

Review

Titanium: An Overview of Resources and Production Methods

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Abstract: For several decades, the metallurgical industry and the research community worldwide have been challenged to develop energy-efficient and low-cost titanium production processes. The expensive and energy-consuming Kroll process produces titanium metal commercially, which is highly matured and optimized. Titanium's strong affinity for oxygen implies that conventional Ti metal production processes are energy-intensive. Over the past several decades, research and development have been focusing on new processes to replace the Kroll process. Two fundamental groups are categorized for these methods: thermochemical and electrochemical. This literature review gives an insight into the titanium industry, including the titanium resources and processes of production. It focuses on ilmenite as a major source of titanium and some effective methods for producing titanium through extractive metallurgy processes and presents a critical view of the opportunities and challenges.

Keywords: titanium; titanium alloys; ilmenite; extractive metallurgy; TiO_2 ; calciothermic reduction



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1. Introduction

Titanium is a transition metal that is used more in the production of high-strength, corrosion-resistant, and thermally stable metal alloys for the aerospace and shielding industries. The titanium production cost has so far hindered the growth in the use of this metal relative to other base metals on the market, even though titanium is the fourth most abundant structural metal in the earth's crust with 0.6%. It comes after iron, magnesium, and aluminum, but remains exotic due to its prohibitive cost [1,2], which prevents the metal from reaching its full potential in marine and automotive industry applications. Older production technology, high energy losses, and loss of material or metal are some of the problems associated with the production of titanium metal [3]. Further, all base metals are inferior to titanium in terms of specific mechanical and chemical properties, but titanium has not yet been fully exploited [1,2,4]. Titanium exhibits unique properties, some of which are proprietary, which could help it replace common metals and alloys such as steel and aluminum in many applications [5].

The current commercial method of titanium production is the Kroll process, marketed by DuPont Germany in 1948 [4]. It is a discontinuous, energy-, and labor-intensive process whose strict conditions make it expensive; therefore, researchers around the world are investigating new methods for extracting titanium from its precursors. Titanium is mainly produced from minerals such as ilmenite FeTiO_3 and rutile (TiO_2) while smaller quantities are produced from perovskite (CaTiO_3) and titanite or sphene (CaTiSiO_5) [6]. The main ilmenite deposits are located in Australia, China, Norway, Canada, Madagascar, India, South Africa, and Vietnam, while rutile deposits are found in Sierra Leone, the United States, India, and South Africa [7].

Ilmenite is a significant mineral [8], which contains between 40% and 65% titanium dioxide. The other elements are either ferrous oxide or ferric oxide and sometimes small amounts of vanadium, magnesium, and/or manganese. Ilmenite's main sources are the

heavy mineral sands (alluvial deposits) but are also commonly distributed in hard rock [9]. Currently, ilmenite accounts for 92% of the world's titanium mineral production. Rutile (TiO_2) has a titanium dioxide content of 93–96% but is difficult to find in natural ilmenite deposits [7]. Thereby, the present review focuses on the alluvial deposit, more precisely the ilmenite, and the extraction of titanium from it.

Titanium metal production consumes a small proportion of total titanium reserves per year [7]. Low density and high tensile strength make titanium attractive for industrial applications, and give titanium-containing alloys the highest strength-to-weight ratio, an important property for metals in the steel industry. In addition, titanium is a valuable metal and can resist corrosion of both seawater and acids. As an alloyed metal, it can also resist corrosion better than copper and nickel alloys and has a low modulus of elasticity that is half that of steel and nickel alloys. The most common titanium alloy is Ti6Al4V (6% aluminum, 4% vanadium, 90% titanium) and is typically used in medical applications such as knee replacement implants. Metal is also one of the main elements in the aerospace industry, architecture, chemical, and automotive applications [10].

The traditional methods of manufacturing Ti follow the same general procedures as steel, including the primary metal production, the melting and casting of alloy ingots, forging and rolling to produce rolling products, and the manufacture of components or structures from rolling products [11]. Many powder production processes are at various stages of development. There are two general approaches for Ti metal production: electrochemical and thermochemical methods. The well-known example of the electrochemical methods is the Fray, Farthing, and Chen (FFC) or Cambridge process [12], which is based on the electrolysis reduction of titanium oxide. The Kroll process [13], is an example of the thermochemical way that is a commercially suitable process for primary Ti metal production today.

This review provides an overview of titanium resources, of which ilmenite is the main source, as well as it focuses on some effective methods for producing titanium powder through extractive metallurgy processes, and highlights a comprehensive view of the opportunities and challenges.

2. Titanium Usage and Market

Titanium, and particularly titanium alloys, have become economically accessible following a drop of nearly 30% in the price of commercially pure titanium over the last five years [14]. Titanium alloys have many physical (lightness, good mechanical properties, resistance to cryogenic temperatures) and chemical (resistance to electrochemical corrosion, biocompatibility) advantages [15,16], which make them an indispensable material for civil and military applications in fields as vast as in energy, transport, medical (MRI magnet for observing the human body), water treatment, and the transport of corrosive liquids and gases (Figure 1) [14].

The uses of titanium have expanded based on its inherent properties as well as the development of new alloys. The main use is still in aerospace and aeronautics applications, such as engines, airframes, missiles, and spacecraft [16]. Aerospace applications are based on the low density (Table 1) and high strength-to-weight ratio of titanium alloyed at high temperatures. Titanium's corrosion resistance makes it a natural material for seawater, marine, and naval applications. In addition, titanium is largely used in seawater-cooled power plant capacitors [16].

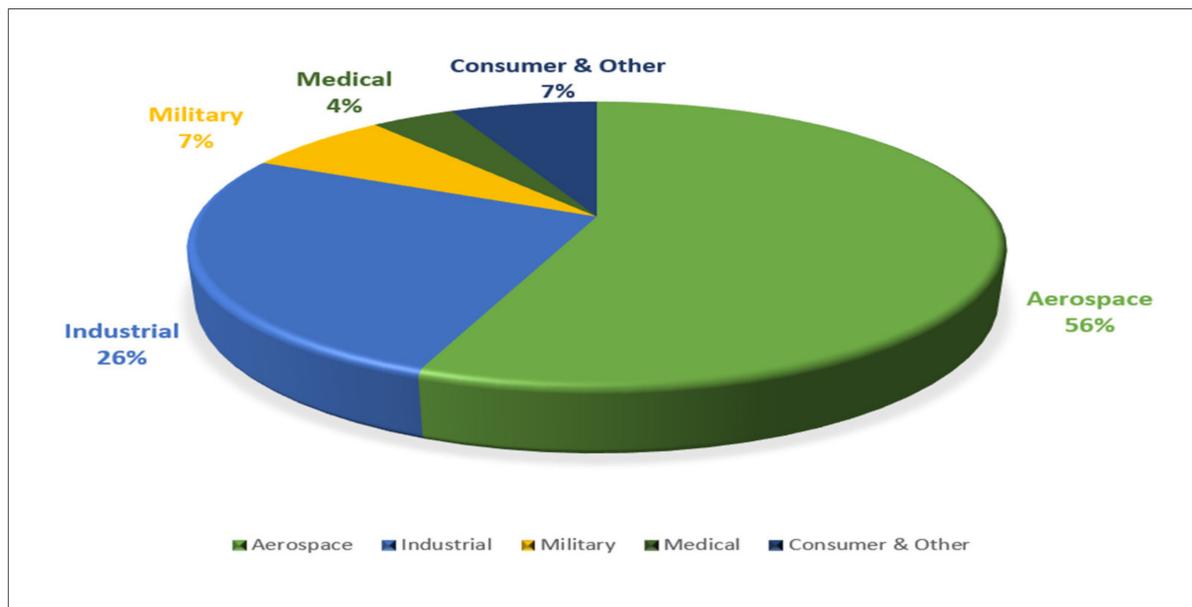


Figure 1. Titanium applications of the Western world by market sector, 2017 [17] (Reprinted with permission from Elsevier, Copyright, (2020)).

