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Review

Research Progress of Titanium Sponge Production: A Review

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Abstract: Titanium has excellent all-round performance, but the high cost of its production limits its widespread use. Currently, the Kroll process used to commercially produce titanium sponge is inefficient, energy-intensive, and highly polluting to the environment. Over the past few decades, many new processes have been developed to replace the Kroll process in order to reduce the cost of producing titanium and make it a common metal with as many applications as iron. These new processes can be divided into two categories: thermal reduction and electrolysis. Based on their classification, this paper reviews the current development status of various processes and analyzes the advantages and disadvantages of each process. Finally, the development direction and challenges of titanium production process are put forward.

Keywords: titanium sponge; Kroll process; thermal reduction; electrolysis

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1. Introduction

Titanium (Ti) is the ninth most abundant element on Earth and the fourth most abundant structural metal after aluminum, iron and magnesium. Meanwhile, titanium and titanium alloys have been widely used in various industries because of their high specific strength, high and low temperature resistance, corrosion resistance and good biocompatibility [1]. Titanium is similar in strength to steel, being five times as strong as aluminum, but about half as dense, so it is also a necessary alloying element for many metals, including iron, aluminum and molybdenum [2]. The high specific strength and high adaptability to different working conditions of titanium and titanium alloy have led them to be widely used in the aerospace (aircraft, engines, spacecraft, etc.) and military fields (missiles, unmanned aerial vehicles, helicopters, etc.) [3–5]. Currently, 60–75% of titanium alloys are used in the aerospace industry. Nowadays, countries all over the world are paying more and more attention to the issue of reducing carbon emissions, among which the lightweighting of transportation is a key step to reduce carbon emissions. The automotive industry has embarked on a quest to achieve lightweighting of structural components through the use of titanium alloys, which can reduce carbon emissions while lowering fuel consumption due to their low density [6–8]. Titanium and titanium alloys are also used in marine engineering, including deep-sea submersible housings and propellers, due to their corrosion-resistant properties [9,10]. The non-magnetic and better biocompatibility of titanium and titanium alloys have made them increasingly interesting as human implants (bone repair, joint prostheses, etc.) in the biomedical field, as well [11–13]. Civilian technology using titanium and titanium alloys in Japan has been at the forefront of the world, and it is used in the manufacture of high-end sports goods (golf clubs, bike racks, etc.) and electronic products (mobile phone, cameras, etc.) [14,15]. According to the Global Titanium Metal Market Research Report 2020, the worldwide market for titanium was valued at USD 435.6 million in 2020 and will grow at a CAGR (Compound Annual Growth Rate) of

approximately 5.4% to USD 631.26 million by 2026 [16]. MRFR (Market Research Future) research indicates that titanium metal will accumulate at a CAGR of 5.36% from 2018 to 2023 to reach a volume of 204.7 KT [17]. From the above data, we can see that titanium has good application prospects and has the potential to become the fourth generation of metal materials after copper, iron and aluminum. However, the global production capacity of titanium sponge only increased from 293 KT in 2018 to 350 KT in 2021, which is not only a very slow growth rate but also a much lower total annual production than that of iron and aluminum [18]. Titanium is about 4–5 times more expensive than stainless steel when market fluctuations are taken into account. Even though the overall performance of titanium is better than that of steel and aluminum, the low production volume and high cost greatly limit its widespread use. This limitation comes, on the one hand, from the high material losses and high energy consumption in the manufacture of titanium products [19]. In the aerospace industry, the purchase-to-fly ratio of titanium is generally 12:1, for example; meanwhile, the purchase-to-fly ratio for the F-22 is 12.2:1, which is equivalent to about 80% of the titanium being wasted [20]. On the other hand, the high cost of titanium production is one of the main reasons why it is difficult to use it widely. Titanium has a strong affinity for elements such as O, C, N and S, which results in high energy consumption. In addition, all operations in the reduction process are required to be carried out in an inert atmosphere, all of which increase the cost of titanium production [21]. For example, the ductility of titanium varies considerably in the absence and presence of oxygen, with its high ductility being lost in the presence of oxygen [22]. With the current production process of titanium parts being the same as steel, including melting, pouring, rolling and manufacturing parts, it is believed that titanium will replace steel as the next generation of general-purpose metal if its production cost drops significantly, allowing it to have a larger production volume.

In 1791, a British mineralogist named R.W. Gregor discovered an unknown oxide, which he named "menaccanite", now known as "ilmenite". Four years later, M.H. Klaproth, a German chemist, isolated a new metal oxide from "rutile" and named the corresponding metal element "Titanium". For some time thereafter, attempts were made to isolate pure titanium without success, and most of the isolated titanium was titanium oxide, titanium tetrachloride and other titanium compounds. In 1825, J.J. Berzelius reduced K_2TiF_6 with potassium to obtain titanium containing large amounts of nitrous compounds. In 1887, L.F. Nilson and O. Petterson, under the protection of CO, first chlorinated TiO_2 with Cl_2 to synthesize $TiCl_4$, and then reduced $TiCl_4$ with Na to obtain pure titanium. In 1910, M.A. Hunter from America obtained 99% pure titanium by heating $TiCl_4$ and Na in a closed steel container, and this method known as the "Hunter process" [23]. In 1940, W.J. Kroll from Luxembourg produced titanium sponge by reducing $TiCl_4$ with Mg instead of Ca, and this method was first successfully used commercially as the "Kroll process" [24]. Although the Kroll process is currently widely used as an effective method for producing titanium sponge, it is also a highly energy intensive and very expensive method. From the discovery of the shortcomings of the Kroll process to the present, there have been continuous attempts to develop new processes to replace the Kroll process and thereby reduce the cost of titanium production. Unfortunately, no new process has been able to replace the Kroll process to date, although some have shown promise in pilot production. New processes aiming to replace existing mature processes to reach commercial application must solve the technical problems of the whole process, which poses certain challenges to the development of new processes. For example, the new process must ensure that O, C and N, or other impurities present very low levels in the final titanium obtained. Obviously, it is not easy to deal with the large number of challenges.

