Research and Development of Ti and Ti alloys: Past, present and future

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Abstract. This study provide an insight of established and future research and development on Titanium metal production, Titanium alloy development, Titanium powder metallurgy, and thermomechanical and manufacturing processes. In the last 60 years, research initiatives were investigating the cost effective alternative ways of producing Titanium metal from rutile, ilmenite and synthetic rutile. The very recent research focuses on the combination of pyro and hydrometallurgical process to produced synthetic rutile from ilmenite. Chloride leaching and solvent extraction will be significant strategies to reduce operating costs and protect the environment. New and developed processed for production of Titanium will be mostly focussed on direct electrowining of synthetic rutile or beach sand. Future perspectives associated with alloy development, biomedical, additive manufacturing, and Titanium powder metallurgy emerging techniques such as hydrogen sintering and phase transformation, and cold gas dynamic spraying or Titonic Kinetic Fusion are discussed.

1. Introduction

The cost of Ti and Ti alloys, product design and manufacturing process as well as emerging biomedical and additive manufacturing have driven the Titanium research and development in recent decades.

Titanium is the ninth most abundant element in the earth's crust. It is five time less than Iron and 200 times more than copper in abundance. However, its usage is 200 times less than copper and 2000 times less than Iron. This may be due to the high cost of the commercialized thermo-chemical processes such as Kroll and Hunter. Thus, the development of electrochemical and in-situ electrolysis may be promising as future production processes. However, some challenging issues such as redox-cycling, feeding, reaction kinetics, control heat balance have to be resolved before scaling-up to commercial production [1][5].

Rutile (95 % of TiO_2), and ilmenite or leucoxene (40-65 % of $FeO.TiO_2$) are the main minerals containing Titanium. Since 1981 the content of rutile in the world has decreased to less than 1 %, therefore Ilmenite is becoming increasingly important and supplying about 91 % of the world's demand for Titanium minerals. Ilmenite has extensive reserves of about 1300 million tons in beach sands and rock deposits and, therefore, ilmenite will remain the principal mineral for the production of Titanium metal in the future[1][2][4][5].

Powder metallurgy techniques which include Additive Manufacturing (AM), Metal Injection Moulding (MIM), Hot Isostatic Pressing (HIP), Cold Isostatic Pressing (CIP), Spark Plasma Sintering (SPS) or Field Assisted Sintering Technology (FAST), Gas Dynamic Cold Spray (GDCS), Direct

Powder Rolling (DPR) and Continuous Rotary Extrusion (CRE) of wire are focused on the production of near-net shapes with acceptable mechanical properties [2][3][5].

Recent research in Ti and Ti alloy has been focused on biomedical and medical applications. Superplastic Ti alloys, low cost composition Ti alloys with good ballistic and mechanical properties and near beta Ti alloys have attracted researchers in this category [5].

Thermomechanical processing and manufacturing techniques have been centred on superplastic forming sheets, forging of fuselage structures and landing gear for future aircraft and manufacturing of highly sophisticated and high performance sport cars [5].

This review therefore, aimed to identify the major drives of Research and Development (R&D) and area of growth for Ti and Ti alloys. Recent research in titanium metal production, titanium alloy development, powder metallurgy of Ti and its alloys, thermomechanical processing and manufacturing process has been reviewed.

2. Titanium metal production

Most research initiatives are currently focussing on investigating the cost effective alternative ways of producing Ti metal from ilmenite or synthetic rutile. Thermo-chemical and pyro-hydrometallurgical process routes are been researched to established the most economical process.

2.1. Thermo-chemical processes

The commercialized thermo-chemical processes such as Hunter and Kroll are very expensive and energy inefficient. Hunter Process (invented in 1910) is similar to Kroll process, however, it uses Na heated to 910 °C to react with $TiCl_4$ in two stages. The first stage reduces continuously the $TiCl_4$ to $TiCl_2$ at approximately 200 °C [1]. The second one, operating in batch, reduces $TiCl_2$ to Ti at 1000 °C.