Table 1. Some properties of pure titanium [15,16].

Parameter	Value
Atomic number	22
Atomic radius (Å)	1.47
Atomic weight	47.9
Boiling point (K)	3273
Chemical valence	2, 3, 4
Electrical resistivity	42.06×10^{-6}
Ion radius (Å) Ti^{+2}	0.9
Ion radius (Å) Ti^{+4}	0.68
Melting point (K)	2073
Density (g/cm^3)	4.51
Specific heat (J/kg–K)	519
Traction modulus $\times 10^3$ (MPa)	101
Modulus of elasticity $\times 10^3$ (MPa)	103
Hardness (1500 kg load) (HB)	65
Fatigue resistance	0.5–0.6

Titanium can also be utilized in petroleum refineries, paper, and pulp bleaching operations, nitric acid plants, and some organic synthesis production [4]. Moreover, Titanium has found its use in the medical field. In particular, depending on clinical needs, titanium and a multitude of its alloys offer high axial flexibility, good expansion behavior, radio-opacity, and hemocompatibility. Even of its sophisticated bio-applications, the main use of titanium in biomedicine is as a structural prosthesis [1,2,18].

3. Resources

Titanium deposits are huge, with current estimates assuming a global reserve of 650 billion metric tons of titanium oxide. The minable deposits are found in South Africa at Namaqualand and Richards Bay, Australia, Canada, Norway, and Ukraine (Figure 2) [1,7]. The two main minerals being considered for use are ilmenite and rutile and although these are the minerals available for economic mining, TiO_2 is part of almost every mineral, sand, and rock [4].

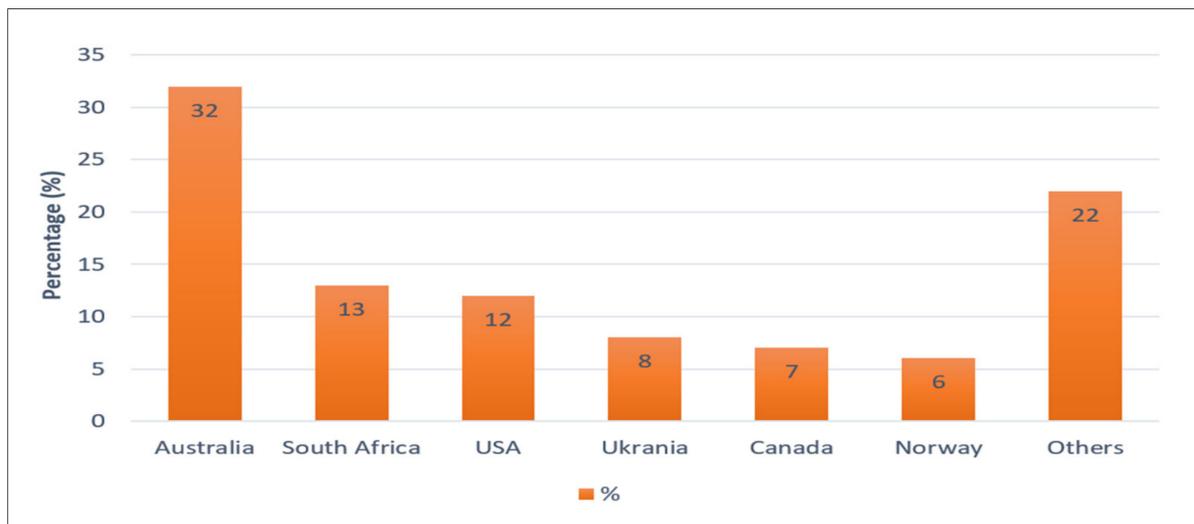


Figure 2. Distribution of the titanium ore reserves in the world [1,4].

The common titanium minerals are anatase, brookite, leucoxene, perovskite, titanite, rutile, and ilmenite. However, only ilmenite, leucoxene, and rutile have crucial commercial value. Ilmenite and rutile are the two main titanium minerals used in industrial applications, mainly for titanium metal production and pigment-grade titanium dioxide [19].

4. Mineral Ilmenite

In 1827, Adolph Theodor Kupffer discovered Ilmenite (titanoferrite) in the Ilmen Mountains of Russia. FeTiO_3 is the typical chemical formula of ilmenite, while its chemical composition is (40–65 wt.%) TiO_2 and (35–60 wt.%) Fe_2O_3 [20]. Table 2 shows the properties of pure ilmenite.

Table 2. Basic properties of pure ilmenite (FeTiO_3) [21].

Property	Value
Chemical classification	Oxide
Color	Black
Luster	Metallic, sub-metallic
Mohs hardness	5–6
Specific weight	4.7–4.8 g/cm ³
Crystalline structure	Hexagonal
Cleavage	Absent
Unit cell	a = b = 508.854 Å, c = 14.0924 Å

Ilmenite is an economically important mineral, mainly because of its role in the production of titanium oxide pigments. Its magnetic properties and those of ilmenite-hematite solid solutions (Fe_2O_3) are particularly important in commercial extraction by magnetic separation. The dependence of the ilmenite structure on temperature, pressure, and composition is strongly related to its electronic, magnetic, and optical properties [22]. Due to the coexistence of ilmenite with geikielite (MgTiO_3) and pyrophanite (MnTiO_3) in these rocks, the typical chemical formula of this mineral in magmatic rocks is $(\text{Fe}, \text{Mn}, \text{Mg})\text{TiO}_3$ [21]. Ilmenite is often confused with other iron-bearing minerals such as hematite and magnetite because of its high magnetic susceptibility (Figure 3). Ilmenite has a hexagonal crystal structure that is similar to corundum (Al_2O_3) and different from other iron minerals and has lower magnetism compared to hematite and magnetite. The crystal presents an octahedral structure alternating and coordinated with iron and titanium layers [22,23].



Figure 3. Ilmenite sand (left) and grinded material (right) from the Metchib company, Quebec, Canada.

The Tellnes (Norway) mines produce 550,000 tons of ilmenite per year [24]. The largest Ti producers in the world are China, Australia, and South Africa (Figure 4). China produces ilmenite in significant quantities, while Australia and South Africa have the world’s largest natural reserves for ilmenite and rutile [7,21].

