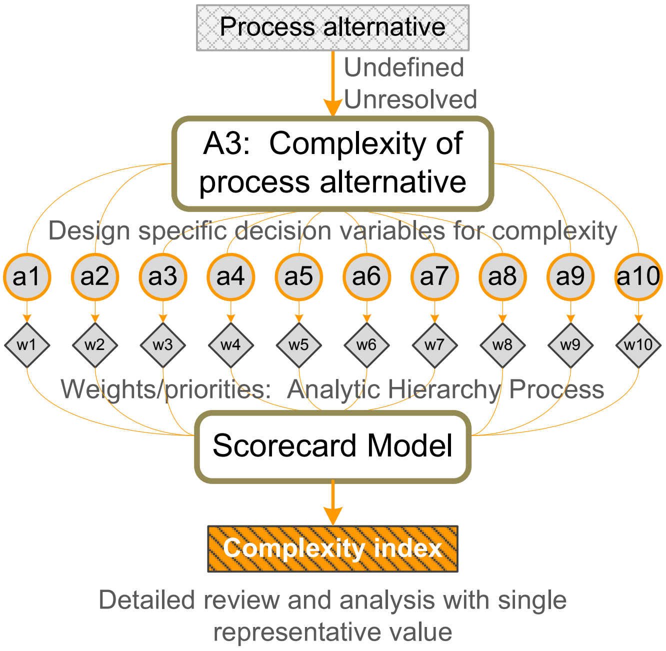


Figure 6.3: Schematic diagram to illustrate the theoretical flow in establishing the complexity index, CI, for each process alternative

The CI for each process alternative is thus, in a sense, a systematic representation of the critical reviews mentioned earlier, together with a simplified check to assess the complexity of these processes.

It is true that this scorecard technique for an important criterion, such as the complexity of the process, might be argued to be too subjective. However, any attempt to calculate exact values for any of the scorecard criteria would be a very difficult and time-consuming task; for some of these criteria, such as the complexity of the reactor, issues with fundamentals and scalability, an impossibility. In order to keep within the scope of this research project, it was decided to advance with this scorecard approach, aware of the subjectivity. The commentary of the industrial experts were reviewed and categorized in such a way as to make it possible to complete the scorecard for each of the investigated processes.

Table 6.2: The evaluation criteria of the Scorecard Model and its pairwise comparison matrix to establish the required specific weights/priorities

**Pairwise comparison matrix:**

| **Scorecard criteria:** | | c1 | c2 | c3 | c4 | c5 | c6 | c7 | c8 | c9 | c10 | Priorities |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Big volume of chemicals | c1 | 1 | 1/7 | 1 | 4 | 1 | 1 | 1/8 | 1/6 | 1/5 | 1/3 | 0.0379 |
| Complex reactor | c2 | 7 | 1 | 6 | 3 | 5 | 4 | 1/2 | 1 | 1 | 8 | 0.1603 |
| Extended high temperatures | c3 | 1 | 1/6 | 1 | 1 | 2 | 1 | 1/6 | 1/6 | 1/4 | 2 | 0.0386 |
| Fluid processing plant | c4 | 4 | 1/3 | 1 | 1 | 1/4 | 1/5 | 1/3 | 1/7 | 1/7 | 5 | 0.0539 |
| Hazardous chemicals | c5 | 1 | 1/5 | 1/2 | 4 | 1 | 2 | 1/2 | 1/8 | 1/3 | 1/2 | 0.0479 |
| High pressures | c6 | 1 | 1/4 | 1 | 5 | 1/2 | 1 | 1 | 1/8 | 1/3 | 1/3 | 0.0545 |
| Issues with fundamentals | c7 | 8 | 2 | 6 | 3 | 2 | 1 | 1 | 1 | 7 | 3 | 0.1961 |
| Reaction efficiency | c8 | 6 | 1 | 6 | 7 | 8 | 8 | 1 | 1 | 2 | 7 | 0.2119 |
| Scalability | c9 | 5 | 1 | 4 | 7 | 3 | 3 | 1/7 | 1/2 | 1 | 7 | 0.1366 |
| Solid processing plant | c10 | 3 | 1/8 | 1/2 | 5 | 2 | 3 | 1/3 | 1/7 | 1/7 | 1 | 0.0623 |
| | | | | | | | | | | | Total | 1 |

The method used to determine the specific weights is dealt with in the section about the analytic hierarchy process, 4.2.3. With these priorities and the completed scorecard, a comparable measurement of the complexity, referred to as the complexity index of each of the processes, was established.

### 6.4.5 Mode of operation: batch, semi-batch or continuous

This is an important technical and economical classification of the process itself.

The mode of operation also plays an important role in the overall feasibility and cost-effectiveness of the proposed process. The Kroll process is a batch process and the dynamics and timeframe associated with producing a single batch, significantly contribute to the cost and labour intensity of the batch process. If it were possible to operate the titanium process in a continuous manner, large savings in both capital and labour costs would be achieved (Van Vuuren, 2008). The actual definition of continuous and batch, the differences between the two and the relevance to the titanium producing process will be discussed in more detail in the following paragraphs.

Continuous operation is basically a series of equipment, with each piece performing a single unit operation. All of the reaction products leave the process reactor continuously and are transported to storage or further processing. Continuous processes are designed to operate 24 hours a day, 7 days a week, throughout the year, with maybe some downtime allowed for maintenance and for some maintenance processes, such as catalyst regeneration.

Batch processes on the other hand, are designed to operate intermittently. Some, even all, the process units are frequently shut down and started up. An acceptable definition of a batch process is one in which a finite quantity of product is made during a period of a few hours, sometimes even days, as is the case with the Kroll process. The batch process most often consists of metering the feedstock into large enough vessels followed by a series of unit operations, such as mixing, heating, reaction and distillation, taking place in discrete intervals. This series of operations is then followed by the removal and storage of the products, by-products and the waste streams. The equipment is then cleaned and made ready for the next process. Normally, because of the costs involved with the start-up and shut down, as well as the lost production time, continuous processes are more economical, especially for large-scale industrial production. Batch processes are used where some flexibility is required in either production rate or product specifications. Batch processes are more difficult to optimize, control, they are labour intensive, the process equipment must be larger to accommodate all the reactants and products, increasing the initial capital expenditure and maintenance costs and, consequently, more expensive to operate. Large-scale operations are performed mostly on continuous basis.

With the techno-economic evaluation in mind, this criterion was included as a stand-alone specification, although there exists an obvious relationship between the capital requirements and the production costs, which is dealt with separately, and the option of either batch or continuous operation. Because of the inherent uncertainty involved in the estimation of the capital requirements and production costs, this criterion was catered for separately, adding an important perspective on the design and decision parameters of the process in question.

### 6.4.6 Economic value of the feedstock and precursors

With regard to the possible reduction in production costs, the raw materials play a large role because the different feedstocks, ilmenite, titania slag, rutile, pure $TiO_2$ or $TiCl_4$, differ significantly in their market prices. From an economic perspective, it is always advisable to start with as inexpensive a feedstock as possible for any process. In the table below the different feedstocks, which form part of this evaluation, are given with their respective compositions, titanium content on a weight basis and the economic value of each. It is true that some other possible precursors do exist and have been, or are currently being researched, such as $TiI_4$, $TiBr_4$ and TiN (Van Vuuren, 2008). However, it appears as if most of these options do not offer very feasible alternatives and were thus excluded from the scope of this research.

A process using a fluorotitanate as precursor is currently being developed by Anglo American, called the Peruke process, and will be discussed in section 7.3.8, but it is important to note that the step prior to the main reduction reaction is included as part of this alternative. The mineral feedstock, such as ilmenite, titania slag or rutile, is first digested in acid, purified by selective precipitation and then the washing of the precipitate. The feedstock of the Peruke process within this techno-economic evaluation is thus assumed to be the cheapest option, ilmenite, since the digestion and precipitation steps account for FeO among the impurities.

Table 6.3: Comparison of the different feedstocks, their composition and respective economic values

| | | | **Titanium mineral and/or metal feedstock:** | | | | | |
|---|---|---|---|---|---|---|---|---|
| **Component:** | Molecular weight | | Ilmenite | Titania slag | Rutile | Pure $TiO_2$ | $TiCl_4$ | Ti Sponge |
| $TiO_2$ | 79.86 | % | 54 | 55 | 95 | 100 | 0 | 0 |
| $Ti_2O_3$ | 143.73 | % | 0 | 27.9 | 0 | 0 | 0 | 0 |
| FeO | 71.84 | % | 42 | 11.8 | 0 | 0 | 0 | 0 |
| Metal oxide* | 120 | % | 4 | 5.3 | 5 | 0 | 0 | 0 |
| $TiCl_4$ | 189.69 | % | 0 | 0 | 0 | 0 | 100 | 0 |
| Titanium fraction, Ti | 47.88 | % | 32.4 | 51.6 | 57.0 | 60.0 | 25.2 | 100.0 |
| Industrial cost, $/tonne | | | 105 | 474 | 525 | 2320 | 2205 | 15930 |
| Cost, $/kg Ti Sponge | | | 0.32 | 0.92 | 0.92 | 3.87 | 8.73 | 15.93 |

* The remainder of metal oxides, such as silicon, manganese, aluminum etc., were grouped and a general molecular weight established to simplify the titanium fraction calculations.

The problem with the titanium value chain, and in most other cases where cheap raw material is compared to a more expensive, but more pure alternative, is the difficulty with impurities. Impurities, not only increase the separation costs and the complexity thereof, but with titanium it actually contributes to the difficulty of obtaining feasible reaction dynamics. Because of the high-reactivity of titanium, especially in its transition phases, the presence of impurities allow unfavourable side-reactions to take place. These reactions basically lock a portion of the titanium product in difficult to remove chemical components, which understandably increases the complexity and costs involved in removing the said titanium product.

The only alternative is then to again make use of a high-purity, intermediate titanium precursor, which could subsequently be reduced to titanium metal. If, however, an effective technology could be developed to successfully make use of low-cost feedstock to produce titanium metal directly, then several processing steps could be skipped to significantly reduce production costs. The influence of this criterion and factor would then be two-fold, firstly, it represents the cost-reduction potential caused by the usage of cheap raw material and secondly, by shortening the process route and eliminating steps, the total production costs could be also reduced.

### 6.4.7 Type and quality of product

The emerging techniques, together with the Kroll process, could easily be categorized according to the type of the final product: titanium sponge, liquid metal or titanium powder. The final product would lead to completely diverging downstream manufacturing routes. Although there has been little work done on methods of using powder to develop alternative routes to products such as bar, wire, sheet, plate and forgings, there appears to be considerable promise of significant cost reduction by avoiding the use of conventional melt and mill processing (Kraft, 2004).

The economic value of the final product is highly dependent on the form and quality of the titanium produced. It has been reported that titanium powder from various parts in the world costs $18/kg to $440/kg depending on the quality alone (Froes, 1998). The quality of the final product is of utmost importance, because even if a process shows great cost-reduction potential, is an efficient method and the capital expenditures be reasonable, but the quality is poor, the process have very limited industrial use, unless the problem could be remedied. Several factors influence and play a significant part in affecting the quality of the final product, such as the initial purity of the feedstock, the presence of impurities, the process conditions and exposure to the external environment.

Once the main titanium reduction reaction is completed, it is necessary to perform separation activities to remove any unwanted chemical species and to obtain the pure titanium product. Even the electrolytic processes operate below the melting point of titanium and the product has to be separated from the by-product, mostly a salt, or excess reactant or the salt medium in which the main reduction reaction takes place. In the Kroll process for example, the final sponge product still contains considerable $MgCl_2$, because of the excess used and this needs to be removed by means of an additional vacuum distillation step.

Separation activities can be sub-divided into enrichment, concentration, purification, refining and isolations techniques (Seader & Henley, 1998). This process involves different modes of operation, conducted in either a continuous or batch-like fashion. The operation may be classified as either:

- Key operations: Changes in chemical composition, such as chemical reaction and/or separation of a mixture of chemicals.
- Auxiliary operations: No changes in chemical composition, but necessary to the success of the key operations. These include separation of phases, heat addition or removal, pressure changes, mixing or dividing of streams or batches of material, solids agglomeration, size reduction of solids and separation of solids by size.

The mixing of chemicals to form a mixture is a spontaneous, natural process that is accompanied by an increase in entropy, but the inverse, the separation of that mixture into its constituent chemical species, is not spontaneous and requires an expenditure of energy (Seader & Henley, 1998). A schematic diagram of a general separation process is shown in Figure 6.4, with the feed mixture either vapour, liquid or even solid. The separation techniques can be grouped into the following: separation by a) phase creation, b) phase addition, c) barrier, d) solid agent and e) force field or gradient.

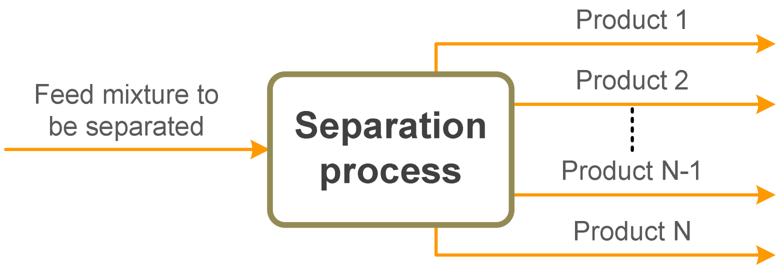


Figure 6.4: A schematic of a general separation process

For all of these general techniques, the separations are achieved by enhancing the rate of mass transfer by diffusion of certain species relative to mass transfer of all species by bulk movement within a particular phase (Seader & Henley, 1998). Physical separation techniques such as decanting, settling or filtration are much cheaper than methods involving a phase transition such as vacuum distillation or leaching, but unfortunately the desired titanium product specifications are of such a standard that physical separation processes are normally not sufficient enough.

An additional step, either leaching or vacuum distillation is then required to obtain the said specifications. Another added shortcoming of physical separation techniques is the difficulty to perform these steps on a continuous basis, because of the high temperatures required to melt the respective salts, the corrosiveness of the chemicals involved and the high purity specification that the titanium product must meet (Van Vuuren, 2008).

The melting points of the various salts and the water solubility thereof are given in the table below. Solid–liquid separation techniques such as filtration and centrifuging are difficult and standard equipment is not readily available for operating with these salts above their melting points. The salts with a very low solubility in water are not suitable to be used in any product removal steps.

Table 6.4: Melting points and the water solubility of various salts

| | Salt | Melting Point | Solubility |
|---|---|---|---|
| No | | °C | g/100cm$^3$ |
| 1 | $AlF_3$ | 1291 | 0.559 |
| 2 | NaF | 988 | 4.22 |
| 3 | $CaCl_2$ | 772 | 74.5 |
| 4 | $Ca(OH)_2$ | | 0.185 |
| 5 | LiCl | 614 | 63.7 |
| 6 | LiOH | | 12.8 |
| 7 | $MgCl_2$ | 708 | 54.25 |
| 8 | $Mg(OH)_2$ | | 0.0009 |
| 9 | NaCl | 801 | 35.7 |
| 10 | NaOH | | 42 |

As seen in Table 6.4, aqueous leaching is well suited to separate the chloride salts, especially magnesium chloride, from the titanium product, but the recovery of anhydrous magnesium chloride is unfortunately complicated by the formation of MgO when dehydrating the $MgCl_2.H_20$. The solution to this problem, as addressed and solved in the

Kroll process is to remove as much salt as possible by means of a physical separation step before the residual amount is removed by vacuum distillation.

chapter | seven

# 7 ALTERNATIVES TO THE KROLL PROCESS

In this chapter all the process alternatives that were investigated in this study are introduced, those removed by the initial screening stage are only briefly mentioned, but the selected 12 options are discussed in detail. The current existing industrial processes are briefly explored followed, by an in depth study of the 10 selected alternatives to the Kroll process, investigated and evaluated in this research project.

The main objective of this chapter is to explore the specific characteristics, both potential advantages and disadvantages, of the studied process alternatives. These 12 options will then be subjected to the designed evaluation criteria, previously introduced as the Filtering Stage B. With the decision criteria in mind, the understanding obtained in this chapter is later used to perform the techno-economic evaluation, with the ranking as the final outcome.

## 7.1 Brief overview of production routes

Numerous titanium production alternatives have been proposed through the years and each generally suffers from different drawbacks. For example, production pathways that require the chemical reduction of titanium-containing compounds typically involve the formation of intermediate products that contain high levels of impurities. The purity or quality of the separation and the oxidation of the final product and intermediaries present the designers and developers with both technical and economical challenges (Hildenbrandt & Thiers, 2004).

In particular, intermediaries formed by the reduction of titanium halides, (with $TiCl_4$ most often used) tend to be highly contaminated with variations of either titanium subchlorides or chlorides of the metal reduction agent. Besides chloride impurities, species such as oxides, carbides and nitrides that are commonly formed not only create purity and separation difficulties, but result in reducing the overall titanium yield of the alternative process.

In addition, plasma thermal reduction of $TiCl_4$ utilizes the chemical separation fundamentals of extremely high temperatures, around 4000°C, and is accordingly very energy intensive.

Electrochemical alternatives suffer from a different set of technical and economical disadvantages. It is relatively simple to deposit metallic titanium onto a suitable electrode, but these reactions must be carried out in a molten salt system. Accordingly, these processes are typically associated with high energy and labour costs, due to the removal and stripping of the electrode.

Although the electrolytic production of aluminum is an economic success, the electrolytic production of titanium faces more challenging obstacles. There are significant differences between aluminum and titanium, and it is because of these differences that the electrolytic reduction of titanium is more challenging. For example, titanium melts at 1660°C, while the melting point of aluminum is 660°C. The lower melting point of aluminium makes it possible for the aluminum electrolytic cell to be operated in a region where aluminum is a liquid, whereas the titanium cells must be operated where titanium is a solid, because the melting point of titanium is so high. Also, titanium can exist in several stable valence states while aluminum has only one. These multiple valence states make it possible for the ions to move between the electrodes resulting in a loss of efficiency.

An important reason for the technological delay in the development of the electrolytic process is the insufficient theoretical understanding of the titanium system. According to Ginatta (1998), most metallurgists get entangled in matters of principles about thermodynamics of electrically charged species, when attempting to interpret the phenomena occurring at a working single electrode. The industrial problem, one of the main challenges in commercialization, with chloride electrolysis is that titanium is deposited in the solid state on the cathodes, with a crystalline morphology that has large surface areas and low bulk densities.

## 7.2 Review of existing industrial processes

Ever since titanium has become an industrial metal, only two processes to produce the metal reached commercialization, namely the Hunter and Kroll processes. These extraction processes, briefly introduced in 2.3.3, coexisted since the early 1950s, but lately the advances in the Kroll process caused this process to become the primary industrial choice in the titanium value chain. In the sections to follow, the Kroll and the Hunter processes will be discussed in detail.

### 7.2.1 Kroll Process

The Kroll process as used today is similar to the process DuPont used to produce titanium metal in 1948 (Gambogi & Gerdemann, 1999). In Figure 7.1 the basic process, although a lot simplified, can be seen. The process starts with $TiO_2$ enriched slag, which is chlorinated in a fluidized bed reactor to form $TiCl_4$, known as the chlorination step (refer to section 2.3.1). This step has been included into the basic process diagram to show the recycling loops of both magnesium and chlorine.

After several purification and distillation steps the formed $TiCl_4$ is fed to the Kroll reactor where the actual reduction reaction takes place. The Kroll process is operated in a batch fashion in an argon-filled retort with enough liquid magnesium to reduce all the $TiCl_4$ leaving approximately 20% excess magnesium. The retort is heated to a temperature of 800°C to 900°C, with $TiCl_4$ slowly fed over a period of several days. It takes roughly two weeks for a batch of 10 tonne, which contributes to the problem that the process is so cost-intensive. The liquid magnesium reduces the titanium tetrachloride according to the reaction:

Equation 24:

$$TiCl_{4(\mathrm{l})} + 2Mg_{(l)} \rightarrow Ti_{(s)} + 2MgCl_{2(\mathrm{l})}$$

The magnesium chloride is tapped off several times during the reduction reaction (Hartman, Gerdemann, & Hansen, 1998). At completion of the reaction, when all the $TiCl_4$ has been reduced, the pressure of the retort rises and it can be opened. Roughly 30% of the initial magnesium charge would still be unreacted and needs to be removed by vacuum distillation. This distillation step involves another batch process where the sponge is heated to 900°C in a vacuum. The impurities are vaporized, removed and condensed in a cold trap. In most cases, the sponge near the retort wall is either left in place or discarded, because it has been contaminated by iron and/or nickel (Kraft, 2004).