Although there have been some reviews on the development of titanium production processes [25–31], many recent advancements have been presented, so an updated and detailed review is necessary. In order to analyze whether the existing titanium production processes have the potential to replace the Kroll process, this paper divides them into two categories: thermal reduction and electrolysis, and provides a comprehensive and critical review of the characteristics and shortcomings of the various processes. In the thermal

reduction process, the raw materials are generally purified TiO_2 or $TiCl_4$. Figure 1 shows the Ellingham diagram of oxides and chlorides using HSC 6.0 software. By comparing Figure 1a,b, it can be seen that TiO_2 is more stable and harder to reduce than $TiCl_4$. Figure 1a shows that TiO_2 can be reduced by Mg, Ca, Y, Al, Ce, Li, La, etc. Meanwhile, it can be seen from Figure 1b that $TiCl_4$ can be reduced by Na, Mg, Ca, K, Li, Y, Al, etc. It should be noted that although Al is thermodynamically feasible as a reducing agent, Al is not used in practical applications due to the easy formation of Ti-Al intermetallic compounds [29]. During the electrolysis process, the titanium-containing material can be used as either the cathode or the anode and can be dissolved into the electrolyte. Finally, the development of titanium production processes is prospected, hoping that this paper will be helpful to scholars in related fields.

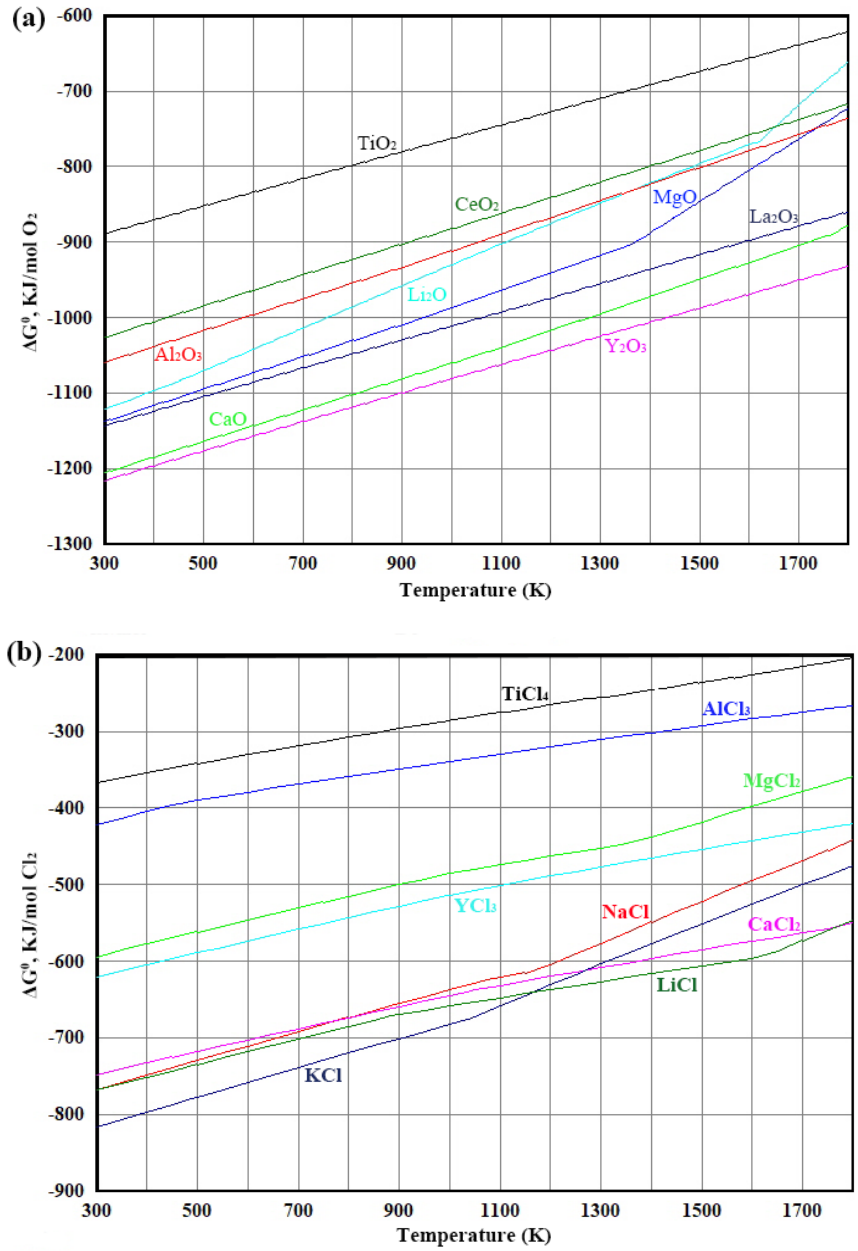


Figure 1. (**a**) Ellingham diagrams for the formation of oxides; (**b**) Ellingham diagrams for the formation of chlorides.

2. Thermal Reduction

All thermal reduction processes involve titanium-containing precursors and reductants. TiO_2 and $TiCl_4$ are the most commonly used precursors. According to Figure 1, it is clear from the thermodynamic feasibility that there are a variety of available reductants, but the most commonly used are Mg, Na and Ca. Mg and Na have a lower price compared to other reductants and the cost of the reductant is an important factor. Ca has a strong reducing ability for TiO_2 and can remove as much oxygen from the precursor as possible, which is also an important factor. In the following, the existing thermal reduction processes will be discussed and analyzed using precursors ($TiCl_4$ and TiO_2) as classification criteria.

2.1. Thermal Reduction of the Precursor $TiCl_4$

The advantage of using $TiCl_4$ as precursor is that the by-products and impurities produced during production can be easily removed by washing or distillation, resulting in higher-purity titanium. The first processes for the reduction of $TiCl_4$ to produce titanium metal are the Hunter process [23] and the Kroll process [24]. In order to overcome their drawbacks and reduce production costs, several improved processes have been developed.

2.1.1. Hunter Process

The Hunter process uses the reduction of $TiCl_4$ by molten metal Na to produce titanium [23], and the main reaction is as follows:

$$TiCl_4 + 4Na = 4NaCl + Ti \quad (1)$$

Figure 2 presents a flowchart of the Hunter process [32], and the whole reduction process is carried out at a temperature above 800 °C. Molten Na and $TiCl_4$ are placed together in the reactor, and after the reaction is completed and the reactor cooled to room temperature, the titanium metal and NaCl mixture is removed, crushed, leached and washed. Then, the titanium metal is dried in vacuum, while Na and Cl_2 are obtained by electrolysis of NaCl solution for reduction and carbon-chlorination. The Hunter process can be used not only to make titanium sponges, but also to produce titanium powder [33]. This is because during actual production, some titanium particles will bond together to form titanium sponge, and others that do not bond together will precipitate to form titanium powder. If the process parameters are adjusted so that most of the titanium particles precipitate independently, then the main product obtained is titanium powder, which is actually achievable. Due to the protective effect of NaCl, the titanium powder will not be exposed to air, avoiding the introduction of more impurities such as oxygen, carbon and iron, so the titanium powder produced by the Hunter process has a high purity, and its typical particle size is 60 mesh and 100 mesh. As raw material, it cannot only be used in the electronics industry, but also can use the HDH (Hydride–Dehydride) process to produce alloy powder with lower oxygen content for powder metallurgy [34]. Although the hunter process has been commercialized, its economics have been questioned. First of all, the reducing agent Na is relatively expensive, and it can be seen from Equation (1) that it takes 4 mol Na to produce 1 mol titanium, that is, it takes about 11 cm^3 NaCl to produce 1 cm^3 titanium. Together with other technical problems, this led to the Hunter process gradually losing its competitiveness and being replaced by the Kroll process. In the 1990s, the Hunter process was officially removed from commercial use with the closure of the Deeside plant in the UK.