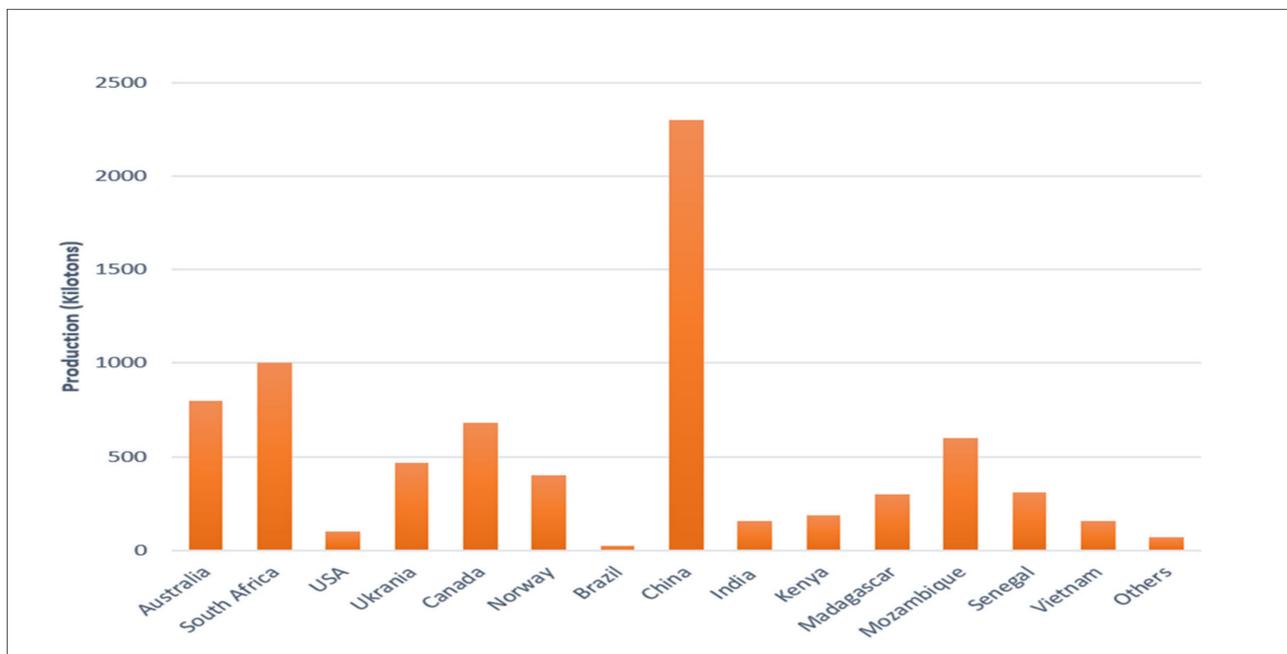


Figure 4. Ilmenite mine production in different countries in 2020 [7].

5. Metallurgical Extraction of Titanium from Its Concentrates

Many methods are used for the production of Ti metal powder. Ti powder is, therefore, the product of extraction processes that produce primary metal by using titanium tetrachloride (TiCl₄) or titanium dioxide (TiO₂) as feed material [25,26]. Processes for the manufacture of titanium powder directly as extractive metallurgical products include the manufacture of Ti from TiCl₄, purified TiO₂, and/or improved titanium slag (UGS) with a TiO₂ content greater than 90%. Upgraded titanium slag (UGS) is one of the fundamental

products of the carbothermal reduction of titanium ore such as ilmenite. Natural rutile and synthetic rutile are also included in this raw material category. These processes can be categorized: (1) thermochemical methods and (2) electrochemical methods [11].

5.1. Thermochemical Processes

5.1.1. Kroll Process

The commercial production of primary Ti metal is generally made either by Kroll [13] or Hunter processes [27]. The standard process against which new technologies are compared is the Kroll process (Figure 5).

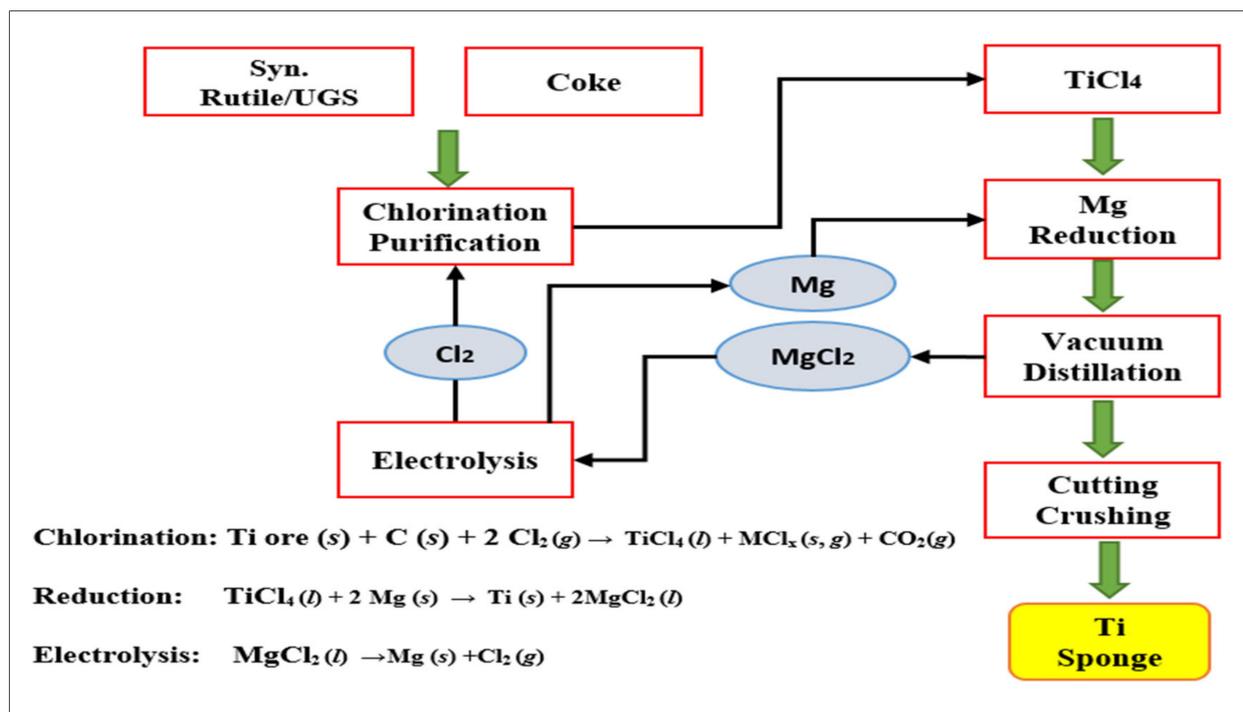


Figure 5. Scheme and reactions of the Kroll process of titanium sponge production [28] (Reprinted with permission from Springer Nature, Copyright, (2020)).

In the process, magnesium metal (the reducing agent) is injected into a retort filled with argon and heated to 800–900 °C. However, the oxides impurity contained in the Ti slag is also chlorinated, so refined TiCl_4 has been produced by purifying the crude TiCl_4 before the Mg reduction [13,29]. Although most of the by-product MgCl_2 , and excess magnesium, is drained during reduction, the product sponge contains residual magnesium and MgCl_2 in its porosity [30]. Magnesium and MgCl_2 are separated by vacuum distillation or helium sweeping followed by leaching. Part of the sponge must be decommissioned due to contamination of the autoclave wall [13,29].

According to one estimate, 70% of the total energy consumption is considered for the distillation to produce the sponge metal. It shows that the cost of metal purification is one of the major cost drivers, in addition to the cost of the precursor and reductant [30].

5.1.2. Hunter Process

The popular process established on TiCl_4 reduction using Na is the Hunter process. The Hunter and Kroll processes are quite similar in that they are considered as thermochemical processes based on the reduction of TiCl_4 to produce Ti [27]. Economically, the Hunter process is considered non-competitive with the Kroll process. The main difficulty is that to produce one mole of Ti by reducing TiCl_4 requires four moles of Na, whereas only two moles of Mg are needed for 1 mole of Ti [11]. In addition, producing Na by electrolysis

is at least as expensive as that of Mg. These problems make the processing of Na more expensive than the use of Mg. However, the Hunter process can also produce Ti powder instead of Ti sponge [31].