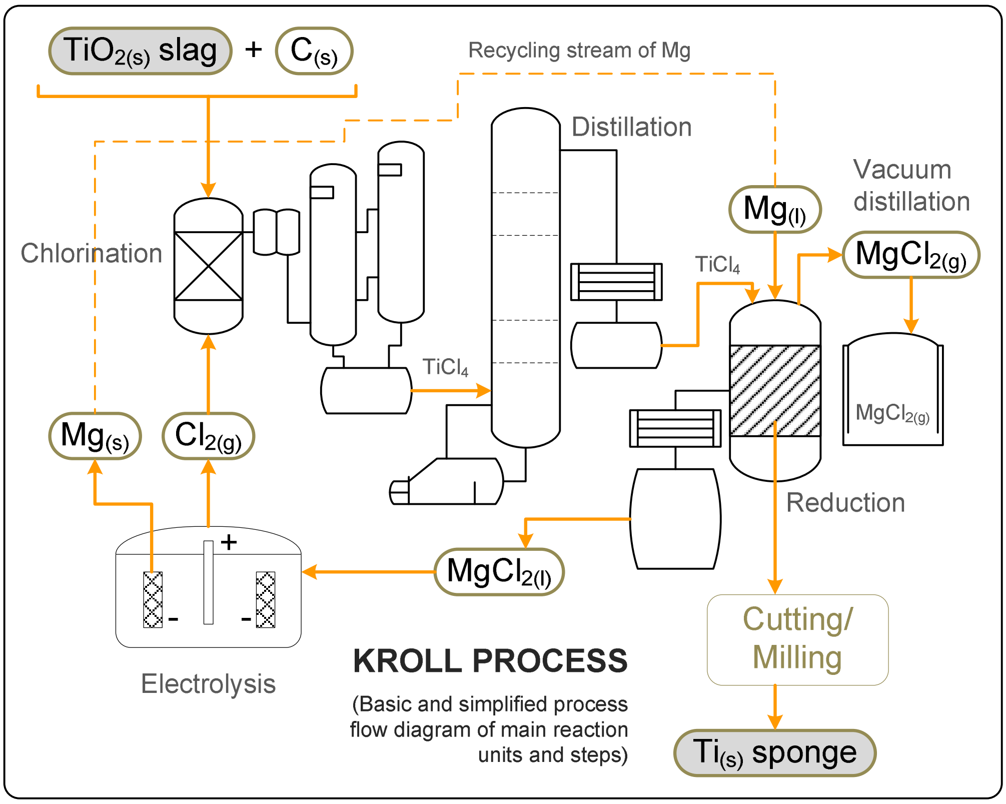


Figure 7.1: A schematic diagram of the Kroll process showing the separate electrolysis plant for the recycle of magnesium and chlorine

Developments and improvements to the Kroll process included the introduction of vacuum distillation, increasing the batch size and the use of more efficient magnesium cells (Ikeshima, 1984). After these progress and advancements, resulting in significant energy savings and also improvement in the quality of the final titanium product, the Kroll reduction step remained very much similar to the process used by the USBM in the late 1940s. However, more fundamental work might make improvements in the process such as means to reduce the portion of sponge that must be downgraded due to vessel contamination at the retort wall or nitride inclusion (Turner, Hartman, Hansen, & Gerdemann, 2001). Besides these potential minor improvements, it could be said that this technology has assumed stagnation and there is hardly any scope existing for bringing down the cost of titanium metal further by this method (Hyado & Ichihash, 2003).

### 7.2.2 Hunter Process

The Hunter process is very similar to the Kroll process; however, there are some differences caused by the solubility of sodium in sodium chloride (NaCl). In the Hunter process, the retort is sealed and filled with molten sodium. Unlike the Kroll process, a slight excess of $TiCl_4$ is used to make sure that no sodium remains in the salt when the reaction is complete. The retort is then heated to the reaction temperature of approximately 910°C and $TiCl_4$ is slowly fed into the retort, where it reacts with the sodium according to the following reaction (Gambogi & Gerdemann, 1999)

Equation 25:

$$TiCl_4 + 4Na \rightarrow Ti + 4NaCl$$

Because the titanium sub-chlorides and sodium are soluble in NaCl, it is not practical to drain off the NaCl that is formed during the reduction. At the end of a run, the retort contains a ratio of 4 moles of NaCl for each mole of titanium and for this reason the retort for the Hunter process must be considerably larger to produce the same amount of titanium as a Kroll retort. When the reduction is finished, the retort is opened and the NaCl-titanium mixture is chipped out. The NaCl is leached away from the titanium with hydrochloric acid. A sub-stoichiometric amount of sodium is used so that excess sodium will not be washed during the leach step. The brine solution is discarded and thus it is necessary that new sodium be bought for every run.

A simple variation of the Hunter process involves a two-stage reduction, as used by RMI. In the first stage, $TiCl_4$ and molten sodium were reacted in a stirred tank to form $TiCl_2$ at approximately 1 200°C according to the reaction below:

Equation 26:

$$TiCl_{4(\mathrm{l})} + 2Na_{(l)} \rightarrow TiCl_2 + 2NaCl$$

This mixture is then fed to a 1 000°C retort containing enough sodium to complete the reduction reaction:

Equation 27:

$$TiCl_2 + 2Na_{(l)} \rightarrow Ti_{(s)} + 2NaCl$$

Although the first step can be operated on a continuous basis, the second is still a batch process and the overall variation is still a batch process (NMAB, 1983). In 1992 RMI shut down its Hunter process sponge plant and Deeside Titanium in the United Kingdom in 1993 also closed its Hunter process plant.

## 7.3 Alternatives investigated in this evaluation

In recent years, there has been an increased focus and intensity in developing more cost-effective alternatives to produce titanium metal. This is primarily because of the fact that this metal promises to answer the call for a structural material with the mechanical properties to reduce the weight of vehicles, both in the aerospace and the automotive industry, but retain the strength of the traditional options, such as stainless steel and aluminum. Overall strong growth in consumption of titanium metal is expected over the next five years. The large projected increase in production, particularly in China, is expected to drive titanium prices back to levels nearer to their long term historical average (ABARE, 2008). Due to this expected increase in consumption and production, the various advances in the research and development of alternative titanium producing processes have to be examined and studied.

As discussed earlier, the Filtering Stage A was used to reduce the total number of process alternatives to 12, including the two existing options above. It must be mentioned and realized that not one of the options listed in Table 7.2 show no potential or promise. Each alternative was founded on a principle and method which was built upon the work of a predecessor and a previous concept or idea. The fact that these options were removed by the first filtering stage of the techno-economic evaluation, based on qualitative analytic principles, might appear subjective.

However, it must be mentioned, that it is not a certainty that the foreseen technological breakthrough would come from the 10 selected emerging processes, but according to the competitive framework developed by Van Vuuren (Van Vuuren, 2008), it is concluded that they show the most potential to reduce the costs associated with the production of titanium.

| No | Process name: | Brief description: | Product |
|---|---|---|---|
| 1 | Armstrong/ITP | Liquid Na reduction of $TICl_4$ vapour | Powder |
| 2 | Cardarelli (QIT Fer et Titane) | Electrolytic reduction of Ti slag as the electrolytic cathode | Ingot |
| 3 | FFC Cambridge | Electrolytic reduction of partially sintered $TiO_2$ electrode in molten $CaCl_2$ | Powder |
| 4 | Ginatta Process | Electrolytic reduction of $TiCl_4$ vapour dissolved in molten electrolyte with multilayer cathodic interface | Ingot |
| 5 | Idaho Titanium Techologies | Hydrogen reduction of $TICL_4$ plasma | Powder |
| 6 | MER Corporation | Anode reduction of $TiO_2$, transport through mixed halide electrolyte and deposition on cathode | Powder |
| 7 | OS Process (Kyoto University) | Calciothermic reduction of $TiO_2$ | Powder |
| 8 | Peruke (Anglo America) | Chemical process involving $M''_2TiF_6$ which forms a hexafluorotitanate | Powder |
| 9 | SRI International | Fluidized bed reduction of Ti halides | Powder |
| 10 | TiRO (CSIRO) | Fluidized bed, vapour Mg, reduction of $TiCl_4$ | Powder |
| 11 | Hunter | Liquid Na reduction of $TICl_4$ vapour | Sponge |
| 12 | Kroll | Liquid Mg reduction of $TICl_4$ vapour | Sponge |

Table 7.1: Selected alternatives, filtered by means of the Filtering Stage A

The remaining processes, beyond the scope of this study, are briefly discussed in section 7.4, to give a complete overview of the research activities within and related to the global titanium industry. Because of the subjectivity of this selection and in defining the scope of this research project, it is recommended that in further studies attention is given to these remaining processes. Attention should be given to the claimed and proven advantages, as well as the cost-reduction potential, so that a thorough comparison with those investigated and evaluated in this study, could be drawn.

### 7.3.1 Armstrong/ITP

The Armstrong process, as developed by International Titanium Powder (ITP), is a continuous process that produces titanium by the reduction of $TiCl_4$ with sodium (Na), as does the Hunter process. $TiCl_4$ vapour, but a mixture of different chloride vapours could also be used to obtain a specific titanium alloy, is injected into a stream of molten sodium (Hansen & Gerdemann, 1998). The reaction occurs immediately downstream of the injection nozzle. The process is designed with excess sodium to bring the temperature of the reaction products down, but also to act as the carrier for the formed titanium powder.

The reduction reaction is highly exothermic, forming molten products. It is important to keep the temperature of the product stream below the sintering temperature of titanium, of about 1 000°C. This is done by controlling the quantity of sodium and quenching the reaction products in the bulk stream. The excess sodium absorbs sufficient heat so that the titanium particles do not sinter to form a solid mass or react with the container walls.

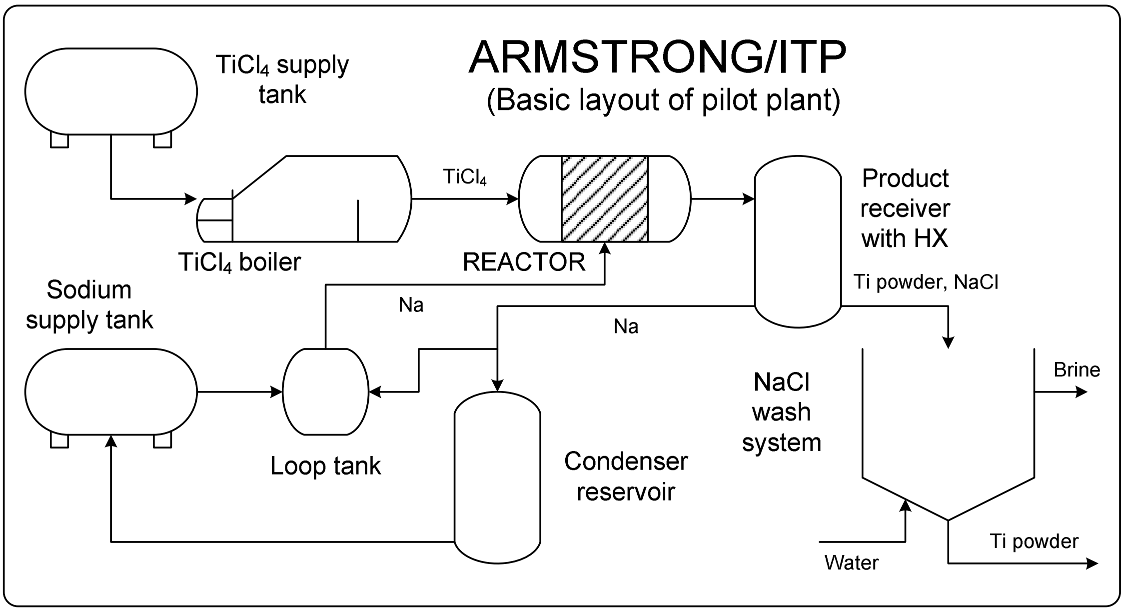


Figure 7.2: Process flow diagram of the original Armstrong/ITP process (Anderson, Armstrong, & Jacobsen, 2004)

The equation for the reaction is as follows:

Equation 28:

$$TiCl_{4(g)} + 4Na_{(l)} \rightarrow Ti_{(s)} + 4NaCl_{(s)}$$

The formed products, titanium powder, NaCl and the remaining molten sodium, are then separated by conventional cyclones or particulate filters. Two options are available however:

a) The first option removes the titanium and NaCl products in separate steps. The bulk stream is maintained at a temperature where titanium is solid and the NaCl is molten, by controlling the ratio of $TiCl_4$ and sodium flowrates. Titanium is removed first, after which the stream is cooled to solidify the NaCl, to be removed.

b) A lower ratio of $TiCl_4$ to sodium flowrate is used for the second option, to ensure that the bulk temperature remains below the solidification temperature of NaCl.

> The products are thus removed simultaneously with the NaCl and any residual sodium present on the particles removed in a water-alcohol wash.

Recent technological advances suggest that excess $TiCl_4$ in combination with excessive cooling measures rather be used to cool the product stream. The use of excess sodium requires that the remaining excess be removed, such as by vacuum distillation, before the products can be separated. The molten sodium may explosively react with water or is insoluble in water whereas the reaction products, in particulate form, can be separated by a water wash. Vacuum distillation is expensive and would be preferred to find systems and methods that would permit the separation steps directly with water without the need for preliminary steps.

In 2003 ITP filed another patent, which incorporated most of these advances (Anderson, Armstrong, & Jacobsen, 2004). In making use of an excess $TiCl_4$, as a heat sink, the products are in particulate form and only a vapour phase chloride. The vapour can be efficiently and inexpensively removed so that the accumulated particles are entirely free of molten sodium metal. A vacuum distillation step would thus not be needed, since the separation can be completed with a water wash. The boiling point of sodium chloride is 1 465°C and it thus becomes the upper temperature limit, whereas the boiling point of $TiCl_4$, becomes the lower limit to ensure that all excess $TiCl_4$ remains in the vapour phase until after separation. An inert gas, such as argon, could then be used to sweep the excess vapour from the reaction products. The excess vapour with the inert sweep gas leaves the reaction chamber at the top, while the particulate products accumulate and are removed at the bottom, after being cooled by the inert gas. Thereafter, the particulates may be introduced to a water wash to separate the metal particulates.

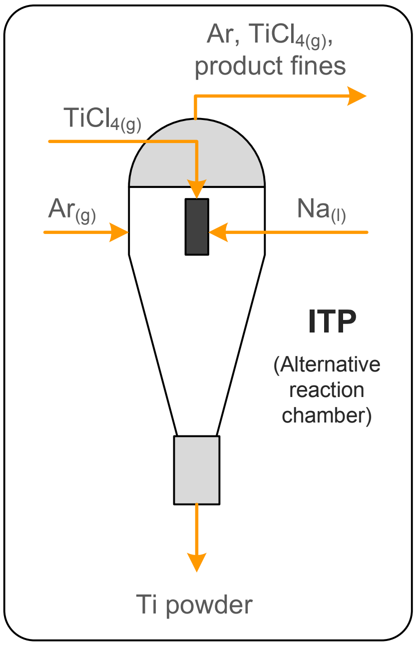


Figure 7.3: A schematic diagram of the alternative reaction chamber for this process (Anderson, Armstrong, & Jacobsen, 2004)

An important aspect of this technique is the removal of any excess vapour prior to separation of the produced metal and salt. However, some technical difficulties, some of which were unknown in the original version of the Armstrong process, unfortunately complicate the process. For instance, when $TiCl_4$ is present in excess of the stoichiometric amount needed to react with the reducing sodium, certain sub-chlorides, such as $TiCl_3$ and $TiCl_2$, may be formed. Sub-chlorides are to be avoided, because they contaminate the produced titanium metal, requiring further processing.

The powder produced has a quality near to that of grade 1 commercially pure titanium, but apparently it is quite difficult to lower the oxygen content much below the 0.2% level (Gerdemann, 2001), but overall the powder produced is usable within the existing titanium industry. ITP has been running tests on a pilot plant for couple years, the basic process flow diagram can be seen Figure 7.2, to experiment and to refine the process operational parameters. The identified issues include the following (Kraft, 2004) and (Van Vuuren, 2008).

- Demonstrating equipment durability, because large parts of the process are to be operated at elevated temperatures to ensure a molten sodium stream. The alternative option, using an excess of $TiCl_4$, is struggling with process fundamentals, such as the formation of sub-chlorides, which needs to be avoided.

- The separation and purification step is difficult, complicated and according to Van Vuuren, need to be optimized.
- The capital cost of an integrated production facility has to be determined.

A key advantage of the Armstrong/ITP process is that if since $TiCl_4$ is used the evaporation step also functions as a second purification after the initial distillation during the manufacturing of $TiCl_4$. Lower grades of rutile could thus be used and a distillation step could be removed, if the $TiCl_4$ manufacturing stage is included in the overall process plant design and not bought from outside vendors (Kraft, 2002).

In 2008, ITP was acquired by Crystal Global, which has extensive experience in the titanium dioxide market. A full-scale facility is expected to start production in 2010

### 7.3.2 Cardarelli (QIT Fer et Titane)

Quebec Iron and Titanium (QIT), owned by Rio Tinto, is a well established mining and smelting company with operations in Quebec in Canada. QIT has recently developed a high-temperature titanium extraction process based on an electrolysis reaction, where molten titania slag is the cathode as seen in Figure 7.4 (Kraft, 2004). The operating temperature of this process should be between 1 570°C and 1 860°C, for that is the temperature where titania slag is in a molten state, depending on the titania content. The titania content is usually for the crude slags (77% to 85% weight $TiO_2$) or upgraded titania slags, natural or synthetic rutile (92% to 96% weight $TiO_2$) (Cardarelli, 2002).

The process is based on the fact that titania slag exhibits semi-conductive behavior and hence can be used without any additional treatments as an electrode (Cardarelli, 2002). The primary concept consists of pouring molten salt electrolyte, such as $CaF_2$ into the chamber, followed by molten titania, the traditional product of primary processing, which is allowed to settle below the electrolyte. Solidified electrolyte, slag and metal forms a protective lining on the walls and floor of the chamber, which solves the contamination issue for the corrosive actions of molten titanium metal.

The operation, or rather the electrolysis, is performed in two steps. Firstly, the impurities, such as iron, chromium, manganese and vanadium, are removed by means of electrolysis as it forms, settles and collects at the bottom of the chamber. This metal mixture can then be removed. The second step is operated at a higher temperature where the titanium can be electrolyzed from the slag, which also settles and collects at the bottom. Liquid titanium metal is then tapped from the chamber (Figure 7.4).

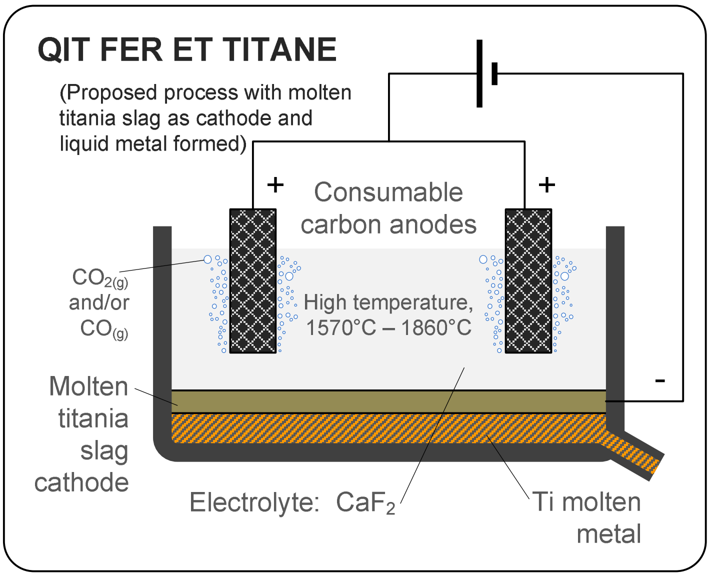


Figure 7.4: A diagram of the QIT process (Cardarelli, 2002)

This process is continuous with considerable work already done and the final configuration is based on multiple iterations of design concepts. The overall electrochemical reaction corresponds to the carbothermic reduction of $TiO_2$ (refer to 7.3.6 for more details thereon) with an overall reaction scheme which is given by:

Equation 29:

$$TiO_{2(l)} + C_{(s)} \rightarrow Ti_{(l)} + CO_{2(g)}$$

According to Cardarelli, the QIT process has the following advantages (Cardarelli, 2002):

1. Deoxidizing electrochemically continuously and in one step a raw feedstock, far less expensive than both $TiCl_4$ and pure $TiO_2$.
2. Molten titania slag is utilized directly as molten cathode without any prior treatment or additives.

3. The combining of the ilmenite smelting step and the electrolytic reduction step, results in an attractive and energy effective alternative.
4. The molten titanium metal can be continuously tapped and cast under an inert atmosphere into large ingots.

Besides these advantages, the QIT process is very similar to the FFC Cambridge process, except that the process is carried out at a temperature above the melting point of titanium, approximately 1 670°C (Loutfy & Withers, 2007)

### 7.3.3 FFC Cambridge

In 2000 a new process was reported in which solid $TiO_2$ was directly electrochemically reduced to metallic titanium in molten $CaCl_2$ (Chen, Fray, & Farthing, 2000). This new process, which is now called the FFC Cambridge process, named after the three authors, Fray, Farthing and Chen, is low in energy consumption, relatively fast compared to the Kroll process with the possibility to be operated on a continuous basis. It thus initially promised to be an economical and environmentally friendly alternative to the Kroll process and in a sense sparked the global eagerness to find a cost-effective alternative to produce titanium metal (Ma, Wang, Hu, Jin, & Chen, 2006).