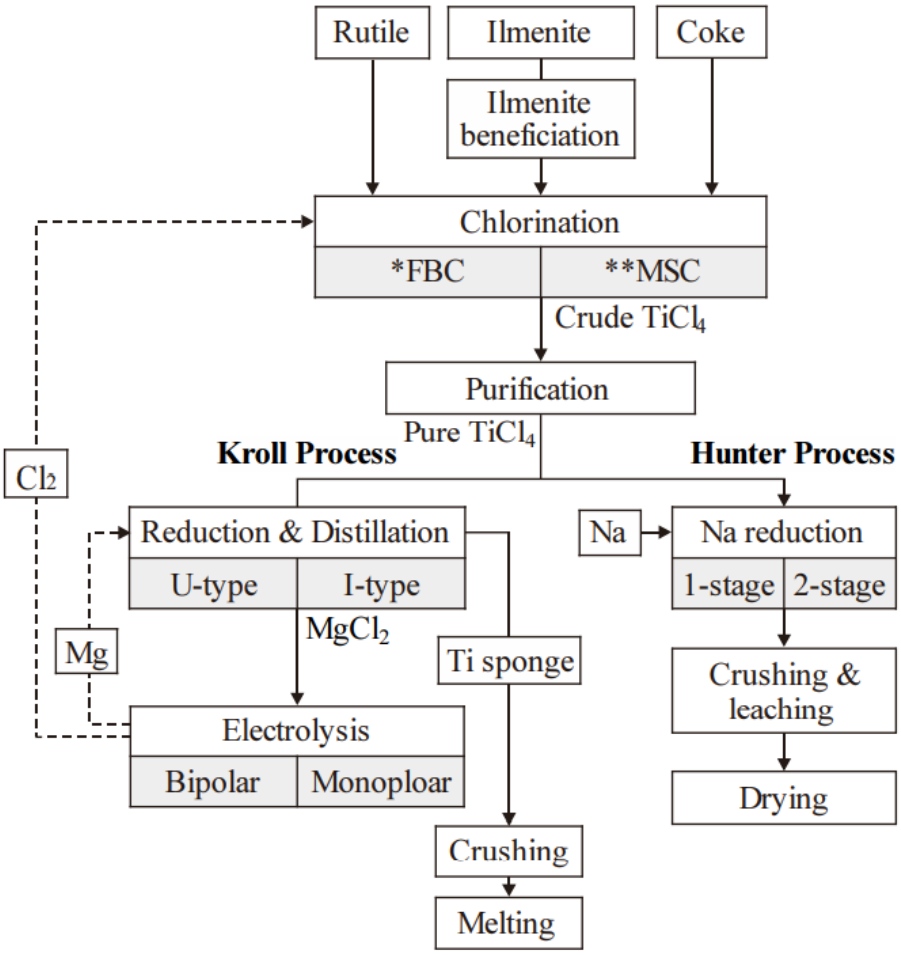


Figure 2. Flowchart of the Hunter process and the Kroll process [32] (Adapted from [32], with permission from The Korean Institute of Resources Recycling, 2020).

2.1.2. Kroll Process

The Kroll process is the main process for the production of commercial titanium at present. The core of the Kroll process is the reduction of $TiCl_4$ with molten metal Mg to obtain titanium sponge [24], and the main reaction is as follows:

$$TiCl_4 + 2Mg = 2MgCl_2 + Ti \quad (2)$$

Figure 2 presents a flowchart of the Kroll process [32]. In addition to the chlorination process shared by the Hunter and Kroll processes to produce $TiCl_4$, there are three sub-processes: reduction, crushing and melting, and electrolysis. $TiCl_4$ and molten Mg are reduced in a sealed vessel filled with argon gas at 800–900 °C, and the reaction products are titanium sponge. The titanium sponge is mechanically crushed into small pieces, and after passing the quality inspection, it is melted into titanium ingots. As the reaction proceeds, a large amount of by-product $MgCl_2$ and excess Mg are produced and must be vacuum distilled (0.1–1 Pa) at 1000 °C for several days to ensure their removal. This is because if they are not, the accumulated $MgCl_2$ will prevent the continuous reaction of $TiCl_4$ with molten Mg, but this step also increases the cost of the Kroll process [35]. It is estimated that the energy consumption of distillation could be close to 70% of the total energy consumption of the Kroll process [36]. At present, the largest reactor can produce 10 tons of titanium, but the distillation and cooling take a long time. According to statistics, a production cycle takes about 10 days. On average, one reactor can only produce 1 ton of

titanium per day [37]. The $MgCl_2$ obtained by distillation is re-electrolyzed to produce Mg and Cl_2, which can be used again in the reduction and chlorination respectively. Although the Kroll process has been optimized over the years, it Is still a complex and long process, and has some drawbacks, such as low production efficiency and high energy consumption.

2.1.3. Armstrong Process

The Armstrong process is an improvement on the Hunter process, and the core reactions of both are the same [38]. Because it can be produced continuously, it is expected to reduce the production cost of titanium, which has attracted a lot of attention. Figure 3a presents a flowchart of the Armstrong process [25]. In this process, the $TiCl_4$ in the reactor is gaseous, and the molten Na is continuously added to the reactor and a reduction reaction occurs. The product titanium and by-product NaCl are carried out of the reaction zone by flowing molten Na and collected. The residual Na is separated by filtration and distillation, then the NaCl is washed away, and the final pure titanium is obtained after drying. The Armstrong process can produce low-oxygen titanium micro-sponge with oxygen concentration of 0.12–0.21 wt%, also known as titanium powder, with unique coral-like morphology and low bulk density [39,40], as shown in Figure 3b. In addition, this process can also produce titanium alloy powders, such as Ti-64 powders [41,42], as shown in Figure 3c. It should be noted that the resulting titanium and titanium alloy powders are not directly used in powder metallurgy and need to be ground into finer particles [43]. The Armstrong process has gained considerable attention because of its potential to make the Hunter process continuous. Based on the results of its pilot production at commercial scale, it is statistically known that its energy consumption is about 50% lower than that of the Kroll process.