In the Hunter process, $TiCl_4$ and Na are gradually introduced into the reactor. The process is generally performed over 800 °C [28,32]. Ti is formed at the surface of the molten bath, where the gas $TiCl_4$ is exposed to the Na. Ti crystals then form and are set at the bottom of the liquid bath. According to the operating parameters, some Ti particles can form Ti sponge, while others are deposited as Ti powder. The purity of the powder produced by the Hunter process is often higher (99%) [11,29]. Table 3 provides a comparison between Kroll and Hunter processes.

Table 3. Comparison between Kroll and Hunter processes [31] (Reprinted with permission from John Wiley and Sons, Copyright, (2013)).

Kroll	Hunter
Batch	Does not last forever
15–50% excess magnesium	A small excess of $TiCl_4$
Few fines	Up to 10% fines
Difficult to rectify	Easy to rectify
Heavy iron contamination from the walls of the autoclave	Little iron contamination from retort walls.
Sponge washed or vacuum distilled	Sponge leached
Retort contains mostly titanium	Retort contains 4 moles of NaCl for each mole of titanium

5.1.3. Armstrong Process

The Armstrong process is considered the most advanced process. It uses the same reactions as the Hunter process [33].

Therefore, the crucial advantage of the Armstrong process [34] is the continuity of the operation, pumping molten sodium in the reactor to react continuously with $TiCl_4$ gas (Table 4). Ti powder and the resulting NaCl are collected from the reactor by the sodium stream. Once the unreacted liquid Na is removed by filtration, as well as Ti powder is purified by washing out the salt. The Armstrong product can be described as mini sponges, i.e., microporous particles [35]. Figure 6 shows the Armstrong process aspects.

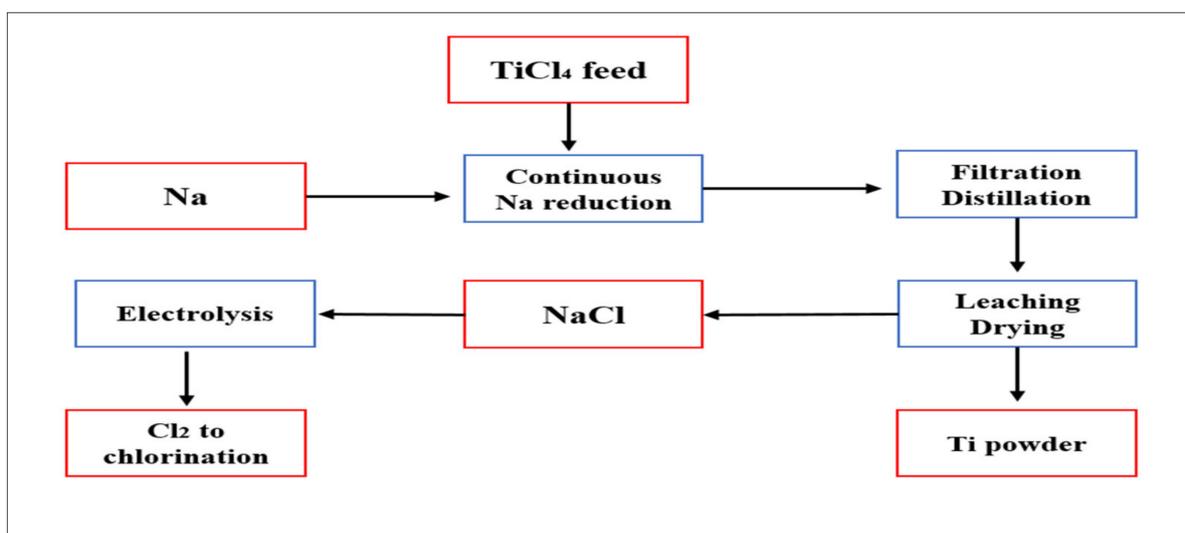


Figure 6. The Armstrong flow diagram [36].

5.1.4. TiRO Process

This process was developed by CSIRO (Commonwealth Scientific and Industrial Research Organization) in Australia and used the same reactions as the Kroll process but in a fluidized bed reactor in which gas–solid fluidization takes place, which considerably increases the reaction rate and reduces both operating and capital costs [37].

The TiRO process consists of two main steps (Figure 7): reduction of TiCl_4 in a fluidized bed with Mg powder and vacuum distillation to remove the by-products MgCl_2 and Mg [38].

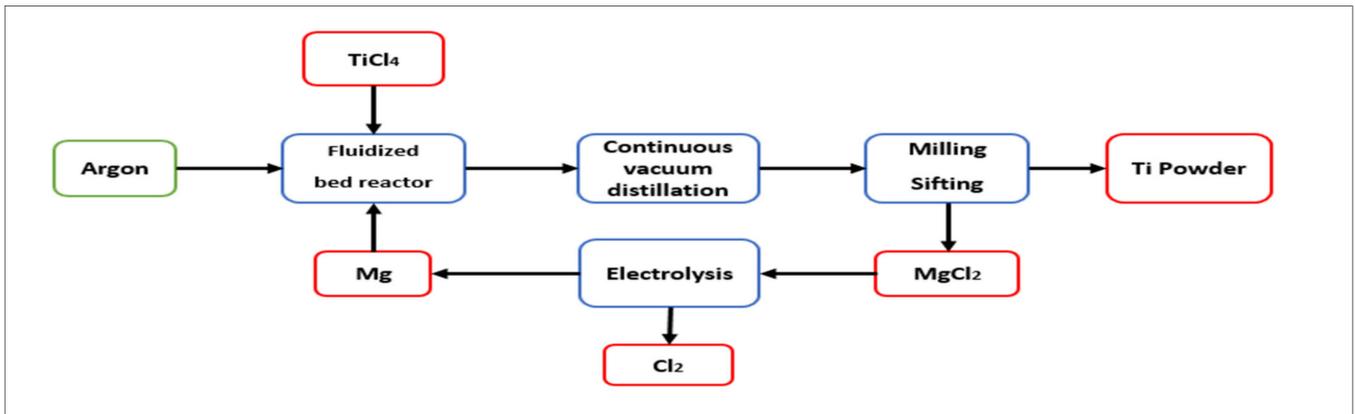


Figure 7. Diagram of the process TiRO™ [39].

According to the information mentioned above, TiCl_4 can be reduced by sodium or magnesium. The main characteristics of the powder are well detailed in Table 4 below.

All these processes below use TiO_2 as raw material to produce titanium powder with high purity.

Table 4. Comparison between characteristics of TiCl₄ reduction-based processes (adapted from [11] Taylor & Francis, an open-access journal).