This process was discovered and developed accidentally, because they, Frey *et al*., were investigating methods to remove the oxide film on the surface of titanium. When they applied an electrical current, they realized that the oxides are being reduced to titanium. In Figure 7.5 the simple processing steps can be seen. $TiO_2$ feedstock is pressed into a preformed mould which is consequently placed in a molten bath of calcium chloride, kept between 800°C to 1 000°C under an argon atmosphere, as the cathode together with a carbon anode for the electrochemical reaction. Following the complete reduction and deoxidation reaction, the cathodes are removed, milled to a uniform particle distribution, followed by a washing step to obtain the final product of titanium powder. Interesting is the fact that the just removed reduced cathodes have a morphology similar to the Kroll sponge (Cardarelli, 2002). It has been noted that the deoxidation step requires a long time because oxygen is present in small amounts in the titanium metal formed at the cathode/electrolyte interface and its diffusion kinetics across solid matter becomes the rate-determining step (Ono & Suzuki, 2002; Cardarelli, 2002).

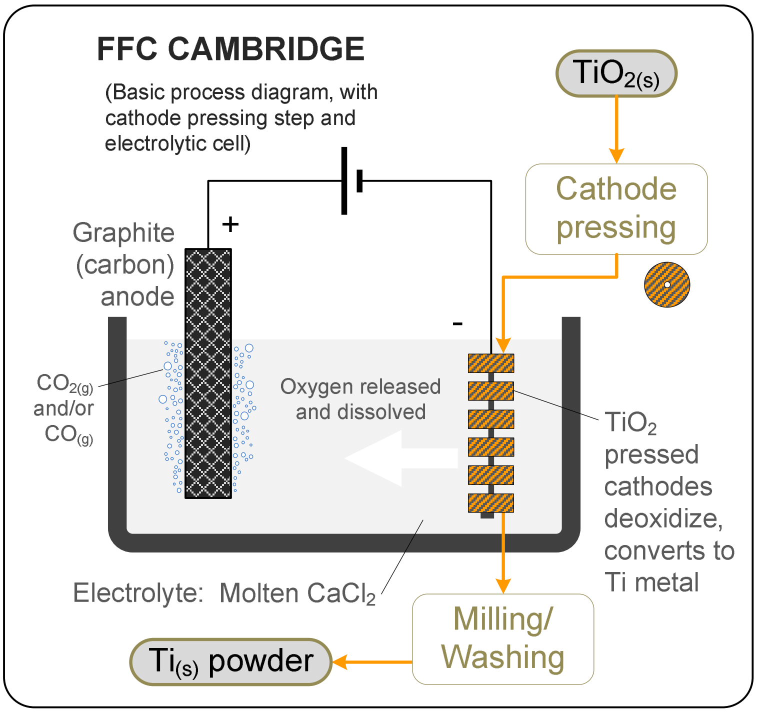


Figure 7.5: A diagram of the FFC Cambridge process (Chen, Fray, & Farthing, 2000)

There is at present a significant uncertainty regarding the $TiO_2$ feedstock used in this process, its cost and the resulting impurities in the produced metal. As shown in Table 6.3, ilmenite and slag contain much too high levels of impurities to be used directly. Rutile contains much lower impurity levels, might be used for non-aerospace titanium metal, but should still be tested and confirmed. The $TiO_2$ currently used in the process is pigment grade and thus very expensive (Kraft, 2002), pushing up the overall economics of this alternative. Another fundamental concern is the formation of calcium titanite, $Ca_xTi_yO_z$, during the electrolytic reaction in the molten $CaCl_2$ bath, especially if the titanium feedstock is $TiO_2$ and thus in the $Ti^{4+}$ valence state (Withers, Cardarelli, Laughlin, & Loutfy, 2008).

Metalysis, a company based in the United Kingdom, acquired the head license for the FFC Cambridge process in January 2006 and started operations at the titanium pilot plant at Farnborough. In October 2006, Metalysis acquired another electrode deoxidation process, developed by BHP Billiton, called the Polar Process. BHP Billiton received a minority stake in the new joint venture company, which is now called Metalysis Titanium.

Metalysis Titanium has combined the expertise and intellectual property of both the FFC Cambridge and Polar processes and in early 2007 consolidated the development of the two titanium extraction processes. BHP Billiton already produced 10kg/day at its technology centre in Australia in 2006 before the intellectual property transfer.

In mid 2006 it was announced that an investment of $4.40 million in an alloy production centre to commercialize the use of the FFC process for a range of alloys, including those based on titanium, has been cleared and by May 2009, Metalysis has raised almost $8.20 million to further scale-up the FFC Cambridge process. The company is currently supplying low volumes of metallurgical grade powders to its partners and is scaling up to enter the titanium markets more significantly in early 2010 (Pudney, 2009). Besides the laboratory and development cells, where quantities of between 100g and 20kg are reduced in each experiment, primarily to establish a fundamental knowledge and understanding of reduction mechanisms, process optimization and cell geometry, an operational batch pilot plant has been set up. In these batch pilot cells, approximately 100kg of feedstock can be reduced in each batch. These cells, commissioned in 2005, have helped characterize and resolve various scale-up issues. Even though these cells are well designed and engineered from an electrochemical perspective, they are not capable of the rapid reduction and turnaround times necessary to make the process economically viable. Currently a new generation of semi-continuous pilot cells are being designed and built (Pudney, 2009).

### 7.3.4 Ginatta Process

Ginatta Tecnologie Titanio, GTT, in Italy developed and piloted a high-temperature, of more than 1 700°C, electrowinning cell for the direct production of liquid titanium from $TiCl_4$. GTT believes that the key to lower cost titanium production is to produce it in liquid form, as with most other metals. Marco V. Ginatta has been working on an electrolytic method of producing titanium since the early 1980s. The technology was supported in part and licensed to RMI from 1985 to 1991. According to the patent registered in 1987 (Ginatta & Orsello, 1987) the leading challenges were addressed:

- The need to carry out the electrolysis in a substantially sealed container to avoid contamination of the bath by atmospheric gases.
- Problems and difficulties with the crystalline morphology of the formed titanium metal.

- The high reactivity of the produced metal when in contact with air at elevated temperatures. The metal must thus be cooled in an inert atmosphere to allow it to be stored subsequently.
- Another difficulty was how to deal with the very low solubility of $TiCl_4$ in molten salts.

However, at that stage engineering issues related to multivalency and liquid metal production resulted in high production costs. In 1992, these issues and a market downturn caused RMI to withdraw from the project (Kraft, 2004).

Ginatta has refined the process and addressed these issues, resulting in a new concept. The reaction dynamics of $TiCl_4$ with calcium is fast; it is for this reason that a concentration of elemental calcium be present in the electrolyte. $TiCl_4$ vapour is injected into the electrolyte where it is absorbed. A multilayer cathodic interphase, consisting of ions of K, Ca, Ti, Cl and F, separates the molten titanium cathode from the electrolyte. The bottom layer produced liquid titanium, which could thus be removed from the bottom of the container.

The current pilot plant produces titanium liquid that is cast into 250mm diameter ingot, but the process is complex and little information is available on likely production costs. Besides the complexity of the reactor, the use of $TiCl_4$ is a limiting factor when the cost reduction potential is considered. Also, the ability to start up and shut down when operated in continuous mode needs to be demonstrated (Kraft, 2004). According to Van Vuuren (Van Vuuren, 2008) the long process times at extreme conditions and the complexity of the reactor are the main drawbacks of this alternative.

### 7.3.5 Idaho Titanium Technologies

Idaho Titanium Technologies originally developed a small-scale, experimental plasma reactor system, incorporating a rapid plasma quench step, to produce titanium hydride powder. In 2001, they obtained funding from a NIST ATP[17] grant, to scale-up the production process to a production rate of 50kg/h at the required purity and quality level. ITT systematically addressed the engineering issues associated with the design and

---

[17] NIST ATP: The National Institute of Standards and Technology's Advanced Technology Program.

performance of the plasma torch operation, reactor, quench system and the powder collection (Cordes & Donaldson, 2001).

The process involves the thermal disassociation and reduction of $TiCl_4$ to produce a fine hydride powder. Research focused on increasing the particle size of the titanium hydride powder and in early 2004 the production rate was reported to be 18.14kg/h.

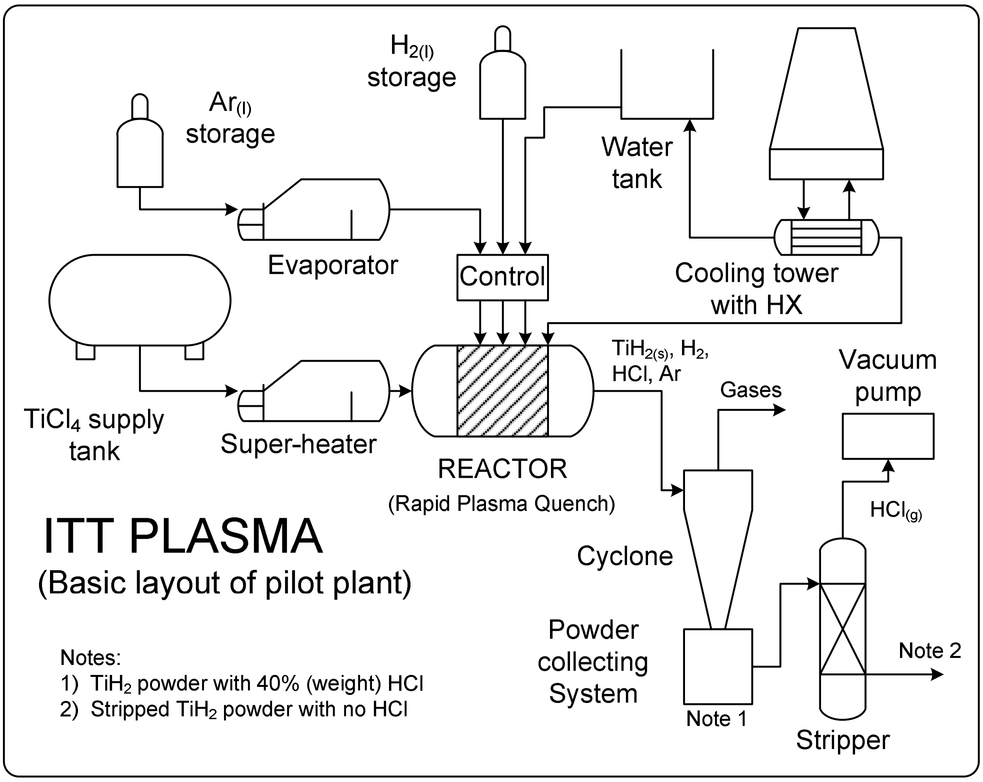


Figure 7.6: Basic process flow diagram of the plasma quench reactor system (Kraft, 2004)

As mentioned earlier, ITT produces an ultra-fine spherically shaped titanium hydride powder using a plasma process, directly followed by a rapid, quenching step and then hydrogenation. The reaction takes place according to the following:

Equation 30 and 31:

$$TiCl_{4(g)} \xrightarrow[Plasma]{} Ti + 4Cl$$

$$Ti + 4Cl + 3H_2 \xrightarrow[Quench]{} TiH_{2(s)} + 4HCl_{(g)}$$

The characteristics that are responsible for the capabilities of this system are apparently the following (Cordes & Donaldson, 2001):

- The arc directly heats the reactants. Most of the arc length is composed of the reactant species, or their dissociated ionized products. Very efficient heat transfer is accomplished by this innovation. As a result, even corrosive species such as chlorine can be directly heated to over 4 500°C without corrosion problems arising for either the reactor or the electrodes.
- This direct heating, as mentioned above, enables very short residence times in a very small reactor.
- The specifically designed and patented reactor (Detering, Donaldson, Fincke, & Kong, 1998) with the Delaval nozzle can cool the reactants at an incredible rate. This unique rapid quench is critical in that it prevents any back-reactions and permits the retention of otherwise unstable products.

There are limited applications for a titanium hydride powder in manufacturing mill products. However, the powder produced by the ITT plasma quench process is much more resistant to oxidation than normal titanium metal powder and according to Froes *et al*. there are some advantages in using titanium hydride in powder metallurgy manufacturing. Apparently the addition of hydrogen as an alloying element has a beneficial effect on the workability, because it leads to an increase in ductility and decrease in strength at high temperature (Froes, Senkov, & Jonas, 1996). The hydrogen can be removed from the powder by heating the titanium above 400°C (Cordes & Donaldson, 2001).

### 7.3.6 MER (Materials & Electrochemical Research Corporation)

MER has developed an overall reduction process that is significantly different from other emerging technologies. The first step and objective of the MER process is to carbothermically reduce the titanium feedstock, mostly rutile, to a lower oxide. Carbothermic reduction has been established as the most economical process to produce a metal in its pure metallic form. However, it is not always possible to completely win the metal from its ore, for undesirable side-reactions, such as the formation of carbides, is a difficulty and drawback. That has been the case for $Al_2O_3$ and traditionally also for $TiO_2$, which has not yet been carbothermically reduced to pure titanium (Withers, Cardarelli, Laughlin, & Loutfy, 2008).

According to MER, $TiO_2$ could be carbothermically reduced to TiO. It is even possible to remove more oxygen from the TiO to produce a suboxide of titanium with a O:Ti ratio of less than 1. Obviously, the more oxygen removed by this step, the less required to be removed by electrons in electrolytic reduction which has been frequently proven to be inefficient. It is known that thermal reduction of metal oxides is more economical than using electrons produced by electrolysis which is why iron and many other metals are won by thermal reduction processes (Loutfy & Withers, 2007).

As seen in Figure 7.7, the $TiO_2$ containing feedstock is mixed with either graphite flakes and a binder or a carbon precursor[18] which also acts as a binder for the sintering step where the powders are consolidated. Carbothermic reduction is then typically performed, Equation 32, in the absence of air under an inert atmosphere or vacuum in the temperature range of 1 200°C – 2 100°C (Loutfy & Withers, 2007). The process, depending on operating parameters, removes most of the metallic iron and some of the metals that alloy with iron, such as Mn, Cr and V.

Equation 32 (Carbothermic reduction):

$$TiO_2 + C \xrightarrow[\Delta:\ HEAT]{} Ti_xO_yC_z + (1-z)CO$$

The values of $x$ and $y$ present any of the possible combinations of the formed titanium suboxides with the O:Ti ratios as described previously, and $z$ is the carbon fraction as part of the solid product.

---

[18] Carbon precursor: A liquid, such as phenolic or resin binder, which when pyrolized will provide a high yield of carbon.

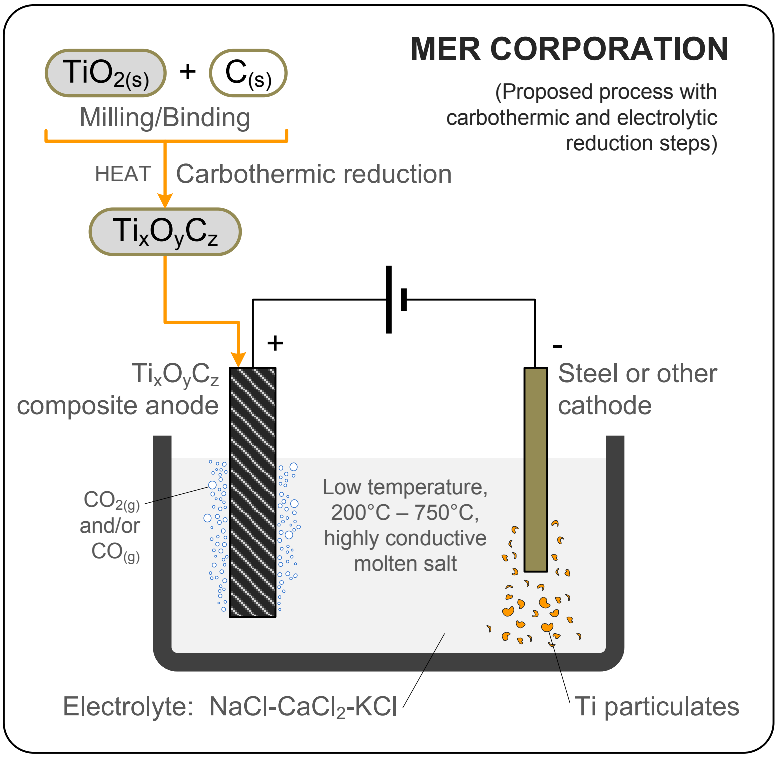


Figure 7.7: Schematic diagram showing the electrochemical cell of the MER process (Kraft, 2004)

If stoichiometrically required, carbon is added to the reduced product, and again consolidated to form the composite anode which is then used in the electrolytic reduction step. $Ti^{3+}$ and $Ti^{2+}$ ions are released into the electrolyte, are further reduced and deposit as titanium metal on the cathode as particulates (Kraft, 2004). The electrolytic reactions are as follows:

Equation 33 (Anode reaction):

$$Ti_xO_yC_z \rightarrow xTi^{2+} + z\,CO/CO_2 + 2e^-$$

Equation 34 (Cathode reaction):

$$xTi^{2+} + 2xe^- \rightarrow xTi_{(S)}$$

DARPA[19] awarded MER a contract for the development of this process in 2003, followed by a further award in 2006 to a consortium of MER and DuPont to further develop the process for making titanium metal powder. The scaled-up facility's design specifications and objectives are to produce 227kg/day of powder (Withers, Cardarelli, Laughlin, & Loutfy,

---

[19] DARPA: The Defence Advanced Research Projects Agency is the central research and development office for the United States of America's Department of Defence.

2008). DuPont supplied the $TiO_2$ as feedstock and participated in the design and development of the scaled-up system, whereas MER provided the core technology for converting $TiO_2$ to metal. MER conducted the experimental work, constructed and operated the scaled up system.

### 7.3.7 OS Process (Kyoto University)

Katsutoshi Ono and Ryosuke Suzuki, hence the OS Process, of the Kyoto University developed an electrolytic process for producing titanium by calciothermic reduction of $TiO_2$. The main electrolytic reaction is as follows:

Equation 35:

$$TiO_2 + 2Ca^+ + 2e^- \rightarrow Ti + 2Ca^{2+} + 2O^{2-}$$

The FFC Cambridge process, refer to section 7.3.3, shares many of the technical fundamentals with the OS Process, for it is also an electrolytic process that uses a molten bath of $CaCl_2$. However, the deoxidation requires a long time because oxygen is present in small amounts in the titanium metal formed at the cathode and its diffusion in solid matter becomes the rate-determining step (Ono & Suzuki, 2002).

$TiO_2$ is reduced in the following manner with the OS Process:

a) A molten salt, consisting of $CaCl_2$ and CaO is prepared as a reaction region inside the reactor.

b) The molten salt in this region is then electrolyzed to generate monovalent calcium ions, $Ca^+$, and elemental Ca, thereby converting the molten salt into a strongly reducing environment.

c) $TiO_2$ is then introduced to this region to be reduced to form titanium metal. The following reactions occur at the cathode and anode respectively:

Equation 36, 37 and 38: (Cathode reactions)

$$Ca^{2+} + e^- \rightarrow Ca^+$$

$$Ca^{2+} + 2e^- \rightarrow Ca$$

$$Ca^+ + e^- \rightarrow Ca$$

Equation 39 and 40: (Anode reactions)

$$C + O^{2-} \rightarrow CO + 2e^-$$

$$C + 2O^{2-} \rightarrow CO_2 + 4e^-$$

d) A partitioning device is installed which allows the monovalent $Ca^+$ generated in the electrolysis zone to migrate to the reduction zone, trading places with the CaO formed in the reduction zone.

e) The formed titanium metal agglomerates, recovered from the reduction zone are washed with either water or dilute HCl for the removal of $CaCl_2$ and CaO adhered to the surface.

f) The final product, the metal agglomerates, is very similar to the sponge formed during the Kroll process, so the further processing is technically and economically similar.

In 2004 it was reported that industrial development of the OS process was going ahead in cooperation with a Japanese aluminum company, Nippon Light Metal but no further reports have been noted. The process has the advantage that low oxygen titanium can be produced in reasonable time and at moderate cost but problems have been identified in transferring the technology to a larger scale and continuous operation, particularly the separation of titanium from the bath constituents and purification to a low Cl level (Kraft, 2004). Also, as mentioned earlier, the fact that the formed product and its processing are similar to the processing of sponge, make the overall cost-reduction potential slightly less attractive.