The Kroll process (invented in 1940s) has been employed for Ti extraction since the 1950s. Its post-processing steps including multiple re-melting and product fabrications make it labour and energy intensive process. Kroll and Hunter need high grade natural rutile or upgraded synthetic rutile as feed and chlorination process to produced $TiCl_4$ [1][4].

The motivation for development of new processes for Ti metal production is mainly establishing a low-cost alternative to Kroll process. In actual research and industrial state no production process available to date has overcome both energy efficiency and scale-up challenges to replace the Kroll process.

The Armstrong® process is a continuous process for the reduction of $TiCl_4$ using Na. The process produces powder particles with a unique, low bulk density, "coral-like" morphology. Post-processing activities such as dry and wet ball milling provide a means of increasing the tap density and narrowing the particle size distribution to meet the requirements for typical powder metallurgy conversion processes. The high degree of interlocking between adjacent powder particles offers distinct advantages in roll compaction, allowing for the direct rolling of powder into titanium sheet [4][5].

2.2. Pyro-hydrometallurgical processes of Titanium

The combination of pyro and hydrometallurgical processes are recently researching ways to upgrade ilmenite to synthetic rutile. Since ilmenite is becoming increasingly important due to the depletion of rutile and, therefore, the synthetic rutile and slag are mostly used for the production of Ti metal. The development and progress on slag and ilmenite upgrading process are shown in **Table 1** [1][4].

The development of electrochemical and in-situ electrolysis have achieved some success. However, some challenging issues such as control redox reactions, feeding, reaction kinetics, control of heat balance have to be resolved before scaling-up to commercial process [1][4].

Electro-chemical processes such as direct hydrometallurgical lixiviation are advantageous in processing abundant ilmenite ores, since low energy consumption is expected and sufficiently high quality of synthetic rutile is produced. A novel sulphate process to improve leaching strategies has been developed by BHP Billiton. This process uses solvent extraction method to separate metals,

reduce wastes and recycle acids. The drawback are high consumption of H_2SO_4 and production of large amount of sulphate waste and high cost for treatment. This process is very promising for commercial applications in the future[2][5][6].

Table 1. Ilmenite and slag upgrading processes.

Process	Pyro-Treatment	Leaching	Advantages	Disadvantages
Becher Sulphate	FeO oxidized to Fe_2O_3 and reduced to Fe with (C+ S) at 1200 °C	a. NH_4Cl/O_2 b. 0.5 M H_2SO_4	Diverse ilmenite type ore feed	Multi steps, high energy, emission of CO_2
Murso	Similar to Becher, but use C and H_2 and fluidized bed at 900-950 °C	20 % HCl at 108-110 °C	Efficient than Becher, easier recycling of HCl	Similar to Becher
Laporte	Oxidation in fluidise bed at 950 °C, reduction with C of Fe_2O_3 to FeO	18 % HCl	Free formation of fine TiO_2, ease leaching of FeO	Similar to Becher , but low temperature
Benelite	Reduce roasting of Fe_2O_3 to FeO using C	18-20 % HCl	One simple step	Limited type of ilmenite
Austpac	Magnetisation of ilmenite by roasting at 800-1000°C	25 % HCl	Magnetic separation, >97 % TiO_2	High acidity, magnetic Fe form
Dunn	Selective chlorination of Fe in ilmenite with Cl_2 in fluidised bed		Recycling of Cl_2 by oxidation of $FeCl_2$ to Fe_2O_3	Large Fe sulphate wastes
Kataoka	Reduction roasting of Fe_2O_3 to FeO	H_2SO_4	Low temperature and less corrosive than HCl leaching	Large Fe sulphate waste
Direct Fe leaching		HCl + Fe powder		

Direct chloride leaching has been investigated intensively, incorporating solvent-extraction to separate Ti from Fe and incidental impurities. This process is a significant strategy to reduce operating costs and protect the environment by enabling the use of low grade ilmenite and eliminate the chlorination process for production of high grade TiO_2 and/or $TiCl_4$.

Caustic leaching with high selectivity of Ti over Fe, Ti dioxide nano-technology for hydrometallurgical processing, and direct leaching of ilmenite in chloride solution and subsequent purification using solvent extraction for Ti oxide and Ti metal production are other alternative lixiviation processes that have been researched and developed nowadays [2][5][6].