Category	Process Identifier	Raw Material	Reducing Agent	Product Size and Morphology	Reported Chemical Product and Composition	Batch or Continuous: Reactions	Salt	Temp (°C)	Ref
Reducing TiCl ₄ using Mg	Kroll	TiCl ₄	Mg Liquid	Sponge	O~0.06%	Batch; 2Mg + TiCl ₄ → Ti + 2MgCl ₂	No salt	800–1000	[13]
	TiRO	TiCl ₄	Mg Powder	Similar spherical shape but sintered to form large chunks	O ≥ 0.3%, Cl < 0.03%	Continuous; 2Mg + TiCl ₄ → Ti + 2MgCl ₂ (s)	No salt	650–712	[38]
	Vapor Phase Reduction	TiCl ₄	Mg Vapor	Sub-micrometer, too fine to be captured	Low levels of Mg and Cl, but O ≥ 0.82%.	Continuous; 2Mg + TiCl ₄ → Ti + 2MgCl ₂	No salt	1000	[40]
	CSIR-Ti	TiCl ₄	Mg	Irregular shape, size be ranging from 1 to 330 μm	Cl < 50 ppm, N < 50 ppm, O > 0.2%	Continuous; Mg + TiCl ₄ → TiCl ₂ + MgCl ₂ TiCl ₂ + Mg → Ti + MgCl ₂	No salt	>900	[41]
Reducing TiCl ₄ using Na	Hunter	TiCl ₄	Na	Sponge and powder	Purer than that produced by the Kroll process (99%)	Batch; 4Na + TiCl ₄ → Ti + 4NaCl	No salt	>800	[27,42]
	Armstrong	TiCl ₄	Na	Mini sponge, particulates with micro porosity	O: 0.12–0.23%, N: 0.009–0.026%, C: 0.013%, Fe: 0.012%	Continuous; 4Na + TiCl ₄ → Ti + 4NaCl	No salt	860	[34,35]
	ARC	TiCl ₄	Na	Powder, small aggregates	Oxide layer contributes a lot to the final high oxygen content	Continuous; 2Na + TiCl ₄ → TiCl ₂ + 2NaCl TiCl ₂ + 2Na → Ti + 2NaCl	No salt	>800	[43]

5.1.5. Metal Hydride Reduction (MHR) Process

The MHR process was first introduced in 1945, and the most remarkable work was reported by Borok [44], in 1965 and Froes et al. in 1998 [45]. Calcium hydride was used to directly reduce TiO_2 . In Russia, a commercial operation has been reported that uses the same procedure [46].

5.1.6. Electronically Mediated Reduction (EMR) Process

EMR process uses calcium as a reducing agent to produce titanium. The TiO_2 reduction is made with no direct contact with the reducing Ca-Ni alloy, and hence the contamination of titanium can be successfully avoided by using EMR. This approach can be exploited to develop another process to produce titanium powder continuously [47].

5.1.7. Process for Reducing Preforms

Okabe et al. [48] have developed this process where TiO_2 is mixed with either CaO or CaCl_2 and sintered in the air. Calcium vapor reduces TiO_2 at temperatures between 800 and 1000 °C, with the calcium oxide dissolving in calcium chloride. A hydrochloric acid solution has been used for leaching the product [46]. Again, these experiments were only conducted in the laboratory [49].

5.1.8. Hydrogen-Assisted Magnesium Reduction (HAMR) Process

The HAMR process is developed to produce a Ti powder with a very low oxygen content, by using a hydrogen atmosphere, molten salt, and deoxygenation step to guarantee that the oxygen amount in titanium powder is sufficiently low (less than 0.15% by weight) [50,51]. Table 5 shows a comparison between the characteristics of these processes based on TiO_2 reduction.

Table 5. Comparison between characteristics of TiO_2 reduction-based processes (reprinted from [11] Taylor and Francis, an open-access journal).

Process Identifier	Raw Material	Reducing Agent	Product Size and Morphology	Reported Chemical Product and Composition	Salt	Temperature (°C)	Ref
MHR	TiO_2	CaH_2	Irregular, sponge	O: 0.19 wt.%, H: 0.34 wt.%, C: 0.03 wt.%, N: 0.06 wt.%	No salt	1100–1200	[52,53]
Calciothermal reduction	TiO_2	Ca	Irregular, sponge	O: <0.2 wt.%, Ca: >0.1 wt.%	CaCl_2	900–1200	[54]
Process for reducing preforms	TiO_2	Ca	Irregular, sponge	O: 0.2–0.3 wt.%	CaCl_2	>900	[48]
EMR	TiO_2	Ca	Irregular, sponge	O: 0.15–0.2 wt.%	CaCl_2 or CaCl_2 + CaO	>900	[47,55]
Combustion synthesis	TiO_2	Mg + Ca	Irregular, sponge	O: 0.2–0.3 wt.%	Ca(OH)_2	850–1000	[56,57]
HAMR	UGS	Mg + Ca	Dense, globular powder	O: <0.15 wt.%	MgCl_2 or MgCl_2 -KCl	<800	[50,58]

There have been several reports and trials to perform continuous processes based on the same chemistry as the above processes. Lu et al. [59] produced a fine titanium powder from a titanium sponge by the shuttle: the disproportionation reaction and its reverse reaction (proportioning reaction) of titanium ions in molten NaCl-KCl at 750 °C. Moreover, some experiments were performed to synthesize TiH_2 from the reaction between CaH_2 and TiCl_4 in the presence of Ni [60].

In another study, porous titanium was obtained in mixtures of molten CaO-CaCl₂ salts dissolved in Ca by self-sintering with the exothermic reaction between porous CaTiO₃ and calcium vapor at 1000 °C for 6 h under vacuum [61]. Development of a new method based on deoxidation of dissolved O from Ti. The process leads to the formation of YOCl using Mg as a deoxidizer at 1027 °C [62].

Daniel Spreitzer et al. [63] have used a laboratory fluidized bed reactor to cut down the hematite kinetic reaction to produce Fe by hydrogen around 600–800 °C by measuring the change in weight of the sample portion during reduction. Moreover, with combining magnesiothermal reduction of TiO₂ and a leaching purification process, titanium metal powder was obtained with only 2.98% of O [64]. The synthesis of a cermet based on Fe-TiC by carbothermal reduction of ilmenite was successfully produced [65]. This method was done in an atmosphere containing argon in a scope of 850–1350 °C. Another study has led to developing an environmentally friendly pre-treatment process to recycle titanium turning waste and ferrotitanium ingots with low levels of gaseous impurities [66]. The number of gaseous impurities in the titanium scrap before the removal of machining oils from the surface reached 2% [66]. Similarly, Nersisyan et al. [67] have developed a combustion synthesis route for single-phase titanium-based compounds (e.g., FeTi, TiC, TiB₂, and TiFeSi₂) from the precursor mixture FeTiO₃ (natural ilmenite)-αMg-C (B, Si)-kNaCl. The method allows the process temperature and the phase composition to be controlled by changing the number of moles of Mg and NaCl [67]. Furthermore, new research has been developed to study the effect of the degree of ilmenite reduction on the chemical and phase characteristics of ferrotitanium and slag produced by the SHS aluminothermic process, which is a highly exothermic thermite reaction [68]. Increasing reduction not only reduces the consumption of aluminum and the amount of slag produced in the preparation of ferrotitanium but also reduces the oxygen content and improves the titanium and iron qualities [68]. Further, the Panzhihua ilmenite carbothermal reduction with activated carbon has been studied by using isothermal trials between 1200 °C and 1500 °C [69]. By decreasing the pressure and increasing the temperature, the impurities (Mg, Mn) in the product have been removed [69]. The carbothermal reduction behavior of ilmenite at high temperatures was studied by thermodynamic calculations [70]. FeTi formation is generated at 1650 °C. By increasing the temperature, a clear increase of TiC is observed, which can also encourage the further reduction of ilmenite slag at high temperatures [70].