### 7.3.8 Peruke (Anglo American)

Peruke, a subsidiary of Anglo American, has patented a process for the production of titanium powder from titanium containing minerals such as ilmenite and rutile, which consists of a hydrometallurgical and a pyrometallurgical stage (Pretorius, 2005). The process can be described in the following steps:

1. Digestion of titanium containing feedstock, such as ilmenite and rutile, with diluted hydrofluoric acid, HF, to form $FeTiF_6$ as shown in Equation 41. To ensure that all the acid has been reacted, an excess of 20% ilmenite is used during this digestion reaction. The unreacted ilmenite, because of its density and coarse particle size, could be easily recovered and recycled. The reaction is strongly exothermic. During this step, iron filings were added to the solution to reduce all soluble $Fe^{3+}$ to

$Fe^{2+}$. Following the completed reaction and related activities, the suspension is filtered and washed.

Equation 41:

$$FeTiO_{3(s)} + 6HF_{(aq)} \rightarrow FeTiF_{6(aq)} + 3H_2O$$

2. The selective precipitation of $(NH_4)_2TiF_6$ by the addition of ammonium chloride ($NH_4Cl$). Based on the solubility difference between $(NH_4)_2TiF_6$ and $(NH_4)_2FeCl_4$ the crystalline product could be removed, washed and filtered, effecting the separation of the titanium from the iron species. If needed, the purity of this titanium precursor could be increased by an additional recrystallization step.
3. The formed and purified $(NH_4)_2TiF_6$ is dissolved in water and reduced with mercury-activated aluminum, Al(Hg). The reaction is exothermic and the precipitated product consists of both $NH_4TiF_4$ and $(NH_4)_3AlF_6$ in the weight ratio of 3:1, but the $(NH_4)_3AlF_6$ could be washed away with diluted HF, because the titanium containing product has a very low HF solubility.
4. This step includes the thermal decomposition of the formed $NH_4TiF_4$ at approximately 700°C in an inert, preferably argon, atmosphere in a mild steel rotary kiln according to the following equation:

Equation 42:

$$NH_4TiF_4 \xleftrightarrow[\Delta:\ HEAT]{} TiF_3 + xNH_4F$$

5. The preferred route for reducing the $TiF_3$ to titanium metal is reduction with aluminum, together with the sublimation of the formed $AlF_3$, but the process can apparently be adapted to produce a variety of metal alloys. According to the inventor (Pretorius, 2005), it is found to be undesirable to sublime all the $AlF_3$, for a fluoride coating acts as a protective layer, increasing the safety of storage, handling and transporting the formed titanium powder.

Peruke has reported that a very pure titanium precursor, $(NH_4)_2TiF_6$ can be produced from ilmenite and be used to produce titanium metal with oxygen levels equivalent to that of Grade 1 titanium. The optional pathways are illustrated in Figure 7.8 with all the shaded species referring to titanium containing components.

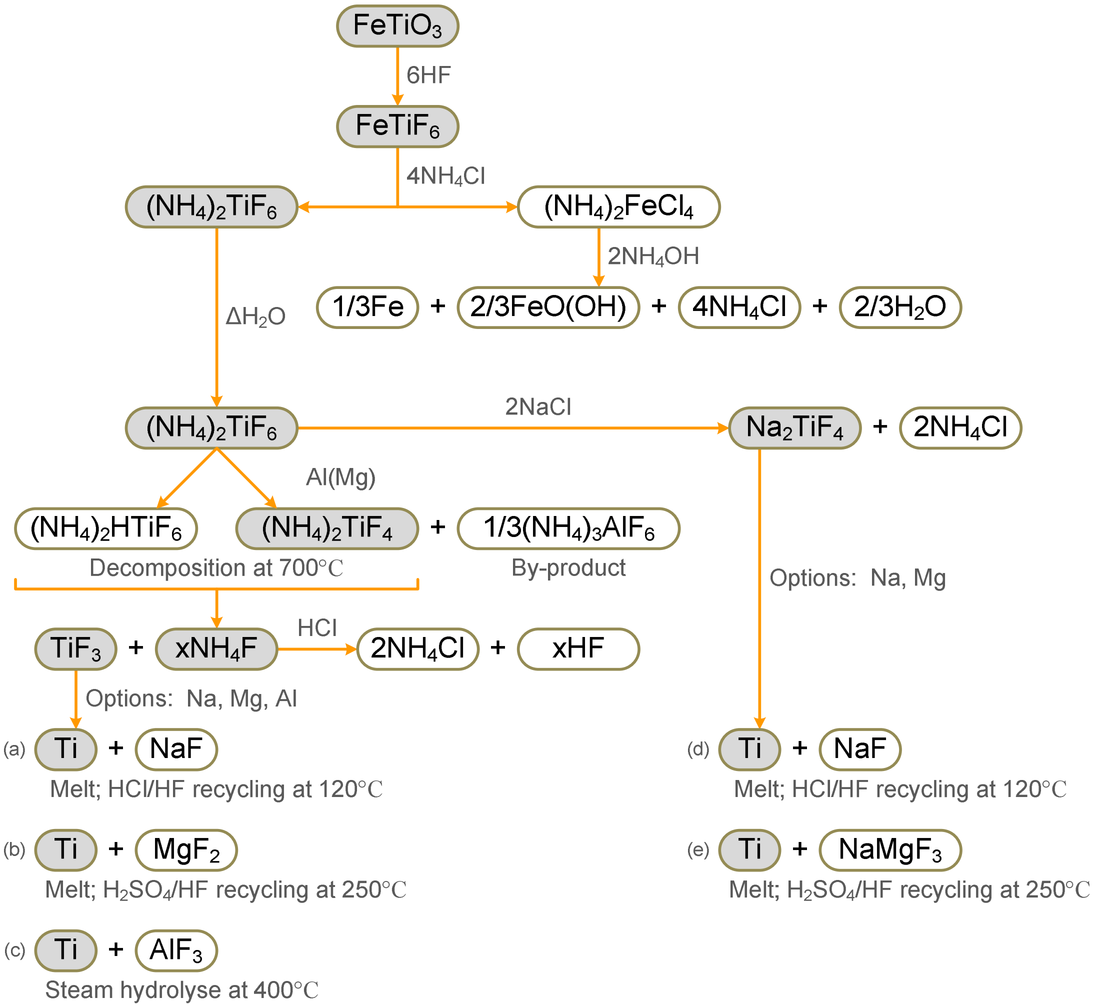


Figure 7.8: Schematic diagram of the Peruke process with the two options: Al(Mg) or NaCl (Pretorius, 2005)

A pilot plant has been commissioned and built at Crown Mines in Johannesburg, South Africa, by Anglo American to test the industrial viability and continuity of the Peruke process (Prinsloo, 2008).

### 7.3.9 SRI International

The process developed by SRI uses a high temperature fluidized bed to convert $TiCl_4$ and other metal chlorides to titanium or titanium alloy by making use of hydrogen, or any other hydrogen releasing compound, as the reduction agent. Several reactor designs are possible, with either one or two reaction chambers, for the two reaction zones are typically maintained at different temperatures (Figure 7.9).

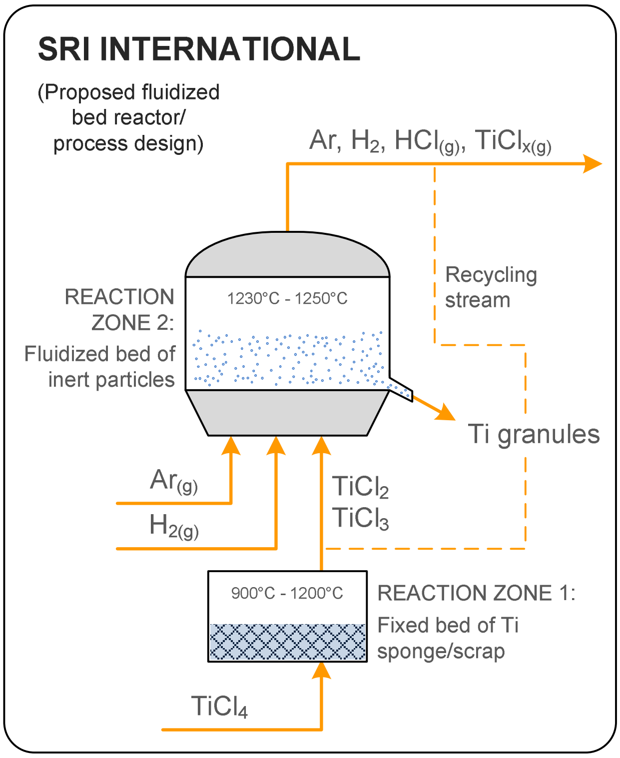


Figure 7.9: Schematic diagram and basic layout of the fluidized bed reactor

In the first zone, kept between 900°C and 1 200°C, $TiCl_4$ vapour is passed through a fixed bed of either titanium sponge or scrap metal and reacts according to the following equations:

Equation 43 and 44:

$$3TiCl_{4(g)} + Ti_{(s)} \rightarrow 4TiCl_{3(g)}$$

$$TiCl_{4(g)} + Ti_{(s)} \rightarrow 2TiCl_{2(g)}$$

The formed titanium subhalides, $TiCl_x$, are moved to the second zone together with an inert carrier gas, argon, disproportionated and reduced by hydrogen to form the reaction product:

Equation 45:

$$2TiCl_{x(g)} + xH_{2(g)} \rightarrow 2Ti_{(s)} + 2xHCl_{(g)}$$

For rapid deposition of titanium, as required for industrial production rates, a temperature above 1 200°C is generally maintained (Hildenbrandt & Thiers, 2004). The use of an atmospheric pressure fluidized bed chemical vapour deposition (FB-CVD) reactor leads to very high efficiency in metal deposition, due to the proven high heat and mass transfer coefficients available in the fluidized bed.

Although $TiCl_4$ and other metallic chlorides for alloying must still be prepared as a starting material, this process produces alloyed powders directly, without the need to mix metallic titanium and other alloying metals. Unlike the Kroll process and several of the other alternatives, this process does not require the formation of any intermediaries containing high levels of halides. As a result, the metallic composition produced as the final product does apparently not need further purification or processing, before commencing with manufacturing steps (Hildenbrandt & Thiers, 2004). Impurity elements, such as carbon and nitrogen present in the titanium sponge and scrap should be relatively stable as carbide and nitride and should thus not be transported and removed from the first reaction zone by means of the carrier gas. Oxygen, however, could possibly form $TiOCl_2$ which results in notable difficulties. Pilot plant construction was scheduled for 2005/6, but there is no evidence of samples of material being available.

### 7.3.10 TiRO (CSIRO)

The Commonwealth Scientific and Industrial Research Organisation[20] (CSIRO) has recently developed the TiRO process as an alternative method for producing titanium. The same chemistry, as used in the Kroll process, is used, but with two important differences: firstly, that the TiRO process turns $TiCl_4$ directly into titanium powder (ABARE, 2008) and secondly, the possibility of producing the powder in a continuous manner.

Grant Wellwood is leading a Light Metal Flagship (LMF) research project as part of CSIRO to develop this new TiRO process. In November 2005, the operational potential of this process had been proved on laboratory scale, producing titanium powder at the rate of 200g/h (Considine, 2005). The CSIRO approach is to use a fluidized bed in conjunction with the magnesiothermic reduction reaction of the Kroll process for a continuous powder making process. The kinetics is apparently favourable, with the fluidized bed mass transfer providing a high single pass conversion. The TiRO process has a high product yield with minimal losses to the iron retort walls and limited losses to subhalides (Wellwood, 2006).

---

[20] CSIRO: The Commonwealth Scientific and Industrial Research Organisation, is Australia's national science agency and one of the largest and most diverse research agencies in the world. CSIRO has established a number of National Research Flagships covering a vast array of different disciplines and fields, including Light Metals. One of the LMF research projects focused on developing the TiRO process as a cost-effective alternative to the Kroll process.

The $TiCl_4$ is reacted with magnesium in a fluidized bed reactor and is operated within a narrow temperature window, but the bed has the capacity to self regulate and therefore this operating window is robust and easily maintained. The reaction starts slowly, but as liquid magnesium chloride begins to be formed, the reaction rate increases substantially. An advantage of the TiRO process is that by producing titanium powder and not sponge, many of the intermediate stages, such as the vacuum distillation and the formation of ingots, if the benefits of powder metallurgy are taken into account, could be avoided. The TiRO process further allows some flexibility with regard to the particle characteristics and thus could be altered to suit different needs.

The laboratory-scale testing of this process has produced titanium metal with unacceptable high oxygen content - above the allowed 0.25% oxygen levels for grade 2 commercially pure titanium. Besides not being able to obtain a pure enough titanium metal as a final product, this process is making use of $TiCl_4$ as feedstock and can thus not take advantage of the economic benefits associated with the use of other alternatives, such as rutile or ilmenite. Scaling-up to a 50kg/day pilot plant should reduce the current high oxygen content and provide a platform to critically investigate the economics of the process (Wellwood, 2006).

## 7.4 Other processes beyond the scope of this study

It has been mentioned previously that globally there are approximately 24 research and development programmes running to find an effective, both technically and economically, alternative to the existing Kroll process. In Table 7.2 the remaining 14 process alternatives are summarized. Some of them have been discontinued, because of economic problems, the difficulty in attracting and maintaining interested investors or maybe even unsolvable technicalities.

It must be mentioned and realized that none of the options listed in the Table 7.2 show no potential or promise. Each alternative was founded on a principle and method which was built upon the work of a predecessor and a previous concept or idea. The fact that these options were removed by the first filtering stage of the techno-economic evaluation, based on qualitative analytic principles, might appear subjective.

Table 7.2: R&D programmes and titanium producing alternatives screened and removed

**Name/Organization involved with this research:**

| No | Process name: | Brief description: |
|---|---|---|
| 1 | AlTi | Reduction of $Na_2TiF_6$ with Al |
| 2 | CSIR | $H_2$ reduction of $TiCl_4$ |
| 3 | DMR | Aluminothermic process to convert $TiO_2$ |
| 4 | DuPont | Na reduction of $TiCl_4$ |
| 5 | EMR/SME | Electronically mediated reduction in molten salt |
| 6 | Japan Titanium Society | Liquid $CaCl_2$, with dissolved Ca, reduction of $TiCl_4$ |
| 7 | MHR Process | CaH reduction of $TiO_2$ |
| 8 | MIR-Chem | $TiO_2$ granules reduced by $I_2$ in shaking reactor |
| 9 | MIT Titanium Initiative | Electrolytic reduction of $TiO_2$ in oxide melt |
| 10 | Norsk | Calciothermic reduction of $TiO_2$ |
| 11 | Norton Wheel | Electrolytic cell for TiC |
| 12 | Preform Reduction Process | Reduction of $TiO_2$ by Ca |
| 13 | Rhone Poulenc | Li reduction of $TiCl_4$ |
| 14 | Vartech | Gaseous reduction of $TiCl_4$ vapour |

It is, however, also important to note that most of these processes never progressed further than laboratory scale and were thus still a considerable way from commercialization. It was one of the aims and objectives of this study to focus primarily on those options with a reasonable chance of being industrialized in the next 5 to 10 years. The first filtering stage was therefore constructed in such a way as to remove the alternatives that either have been terminated or are close to be terminated by their respective researchers or investors, or those that have no likely chance of developing into an industrial process within the next 5 to 10 years. Future research projects could thus fit the remaining alternatives listed in Table 7.2 into their scope.

chapter | eight

# 8 RESULTS OF EVALUATION AND DISCUSSION

The processes to produce and refine titanium metal studied in chapter 7, were subjected to the decision criteria of the techno-economic evaluation as designed in section 6.4 and the results were compiled in this chapter. As shown in Table 8.1, it was decided to make use of an index, to enable easy reference to any of the selected 12 options. This Alternative Process Index (API) will therefore be used throughout the results, the tables and figures of this chapter.

Table 8.1: The Alternative Process Index (API) and the relevant author(s)

| No | API | Process name: | Author(s): |
|---|---|---|---|
| 1 | ArmITP | Armstrong/ITP | Anderson, Armstrong, Jacobsen |
| 2 | CardQIT | Cardarelli (QIT Fer et Titane) | Cardarelli, Turgeon |
| 3 | FFC | FFC Cambridge | Chen, Farthing, Fray |
| 4 | Ginatta | Ginatta Process | Ginatta, Orsello |
| 5 | Hunter | Hunter | Hunter |
| 6 | ITT | Idaho Titanium Technologies | Cordes, Donaldson |
| 7 | Kroll | Kroll | Kroll |
| 8 | MER | MER Corporation | Loutfy, Withers |
| 9 | OS | OS Process (Kyoto University) | Ono, Suzuki |
| 10 | Peruke | Peruke (Anlo American) | Pretorius |
| 11 | SRI | SRI International | Hildenbrand, Thiers, Sanjurjo |
| 12 | TiRO | TiRO (CSIRO) | Wellwood |

Furthermore, this chapter is divided into three sections:

a) All the intermediate findings noted during the evaluation process on the results of the decision criteria and the respective outcome of each criterion. The three criteria with sub-levels and not simply a definite answer to the options posed by the decision criteria are discussed in detail. The methods and techniques used to calculate a representative value for each process alternative for these three criteria are explained. Thereafter, the results based purely on the values the alternatives scored for the decision criteria, but prior to TOPSIS, will be presented.

b) The main results of the techno-economic evaluation, with the specific weights calculated by means of the AHP and ranked using the TOPSIS technique. The correlation coefficients were then calculated to see which pairs of the decision criteria could be judged faulty.

c) The outcome and results of the sensitivity analysis has been compiled and are represented in this section.

## 8.1 Results on decision criteria

In the following paragraphs the intermediate findings on the characteristics of the decision criteria as noted during the evaluation are discussed. Special attention is given to the following three criteria: 1) Academic coverage and innovation activity, 2) Commercial readiness and 3) Complexity of process alternative.

### 8.1.1 Academic coverage and innovation activity

According to the IP (intellectual property) solutions business of Thomson Reuters[21] it is possible to track the innovation hubs by analyzing global patent activity. By recording the total number of unique inventions in published patent applications and granted patents over a given period, researchers are able to identify segments within an industry that are receiving growing attention from investors (Roderick & Gaze, 2009). In a similar way, although in not as much detail, the WIPO database was analyzed and used in this study to obtain relevant insight in the innovation trends within the titanium industry. The innovation activity, AC1, was determined by counting the number of relevant patents filed per author and calculating the average per process. The final results of this analysis are given in Table 8.2, together with a normalized representation of the amount of academic articles (AC2) available, directly and indirectly related to the specific process in question.

---

[21] Thomson Reuters is the world's leading source of intelligent information. Among several market and professional divisions (Sales & Trading, Enterprise, Investment & Advisory, Media, Legal, Tax & Accounting and Healthcare & Science) it provides critical information to decision making authorities.

Table 8.2: The number of filed patents and academic articles for each process

| | | | | | Normalized: | |
|---|---|---|---|---|---|---|
| No | Author(s): | # Patents: | | | AC1 | AC2 |
| 1 | Anderson, Armstrong, Jacobsen | 1 | 6 | 5 | 0.084 | 0.079 |
| 2 | Cardarelli, Turgeon | 2 | 1 | | 0.032 | 0.026 |
| 3 | Chen, Farthing, Fray | 5 | 3 | 4 | 0.084 | 0.108 |
| 4 | Ginatta, Orsello | 1 | | | 0.021 | 0.036 |
| 5 | Hunter | 9 | | | 0.189 | 0.173 |
| 6 | Cordes, Donaldson | 1 | 0 | | 0.011 | 0.029 |
| 7 | Kroll | 14 | | | 0.295 | 0.289 |
| 8 | Loutfy, Withers | 4 | 4 | | 0.084 | 0.079 |
| 9 | Ono, Suzuki | 4 | 5 | | 0.095 | 0.079 |
| 10 | Pretorius | 3 | | | 0.063 | 0.017 |
| 11 | Hildenbrand, Thiers, Sanjurjo | 1 | 2 | 3 | 0.042 | 0.055 |
| 12 | Wellwood | 0 | | | 0.000 | 0.029 |
| | | | | | 1.000 | 1.000 |

In the figure below, the adjusted academic coverage, AC2, and innovation activity, AC1, for the process alternatives investigated in this study are illustrated graphically.