Fray-Farthing-Chen (FFC) Cambridge (developed in the late 1990s) has developed a process called Metalysis®, to generate Ti powder of different morphologies and alloy chemistries. The FFC process has the capability to combine different metallurgical steps, including metal extraction, alloying, and shaping, into one step. FFC Cambridge process extracts Ti from Ti oxides at lower energy consumption via electrochemical reduction in molten salts. Its ability to produce alloys and powders, while retaining the cathode shape also promises energy and material efficient manufacturing. This process can be run with lower cost feedstocks such as Ti oxides, synthetic rutile and slags, and recycled Ti wastes. Recycling Ti scrap using FFC process will reduce the huge "buy to fly" ratio in the aerospace industry. The use of inert anodes can also improve the process sustainability by improving the current efficiency and product purity [2][5][6].

A recently developed process, Hydrogen-Assisted Magnesium Reduction (HAMR), is based on the destabilisation of the Ti–O system using hydrogen as a temporary alloying element during the magnesio-thermic reduction of TiO_2. It is a very promising process for the production of Ti metal [5].

3. Titanium alloy development

The application of Ti and Ti alloys in the field of medical and biomedical science is increasing due to its unique physical, chemical and biological properties. Ti and its alloys offer excellent biocompatibility and good osseointegration. Recent research in this area is focused on Bioactive Surface Modifications (BSM) of Ti and its alloys, in order to achieve improved biocompatibility. The current techniques that are used for BSM are intended to improve either the interaction of hard tissues with Ti and its alloys (Physio-chemistry) or the hard and soft tissues interaction with Ti and its alloy. Advanced surface modification approaches are needed to widen the possibility of applications of Ti and its alloys in medical and biomedical applications.

Low-rigidity Ti alloys containing nontoxic and allergy-free elements (Nb, Ta and Zr) are given considerable attention in biomedical applications. Low-rigidity (low Young's modulus) Ti alloys have the advantage of healing bone fractures and adapting bone properties. Ni-free superelastic and shape memory Ti alloys for biomedical applications are being actively developed. Additionally, mechanical properties such as strength, ductility, fatigue strength, fretting fatigue strength, and wear resistance have been included in the recent research [7][8][9].

New Ni-Ti shape memory alloys have been developed for intravascular devices such as stents and occlusion coil; for osteosynthesis, osteoconductivity and osseointegration. The texture and shape of the Ni-Ti device can be modified by stress and temperature variations for hard and soft tissue interactions [3],[7],[10].

Alloy development has recently been focussed on improving high temperature performance and superplasticity of α-β Ti alloy (4.5-5.5Al-3.0-5.0V-0.3-1.8Mo-0.2-1.2Fe-0.12-0.25O-0.1-0.4Si-Ti) [14]. This includes designing α-β Ti alloy with good ballistic and mechanical properties using low-cost composition, 4.2-5.4Al-2.5-3.5V-0.5-0.7Fe-0.15-0.19O-Ti [15]. The focus also includes developing a high strength, deep hardenability, and excellent ductility near-β Ti alloy for an aviation system component, including 5.3-5.7Al-4.8-5.2V-0.7-0.9Fe-4.6-5.3Mo-2.0-2.5Cr-0.12-0.16O-Ti [16].

In a joint effort, German scientists have developed a new γ-TiAl (Ti-43Al-4Nb-1Mo-0.1B at. %) which is characterized by β-solidification. This alloy exhibits a more homogenous and fine microstructure due to solidification via the bcc β-phase and can be extruded and fine grain achieved [11].

A metastable Ti-5Al-5V-5Mo-3Cr alloy has been developed recently. This alloy is expected to replace Ti6Al4V and high strength steels in the future aircraft as forged fuselage structures and forged landing gears. The new alloy offers attractive mechanical properties such as moderate strength, acceptable ductility and fracture toughness, and less residual stresses and distortion after machining, forging and heat treatment [11].