Otherwise, for patents published in this sense, Mu et al. [71] invented a method that aimed to improve the metallic titanium production with a low-energy titanium-containing material by a molten salt electrolysis process (Table 6).

Similarly, in 2016, Fang et al. [51] presented a research procedure for producing a titanium powder or sponge. For instance, the method may include obtaining a TiO₂-rich material, reducing impurities to produce purified TiO₂, reducing the purified TiO₂, using a metallic reducer at the same temperature and pressure to produce a TiH₂ product [51]. RMI (now part of Arconic) has patented a process that carries out above 900 °C to reduce oxygen in Ti-6Al-4V powder [72].

Table 6. Advantages and disadvantages of some patents in titanium production based on thermochemical methods.

Publication N°	Title	Advantages	Disadvantages	Reference
US 2016/0108497 A1 (2016)	Methods of producing a titanium product	<ul style="list-style-type: none"> - Hydrogen helps destabilize the Ti-O system. - Titanium hydride is known to be more impermeable to oxidation in the air than α-Ti, making it easier to handle the material after reduction and controlling the oxygen content in the final product - The oxygen content can be reduced to less than 0.2%. - The use of molten salt, especially salt-containing Mg such as $MgCl_2$ to facilitates the reaction and greatly improves the kinetics of the reduction process 	<ul style="list-style-type: none"> - High reduction temperatures - High pressures 	[51]
US 9,963,796 B2 (2018)	Method of producing titanium metal with titanium-containing material	<ul style="list-style-type: none"> - Low energy consumption - Low cost of production - Fewer titanium losses 	<ul style="list-style-type: none"> - Fine powder 	[71]
US 10,066,308 B2 (2018)	System and method for extraction and refining of titanium	<ul style="list-style-type: none"> - Reduce the use of hazardous chemicals - Reduce the production of greenhouse gases, such as CO_2 - High purity up to 90% 	<ul style="list-style-type: none"> - High temperatures - Consumable anode - Relatively high energy consumption 	[73]
US 9,067,264 B2 (2015)	Method of manufacturing pure titanium hydride powder and alloyed titanium hydride powders by combined hydrogen-magnesium reduction of metal halides	<ul style="list-style-type: none"> - To provide cost-effective and highly productive manufacturing of purified titanium hydride powders and alloyed titanium hydride powders from porous titanium compounds with reduced magnesium and hydrogen content - Reduce the thermal reduction reaction time in the horn by 15% to 20% and simultaneously improve the percentage of magnesium used from 40% to 50% to 70% to 80% 	<ul style="list-style-type: none"> - Use of large quantities of hydrogen. - Production of small quantities of titanium powder. - The use of hazardous chemicals such as $TiCl_4$. 	[74]
US 8,388,727 B2 (2013)	Continuous and semi-continuous process of manufacturing titanium hydride using titanium chlorides of different valency	<ul style="list-style-type: none"> - A continuous process for the manufacture of titanium hydride powder - Significantly lower oxygen content in the titanium powder due to the absence of grinding steps and limited contact with atmospheric humidity - Manufacture of pure titanium hydride powder from titanium slag with the recycling of the main amount of hydride and chlorine without an electrolysis process - Use the same equipment as that used in the manufacture of said porous hydrogenated titanium compound - Cost-effective and highly productive production of purified titanium hydride powder 	<ul style="list-style-type: none"> - Carbon monoxide emission - Powder too fine - Formation of intermediate products 	[75]
Re. 34,598 (1994)	Highly pure titanium	<ul style="list-style-type: none"> - A fairly low temperature - Production of high purity titanium - Oxygen content does not exceed 200 ppm 	<ul style="list-style-type: none"> - Contamination problem. 	[76]
US 4,923,531 (1990)	Deoxidation of titanium and similar metals using a deoxidant in a molten metal carrier	<ul style="list-style-type: none"> - The process is effective for most refractory metal alloys - Low-pressure operation - The oxygen level can be reduced to between 10 and 90% of the initial oxygen content, depending on the alloy and conditions 	<ul style="list-style-type: none"> - Deoxidation is limited; it concerns metals and metal alloys containing small quantities of oxygen - Fairly high temperature - Consumable proces 	[72]

Table 6. Cont.

Publication N°	Title	Advantages	Disadvantages	Reference
US 8,007,562 B2 (2011)	Semi-continuous magnesium-hydrogen reduction process for manufacturing of hydrogenated, purified titanium powder	<ul style="list-style-type: none"> - Reaction temperatures are quite low - High productivity due to the use of a small mass of $TiCl_4$ - Less electricity consumption - Total powder production time is reduced 	<ul style="list-style-type: none"> - Use of high pressures. - A large amount of hydrogen - Use of large quantities of magnesium - Fine powder - The use of hazardous chemicals such as $TiCl_4$. 	[77]
US 10,689,730 B2 (2020)	Methods of producing a titanium product	<ul style="list-style-type: none"> - Oxygen content can be reduced to less than 0.2% 	<ul style="list-style-type: none"> - Multi-step process 	[78]
US 583,492 B2 (2020)	Titanium powder production apparatus and method	<ul style="list-style-type: none"> - Preventing contamination of titanium powder 	<ul style="list-style-type: none"> - Preparation conditions are difficult 	[79]

5.2. Electrochemical Processes

5.2.1. Cambridge FFC Method

For several decades, it was considered difficult to synthesize titanium with a low amount of oxygen. However, in 2000, a new method was introduced [80], which showed that it is possible to reduce TiO_2 , completely in the solid-state, to the metal in molten calcium chloride, which is a cheap and non-toxic product. This technique is known as the Cambridge FFC process (Figure 8). It operates in a molten saline environment, typically in the scope of $800\text{ }^\circ\text{C}$ to $1100\text{ }^\circ\text{C}$. CaCl_2 is used as a salt since CaCl_2 can dissolve and transport oxygen ions. The TiO_2 reduction during the FFC process has been reached by the ionization of oxygen from the titanium-containing cathode, which diffuses to the anode and is discharged [46].