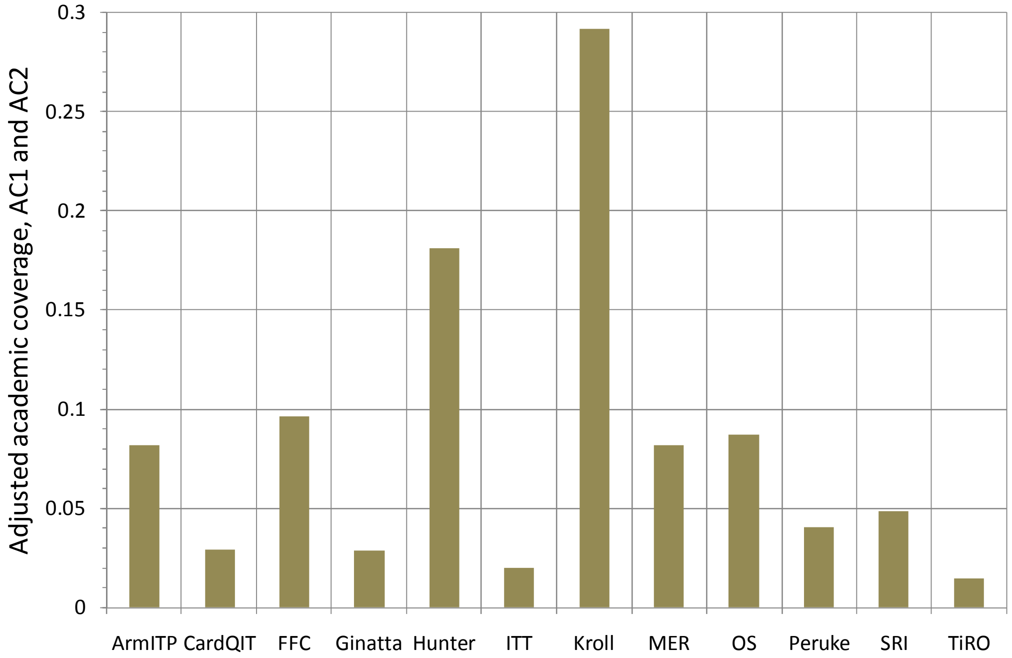


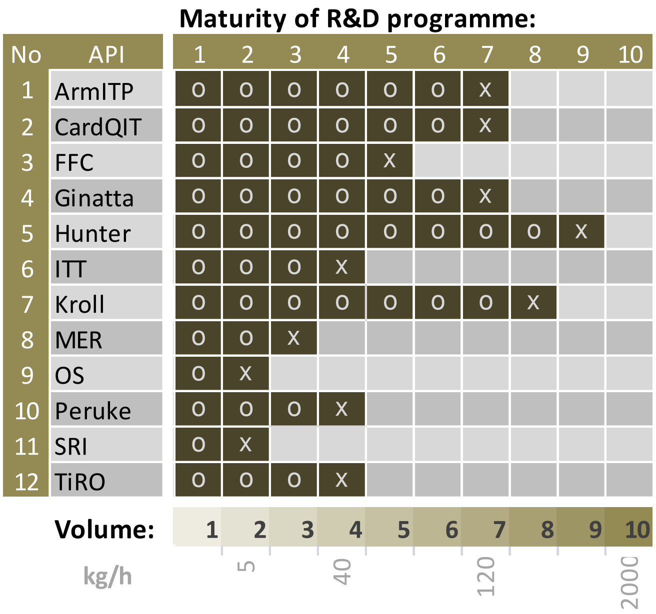
Figure 8.1: Representation of the combined academic and innovation coverage

The existing options, the Hunter and Kroll processes, recorded high values, as can be observed in Figure 8.1. Since both processes have been in operation and thus part of research and development programmes for a considerable longer period of time, compared to the other process alternatives.

### 8.1.2 Commercial readiness

As discussed in section 6.4.3, the development status of the investigated alternatives is at the heart of the technology management and implementation strategy. In Table 8.3, the level of commercial readiness is listed for each alternative, together with a production volume index.

Table 8.3: The respective development status of the investigated alternatives



| | | Maturity of R&D programme: | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| No | API | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| 1 | ArmITP | O | O | O | O | O | O | X | | | |
| 2 | CardQIT | O | O | O | O | O | O | X | | | |
| 3 | FFC | O | O | O | O | X | | | | | |
| 4 | Ginatta | O | O | O | O | O | O | X | | | |
| 5 | Hunter | O | O | O | O | O | O | O | O | X | |
| 6 | ITT | O | O | O | X | | | | | | |
| 7 | Kroll | O | O | O | O | O | O | O | X | | |
| 8 | MER | O | O | X | | | | | | | |
| 9 | OS | O | X | | | | | | | | |
| 10 | Peruke | O | O | O | X | | | | | | |
| 11 | SRI | O | X | | | | | | | | |
| 12 | TiRO | O | O | O | X | | | | | | |
| | Volume: | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| | kg/h | | 5 | | 40 | | | 120 | | | 2000 |

It is senseless to fix the production volume to a specific index, which would then be misused to categorize the technological progress only based on the amount of product produced. The four categories introduced in section 6.4.3, were incorporated into a 1 to 10 scale, and based on the appropriate commercial readiness, as follows:

- **1 and 2:** Laboratory scale production with volume no greater than a few kilograms per experimental run or batch. Mostly, only fundamental research with typical product batches of a 100g.
- **3 and 4:** Bench scale production would commence once the fundamentals have been found promising and feasible. Either, batch or continuous bench scale operations with volumes between 5kg/h and approximately 40kg/h, but mostly much smaller.

- **5, 6, and 7:** Pilot plants are built, mostly to test the commercial and operational viability of an alternative, but sometimes the production volumes are within a given order, 40kg/h and 120kg/h, that it could be marketed and sold.
- **8, 9 and 10:** Fully operational industrial plants with production volumes that even surpasses the 2000kg/h, which translates to a capacity of 17000 tonnes per annum, based on the index. The Hunter ranked higher than the Kroll process, because it is operated as a semi-batch and more advanced based on the index, although the production volumes of the plants that still use the Hunter process, are considerably smaller than the Kroll plants.

### 8.1.3 Complexity of process alternative

This is one of the most important criteria of this techno-economic evaluation and on which the outcome rests heavily, because the complexity of the processes investigated largely adds to the difficulty of conducting an objective evaluation. As discussed in chapter 7, it is clear that each process alternative faces a different set of technical and fundamental obstacles. Some of the alternatives struggle with up-scaling because of reaction dynamics, others are experiencing troubles with process fundamentals and impurities, and others with the formation of unwanted products and side-reactions. The critical reviews, mentioned in 6.4.4, such as the study performed by EHK Technologies in 2004, the Roskill's technical report in 2007 and the academic articles and works of authors like Froes, Gambogi, Gerdemann, Kraft and Van Vuuren, were used as a guideline to assess this criterion.

In Table 8.4, the results of the model are given, where M* is the pre-worked marks achieved, Mw the weighted marks, which normalized is given by the complexity index, CI.

The Scorecard Model was completed and a summary of the comments made by Kraft and Van Vuuren has been compiled in Appendix B: Additional Tables, for each process alternative and the CI calculated. The index is a compilation of the 10 criteria, introduced in 6.4.4, and the higher the representative value, the more complex the process in question.

Table 8.4: Computed results of the Scorecard Model

| No | ATP | M* | $M_w$ | CI |
|---|---|---|---|---|
| 1 | ArmITP | 4 | 0.301 | 0.053 |
| 2 | CardQIT | 4 | 0.327 | 0.057 |
| 3 | FFC | 3 | 0.395 | 0.07 |
| 4 | Ginatta | 7 | 0.845 | 0.149 |
| 5 | Hunter | 8 | 0.777 | 0.137 |
| 6 | ITT | 5 | 0.453 | 0.08 |
| 7 | Kroll | 6 | 0.453 | 0.08 |
| 8 | MER | 5 | 0.767 | 0.135 |
| 9 | OS | 3 | 0.395 | 0.07 |
| 10 | Peruke | 4 | 0.276 | 0.049 |
| 11 | SRI | 3 | 0.27 | 0.048 |
| 12 | TiRO | 3 | 0.419 | 0.074 |

For example, in Figure 8.2, it is interesting to note that two of the most complex processes, the Ginatta and MER alternatives, both electrolytic options, ranked high on the index. The one, Ginatta, makes use of a multilayer cathodic interphase, complex cell configuration and extreme conditions to allow a molten product, whereas the other, MER, makes use of a pre-carbothermic step to reduce and deoxidize the feedstock as far as possible and then sinter the product with a carbonaceous binder to form the anode, subsequently used in the electrolytic reduction step.

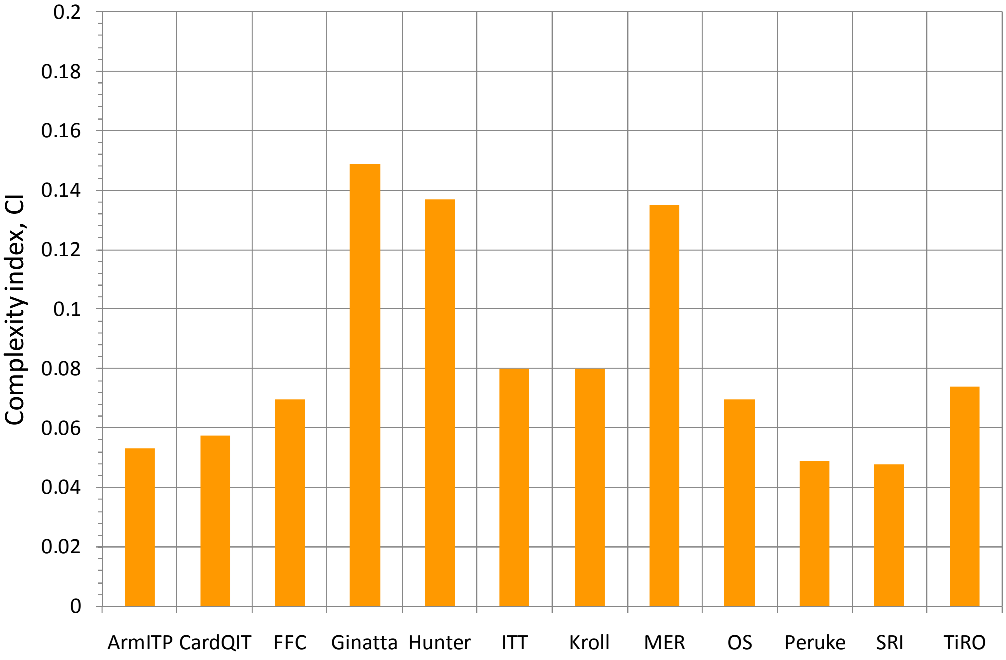


Figure 8.2: Representation of the complexity index, the CI

### 8.1.4 Compiled results of all the benefit and cost criteria

In the following section, the results of all the decision criteria, grouped as either benefit or cost criteria, are represented in Figure 8.3 and Figure 8.4. As part of the methodology of the TOPSIS evaluation, the decision criteria were grouped as either:

- **Benefit:** Which implies that for any incremental increase in the value each process alternative scored for the respective criteria, the accumulated result would be positively influenced. The benefit criteria: 1) academic coverage, 2) commercial readiness and 3) type of product.
- **Cost:** On the other hand, an incremental increase in the value scored for the remaining criteria would cause the result to be negatively influenced. The cost criteria: 1) complexity of process, 2) mode of operation and 3) economics of raw material.

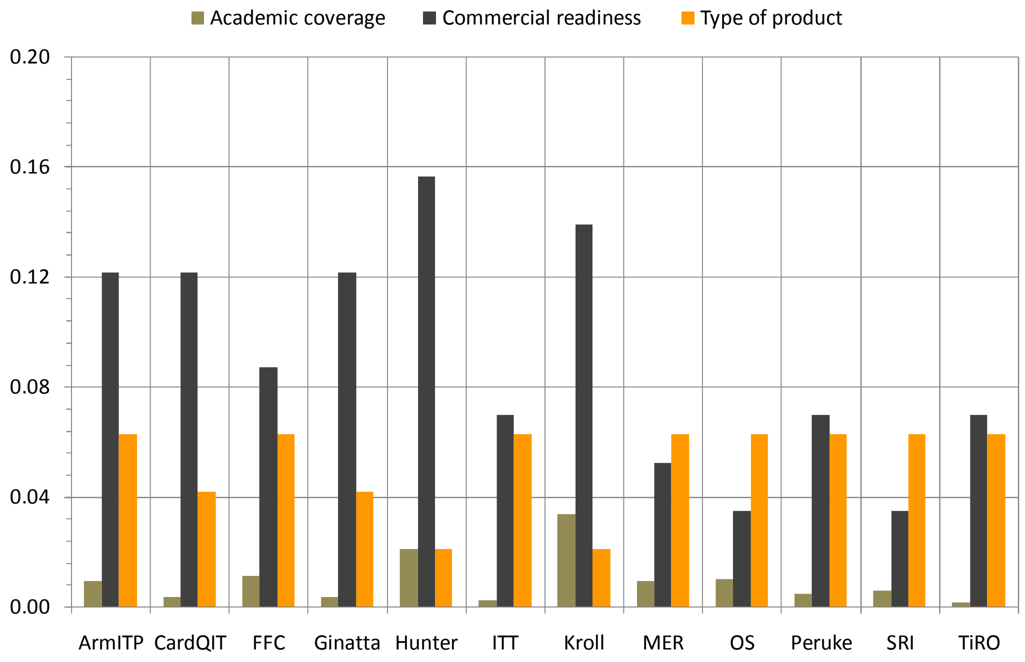


Figure 8.3: The respective scores for the three benefit decision criterions, C1 (academic coverage), C2 (commercial readiness) and C6 (type of product)

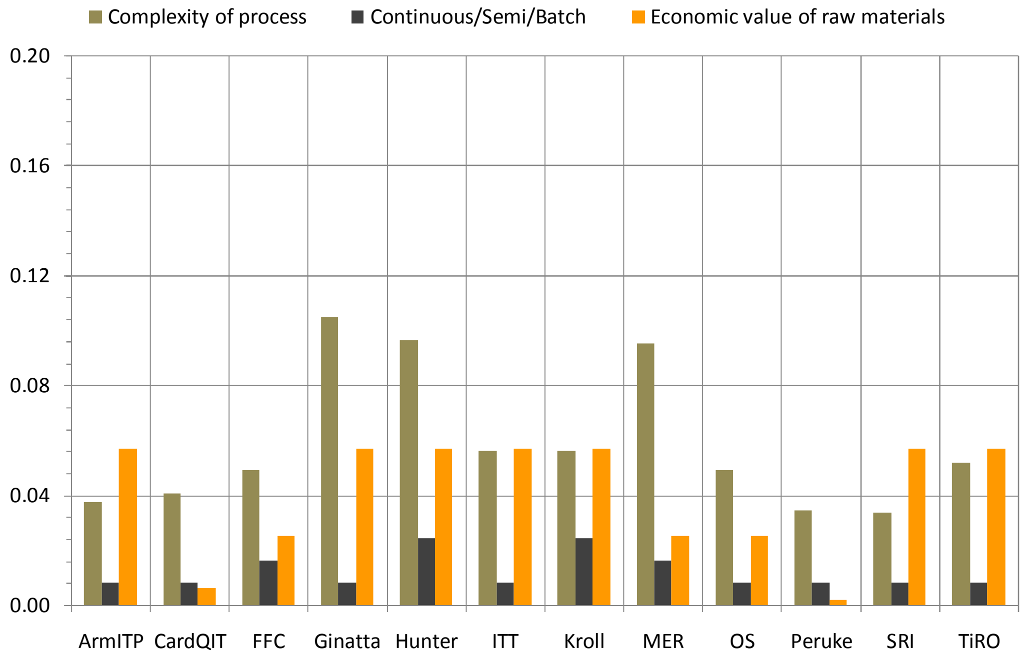


Figure 8.4: The scores for the three cost decision criterions, C3 (complexity of process), C4 (mode of operation) and C5 (economic value of raw material)

## 8.2 Main results of the evaluation

It is the objective of this section to introduce the main results of the techno-economic evaluation. All the decision criteria and their respective results have been discussed previously and compiled in section 8.1.4. To calculate the main results of the evaluation, the following steps have been taken and are introduced in this section accordingly:

1. Determining the specific weights of the decision criteria by means of the AHP.
2. Completing the decision matrix at the onset of TOPSIS. Thereafter it is normalized and the just determined specific weights used to allocate appropriate weighing.
3. Identifying the positive and negative ideal solutions.
4. Performing the TOPSIS algorithm with Euclidean distances to calculate the final ranking.
5. Calculating the correlation coefficients of the decision matrix to see which of the criteria pairings fall beyond the preferred range.

### 8.2.1 AHP with the decision criteria

In the following table, all the evaluation criteria were pairwise compared according to the AHP, described in section 4.2.3, to assess their 'relative preference' with respect to each other and the overall objective of the evaluation.

Table 8.5: The AHP to calculate the specific weights (priorities) of the decision criteria

| | | Pairwise comparison matrix: | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **Evaluation criteria:** | | C1 | C2 | C3 | C4 | C5 | C6 | Priorities |
| Academic coverage | C1 | 1 | 1/6 | 1/5 | 2 | 1/7 | 1/5 | 0.0455 |
| Commercial readiness | C2 | 6 | 1 | 2 | 3 | 2 | 4 | 0.3396 |
| Complexity of process | C3 | 5 | 1/2 | 1 | 4 | 3 | 1 | 0.2204 |
| Mode of operation | C4 | 1/2 | 1/3 | 1/4 | 1 | 1/3 | 1/8 | 0.0476 |
| Economics of raw material | C5 | 7 | 1/2 | 1/3 | 3 | 1 | 1 | 0.1573 |
| Type of product | C6 | 5 | 1/4 | 1 | 8 | 1 | 1 | 0.1896 |
| | | | | | | | Total | 1 |

The method compares and aggregates eigenvectors until the final vector for weight coefficients is obtained (Saaty, 1980). The final vector then reflects the relative importance of each criterion with respect to the objective of the techno-economic evaluation.

### 8.2.2 TOPSIS evaluation to determine ranking

The TOPSIS method is based on the concept that the chosen alternative should have the shortest distance from the positive ideal solution and the longest distance from the negative ideal solution. Three possible techniques are commonly used to calculate these distances, but the option to use Euclidean distances was considered most relevant and is discussed in detail in section 4.3.4.

The completed decision matrix is given in Table 8.6.

Table 8.6: The completed results for each of the decision variables

**Decision criteria:**

| | |
|---|---|
| Academic coverage | C1 |
| Commercial readiness | C2 |
| Complexity of process | C3 |
| Continuous/Semi/Batch | C4 |
| Economics of raw material | C5 |
| Type of product | C6 |

| No | ATP | | C1 | C2 | C3 | C4 | C5 | C6 |
|---|---|---|---|---|---|---|---|---|
| 1 | ArmITP | A1 | 0.082 | 0.113 | 0.053 | 1 | 8.73 | 3 |
| 2 | CardQIT | A2 | 0.029 | 0.113 | 0.057 | 1 | 0.92 | 2 |
| 3 | FFC | A3 | 0.096 | 0.081 | 0.07 | 2 | 3.87 | 3 |
| 4 | Ginatta | A4 | 0.029 | 0.113 | 0.149 | 1 | 8.73 | 2 |
| 5 | Hunter | A5 | 0.181 | 0.145 | 0.137 | 3 | 8.73 | 1 |
| 6 | ITT | A6 | 0.02 | 0.065 | 0.08 | 1 | 8.73 | 3 |
| 7 | Kroll | A8 | 0.292 | 0.129 | 0.08 | 3 | 8.73 | 1 |
| 8 | MER | A9 | 0.082 | 0.048 | 0.135 | 2 | 3.87 | 3 |
| 9 | OS | A10 | 0.087 | 0.032 | 0.07 | 1 | 3.87 | 3 |
| 10 | Peruke | A11 | 0.04 | 0.065 | 0.049 | 1 | 0.32 | 3 |
| 11 | SRI | A12 | 0.048 | 0.032 | 0.048 | 1 | 8.73 | 3 |
| 12 | TiRO | A13 | 0.014 | 0.065 | 0.074 | 1 | 8.73 | 3 |

Table 8.7: Defining the positive and negative ideal solutions from

**Positive and Negative IDEAL:**

| | $C1_{nw}$ | $C2_{nw}$ | $C3_{nw}$ | $C4_{nw}$ | $C5_{nw}$ | $C6_{nw}$ |
|---|---|---|---|---|---|---|
| A+ | 0.034 | 0.156 | 0.034 | 0.008 | 0.002 | 0.063 |
| A- | 0.002 | 0.035 | 0.105 | 0.024 | 0.057 | 0.021 |

In the table below, the results of the TOPSIS evaluation are given, with the Euclidean distances for each process alternative, ranked based on the final outcome. The CardQIT process appears to be the winning alternative, by a notable margin, with the ArmITP, Kroll and FFC in second, third and fourth place respectively.

Table 8.8: Main results of the TOPSIS evaluation ranked according to the Euclidean distances from the positive and negative ideal solutions

| No | $d^{+}_{j}$ | $d^{-}_{j}$ | $R_j$ | ATP |
|---|---|---|---|---|
| 1 | 0.051 | 0.128 | 0.714 | CardQIT |
| 2 | 0.070 | 0.127 | 0.646 | ArmITP |
| 3 | 0.077 | 0.126 | 0.623 | Kroll |
| 4 | 0.079 | 0.127 | 0.617 | FFC |
| 5 | 0.092 | 0.127 | 0.580 | Peruke |
| 6 | 0.096 | 0.124 | 0.564 | Hunter |
| 7 | 0.103 | 0.123 | 0.543 | Ginatta |
| 8 | 0.109 | 0.125 | 0.534 | TiRO |
| 9 | 0.110 | 0.125 | 0.532 | ITT |
| 10 | 0.127 | 0.125 | 0.496 | OS |
| 11 | 0.126 | 0.123 | 0.493 | MER |
| 12 | 0.136 | 0.124 | 0.476 | SRI |

An interesting observation is the fact that the ageing Kroll process is not lagging far behind the newer novel technologies. The reason for this is that the commercial readiness of the process alternative was given a weighted importance and since the Kroll process has been in operation for almost 60 years, it outperformed the others with regard to this criterion.