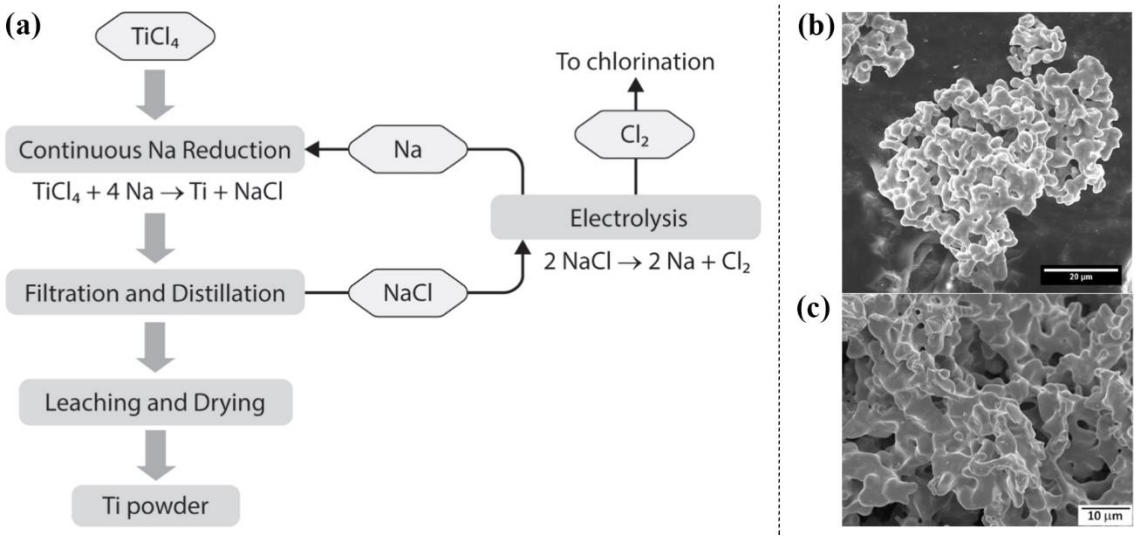


Figure 3. (**a**) Flowchart of the Armstrong process [25] (Adapted from [25], with permission from IOP Publishing, 2021); (**b**) SEM image of titanium powder produced by Armstrong process [39] (Adapted from [39], with permission from Springer, 2017); (**c**) SEM image of Ti-64 powder produced by Armstrong process [41] (Adapted from [41], with permission from Elsevier, 2011).

2.1.4. ARC (Albany Research Center) Process

In order to alleviate the problem of too fast reduction of $TiCl_4$, Albany Research Center (ARC) in the United States also developed a continuous production process based on Hunter process, known as the ARC process [44]. $TiCl_4$ is reduced in a two-step process using Na in molten salt bath, and $TiCl_4$ is first reduced to $TiCl_2$ and then to titanium metal. the main reaction is as follows:

$$TiCl_4 + 2Na = TiCl_2 + 2NaCl \quad (3)$$

$$TiCl_2 + 2Na = Ti + 2NaCl \quad (4)$$

In this process, melting NaCl will dilute the mixture of $TiCl_4$ and Na, thus slowing the rate of reduction reaction. The diluted reactants undergo a reduction reaction in continuous stirring tank, and the newly generated titanium will adhere to the existing small titanium particles. As the reaction progresses, when the titanium particles become too large to suspend, they fall to the bottom of the reaction tank and are removed. Although the feasibility of the ARC process has been demonstrated in the laboratory, this process has not gained commercial attention due to problems such as the difficulty of controlling the oxygen content in its products.

2.1.5. Vapor-Phase Reduction Process

In order to reduce the production cost of titanium, the Albany Research Center in the United States developed not only the ARC process by improving the Hunter process, but also the Vapor-phase reduction process by improving the Kroll process [45]. In fact, companies have been working on the gas reduction process since 1953, and it was not until 1989 that the Albany Research Center improved this process and the oxygen content in titanium nitride powders was greatly reduced to about 0.23 wt% [45,46]. Hansen et al. [45] obtained titanium by placing molten $TiCl_4$ under argon protection with magnesium wire in a shaft reactor at 1000 °C. The resulting mixture of Ti, $MgCl_2$ and Mg is removed from the argon stream by electrostatic precipitator and separated by vacuum distillation or leaching. However, due to the submicron titanium powder obtained, a large amount of surface oxidation will occur in the subsequent processing such as leaching, resulting in high oxygen content. In order to realize the original Vapor-phase reduction process, Goldsteins et al. [47] used the method of numerical simulation and experiment to optimize the parameters of niobium reactor electrical heating under vacuum, and obtained good results. In general, the control of oxygen content is the challenge presented by this process.

2.1.6. CSIR-Ti (Council for Scientific and Industrial Research) Process

South Africa is a major supplier of titanium ore in the world, but there is no titanium manufacturing industry. Most of the titanium metals they use are imported. Therefore, the Council for Scientific and Industrial Research (CSIR) in Pretoria, South Africa, is developing a low-cost titanium production process, named the CSIR-Ti process [48]. The process is a continuous two-step reduction process based on the Kroll process. $TiCl_4$ is first reduced to $TiCl_2$ by Mg, and then reduced to titanium powder. The main reactions are as follows:

$$TiCl_4 + Mg = TiCl_2 + MgCl_2 \quad (5)$$

$$TiCl_2 + Mg = Ti + MgCl_2 \quad (6)$$

The CSIR-Ti process can produce commercially pure (CP) 4 Grade titanium powder, and the SEM images of different morphologies of titanium produced by this process are shown in Figure 4 [49]. During the continuous production of the CSIR-Ti process, several reactions take place, and the morphology of titanium obtained will be affected by controlling the reactions course. By adjusting the process parameters, the required specific morphology of titanium can be preferentially generated. For example, the four morphologies shown in Figure 4 are what the developers have implemented in practice and named, i.e., Mixed, Plates, Powder and Crystal. In consideration of production cost, the acid leaching method was used instead of vacuum distillation to remove by-products from titanium powder. The problem of high oxygen content in titanium powder caused by acid leaching can be overcome by controlling PH value and temperature, so that the oxygen content after leaching is lower than 0.4 wt% specified for CP 4 Grade titanium [50]. Through pilot production, the developers believe that the CSIR-Ti process has demonstrated its ability to reduce the cost of titanium production, and believe that it can influence the titanium market when truly industrialized.