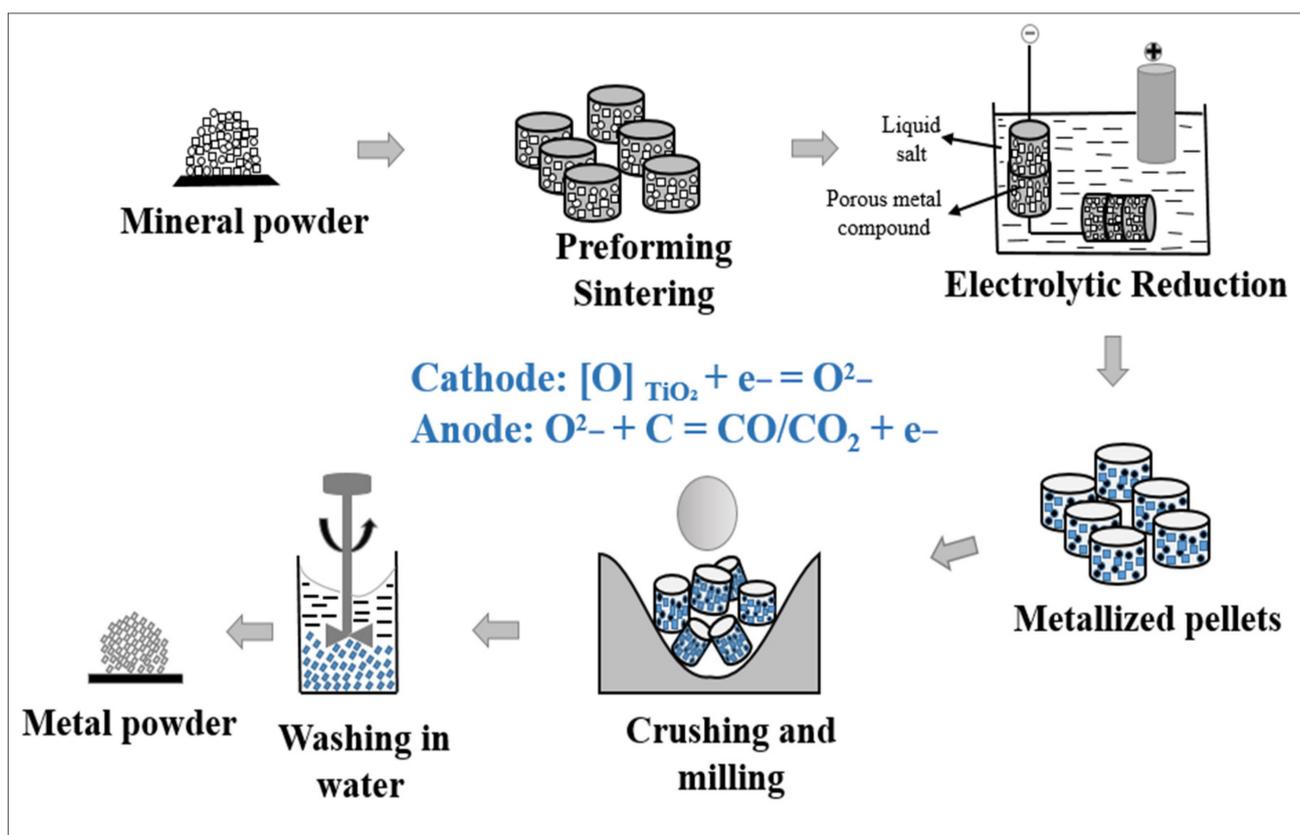


Figure 8. A schematic illustration of the CTF's Cambridge process [81] (Reprinted with permission from Taylor & Francis, Copyright, (2015)).

5.2.2. Ono and Suzuki Process

The (OS) process invented by Ono and Suzuki et al. [54,82,83] is based on a reduction of TiO_2 by Ca. Ca is generated by electrolysis of CaO in molten salt CaCl_2 . A layer of calcium oxide that inhibits any further reaction was generated by the simple reaction of calcium with titanium dioxide generated (Figure 9); however, the ability of calcium chloride to dissolve significant amounts of calcium oxide may be effective in overcoming this problem [49].

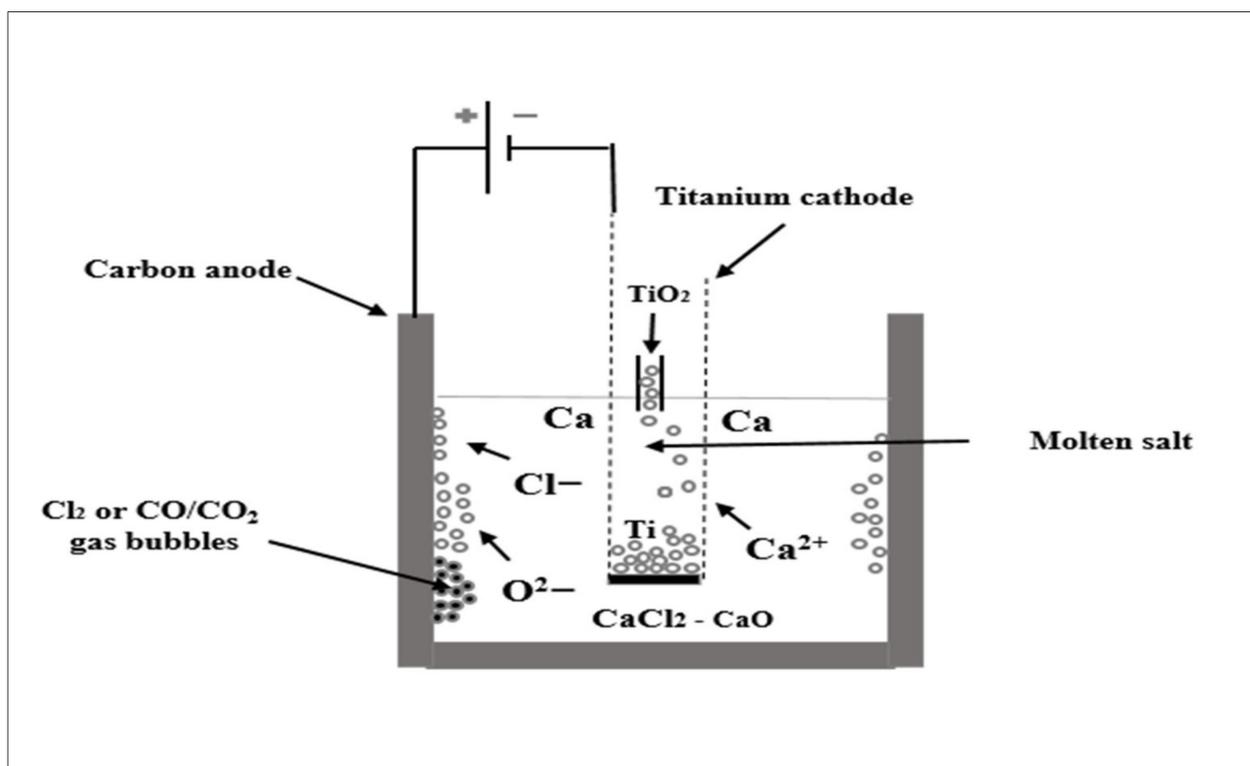


Figure 9. Diagram of the cell used in the OS process [83] (Reprinted with permission from Elsevier, Copyright, (2015)).

5.2.3. Quebec Iron and Titane (QIT) Process

The QIT process, patented by François Cardarelli in 2009 [84], is a process for the electrolytic extraction of Ti metal from compounds containing TiO₂ in a liquid state. Specifically, this process uses a molten compound containing TiO₂ as the cathode on the bottom and a consumable carbon as the anode. A layer of electrolyte, such as molten salts (e.g., CaF₂) or a solid-state ion conductor is used as the O²⁻ ion carrier in the middle. The temperature ranges between 1700 °C and 1900 °C in this process [76].

There have been several reports on the development of continuous processes based on the same chemistry as the above processes. A new process was presented, which integrates carbochlorination and electrolyzation to elaborate metallic titanium in molten NaCl-CaCl₂ electrolyte [82]. This experiment was made at 577 °C using some specific precursors like carbon-doped TiO₂. Likewise, a pre-treatment is performed to partially reduce TiO₂ to titanium sub-oxides with lower valence. The compacted pre-treated mass is electrolyzed at a temperature of 1000 °C in a molten CaCl₂ bath for 1–5 h [85].