### 8.2.3 Correlation coefficients of evaluation criteria

Like the covariance, the correlation coefficient, is a measure of the extent to which two measurement variables ‘vary together’. Unlike the covariance, the correlation coefficient is scaled so that its value is independent of the units in which the two measurements are expressed. Three possible conclusions, based only on the values of these coefficients could be made:

- A value close to zero should be interpreted that the two criteria are for practical purposes unrelated.
- A large positive correlation coefficient means that large values of the one variable tend to be associated with large values of the other.
- A large negative correlation coefficient means exactly the opposite. That is that large values of the one variable tend to be associated with small values of the other.

For the purpose of this study, four correlation coefficients were highlighted in Table 8.9 with values outside the preferred range of positive and negative 70%. For any values bigger, it should be interpreted and understood that the coefficient’s two criteria are measuring partially the same qualities of the alternatives.

Table 8.9: The calculated correlation coefficients of the decision criteria with values outside the preferred range identified

| | C1 | C2 | C3 | C4 | C5 | C6 |
|---|---|---|---|---|---|---|
| C1 | 1.000 | - | - | - | - | - |
| C2 | 0.510 | 1.000 | - | - | - | - |
| C3 | 0.178 | 0.334 | 1.000 | - | - | - |
| C4 | 0.885 | 0.529 | 0.435 | 1.000 | - | - |
| C5 | 0.241 | 0.255 | 0.282 | 0.193 | 1.000 | - |
| C6 | -0.714 | -0.818 | -0.440 | -0.714 | -0.258 | 1.000 |

Although this finding does not have harmful implications on the outcome of the evaluation, it should be remedied by either removing the faulty criterion or adjusting the scope thereof in order to obtain a well-balanced assessment.

## 8.3 Sensitivity analysis

Following the TOPSIS evaluation and obtaining the ranking as given in Table 8.8, it was necessary to assess the outcome's sensitivity to any variations or disturbances in the values of the decision variables. This was done to test and ensure the robustness of the final ranking. The sensitivity analysis was divided into two legs. The aim of the first leg was to investigate the sensitivity of the final ranking to a complete range of both positive and negative offsets to the allocated weights. The second leg was conducted by removing a criterion from the evaluation, so that the overall effect and impact this respective criterion has on the final ranking, were studied. This was achieved by zeroing the specific weight of the criterion in turn and adjusting the remaining weights to normalize the evaluation.

For both cases, six representative process alternatives were selected and are represented in Figure 8.5 and Figure 8.6. The top four alternatives, as given by the final ranking (see Table 8.8), with a further two randomly selected options, were used to illustrate the overall sensitivity of the experimental results. These selected processes, in API format, are: CardQIT, ArmITP, Kroll, FFC, Peruke and ITT. For the sake of comprehensibility, only these six were chosen and the other processes just do not appear in the figures because they would only clutter the graphical representation and have no significant impact on the final outcome and conclusion.

### 8.3.1 Introduction and overview

The two-legged sensitivity analysis was designed to investigate firstly what the redistribution of the criteria's specific weights would have on the final ranking and secondly, what zeroing a criteria and thus the removal of its influence would have on the ranking.

### 8.3.2 Decision criteria adjusted by introducing percentage offset

Within the first leg of the sensitivity analysis, the local parameters were allowed to vary by redistributing the allocated specific weight of each decision criteria, according to the process introduced below.

- **Good cases:** For these cases, the specific weight of the benefit criteria was increased with the allocated percentage offset and the reverse for the bad cases.
- **Bad cases:** The specific weight of the cost criteria, for these cases, was increased with the allocated percentage offset and the reverse for the good cases.

The process was divided into 8 different cases, with the first and last case the normal scenario, with the AHP calculated specific weights with no adjustments. For each case, a percentage offset was introduced, as specified below:

Table 8.10: Offset details and specifications of the first leg of the Sensitivity Analysis

| No | Description | Type | Offset |
|---|---|---|---|
| 1 | Normal | - | 0 |
| 2 | Small | Good | 10 |
| 3 | Small | Bad | 10 |
| 4 | Medium | Good | 40 |
| 5 | Medium | Bad | 40 |
| 6 | Large | Good | 80 |
| 7 | Large | Bad | 80 |
| 8 | Normal | - | 0 |

The process alternatives vary in their dynamic nature with respect to the final ranking, as can be seen in Figure 8.5. During this analysis, the decision criteria were adjusted through a range of good/bad cases by introducing a percentage offset. For example, some of the alternatives, such as the CardQIT, Peruke, FFC and ITT processes, recorded a wide envelope during the sensitivity analysis, as compared to the others, which performed within a much narrower envelope.

Those options, such as the ArmITP and Kroll processes, thus represent the more stable, robust, predictable and less risky alternatives.

The final ranking stayed relatively unchanged with the leading options, CardQIT, ArmITP and Kroll, unchallenged for the first five cases, but when the medium to large offsets were introduced, the final ranking changed. This is especially true for case 5 and more so case 7, which significantly favours the process alternatives that were not as attractive in the benefit criteria (academic coverage, commercial readiness and type of product), but scored well in the cost criteria (complexity of process, mode of operation and the economics of the raw material). It could be observed in Figure 8.5 that the standing of two options, the Peruke and FFC processes, dramatically improved under these new adjusted conditions.

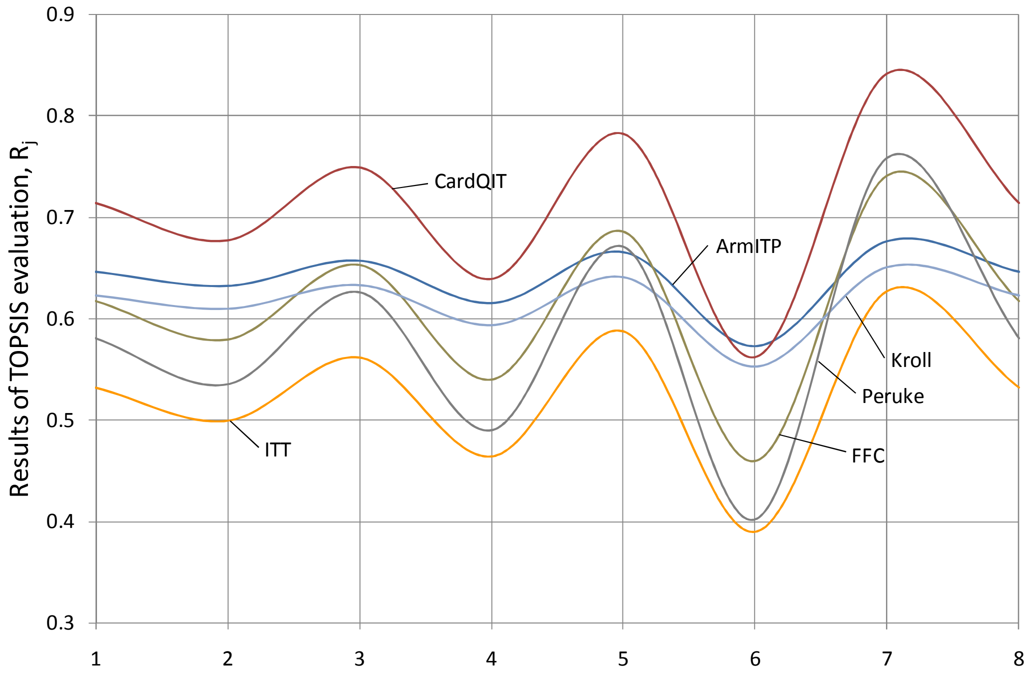


Figure 8.5: Results of TOPSIS, following the first leg of sensitivity analysis

### 8.3.3 Decision criteria zeroed to observe influence on ranking

In a similar way as the previous analysis, this process was also divided into 8 different cases, again starting and ending with the normal case. For the six steps in between, the specific weight of each criterion was zeroed and the remaining weights redistributed. For example, for the case 2, a specific weight of 0 was allocated to C1 (academic coverage) and the other weights recalculated to ensure that the summation still adds to 1. This procedure was then repeated for all of the other criteria in order for cases 3 to 7. The results were compiled and are represented in Figure 8.6, where the respective influence each of the criteria has on the final ranking, can be observed.

- **Cases 1 and 8:** Normal, nothing has been altered or changed.

- **Case 2:** C1, the decision criterion, academic coverage, has been zeroed by giving the specific weight of this criterion a value of 0. It could be noted that the influence, this criterion has on the final ranking is indeed minor.
- **Case 3:** The commercial readiness, C2, has been zeroed in this case to simulate a scenario and thus a ranking where all of the process alternatives are at the same level of commercialization.
- **Case 4:** The cost criterion C3, the complexity of the process alternatives, has been zeroed. This was done to simulate an environment where the variety of issues and difficulties, as identified by the industrial experts and compiled in the Scorecard Model as the complexity index, were removed.
- **Case 5, 6 and 7:** This zeroing procedure was then repeated for these remaining criteria.

Several important observations could be made, when studying the figure below. At cases 2, 5 and 7, nothing significant or important could be noted because the final ranking remained unaltered for the six process alternatives selected for the sensitivity analysis.

For case 3, the processes that show a lot of potential were catapulted into more favourable positions, but according to their level of commercialization, scored relatively low in the overall evaluation, see Table 8.8 . Process alternatives, such as Peruke and FFC, jumped to the first two positions, which demonstrate their underlying potential and the difficult nature of conducting this evaluation.

These two options thus represent a high risk, high reward investment due to the level of uncertainty involved. From a South African perspective, it is of interest to note that the Peruke process outranked all the other alternatives in this case. As explained and discussed in the appropriate section, 6.4.3, dealing with the characteristics of this criterion, several obstacles stand in the way of a novel technology and full-scale industrial implementation, but with sufficient financial input this strategy has increased odds of success and commercialization.

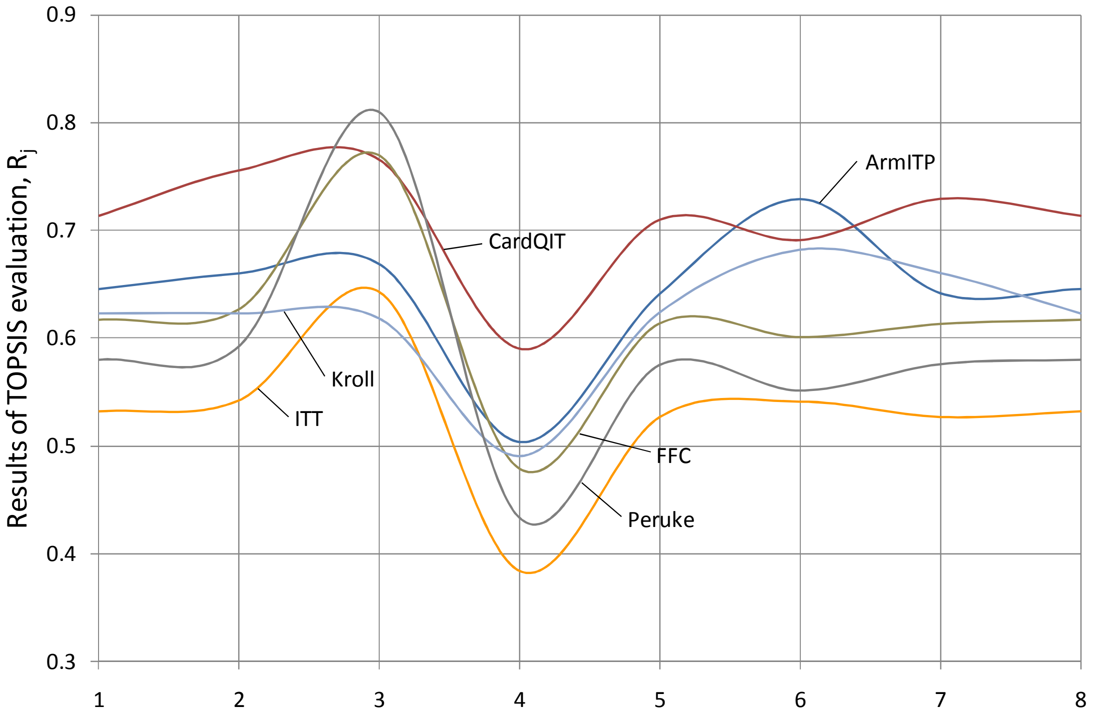


Figure 8.6: Results of TOPSIS, following the second stage of sensitivity analysis

The general large drop, observed for the settings of case 4, is explained by understanding that the influence the complexity index (CI) has on the overall evaluation has been nullified for this case. By doing this, an important conclusion on the validity of the Scorecard Model could be drawn. For example, if the techniques used to compile and represent the findings of the industrial experts into the CI, were questionable, the final ranking would have experienced a more notable disturbance on the removal of this index from the evaluation. The inverse is observed and thus confirms the use of the said model.

The other case where the ranking is reshuffled is for case 6, which deals with the economics of the raw material used as feedstock. The process alternatives that make use of expensive $TiCl_4$ as the precursor for the reduction reaction, such as the ArmITP, Kroll and ITT, greatly benefit from the adjusted weights of the decision criteria. Whereas, the two options that use either enriched titania slag or the mineral ilmenite, CardQIT and Peruke respectively, are not penalized, but one of their main advantages has been nullified. This scenario is not impossible, for several industrial experts argue that the $TiCl_4$ route has been optimized to such an extent through the almost 60 years of industrial usage and research that the handicap is too big to overcome in the next 5 to 10 years.

chapter | nine

# 9 CONCLUSIONS AND RECOMMENDATIONS

The objective of this chapter is to conclude this study, present the conclusions based on the findings and results of the research, and to discuss possible and recommended future work. However, it is first necessary to give an overview of the evaluation and the final ranking and thereafter the conclusions and recommendations.

## 9.1 Overview of evaluation and final ranking

The purpose of this study was to provide the decision making authorities with a ranking and evaluation of the emerging alternatives to produce titanium metal. A 2-Phase Filtering System, based on both qualitative and quantitative techniques, was designed to assess, evaluate and formulate a final ranking. This evaluation was followed by a detailed sensitivity analysis of both local and global parameters.

The complete ranking is given in Table 8.8, and the four leading process alternatives, based on this evaluation and the findings of the sensitivity analysis, are as follows:

1. **CardQIT:** The Canadian affiliate of Rio Tinto, QIT, developed a high-temperature titanium extraction process based on an electrolysis reaction, where molten titania slag is the cathode. This alternative, according to this research, is very mature with regards to the commercial readiness of the technology itself and outranked many of the others, except the Kroll and Hunter processes. It also managed a relatively low score on the complexity index, which weighed heavily in the evaluation. Although the final product of this process alternative is not titanium powder, as is

almost the norm, but rather molten metal, it still eliminate the production and refinement steps associated with sponge. Another significant advantage of this alternative is the fact that it makes use of molten titania slag as the titanium-containing feedstock, which compares very favourably with the more expensive $TiCl_4$ option.

2. **ArmITP:** The Armstrong process is a continuous process that produces titanium in a very similar fashion as with the Hunter process, by the reduction of $TiCl_4$ with sodium. $TiCl_4$ vapour is injected into a stream of molten sodium to form titanium powder as the reaction product. Similar to the CardQIT, the Armstrong process is in its last stages of commercialization; only struggling with the final difficulties, such as the optimization of product separation and purification steps. A full-scale production facility based on this technology is scheduled to start production in 2010. Unlike the CardQIT, however, this alternative makes use of expensive $TiCl_4$ as feedstock and only when this respective criterion was zeroed, as seen in case 6 of Figure 8.6, could it upstage the leader.
3. **Kroll:** The final ranked standing of this existing process was an interesting observation. This process was developed in the 1950s, and although much research has been invested in progress and advancements, resulting in significant energy savings and also improvement in the quality of the final titanium product, the Kroll reduction step remains very imilar to the original process used by the USBM back then. Two criteria played a big part in the unexpected high ranking of the Kroll process, and these were academic coverage and commercial readiness. If it were not for these two criteria, both existing processes would have struggled even more against the emerging alternatives.
4. **FFC:** This process was developed in 2000 and initially promised to be an economical and environmentally friendly alternative to the Kroll process; it thus in a sense sparked the global eagerness to find a cost-effective alternative to produce titanium metal. Solid $TiO_2$ is directly electrochemically reduced to metallic titanium in molten $CaCl_2$. However, ever since 2000, a lot of research has been invested in the attempt to implement the technology successfully, but several obstacles and difficulties still remain. The final product is also a powder, but unfortunately the

feedstock is the expensive pigment grade $TiO_2$, and therefore limits the potential cost-reduction.

## 9.2 General conclusions

In this section, several important conclusions drawn from this investigation are listed. In Figure 9.1 the complete upstream value chain of titanium metal can be seen, together with all 10 emerging alternatives and 2 existing processes, investigated in this research project and their respective chemical/technical routes.

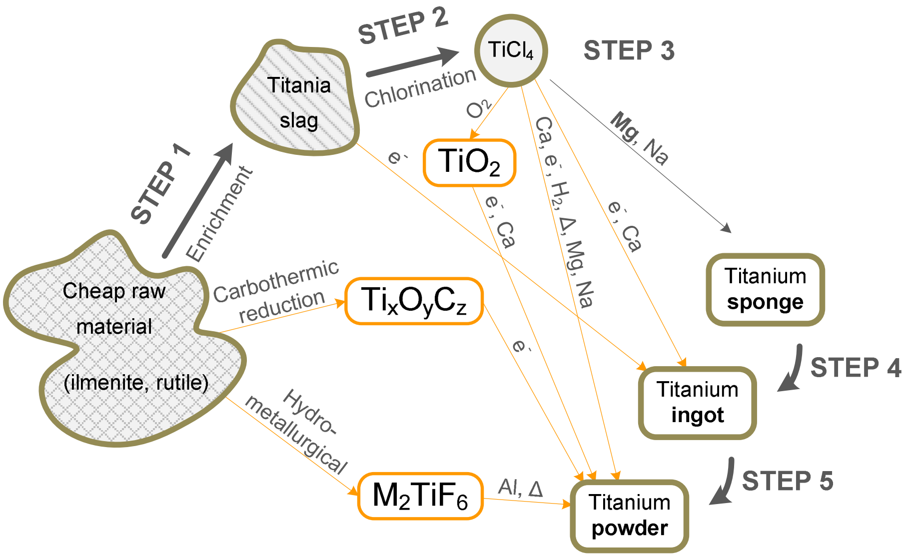


Figure 9.1: Graphical representation and summary of the upstream value chain

The AMTS has recently launched a project involving high performance titanium machining, with the operational head at the University of Stellenbosch, as discussed in section 1.2. The starting material of the downstream value chain and for this research would commonly be either ingot or powder, and it is thus important to note the multitude of routes to produce these products.

### 9.2.1 $TiCl_4$ as intermediate and precursor

When considering the upstream value chain of titanium metal it is advisable when comparing all the alternatives to start with the same raw material, either ilmenite or rutile. Various precursors are available to use in producing titanium, listed in Figure 6.2, but it must be remembered that all of these precursors are the purified product of several steps prior and therefore already an intermediate in the production route of titanium metal. For example, to produce $TiCl_4$ from ilmenite at least three reaction steps are required: a) ore enrichment, b) chlorination and c) purification (not included in the figure above). These production steps have been optimized through the 60 years of industrial usage and development. Even though $TiCl_4$ is quite expensive as a metal feedstock when compared to either aluminium or steel production, according to several critical reviews (Gambogi & Gerdemann, 1999; Hurless & Froes, 2002; Kraft, 2004; Roskill, 2007; Van Vuuren, 2008) it is the cheapest, most practical intermediate and precursor for the reduction reaction. However, a critical question has remained unanswered: if the complete upstream value chain of titanium metal is taken into consideration, it should be possible to design a more cost-effective alternative route based on less expensive feedstock.

Now it is true that several promising emerging alternatives are being researched and developed using $TiCl_4$ as precursor, such as Armstrong/ITP, Ginatta, ITT and TiRO to mention only those in this study, but the overall cost-reduction potential is limited. Most of the economic implications and reductions for these options are realized in not producing titanium sponge, but rather directly ingot or powder as can be seen in Figure 9.1. The benefits of using these options and routes should thus be categorized under a different heading and are accordingly discussed in the following, section 9.2.4.

It is concluded that even though $TiCl_4$ is the cheapest, most practical intermediate and precursor for the reduction reaction, the alternative processes that do not make use thereof register notably more cost-reduction potential.