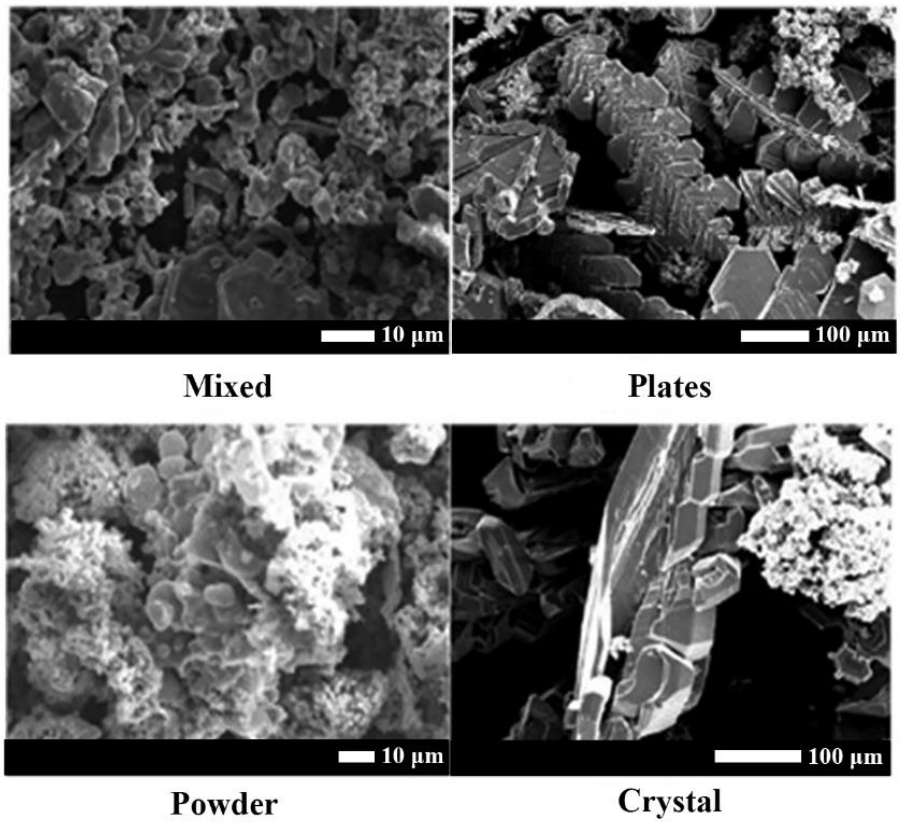


Figure 4. SEM images of different morphologies of titanium produced by CSIR-Ti process [49] (Adapted from [49], with permission from IOP Publishing, 2018).

2.1.7. TiRO Process

The Commonwealth Scientific and Industrial Research Organization (CSIRO) has developed a new process based on the Kroll process for the direct and continuous production of CP 2 Grade titanium powder, the TiRO process [51]. This process consists of two steps, and its flowchart is shown in Figure 5 [52,53]. The first stage is in a fluidized bed reactor, $TiCl_4$ reacts with Mg to form small titanium particles with an average diameter of about 1.5 μm, which are evenly distributed in the by-product solid $MgCl_2$ particles with an average diameter of about 350 μm. The fluidized bed reactor allows precise temperature control, ensuring $MgCl_2$ remains solid. The second step is continuous vacuum distillation, the small titanium particles are separated from the $MgCl_2$ particles, and then sintered into porous titanium balls with an average diameter of about 250 μm. Finally, after grinding, the volume of titanium powder is smaller. The grinding process can only be carried out for a short time; grinding for too long will cause titanium powder agglomeration, and it cannot be carried out in the air, because this will lead to an increase in oxygen content of titanium powder. Mg and Cl_2 produced by electrolysis of $MgCl_2$ can also be reused. This process can be used to produce titanium alloy powder if a variety of precursors are added to the fluidized bed reactor, and PM (Powder Metallurgy) can be combined to produce titanium alloy ingot [54]. The TiRO process has a much higher reaction rate than the Kroll process, and requires relatively simple equipment. A production plant with a capacity of 50 tons is known to have been established in Melbourne.

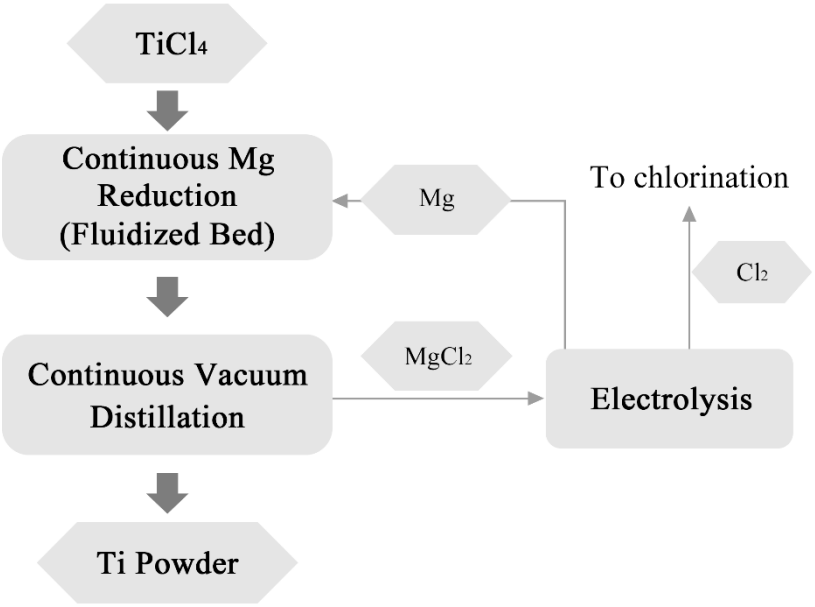


Figure 5. Flowchart of the TiRO process [52] (Adapted from [52], with permission from Elsevier, 2020).

2.1.8. Other Processes

In addition to the processes described above, there are others that have been reported but not named, which are briefly introduced below. Suzuki et al. [55] proposed conducting a magnesiothermic reduction of $TiCl_4$ in molten salt medium to generate $TiCl_2$ and regenerate titanium powder. However, normally, titanium powder is high in oxygen and nitrogen. Ardani et al. [56] proposed a process in which titanium hydride powder is first prepared and then titanium powder is obtained by deoxidation. The main reaction occurs between $TiCl_4$ and MgH_2, and TiH_2 is formed by reduction reaction under hydrogen. Thermodynamic evaluation was carried out by experiments, and the results show that this process is not only feasible in technology, but also in economy [57,58]. Kado et al. [59] proposed a continuous process of molten Bi-assisted magnesiothermic reduction of $TiCl_4$, which resulted in molten Ti-Bi alloy. After bismuth is removed, the titanium metal can be recovered.