An investigation of the CaCl₂ effect on the calcium vapor reduction process of Ti₂O₃ has been performed [86]. The compound CaCl₂ plays a crucial role in the calciothermic reduction process of Ti₂O₃ to prepare porous titanium [86]. Likewise, the generation of a low oxygen Ti powder was carried out by electrolytic reduction of CaTiO₃ in a CaCl₂-CaO melt. By using different sizes of raw oxide particles, the concentration of residual oxygen in the cathode imposes a reduction mechanism using calcium from the cast iron [87]. Another method was introduced for the preparation of titanium metal by reduction of TiCl₄ in NaCl-KCl-NaF eutectic melts [88]. A new method for manufacturing porous titanium by in situ calcium vapor reduction of titanium sesquioxide was presented by Yang et al. [89]. By calcium vapor, Ti₂O₃ and CaCl₂ powders have been reduced. The product was leached with hydrochloric acid and deionized water and the porous structure of Ti was obtained [89]. Furthermore, LiCl-KCl molten salt was used as an electrolyte due to its relatively low melting point to produce metallic titanium. The oxygen content in the titanium crystal is 1200 ppm [90].

Commercial TiO_2 has been reduced by Mg in a hydrogen atmosphere [91]. A mandatory deoxygenation process was added to ensure that the purity met standard specifications for titanium. The magnesium reduction and deoxygenation combination process is a holistic approach that produces Ti powders meeting ASTM specifications [91].

Otherwise, for patents published in this sense, Zhu et al. [92] invented a method for the electrowinning of titanium metal from a soluble anode molten salt containing titanium and concerns the technical field of non-ferrous metal metallurgy. In 2009, François Cardarelli [84] also invented a process for the electrowinning of Ti metal from compounds containing a liquid TiO_2 (Table 7). This process uses a molten compound containing TiO_2 as the cathode in the bottom. The anode can be a consumable carbon, a stable inert anode, or a gas diffusion anode powered by a combustible gas (e.g., H_2 , CO, etc.). The temperature reaches 1700 °C to 1900 °C for this process [76].

As shown above, there are many methods and newly developed technologies to produce titanium powder. Kroll process the most utilized one can produce titanium with less oxygen content and metallic impurities, but its productivity is still very low, magnesium as a reductant has a high cost compared to other metals such as calcium and aluminum, and it is a labor-intensive batch process. Furthermore, the Hunter process produces titanium powder purer than Kroll's powder but uses an expensive sodium reductant and heterogeneous exothermic reactions. For other processes, they present advantages at the production level but they are still at the laboratory scale and require more time to be developed in the industry. It is possible to develop a method to directly reduce oxides to efficiently produce Ti with low oxygen amount in the next few years. In principle, the production of high purity metallic Ti by direct reduction of Ti precursors is possible; hence, a method that relies on the melting of these oxides and is based on the principles of the Kroll process should be developed as a new approach to establish a low-cost Ti reduction process.

On the other hand, new technologies are developed as an alternative to the Kroll process. The electrochemical road is the best choice for many industries. The FCC Cambridge provides a product with almost 0.3 mass% oxygen, and it is a semi-continuous operation. However, this method exhibits many drawbacks: low current efficiency (20–40%), slow oxygen diffusion, difficult separation of metal/salt, and is costly for the TiO_2 pellet feed. On the other hand, the OS process can produce titanium directly from TiO_2 reduction in molten salt, but it still has some problem contamination because of the presence of carbon. Furthermore, many electrochemical procedures have been performed recently. They dictate a good enhancement in the cost and production issues, but they are difficult to scale up for the difficulty in facilitating a homogeneous reaction.

Table 7. Advantages and disadvantages of some patents in titanium production based on electrochemical technics.

Publication N°	Title	Advantages	Disadvantages	Reference
US 10, 081, 874 B2 (2018)	Method for electrowinning titanium from titanium-containing soluble anode molten salt	- This invention has the advantages of a short process flow, high carbothermal reduction efficiency, fewer intermediate products, direct availability of high-purity titanium, low purity requirements for anodic raw materials, low energy consumption, environmental friendliness, etc	- Use of toxic products. - High temperatures	[92]
US 7,790,014 B2 (2010)	Removal of substances from metal and semi-metal compounds	- CaCl ₂ is used as a salt (can dissolve and transport oxygen ion), cheaper and less toxic than MgCl ₂ - One-step process that does not use Mg as a reducing agent - Can also be used for the direct production of alloys, which could lead to savings in other ways	- Low yield. - Possibility of incomplete or partial reduction of TiO ₂	[93]
US 7,504,017 B2 (2009)	Method for electrowinning of titanium metal or alloy from titanium oxide containing compound in the liquid state	- Electrochemical deoxidation is a one-step process - Cheaper raw material. - Use of molten titanium oxide slag as cathode material, preferably as such, without prior treatment and without the introduction of additives - Operation of the electrolysis at a temperature above the liquidus temperature of the titanium oxide slurry and the melting point of the titanium metal, allowing the electrodeposited titanium droplets to be rapidly collected by gravity - Providing a molten material for use as a molten cathode material	- High reaction temperatures - High temperature furnace with consumable carbon anodes - Exhaust of CO ₂ gas	[84]
US 7,410,562 B2 (2011)	Thermal and electrochemical process for metal production	- Titanium can be electrolyzed from other titanium compounds that are not oxides - The use of a strong Lewis acid stabilizes and thus increases the activity of the titanium ion. - Extraction of a 99.9% pure titanium sponge - Possibility to produce titanium alloys - Permission to produce titanium with very low oxygen content	- High temperatures and pressures - Problem of oxidation. - Very energy consumable	[94]
EP 2 322 693 B1 (2004)	Electrochemical process for titanium production	- Use of cheaper and less toxic molten salts - Reduction of oxygen content (<400 ppm) - Use of cheaper and non-consumable graphite cathodes	- High temperatures - Difficulty controlling contamination.	[95]
US 2007/0029208A1 (2008)	Thermal and electrochemical process for metal production	- Extraction of the titanium sponge with a purity of 99.9% - Possibility to produce titanium alloys. - Production of titanium with very low oxygen content	- High temperatures and pressures - Oxidation problem - Very energy consumable	[96]

6. Conclusions

Titanium has remained an essential metal because of its wide use in different fields. Its demand in the industry has prompted unprecedented technical progress. Natural ilmenite is the most abundant titanium-bearing mineral in the earth's crust. The mineral ilmenite has been significantly grown since his discovery. Nowadays, it is the most crucial ore of titanium. The presented review shows the presence of enormous techniques for manufacturing titanium powder and titanium metal. Many of these processes are at various stages of development. The incentive for the development of new processes is often firmly rooted in the ambition to achieve a low-cost alternative to the Kroll process for the production of primary Ti metal. Marketed chloride-based thermochemical processes, such as the Kroll and Hunter processes, are batch operations and require high-quality natural rutile or improved synthetic slag, such as feeding and using cost-sensitive chlorination and thermochlorination steps. Many improvements have been made to thermochemical processes, but they offer few opportunities for cost reduction beyond current technology. Several development methods have generated considerable interest and scale-up efforts, including the Armstrong process and the FFC Cambridge process. The former is an example of using a continuous process for the reduction of $TiCl_4$ with Na or Mg while the latter is an example of the various electrochemical methods that convert TiO_2 into Ti metal in molten salt. A recently developed method, named the HAMR process, is based on destabilizing the Ti-O system by using hydrogen as a temporary alloying element during the magnesium thermal reduction of TiO_2 . However, compared with the Kroll, these producers are expanding their production to meet the unprecedented demand for titanium. Overall, it is expected that it will take several years before any new process will be in commercial production and compete with the Kroll process.

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