### 9.2.2 Attractive alternative precursors and routes

In this study, three alternatives were investigated which respectively use ilmenite, rutile or titania slag, and not $TiCl_4$ as the direct precursor for titanium metal production.

They are summarized below:

- QIT Fer et Titane developed a high temperature electrolytic process based on the work of Cardarelli, where enriched titania slag, known as UGS or upgraded slag, is melted and utilized as the cathode. The product of this process is liquid metal tapped from the bottom of the electrolytic cell, which can be cast into ingot.

- The MER Corporation designed an electrolytic process, but instead of using $TiCl_4$ or $TiO_2$ as precursor, it incorporates a carbothermic reduction step. During this step titanium containing mineral, such as ilmenite or rutile, is reduced and deoxidized before being sintered together with a carbonaceous binder as the anode for the electrolytic reduction step. Titanium metal is deposited on the steel cathode and removed as particulates, which with further processing is refined as titanium powder.
- The research department of Anglo American is investigating the option of a hydro/pyrometallurgical route called the Peruke process. Titanium containing mineral, such as ilmenite or rutile, is digested in hydrofluoric acid and selectively precipitated as a fluorotitanate. Besides the used of cheap feedstock, the process conditions of this step are also attractive: aqueous media at atmospheric pressure and relatively low temperatures. The washed and purified fluorotitanate is then decomposed at an elevated temperature and reduced with aluminum to again precipitate as titanium metal particulates.

### 9.2.3 Several options to reduce $Ti^{4+}$

It should be clearly understood that irrespective of what starting material is used, there comes a point where $Ti^{4+}$ has to be reduced, either directly to Ti or with intermediate steps, in order to obtain the refined metal. The fact that titanium has several stable intermediate valence states, significantly contributes to the difficulties of separating the metal from its ore. These intermediaries thus make the reduction reaction a complicated process. Several optional routes have been developed and tried through the years.

These alternatives can be categorized as follows:

- Metallothermic reduction refers to the use of another metal to complete the reaction. Normally, the alkali metals, lithium or sodium, the earth alkali metals, calcium or magnesium, or alternative metal with a lower, more negative, reduction potential[22] than titanium, such as aluminium could be used as could be deducted from the set of equations below:

---

[22] Reduction potential: A metal with a higher, more positive reduction potential than the other, will have a tendency to gain electrons from the metal in question. For example, $Ca^{2+}$ has a reduction potential of -2.868V compared to that of $Al^{3+}$, -

Equations 46, 47, 48, 49 and 50:

$$Li^{2+} + e^{-} \leftrightarrow Li_{(s)}; \quad -3.041V$$

$$Na^{2+} + e^{-} \leftrightarrow Na_{(s)}; \quad -2.710V$$

$$Ca^{2+} + e^{-} \leftrightarrow Ca_{(s)}; \quad -2.868V$$

$$Mg^{2+} + e^{-} \leftrightarrow Mg_{(s)}; \quad -2.372V$$

$$Al^{3+} + e^{-} \leftrightarrow Al_{(s)}; \quad -1.660V$$

Whereas the respective equations for the reduction of titanium containing species are as follows:

Equations 51, 52 and 53:

$$2TiO_{2(s)} + 2H^{+} + 2e^{-} \leftrightarrow Ti_2O_{3(s)} + H_2O; \quad -0.560$$

$$Ti_2O_{3(s)} + 2H^{+} + 2e^{-} \leftrightarrow 2TiO_{(s)} + H_2O; \quad -1.230$$

$$TiO_{(s)} + 2H^{+} + 2e^{-} \leftrightarrow Ti_{(s)} + H_2O; \quad -1.310$$

- Alternatively, carbon or hydrogen can be used as the reductive agents but then it becomes increasingly difficult to control and manipulate reaction(s) in such a way as to not form any unwanted products, such as carbides and hydrides. The process developed by the MER Corporation is making use of a first carbothermic reduction step to deoxidize the feedstock as much as possible without excessively forming TiC, before moving onto the electrolytic reduction step with a sintered anode. Another option is the thermal decomposition of titanium halides, such as $TiCl_4$, providing a suitable electron donor, ITT uses hydrogen, to react with the $Cl^-$ to form gaseous hydrochloric acid. The product stream must be cooled extremely fast to prevent any back-reactions from taking place, leading to complex reactor designs.
- As mentioned before, the other option is to reduce the $Ti^{4+}$ electrolytically, which means that the required electrons are provided and delivered by electric current through the cathode and removed from the electrolyte at the anode. The fact that none of the attempts to develop an economic process to produce titanium electrolytically have been commercially successful in spite of significant efforts globally over a period of more than sixty years, lead many industrial experts and

---

1.660V, which means that aluminium would thus have a tendency to gain the valence electrons of elemental calcium to form elemental aluminium.

investors to believe and conclude that it is unlikely that success would be achieved in the near future. However, on the contrary, there are a notable number of research and development programmes that are willing and attempting to solve the difficulties with electrolytic reduction. Because of the plentitude of researchers and alternatives making use of electrolytic reduction, is it concluded in this study that this route holds significant potential.

### 9.2.4 Eliminating titanium sponge as intermediate reduction product

Production steps 4 and 5 in Figure 9.1, represent a significant proportion of the total costs involved in manufacturing a final titanium metal product, approximately 62% if plate is produced starting with titanium sponge (Figure 9.2). Most research agrees that titanium sponge, as an intermediate reduction product, should be eliminated. The product fabrication phase, steps 4, 5 and post-ingot steps, require extensive handling from one step of the process to the next. The rolling and forging operations require large capital investment equipment and because of the small volume market of titanium, most titanium companies utilize the equipment available in the steel industry for forming operations (DOD, 2004).

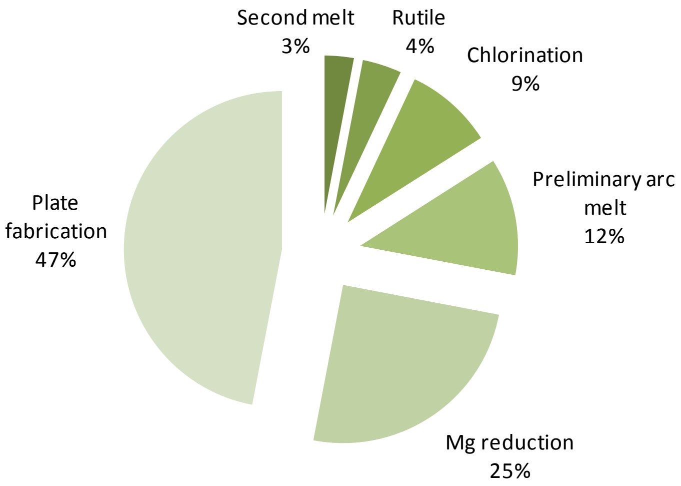


Figure 9.2: Percentage breakdown of the costs involved in the fabrication of a standard plate of titanium (Gambogi & Gerdemann, 1999)

The fabrication of titanium products into final parts requires special attention because of the peculiarities of the material compared to conventional metals. Welding of titanium can be done using mostly ordinary processes, but because of the high reactivity of titanium with nitrogen and oxygen, exposure to these contaminants during welding can adversely effect the properties of the bondage and compromise the performance of the structure (DOD, 2004). This problem can be addressed by ensuring an inert atmosphere until the weld has cooled below a certain temperature, but this requirement becomes difficult to maintain when welding complex structures in tight confines. Productivity is thus lowered and again translates to higher costs.

Another characteristic of titanium which leads to increased fabrication costs is the very low thermal conductivity, which inhibits heat dissipation in the machining of parts. Large amounts of cooling must therefore be provided, together with lower cutting speeds in an attempt to limit the wear of cutting tools. Again these requirements mean lower productivity and higher costs than conventional steel machining.

One possible technology that can reduce the fabrication costs considerable was introduced in section 2.5, titanium powder metallurgy (PM). Although titanium PM is still not fully developed and integrated into the value chain, the potential cost reduction is significant. NNS technology eliminates several fabrication steps and can thus lead to high rates of production. The majority of the processes investigated in this study are designed in such a way that titanium powder is the final product. An important conclusion of that chapter was to ensure that enough weight was given to the alternatives that shorten the production route of titanium metal in such a way that 1) the production of titanium sponge is eliminated and 2) that the cost-reduction potential of titanium PM and NNS be accounted for.

### 9.2.5 Continuous production of titanium product

Lastly, it is important to highlight the importance of developing a continuous process to produce a titanium product, be it sponge, ingot or powder. As mentioned in section 6.4.5, the matter whether the alternative is operated on a continuous basis or as a batch, plays a significant role in the overall economics of the process. The fact that the Kroll process is operated as a batch and the dynamics and timeframe associated with producing a single batch, have been repetitively mentioned as one of the reasons the costs associated in the production of titanium metal via this route, are so expensive. Batch operations require large process equipment to accommodate all the reactants and products, increasing the initial capital expenditure and maintenance costs.

If it was possible to operate the titanium process in a continuous manner, large savings in both capital and labour costs would be achieved (Van Vuuren, 2008). It can be concluded and confirmed from the findings of chapter 7 that most of the research and development programmes are attempting to find a suitable continuous solution to produce titanium metal. Those alternatives that have settled for a compromise batch or semi-batch, such as the FFC Cambridge and MER Corporation, have been heavily penalized in the evaluation in chapter 8.

## 9.3 General recommendations

In the following section, the recommendations based on the results of this study and the conclusions drawn, are introduced and discussed. Most of the recommendations are involved or related to future work and research possibilities that follow from this study.

### 9.3.1 Research simplifications

Originally, this research project had a total of 8 evaluation criteria and after the first 5 were solved, the problems started with the 6th: production and separation costs. The initial plan was to design a model to estimate the capital investment costs for each process alternative investigated. Either the capital cost or the production and manufacturing cost or maybe even both were to be considered, but this has become an almost impossible and difficult assignment, because of the chosen level of detail for this study.

The difficulty was to evaluate whether this criterion was even possible to address, assess and evaluate effectively at all, irrespective of the level of detail and complexity originally chosen. Most of the chosen process alternatives have, at present, not been finalized and are not commercially tested. Therefore, no production data exists.

What is available is the following information:

- The work done by DS Van Vuuren, and his proposed titanium reduction costs.
- Patent information available on the online database such as WIPO and Delphi.
- Design, construction and production costs for Kroll and Hunter processes.
- The DST strategic process does indeed have predictions and estimates on the proposed costs involved in establishing a small-scale Kroll process plant.

If it was decided to continue with the level of detail and complexity associated with this criterion then it would have been possible to make use of the methodology given in Turton's textbook: Analysis, Synthesis and Design of Chemical Processes. Chapter 6 deals exclusively with capital cost estimations and the final output of these calculations would then have been the Bare Module Cost, also called the grass roots cost. In the latter chapters in the book, other economic and feasibility issues are discussed, such as profitability, engineering economic and sensitivity analysis.

It was concluded that it are not completely irrelevant and unnecessary to repeat this process for every alternative investigated in this techno-economic evaluation. If the overall decision analysis model be divided into two filtering steps, then it could just as well be increased to three steps. The Van Vuuren framework, called Filtering Stage A, is a competitive framework and has a systematic and rational basis to assess the 26 possible emerging alternatives to the Kroll process. 12 processes in total, including the Kroll and Hunter, were selected and advanced to the second step, called Filtering Stage B. This filtering step is at the core of the techno-economic evaluation of this study with the 8 mentioned criteria.

The proposed outcome or solution to this difficulty was to remove the following two criteria, 6th (production and separation costs) and 7th (reaction dynamics). These two criteria could be grouped together and in effect be a completely stand-alone third filter, and thus referred to as Filtering Stage C. This third and last step in the techno-economic evaluation would involve an estimation of the economic feasibility of the selected alternatives. Following the second stage, 4 processes could be chosen which after the first two filtering steps show the most potential. The techniques as given in Turton could then be used to calculate the needed economic values, such as Bare Module Costs, Cost of Manufacturing and the consequent profitability/sensitivity analysis.

### 9.3.2 Additional filtering stage: Profitability & Cost analysis

It is recommended that an additional filtering stage be added to the decision model, which could be described as a profitability analysis. The top 4 alternatives, as placed based on the existing ranking, could be chosen as the input for this filtering stage. The profitability analysis would then basically be an estimation of the cost-reduction potential as well as the capital investment and production costs based on process, industrial and economic engineering fundamentals. These calculated economic representations could thus also be ranked to obtain the final recommendable alternative.

The profitability analysis should be followed by a detailed cost-analysis of the chosen alternative from a South African perspective. Part of this analysis would be to estimate the total cost-reduction that would occur within the complete titanium value chain if the new technology completely replaces the aged process. Also, an approximation of the amount of capital investment required to take the technology from the existing level of commercial readiness to the point of producing titanium metal, with the plant upgrade and improvements included.

# 10 LIST OF REFERENCES

ABARE. (2008). *Research and Development in Titanium.* Australian Bureau of Agriculture and Resource Economics.

Abiko, T., Park, I., & Okabe, T. H. (2003). Reduction of titanium oxide in molten salt medium. *10th World Conference on Titanium.* Hamburg, Germany.

Agrawal, V. P., Kohl, V., & Gupta, S. (1991). Computer-Aided Selection - The multiple attribute decision-making approach. *International Journal of Production Research* .

Anderson, R., Armstrong, D., & Jacobsen, L. (2004). *Patent No. WO/2004/033737.* United States of America.

Askeland, D. R., & Phulé, P. P. (2003). *The science and engineering of materials, 4th Edition.* Pacific Grove, California: Thomson Brooks/Cole.

Babkin, A. G., Maiorov, V. G., & Nikolaev, A. I. (1988). Extraction of Niobium, Titanium and other elements from Fluoride Solutions.

Boucher, T. O., Luxhoj, J. T., Descovich, T., & Litman, N. (1993). Multicriteria evaluation of automated filling systems - a case study. *Journal of Manufacturing Systems* .

Buch, J. (2006). Meeting the Demand Challenge. *22nd Annual International Titanium Association (ITA) Conference and Exhibition.* San Diego: Materials Technology.

Buchhovecky, K., & Patton, W. (1969). *Patent No. 3478136.* United States of America.

Cardarelli, F. (2002). *Patent No. WO/2003/046258.* Canada.

Chen, G. Z., Fray, D. J., & Farthing, T. W. (2000). Direct Electrochemical Reduction of Titanium Dioxide to Titanium in Molten Calcium Chloride. *Nature* .

CoMSA. (2008). *Annual Report 2007 - 2008.* Chamber of Mines of South Africa.

Considine, M. L. (2005, November). *TiRO: Titanium powder for making metal.* Retrieved from CSIRO Light Metals: http://www.csiro.au/news/newsletters/0511_metals/meet.htm

Cordes, R. A., & Donaldson, A. (2001). *Titanium Metal Powder Production by the Plasma Quench Process.* Idaho Titanium Technologies, United States Department of Energy.

Cowey, A. (1994). *Mining and Metallurgy in South Africa - A Practical History.* MINTEK.

Detering, B. A., Donaldson, A. D., Fincke, J. R., & Kong, P. C. (1998). *Patent No. US 5749937.* United States of America.

Doan, P. H. (1992). High-Grade Chlorinatable Feedstocks for Titanium Dioxide Pigments. *Industrial Minerals.*

DOD. (2004). *An Integrated Plan for the Development and Processing of Low-Cost Titanium Materials and Associated Manufacturing Processes.* Washington DC: Department of Defence of the United States of America.

Dombrowski, H. (1961). *Patent No. 2984560.* United States of America.

Dombrowski, H. (1963). *Patent No. 3072347.* United States of America.

Drechsler, M. (2004). Model-Based Conservation Decision Aiding in the Presence of Goal Conflicts and Uncertainty. *Biodiversity and Conservation* .

Du Plessis, A. J., & Bekker, J. (2008). *Determining tactical operations policies for an auto carrier using discrete-event simulation.* Stellenbosch: University of Stellenbosch, Thesis in MScEng (Industrial).

Elton, E. J., & Gruber, M. J. (1997). Modern portfolio theory: 1950 to date. *Journal of Banking and Finance* .

Fan, Z. P., Ma, J., & Zhang, Q. (2002). An approach to muliple attribute decision making based on fuzzy preference information on alternatives. *Fuzzy Sets and Systems* .

Froes, F. H. (1998). The Production of Low-Cost Titanium Powders. *JOM Journal of the Minerals, Metals and Minerals Society* .

Froes, F. H., Senkov, O. M., & Jonas, J. J. (1996). Recent Advances in the Thermohydrogen Processing of Titanium Alloys. *Journal of MEtals* .

Gambogi, J., & Gerdemann, S. J. (1999). *Titanium metal: Extraction to Application.* Albany: USGS - National Center, DOE - Albany Research Center.

Garcia, M. L., & Bray, O. H. (1997). *Fundamentals of Technology Roadmapping.* Albuquerque: Strategic Business Development Department, Sandia National Laboratories.

Gerdemann, S. J. (2001). *Titanium: Process Technologies.* Albany Research Center.

Ginatta, M. V. (1998). *Patent No. WO/1998/033956.* Italy.

Ginatta, M. V., & Orsello, G. (1987). *Patent No. US 4670121.* Italy.

Goetzmann, W. N. (1997). *An introduction to investment theory.* New Haven: YALE, School of Management.

Gous, M. (2006). An Overview of the Namakwa Sands Ilmenite Smelting Operations. *Journal of South African Institute of Mining and Metallurgy* .

Guthrie, K. M. (1969). Capital Cost Estimating. *Chemical Engineering* .

Habashi, F. (1997). *Handbook of Extractive Metallurgy, 2nd Volume.* University of Michigan: Wiley-VCH.

Hansen, D. A., & Gerdemann, S. J. (1998). Producing Titanium Powder by Continuous Vapor-Phase Reaction. *JOM Journal of the Minerals, Metals and Materials Society* .

Hartman, A. D., Gerdemann, S. J., & Hansen, J. S. (1998). Producing Lower Cost Titanium for Automotive Applications. *JOM Journal of the Minerals, Metals and Materials Society* .

Hildenbrandt, D. L., & Thiers, E. (2004). *Patent No. WO/2005/035807.* United States of America.

Hogan, L., McGinn, E., & Kendall, R. (2008). *Research and Development in Titanium: Implications for a titanium metal industry in Australia.* Carberra: Australian Bureau of Agricultural and Resource Economics.

Hubbard, G. R., & Weiner, R. J. (1985). *Nominal contracting and price flexibility in product markets.* Cambridge: NBER: National Bureau of Economic Research.

Hurless, B. E., & Froes, F. H. (2002). Lowering the cost of titanium. *The AMPTIAC Quarterly, Volume 6* .

Hwang, J. L., & Yoon, K. (1981). Multiple attribute decision making: Methods and applications. *Lecture notes in Economics and Mathematical Systems.*

Hyado, T., & Ichihash, H. (2003). Establishment of the Manufacture of 5N Super Purity Titanium Billets by Kroll Process. *Titanium: Science and Technology* .

Ikeshima, T. (1984). Recent Developments in Titanium Sponge Production. *Titanium - Science and Technology* .

ITA. (1999). *Titanium: The Ultimate Choice.* The International Titanium Association.

Jahanshahloo, G. R., Lotfi, F. H., & Izadikhah, M. (2006). An algorithm method to extend TOPSIS for decision making problems with interval data. *Applied Mathematics and Computation* .

Ketter, H. (1998). *William J. Kroll: A Luxembourg Scientist.* Foundation Nicolas Lanners.

Kotzé, H., Bessinger, D., & Beukes, J. (2006). Ilmenite Smelting at TICOR SA. *Journal of South Africa Institute of Mining and Metallurgy* .

Kraft, E. H. (2002). *Opportunities for Low-Cost Titanium in Reduced Fuel Consumption, Improved Emissions, and Enhanced Durabiltiy of Heavy Vehicles.* Vancouver: EHK Technologies; Oak Ridge National Laboratory.

Kraft, E. H. (2004). *Summary of Emerging Titanium Cost Reduction Technologies.* EHK Technologies; Oak Ridge National Laboratory.

Lang, H. J. (1947). Engineering Approach to Preliminary Cost Estimates. *Chemical Engineering* .

Lee, Y. H., & Poggi, D. (1978). Mine, Mill and Smelting Complex at Richards Bay, South Africa. *Canadian Institute of Mining and Metallurgy, Metallurgical Society of CIM* .

Loutfy, R. O., & Withers, J. C. (2007). *Patent No. US 2007/0029208.* United States of America.

Lynd, L. E., & Lefond, S. J. (1983). *Industrial Minerals and Rocks, 5th Edition.* New York: AIME.

Ma, J., Fan, Z. P., & Huang, L. H. (1999). A subjective and objective integrated approach to determine attribute weights. *European Journal of Operational Research* .

Ma, M., Wang, D., Hu, X., Jin, X., & Chen, G. Z. (2006). Extraction of Titanium from DifferentTitania Pre-Cursors by the FFC Cambridge Process. *Journal of Alloys and Compounds* .