2.2. Thermal Reduction of the Precursor TiO_2

In addition to the process of thermal reduction of $TiCl_4$ mentioned above, there is also a part of the process that utilizes thermal reduction of TiO_2 to produce titanium. Using TiO_2 as precursor not only shortens the process, eliminating the chlorination process, it also avoids the production of $TiCl_4$, making the whole process safe for human beings. The applicable reducing agents are mainly Ca and Mg, and the by-products CaO and MgO obtained from the reaction with TiO_2 can be removed by acid leaching and filtration, replacing the high energy-consuming vacuum distillation. Rare earth elements have also been studied, such as lanthanum [60], but of course there is no advantage to rare earth elements in terms of economic analysis.

2.2.1. PRP (Preform Reduction Process) Process

The preform reduction process (PRP) was developed by Okabe et al., University of Tokyo [61]. The schematic illustration of experimental apparatus of this process is shown in Figure 6a, and its core reaction is as follows:

$$TiO_2(s) + 2Ca(g) = Ti(s) + 2CaO(s) \quad (7)$$

First, TiO_2 is pre-formed with $CaCl_2$ or CaO as flux using binder. The pre-formed billet is sintered at 800 °C to remove the binder and placed on stainless steel plate. The reductant Ca is placed below the billet, and they are not in direct contact. At 800–1000 °C,

calcium vapor reacts with TiO_2, and titanium powder can be obtained after acid leaching. It is proved that this process can obtain titanium powder with 99.55% purity and irregular shape [62]. Figure 6b,c are SEM images of titanium powder obtained when experimenting with $CaCl_2$ and CaO as fluxes, respectively [61]. Wan et al. [63] improved the PRP process by mixing $CaCl_2$ with TiO_2 and pressing into flakes, which also reacted with calcium vapor, and the results showed that the addition of $CaCl_2$ improved the reaction between calcium vapor and TiO_2. This is because at high temperature, $CaCl_2$ will volatilize and release some gas, which will lead to the formation of some holes in the billet, thus promoting the reduction reaction [64]. Further studies revealed that the addition of the right amount of $CaCl_2$ would promote the reduction reaction, but too much $CaCl_2$ would slow down the reaction due to the occurrence of melting, while demonstrating that $CaTiO_3$ is an important intermediate product [65]. Jia et al. [66] demonstrated experimentally that $CaTiO_3$ is produced by the reaction of TiO_2 and the by-product CaO and is more easily reduced to Ti than TiO_2. The advantage of this process is that since the reductants are not in direct contact with the precursors, a higher-purity titanium powder can be obtained. It should be noted that the above results were obtained only under laboratory conditions, and no industrial trial production was carried out.

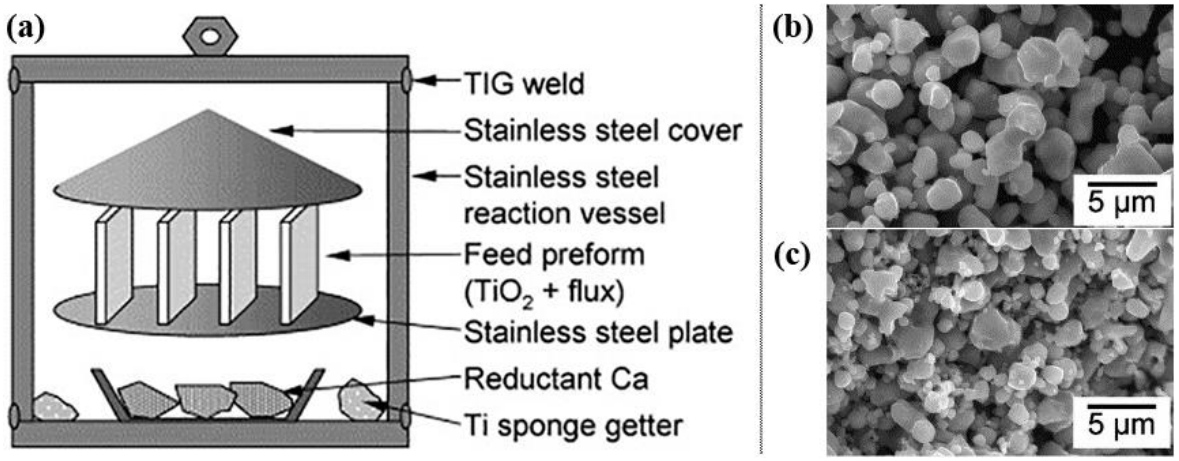


Figure 6. (**a**) Schematic illustration of experimental apparatus of the preform reduction process (PRP); (**b**) SEM image of titanium powder produced by PRP process with flux $CaCl_2$; (**c**) SEM image of titanium powder produced by PRP process with flux CaO [61] (Adapted from [61], with permission from Elsevier, 2004).

2.2.2. MHR (Metal Hydride Reduction) Process

The MHR process is a method of producing titanium powder using metal hydrides, such as CaH_2 and MgH_2, as reducing agents. The preparation of alloy and steel powders using CaH_2 by Borok et al. can be regarded as the pioneering work of this method [67]. Froes et al. [68] first used this method to produce titanium. At 1100 °C, TiO_2 is directly reduced by CaH_2 and titanium powder is prepared in one step. The core reaction is as follows:

$$TiO_2 + 2CaH_2 = Ti + 2CaO + 2H_2 \quad (8)$$

TiH_2 is unstable at high temperature, but stable at low temperature. If this reaction takes place at low temperature, TiH_2 will be formed, and dehydrogenation will be required to produce titanium powder. Similarly, Fang et al. [69] used MgH_2 to produce titanium from TiO_2-based titanium slag with about 62% lower energy consumption than the Kroll process. The schematic illustration of this process is shown in Figure 7 [69], which is divided into three steps: reduction, leaching and dehydrogenation. Since CaH_2 is expensive, MgH_2 should be used instead of CaH_2 as much as possible in the development of this process. Although industrial production based on this process is reported to have landed in Russia, there is no specific information publicly available.