4. Powder Metallurgy of Titanium and its alloys

Powder metallurgy consists of consolidating and sintering (pressure-less and pressure-assisted) Ti and Ti alloy powders. Vacuum sintering is the mostly used process due to the minimum oxygen contamination. Unfortunately the microstructure and mechanical properties of conventionally sintered Ti powder cannot match those of wrought Ti. Thus, the conventional powder metallurgy approaches have not met the performance-to-cost ratios required to substitute wrought Ti and its alloys.

Nevertheless, the recently developed Hydrogen Sintering and Phase Transformation (HSPT) process has shown the capability of yielding microstructures that are equivalent to those of wrought Ti. This process can potentially maximise the performance-to-cost ratio by producing wrought-like Ti using press-and-sinter and conventional heat treatment processes [5].

HIP, which is the traditional TMP to close remaining porosities, will be probably replaced by a more promising low cost alternative Gaseous Isostatic Forging (GIF) process [5].

Titomic® will be commercializing the Titomic Kinetic Fusion (TKF) or Cold-Gas Dynamic Spraying (CGDS) developed by CSIRO. CGDS consists of spraying Ti or Ti alloy particles onto a scaffold to produce a load-bearing structure. The new process is able to use powders costing approximately one fifth to one tenth that of traditional AM powders, resulting in components up to 50 % cheaper, and it can produce large scale parts thirty times faster than other metal AM processes [18].

5. Manufacturing technologies

5.1. Thermomechanical processing
A method of manufacturing fine grain α/β Ti-Al-V-Mo-Fe alloy sheets that is suitable for superplastic forming has been developed. The alloy is forged and hot rolled to sheet bar, then fast-cooled from a temperature above beta transus. The sheet bar is heated between 760 °C.and 843 °C and rolled down. After reheating from about 760 °C to about 843 °C, hot rolling is performed in a direction perpendicular to the previous rolling direction to minimize anisotropy of mechanical properties. The sheets are then annealed at temperatures between 705 °C and 843 °C followed by grinding and pickling [8].

In order to increase the tensile and fatigue strength while keeping sufficient ductility, the Thermohydrogen Process (THP) has been developed. The process consists of hydrogenation of Ti below β-transus followed by air cooling, solution annealing and dehydrogenation below β-transus, solution annealing slightly above β-transus and air cooling (formation of β-phase), then ageing below β-transus followed by vacuum cooling (α precipitation hardening) [11].

The integration of design with manufacturing process and developing bioengineering have driven research in Ti and Ti alloys towards the computational materials engineering to predict fundamental phenomena focused on phase transformations, role of alloying elements and mechanical behaviour of alpha and beta phases. The comprehension through thermal modelling and compositional effects on phase transformation will be the future research focus [12].

5.2. Manufacturing processes
In manufacturing, Laser Beam Forming (LBM) technique has been established for joining of metallic components. Recent research in LBM is focused more effort on improving the laser-Ti and its alloys interaction [13].

MTU Aero Engine (Germany) has developed a linear friction welding process for the production of a new "Dual Material Ti alloy Linear Friction Welded Blisk" (DUTIFRISK). The produced linear friction welded blisks are made from a wide variety of different alloys and/or microstructures for the disk and blade [11].

A skull melting route for serial production has been developed by two companies; ThyssenKrupp Titanium GmbH®, in Germany, and Thyssen-Krupp Titanium S.p.A., in Italy. The melting process is similar to the Vacuum Arc Melting Process (VAR) [11].

Highly sophisticated, and high performance sport cars have been made by Bugatti Engineering GmbH® (Germany). The new sport car is currently the most powerful automobile with an engine performing at 1001 horsepower. The car parts are made of different Ti and Ti alloys in order to limit the weight and fulfil the specific requirement of heat shielding. The total amount of the built in parts is about 40 kg. Ti and Ti alloys used include Ti grade 1 & 2, Ti grade 1 plated with Al (leading to Ti-Al heat resistant for the exhausting system), Ti6Al4V coated with MoS (bolts suspension), Ti6Al4V bi-modal structure (Engine connecting rods), Ti6Al4V superplastically formed, β-Ti alloy (suspension springs) [11].