Mackey, T. S. (1994). Upgrading Ilmenite into a High-Grade synthetic Rutile. *Journal of Metals* .

Macpherson, R. D. (1982). Mineral Processing at Richards Bay Minerals. *CIMM Congress, Canadian Insitute of Mining and Metallurgy* .

Markowitz, H. (1952). Portfolio theory. *The Journal of Finance* .

Méndez, M., Galvan, B., Salazar, D., & Greiner, D. (2006). Multiple-objective genetic algorithm using the multiple criteria decision making method TOPSIS. *MOPGP 2006: 7th International Conference on Multi-Objective Programming and Goal Programming.* Tours, France.

Montgomery, J. S., Wells, M. G., Roopchand, B., & Ogilvy, J. W. (1997). Low-cost titanium armour for combat vehicles. *JOM* .

Morse, P. M., & Kimball, G. E. (1952). *Methods of Operations Research.* New York: MIT Press and John Wiley & Sons, Inc.

Motsie, R. (2008). *An Overview of South Africa's Titanium Mineral Concentrate Industry.*

Nikolaev, A. I., & Kalinnikov, V. T. (2001). Combined Technologies of Processing of Complex Titanium-Rare-Metal Raw Materials. *Khimicheskaya Tekhnologiya* .

Nikolaev, A. I., Larichkin, F. D., & Nikolaeva, O. A. (2008). Choosing the Technology of Combined Processing of Titanium-Rare-Metal Raw Materials. *Theoretical Foundations of Chemical Engineering* .

NMAB. (1983). *Titanium: Past, Present and Future.* National Materials Advisory Board.

Ono, K., & Suzuki, R. (2002). *Patent No. US 2004/0237711.* Japan.

Patton, W. (1970). *Patent No. 3530210.* United States of America.

Pawlek, R. P., & Froes, F. H. (1999). Titanium 1999: Annual Review. *Light Metal Age* .

Peters, M. S., & Timmerhaus, K. D. (1991). *Plant Design and Economics for Chemical Engineers, 4th Edition.* New York: McGraw-Hill.

Pistorius, P. C., & Coetzee, C. (2003). Physicochemical Aspects of Titanium slag Production and solidification. *Metallurgical and Materials Transactions B* .

Pohekar, S. D., & Ramachandran, M. (2004). Aplication of multi-criteria decision making to sustainable energy planning - a review. *Renewable and sustainable energy reviews* .

Prattley, D. J., Morris, R. S., Stevenson, M. A., & Thornton, R. (2007). Application of portfolio theory to risk-based allocation of surveillance resources in animal populations. *Preventive Veterinary Medicine* .

Pretorius, G. (2005). *Patent No. WO/2006/079889.* South Africa.

Prinsloo, L. (2008). *Pyrometallurgy specialist celebrates forty years of production.* Retrieved October 3, 2009, from Creamer Media's Mining Weekly Magazine: http://www.miningweekly.com

Pudney, M. (2009, May 21). *Metalysis attracts $8.20 million capital investment.* Retrieved from Metalysis: http://www.metalysis.com

Ragsdale, C. T. (2004). *Spreadsheet Modeling & Decision Analysis: A practical introduction to Management Science.* Virginia: Thomson South Western.

Roderick, K., & Gaze, L. (2009). *IP Market Report: Innovation Hot Spots.* New York: Thomson Reuters.

Roskill. (2007). *The Economics of Titanium.* Roskill Information Services, 4th Edition.

Saaty, T. L. (2008). Decision making with the analytic hierarchy process. *International Journal of Services Sciences* .

Saaty, T. L. (2008). Decision Making with the Analytic Hierarchy Process. *Internation Journal of Services Sciences* .

Saaty, T. L. (1980). *The Analytic hierarchy process: Planning, Priority Setting and Resource Allocation.* New York: McGraw-Hill.

Salo, A., & Cuhls, K. (2003). Technology Foresight: Past and Future. *Journal of Forecasting* .

Seader, J. D., & Henley, E. J. (1998). *Separation process principles.* Houston: John Wiley & Sons, Inc.

Seong, S., Younossi, O., & Goldsmith, B. W. (2009). *Titanium: Industrial Base, Price Trends and Technology Initiatives.* Santa Monica, California: RAND Corporation.

Sinnott, R. K. (2004). *Coulson and Richardson's Chemical Engineering: Volume 6, 3rd Edition.* Amsterdam: Elsevier Butterworth-Heinemann.

Sones, J. (2003). *Environmental quality indexing of large industrial development alternatives using AHP.* Environmental Impact Assessment Review.

Spronk, J., & Hallerbach, W. (1997). Financial modeling: Where to go? With an illustration for portfolio management. *European Journal of Operational Research* .

Stamper, J. (1957). *Minerals Yearbook: Titanium 1st Volume.* USBM.

Turner, P. C., Hartman, A., Hansen, J. S., & Gerdemann, S. J. (2001). Low Cost Titanium: Myth or Reality. *DOE Scientific and Technical Information* .

Turton, R., Bailie, R. C., Whiting, W. B., & Shaeiwitz, J. A. (2003). *Analysis, Synthesis and Design of Chemical Processes, 2nd Edition.* Upper Saddle River, New Jersey: Prentice Hall PTR.

USBLS. (2008). *Producer Price Index: Titanium Mill Products.* US Bureau of Labour Statistics.

USBM. (1980). *Principles of a Resource/Reserve Classification for Minerals.* United States Bureau of Mines.

USGS. (2009). *Mineral Commodity Summaries.* US Geological Survey.

Van Vuuren, D. S. (2008). A critical evaluation of processes to produce primary titanium. *AMI Conference.* Pretoria: CSIR, Department of Science and Technology.

Wang, X. T., & Triantaphyllou, E. (2008). Ranking irregularities when evaluating alternatives by using some ELECTRE methods. *OMEGA-International Journal of Management Science* .

Wartel, W., Wasilewski, R., & Pollock, W. (1963). *Patent No. 3084042.* United States of America.

Wellwood, G. (2006). Low Cost Titanium Powder Processes to facilate Near Net Shape Manufacture. *22nd Annual International Titanium Association (ITA) Conference And Exhibition.* San Diego: Materials Technology.

Williams, G. E., & Steenkamp, J. D. (2006). Heavy Mineral Processing at Richards Bay Minerals. *South African Pyrometallurgy, Journal of South African Institute of Mining and Metallurgy* .

Withers, J. C., Cardarelli, F., Laughlin, J., & Loutfy, R. O. (2008). *Recent Improvements for Electrowinning Titanium Metal from Composite Anodes.* Tucson: Materials & Electrochemical Research (MER) Corporation.

Yang, T. H., Chen, M. C., & Hung, C. C. (2007). Multiple attribute decision-making methods for the dynamic operator allocation problem. *Mathematics and computers in simulation* .

# 11 APPENDIX A: DECISION ISSUES

## 11.1 Characteristics of decision problems

Although all decision problems are somewhat different, they share certain characteristics. A decision must involve at least two alternatives for addressing or solving a problem, whereas an alternative is a course of action intended to solve a problem and is evaluated on the basis of the value it adds to one or more decision criteria. The criteria in a decision problem represent various factors that are important to the decision maker and are influenced by the alternatives. The impact of the alternatives on the criteria is of a primary importance to the decision maker, however not all criteria can be expressed in terms of measurable units, such as a monetary value (Ragsdale, 2004).

The values assumed by the various decision criteria under each alternative depend on the different states of nature that can occur and these states correspond to future events that are not under the decision making authority's control. Normally, an infinite number of possible states of nature could exist, but in decision analysis a relatively small discrete set of states is used to summarize the future events that might occur.

## 11.2 Decisions for the upstream value chain

The main rules and principles of chemical technology for any raw material, including titanium, are common and based on the fundamental laws of chemistry. Some data on the technology of non-traditional titanium–rare-metal raw materials are given in (Nikolaev & Kalinnikov, 2001). Any technology can be described from the viewpoint of its efficiency, which implies the concepts of technological, economical, and ecological effectiveness and social significance for the surrounding region.

The concept of the technological efficiency of an alternative process is very wide and includes the feasibility of implementing the apparatus of the process, the specific expenditure of reagents, energy resources, time and temperature regimes, and other characteristics. The optimum conditions by no means always coincide for the chemistry of the process and its technological regime. The factor that can be optimal for a separate operation from the viewpoint of chemistry can frequently be non-optimal or, to be exact, impractical for the technology (Babkin, Maiorov, & Nikolaev, 1988).

The costs of raw materials, reagents, energy resources, and end products under conditions of a market economy can change over wide limits. For a quantitative estimation of the efficiency of the various schemes for processing of raw materials, a calculation algorithm should be developed that would make it possible to correct the estimation of the efficiency and, consequently, the rationality of using the chosen raw materials with allowance for changing prices and coefficients (Nikolaev, Larichkin, & Nikolaeva, 2008).

# 12 APPENDIX B: ADDITIONAL TABLES

Table 12.1: Results of the Scorecard Model with the complexity index calculated

| No | ATP | a1 | a2 | a3 | a4 | a5 | a6 | a7 | a8 | a9 | a10 | Totals | CI |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | ArmITP |  | o | o | o | o |  |  |  |  |  | 0.3007 | 0.053 |
| 2 | CardQIT | o |  | o | o |  |  | o |  |  |  | 0.3265 | 0.057 |
| 3 | FFC |  |  |  |  |  |  | o |  | o | o | 0.3949 | 0.07 |
| 4 | Ginatta |  | o | o | o | o |  | o | o | o |  | 0.8453 | 0.149 |
| 5 | Hunter | o |  | o | o | o | o | o | o | o |  | 0.7774 | 0.137 |
| 6 | ITT |  | o |  | o | o | o |  |  | o |  | 0.4532 | 0.08 |
| 7 | Kroll | o |  | o |  | o | o |  | o |  | o | 0.453 | 0.08 |
| 8 | MER |  | o |  |  |  |  | o | o | o | o | 0.7671 | 0.135 |
| 9 | OS |  |  |  |  |  |  | o |  | o | o | 0.3949 | 0.07 |
| 10 | Peruke | o |  |  | o | o |  |  |  | o |  | 0.2763 | 0.049 |
| 11 | SRI |  | o |  |  | o |  |  |  |  | o | 0.2704 | 0.048 |
| 12 | TiRO |  | o |  |  |  |  | o |  |  | o | 0.4186 | 0.074 |
|  | Weights | 0.038 | 0.16 | 0.039 | 0.054 | 0.048 | 0.055 | 0.196 | 0.212 | 0.137 | 0.062 | 5.6783 | 1 |

**Scorecard Model decision variables:**

|  |  |
|---|---|
| Big volumes of chemicals | a1 |
| Complex reactor | a2 |
| Extended high temperatures | a3 |
| Fluid processing plant | a4 |
| Hazardous chemicals | a5 |
| High/low pressure | a6 |
| Issues with fundamentals | a7 |
| Reaction efficiency | a8 |
| Scalability | a9 |
| Solid/fluid processing plant | a10 |

Table 12.2: The comments and concerns made by EH Kraft and DS Van Vuuren (a)

| | | **EH Kraft:** | | **DS Van Vuuren:** |
|---|---|---|---|---|
| ATP | No | Concern | No | Concern |
| ArmITP | 1 | Produce usable powder | 5 | Complex purification |
| | 2 | Demonstrating equipment durability | 6 | Pilot-scale demonstration |
| | 3 | Optimization of the separation equipment | | |
| | 4 | Processes to produce the required particle size and morphology | | |
| CardQIT | 1 | Repeated demonstration of compositional control and quality measures required | 3 | Does not work, projects at CSIR terminated |
| | 2 | No cost-analysis available | 4 | |
| FFC | 1 | Difficult to up-scale | 1 | Long process time |
| | 2 | Electrolytic and chemistry fundamentals | 2 | Inefficient |
| | 3 | Cost of $TiO_2$ | 3 | Ungoing development |
| | 4 | Cost of steps to take reduced mass to usable powder | | |
| Ginatta | 1 | Quite complex, multilayer with various oxidation states of the species (K, Ca, Ti, Cl, F) | 4 | Long process times at extreme conditions |
| | 2 | Use of $TiCl_4$ a cost burden | 5 | Status uncertain |
| | 3 | The ability to start/stop molten liquid stream needs to be demonstrated | 6 | |
| ITT | 1 | Product a hydride, limited use in mill production | 5 | Harsh plasma process |
| | 2 | Use of $TiCl_4$ a cost burden | 6 | Low thermal efficiency |
| | 3 | Required particle sizes not yet met | 7 | HCl recycle |
| | 4 | HCl product, must be sold | 8 | Continuation uncertain |
| OS | 1 | Long reaction times to achieve required quality | 3 | Inefficient |
| | 2 | Fundamentals relating to titanium suboxides | 4 | Continuation uncertain |
| SRI | 1 | High temperature | 4 | Large gas recycle loop |
| | 2 | Early lab staged, 2004 | 5 | H2/HCl separation difficulty |
| | 3 | Unknown energy efficiency vs. Deposition rate | 6 | Continuation uncertain |

Table 12.3: The comments and concerns made by EH Kraft and DS Van Vuuren (b)

| | | EH Kraft: | | DS Van Vuuren: |
|---|---|---|---|---|
| ATP | No | Concern | No | Concern |
| MER | | Impurities are reported to be low, but confirmation is necessary | | Product quality |
| | | Processing costs should be determined | | Continuation uncertain |
| | | Consistent production | | |
| | | Solid deposits with suitable density, uniformity and configuration, to be confirmed | | |
| | | Scalability | | |
| Peruke | | | | Product purity and quality |
| | | | | Extensive distillation |
| | | | | Bound to the $AlF_3$ market |
| | | | | Ongoing development |
| TiRO | | | | Complex reactor |
| | | | | Complex purification |
| | | | | Ongoing development |

Tables 12.4 & 12.5: Normalized and weighted decision matrices

| | C1 | C2 | C3 | C4 | C6 | C8 |
|---|---|---|---|---|---|---|
| A1 | 0.2082 | 0.3582 | 0.1694 | 0.1715 | 0.3627 | 0.3313 |
| A2 | 0.0732 | 0.3582 | 0.1839 | 0.1715 | 0.0382 | 0.2209 |
| A3 | 0.2449 | 0.2558 | 0.2224 | 0.3430 | 0.1608 | 0.3313 |
| A4 | 0.0727 | 0.3582 | 0.4762 | 0.1715 | 0.3627 | 0.2209 |
| A5 | 0.4615 | 0.4605 | 0.4379 | 0.5145 | 0.3627 | 0.1104 |
| A6 | 0.0501 | 0.2047 | 0.2553 | 0.1715 | 0.3627 | 0.3313 |
| A7 | 0.7424 | 0.4093 | 0.2552 | 0.5145 | 0.3627 | 0.1104 |
| A8 | 0.2082 | 0.1535 | 0.4321 | 0.3430 | 0.1608 | 0.3313 |
| A9 | 0.2216 | 0.1023 | 0.2224 | 0.1715 | 0.1608 | 0.3313 |
| A10 | 0.1024 | 0.2047 | 0.1556 | 0.1715 | 0.0133 | 0.3313 |
| A11 | 0.1234 | 0.1023 | 0.1523 | 0.1715 | 0.3627 | 0.3313 |
| A12 | 0.0367 | 0.2047 | 0.2358 | 0.1715 | 0.3627 | 0.3313 |

| | C1 | C2 | C3 | C4 | C6 | C8 |
|---|---|---|---|---|---|---|
| A1 | 0.0095 | 0.1216 | 0.0373 | 0.0082 | 0.0571 | 0.0628 |
| A2 | 0.0033 | 0.1216 | 0.0405 | 0.0082 | 0.0060 | 0.0419 |
| A3 | 0.0111 | 0.0869 | 0.0490 | 0.0163 | 0.0253 | 0.0628 |
| A4 | 0.0033 | 0.1216 | 0.1049 | 0.0082 | 0.0571 | 0.0419 |
| A5 | 0.0210 | 0.1564 | 0.0965 | 0.0245 | 0.0571 | 0.0209 |
| A6 | 0.0023 | 0.0695 | 0.0563 | 0.0082 | 0.0571 | 0.0628 |
| A7 | 0.0338 | 0.1390 | 0.0562 | 0.0245 | 0.0571 | 0.0209 |
| A8 | 0.0095 | 0.0521 | 0.0952 | 0.0163 | 0.0253 | 0.0628 |
| A9 | 0.0101 | 0.0348 | 0.0490 | 0.0082 | 0.0253 | 0.0628 |
| A10 | 0.0047 | 0.0695 | 0.0343 | 0.0082 | 0.0021 | 0.0628 |
| A11 | 0.0056 | 0.0348 | 0.0336 | 0.0082 | 0.0571 | 0.0628 |
| A12 | 0.0017 | 0.0695 | 0.0520 | 0.0082 | 0.0571 | 0.0628 |

Table 12.6: Cost-breakdown per stage by Gerdemann

**Gerdemann (2001) Cost Built-Up**

| No | Stage | $/tonne | $/kg Ti sponge | $/kg |
|---|---|---|---|---|
| 1 | Ilmenite | 88.18 | 0.26 | 88185 |
| 2 | Rutile | 551.16 | 0.99 | 551156 |
| 3 | Slag | 374.79 | 0.73 | 374786 |
| 4 | TiCl4 | 771.62 | 3.09 | 771618 |
| 5 | Raw Materials | 1895.98 | | 1895975 |
| 6 | Ti Sponge | 4938.35 | 4.94 | 4938355 |

Table 12.7: Cost-breakdown per stage by Van Vuuren

**Van Vuuren Production Costs (2006):**

| No | Stage | $/kg Ti sponge |
|---|---|---|
| 1 | Ilmenite | 0.27 |
| 2 | Slag | 0.75 |
| 3 | $TiCl_4$ | 3.09 |
| 4 | Raw Materials | 5.50 |
| 5 | Ti Sponge | 9.00 |

# 13 APPENDIX C: TECHNOLOGY ROADMAPPING

Technology roadmapping is a needs-driven technology planning process to help identify, select and develop technology alternatives to satisfy a set of pre-determined needs. The main benefit of technology roadmapping is that it provides information to make better technology investment decisions by identifying critical technologies and technology gaps (Garcia & Bray, 1997). Technology roadmapping is essential and critical when the investment decision is not an obvious and straight forward decision. This occurs when it is not clear which alternative to pursue, how quickly the technology is needed, or when there is need to coordinate the development of multiple technologies.

With regards to the South African titanium industry, technology roadmapping could be seen as an essential part in devising a strategy and development plan for the future. In recent years, the global titanium industry has seen several research and development programmes, working towards the single objective of finding a more cost-effective alternative to the Kroll process of producing titanium metal. In this study, 24 of the novel alternatives to produce titanium metal, has been investigated and studied in order to conduct the techno-economic evaluation. The fundamentals of technology roadmapping could be used to:

- Identify the critical product needs that will drive technology selection and development.
- Determine the technology alternatives that can satisfy the critical product needs.
- Select the appropriate technology alternatives.
- Generate and implement a plan to develop and deploy the appropriate technology alternatives.

Technology roadmapping is an iterative process that fits within the broader strategic planning, technology planning and business development context. The effective integration of technological considerations into business strategy is an important aspect of business planning. Within the mining industry, technical innovation and chemical process improvements influence the economies and feasibilities of the companies involved, greatly; it is thus of notable significance for the South African titanium industry to consider a technology roadmap with the objective of completing the titanium value chain. In the following section an overview of the roadmapping process is given. The first phase involves preliminary activity without which the roadmapping should not be done. The second phase is the development of the technology roadmap itself, whereas the third phase is the follow-up and use of the roadmap document.

## 13.1 Phase I: Preliminary Action

During this phase, several criteria must be formulated, ensured and checked before the second phase could be commenced. 1) There must be a perceived need for a technology roadmap and collaborative development. 2) The technology roadmapping effort needs input and participation from several different groups, which brings different perspectives and planning horizons to the process. 3) The technology roadmapping process should be needs-driven and not solution-driven.

The scope and boundaries of the roadmap should then also be specified. A roadmap starts with a set of needs and the intended use of the roadmap determines the planning horizon and the level of detail.

## 13.2 Phase II: Development of Technology Roadmap

During this phase the actual technology roadmap is created and could be broken-down into seven steps:

1. The product or the planned outcome of the technology roadmap should be as closely and clearly as possible defined.
2. The critical system requirements which provide the overall framework for the roadmap, and their respective targets should be identified.
3. The major technology areas should then be specified.
4. The critical system requirements should at this stage be transformed into technology-orientated drivers for the specific technology areas.
5. Technology alternatives and their time lines should be identified.
6. Make recommendations about the technology alternatives that should be pursued.
7. Create the technology roadmap report or document.

## 13.3 Phase III: Follow-Up Activity

During this phase the designed technology roadmap should be evaluated, validated and accepted by the industry involved with the implementation step. An implementation plan therefore needs to be developed using the information generated by the technology roadmapping process to make and implement the appropriate investment decisions.