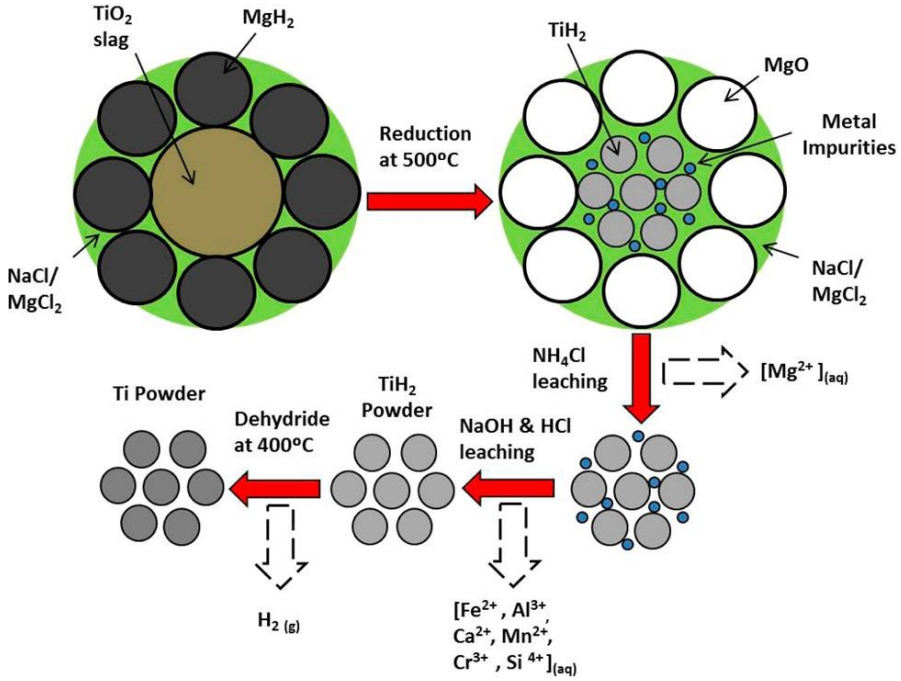


Figure 7. Schematic illustration of producing titanium from TiO_2-based titanium slag using MgH_2 [69] (Adapted from [69], with permission from ACS Publications, 2013).

2.2.3. EMR (Electronically Mediated Reaction) Process

Okabe et al. [70] found that metallothermic reduction is not a strict chemical reaction, and the overall rate of the reaction is limited by the electron transport between the reactants, which indicates that metallothermic reduction is an electronically mediated reaction (EMR), and they first applied this process to the preparation of titanium [71]. Park et al. [72] used the EMR process to directly reduce TiO_2 with reductant Ca to obtain titanium powder with a purity of 99.5%. Figure 8 shows the schematic illustration of experimental apparatus of EMR process and the SEM image of obtained titanium powder [72]. It can be seen that the advantages of this process are similar to the PRP process in that there is no direct physical contact between TiO_2 and the reductant during the reduction process, which can avoid the contamination of titanium powder by impurities to a certain extent.

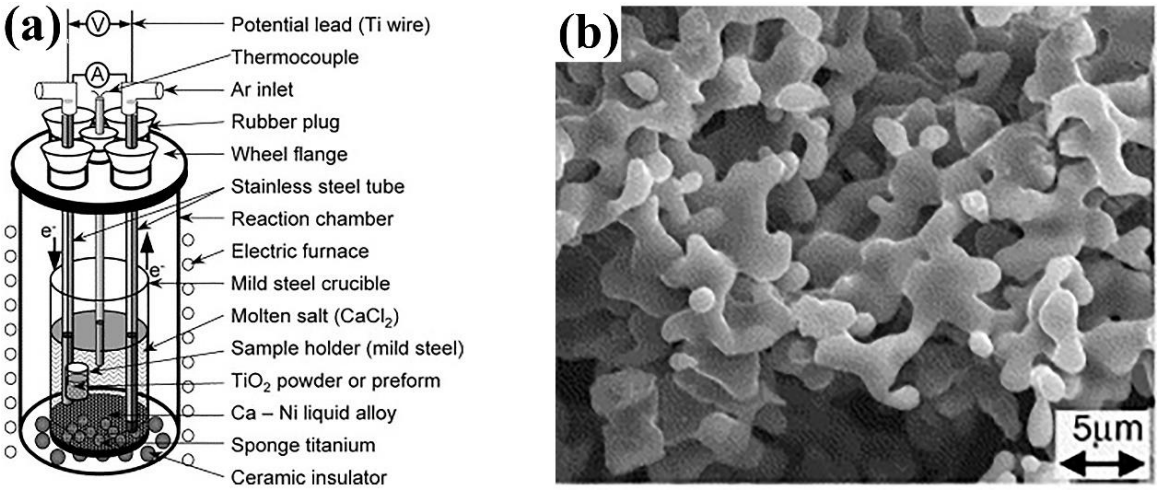


Figure 8. (**a**) Schematic illustration of experimental apparatus of the EMR process; (**b**) SEM image of titanium powder produced by the EMR process [72] (Adapted from [72], with permission from Elsevier, 2005).

2.2.4. HAMR (Hydrogen-Assisted Magnesiothermic Reduction) Process

Zhang et al. [73,74] proposed a process that can prepare high-purity titanium powder with oxygen content less than 0.15%, called the HAMR process. Purified TiO_2 obtained from upgraded titanium slag (UGS) is used as raw material to react with reductant Mg under hydrogen atmosphere to form porous TiH_2 particles. Then, the TiH_2 is heat-treated, which not only eliminates porosity but also dehydrogenates to obtain titanium particles, but the titanium particles at this time contain high oxygen content. The final deoxidation using Ca can yield titanium powder that conforms to ASTM standards (ASTM-B299-13). The morphology of final titanium powder obtained after deoxidation treatment is shown in Figure 9a, and Figure 9b is an enlarged view of Figure 9a [73]. It can be seen from Figure 9 that the microstructure of titanium powder presents irregular granularity. The use of hydrogen, not only helps to destabilize the Ti-O system, but also increases the thermodynamic driving force for the reaction of Mg with oxygen [75,76]. Li et al. [77] found that the relative density of precursor TiO_2 has great importance, which not only affects the oxygen content in titanium powder, but also the morphology of titanium powder, and the experimental results prove that porous TiO_2 should be selected as the precursor. The combination of magnesiothermic reduction and deoxidation is a key factor in the production of low oxygen content titanium powder by this process, and in addition the overall energy consumption of this process is reduced compared to the Kroll process due to the omission of vacuum distillation.