An erosion inhibiting coatings of thin vapour-deposited TiN/Ceramic (ERCoat) to protect compressor blades from premature loss of materials has been developed by MTU Aero Engine, in Germany. The TiN coat is applied by Physical Vapour Deposition (PVD), resulting in alternating deposition of hard and soft intermediate multi-layer structure (Pending Patents) [11].

6. Conclusion

The future of the titanium research and development remains bright, with high market demand which is driven by the growth of biomedical applications, additive and manufacturing industry. This provides the driving force for the Titanium alloy development and Titanium metal production.

References

[1]   J. Gambogi, S.J. Gerdemann, Titanium Metal: Extraction to Application, Doe/Arc. (1999) 0–36. doi:10.1002/9781118788417.ch5.

[2]   I. Mellor, G. Doughty, Novel and Emerging Routes for Titanium Powder Production -An Overview,*Key Eng. Mater.* **704** (2016) 271–281. doi:10.4028/www.scientific.net/KEM.704.271.

[3]   Z. Abdullah, R. Razali, I. Subuki, M.A. Omar, M.H. Ismail, An Overview of Powder Metallurgy (PM) Method for Porous Nickel Titanium Shape Memory Alloy (SMA), *Adv. Mater. Res.* **1133** (2016) 269–274. doi:10.4028/www.scientific.net/AMR.1133.269.

[4]   G. Crowley, How to Extract Low-Cost Titanium, *Adv. Mater. Process.* **161** (2003) 25–27.

[5]   Z.Z. Fang, J.D. Paramore, P. Sun, K.S.R. Chandran, Y. Zhang, Y. Xia, F. Cao, M. Koopman, M. Free, Powder metallurgy of titanium – past, present, and future, *Int. Mater. Rev.* **0** (2017) 1–53. doi:10.1080/09506608.2017.1366003.

[6]   D. Hu, A. Dolganov, M. Ma, B. Bhattacharya, M.T. Bishop, G.Z. Chen, Development of the Fray-Farthing-Chen Cambridge Process: Towards the Sustainable Production of Titanium and Its Alloys, *Jom.* **70** (2018) 129–137. doi:10.1007/s11837-017-2664-4.

[7]   J. Sharan, S. V Lale, V. Koul, M. Mishra, O.P. Kharbanda, An Overview of Surface Modifications of Titanium and its Alloys for Biomedical Applications, Trends *Biomater.Artif. Organs.* **29** (2015) 176–187.

[8]   M. Niinomi, Biologically and Mechanically Biocompatible Titanium Alloys, *Mater. Trans. 49* (2008) 2170–2178. doi:10.2320/matertrans.L-MRA2008828.

[9]   Y. Li, C. Yang, H. Zhao, S. Qu, X. Li, Y. Li, New developments of ti-based alloys for biomedical applications, *Materials (Basel).* **7** (2014) 1709–1800. doi:10.3390/ma7031709.

[10] M. do A. Ferreira, M.A. Luersen, P.C. Borges, Nickel-titanium alloys: a systematic review, Dental Press *J. Orthod.* **17** (2012) 71–82. doi:10.1590/S2176-94512012000300016.

[11] D. Helm, O. Roder, Recent Titanium Research and Development in Germany, (n.d.). http://www.mtu.de/en/technologies/engineering_news/others/Helm_Recent_titanium_research.pdf).

[12] D. Banerjee, J.C. Williams, Perspectives on titanium science and technology, *Acta Mater.* **61** (2013) 844–879. doi:10.1016/j.actamat.2012.10.043.

[13] E.T. Akinlabi, M. Shukla, S.A. Akinlabi, Laser forming of titanium and its alloys – An Overview, *World Acad. Sci. Eng. Technol.* **71** 2012. (2012) 1522–1525.

[14] Yoji Kosaka, Patent no. 2017020607, March 2017, Titanium Metals Corporation

[15] John Fannig, Patent no. 9631261, April 2017, Titanium Metals Corporation.

[16] John Fanning, Patent no. 8454768, June 2013, Titanium Metals Corporation

[17] Yoji Kosaka, Phani Gudipati, Patent no. 8551264, October 2013, Titanium Metals Corporation)

[18] CSIRO, US patent, March 2013, Titomic Limited, Melbourne, Australia.