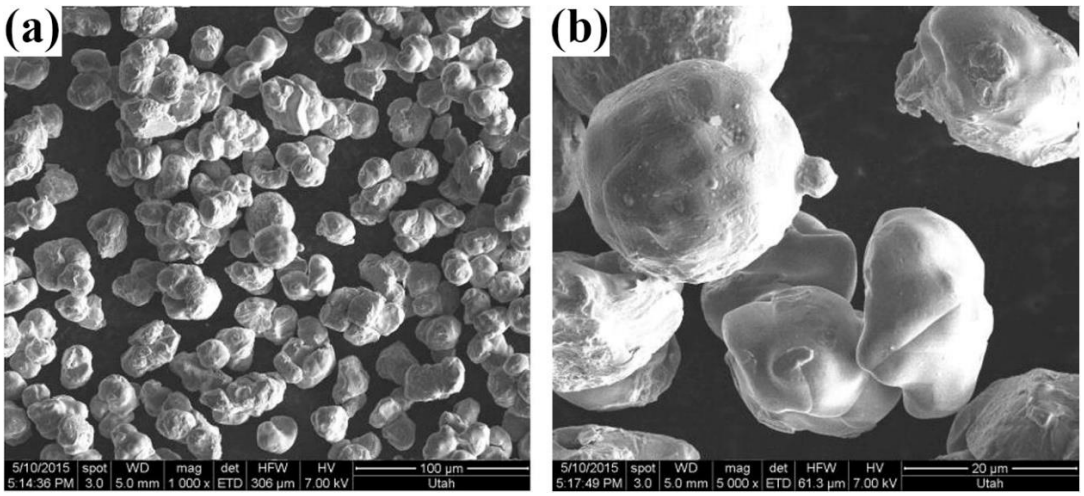


Figure 9. SEM images of titanium powder produced by HAMR process: (**a**) 1000×; (**b**) 5000× [73] (Adapted from [73], with permission from Elsevier, 2016).

2.2.5. SHS (Self-Propagating High-Temperature Synthesis) Process

Self-propagating high-temperature synthesis (SHS) [78,79], also known as combustion synthesis, is based on the principle of using external energy to induce local chemical reactions to form a front of chemical reactions. The chemical reactions will release heat by itself, so that the combustion will spread to the whole reaction system, and finally the required materials will be synthesized.

Fan et al. [80] applied the SHS process to the production of titanium powder in order to overcome the defect of incomplete deoxidation by direct metallothermic reduction TiO_2. The experimental results showed that the oxygen content of the obtained titanium powder is only 0.21 wt% and the purity is greater than 99.0%, reaching the level of commercial application. They also studied the effects of different factors on the chemical reactions of this process [81,82]. Compared with the loose raw material, compaction can increase the effective contact interface of the reactant, make the reaction more fully, and facilitate the acquisition of titanium powder with lower oxygen content. Moreover, the preparation pressure also affects the oxygen content of the final titanium powder. The SHS process can

also be used to directly prepare titanium alloys, such as Ti-Al-Si [83], Ti-Al-Mg [84] and Ti-Fe [85–88]. The SHS process can also be combined with electrolysis to produce titanium powder [89]. TiO_2 powder is first converted to $TiO_{x<1}$ powder by the SHS process, and then $TiO_{x<1}$ powder is converted to titanium powder by electrolysis in molten $CaCl_2$.

2.2.6. Other Processes

Reductants Ca and Mg are most commonly used to reduce TiO_2 to produce titanium powder and several other processes have also been reported [90–96]. The general process can be described as the reduction reaction between Ca or Mg and TiO_2 to obtain titanium powder with the assistance of molten salt. Xu et al. [97] used the first-principles method to calculate the interactions among elements in reduction process, and the results showed that Ca atoms would diffuse into the TiO_2 structure and combine with O to deoxidize TiO_2 and generate titanium. Bayat et al. [98] studied the influence of TiO_2 particle size on the reduction reaction, and the results showed that with the decrease in TiO_2 particle size, the reaction could still be carried out even if reaction temperature is reduced to a certain extent. In addition, the particle size of titanium powder also decreases with the decrease in TiO_2 particle size. Titanium powder can also be prepared by using double reductants at the same time, such as the double reductants Al-Mg [99] and Ca-Mg [100]. Many new processes have been reported, but they are mostly in the laboratory stage.

2.3. Thermal Reduction of Other Precursors

Besides $TiCl_4$ and TiO_2, Ti_2O_3 [101], $TiCl_2$ [102] and Na_2TiF_6 [103] are also used as precursors to produce titanium powder by metallothermic reduction. Yang et al. [101] showed that during the calciothermic reduction of Ti_2O_3, $CaCl_2$ will volatilize and transfer to the surface of Ti_2O_3, which is conducive to the formation of titanium particle with smooth surface. Song et al. [104] considered $TiCl_2$ to be a promising precursor for the production of titanium and titanium alloys and investigated the high-quality synthesis of $TiCl_2$. In order to develop a new process for continuous production of titanium powder by reducing $TiCl_2$, Takeda et al. [105] firstly synthesized $TiCl_2$ with $TiCl_4$ and titanium metal at 1000 °C by using molten salt as medium. Then, $TiCl_2$ and Mg are placed in reactor filled with argon for reduction reaction, and titanium powder with purity of 99.7% is obtained [102]. Zhao et al. [103,106] and Wang et al. [107] found that the two-stage aluminothermic reduction process with Na_2TiF_6 as the precursor could not only produce titanium powder, but also Ti-Al intermetallic compound powder and Ti-6Al-4V alloy powder.

In order to develop new processes that can be used commercially to overcome the disadvantages of high energy consumption and low productivity of the Kroll process, thermal reduction is being studied extensively.

3. Electrolysis

With reference to the development of aluminum industry, the use of electrolytic process to produce titanium is considered to be more economical and environmentally friendly than the thermal reduction process, and is the future development direction. At present, many electrolytic processes have been reported. In 1968, Oki et al. [108] used the electrolytic process to directly reduce TiO_2 in molten $CaCl_2$ to obtain titanium powder. Although the titanium powder is of lower purity, it was also considered to be groundbreaking work and laid the foundation for the production of titanium using the electrolytic process. In the existing electrolytic processes, titanium-containing materials can be used as cathode, anode or in the electrolyte. This paper will also take this as the classification standard a introduce various processes.

3.1. Electrolysis with Titanium-Containing Materials as the Cathode

The processes of producing titanium by electrolysis using titanium-containing material as cathode have a similar operation flow. Several typical processes will be selected for analysis and discussion below.

3.1.1. FFC (Fray–Farthing–Chen) Process

In 2000, Chen et al. [109] developed a new process to produce titanium by electrolyzing TiO_2, which is called the FFC process. The schematic illustration of this process is shown in Figure 10, with molten $CaCl_2$ as the electrolyte, graphite as the anode and pre-sintered block TiO_2 as the cathode. When external electric field is connected, oxygen is ionized from TiO_2 at the cathode, resulting in titanium metal. The ionized oxygen combines with graphite at the anode to form CO or CO_2 [110]. The conversion of all TiO_2 to titanium metal represents the completion of the reaction. The anode and cathode reactions are listed as follows:

$$Anode: 2O^{2-} + C = CO_2 + 4e^- \quad (9)$$

or $O^{2-} + C = CO + 2e^-$

$$Cathode: TiO_2 + 4e^- = Ti + 2O^{2-} \quad (10)$$

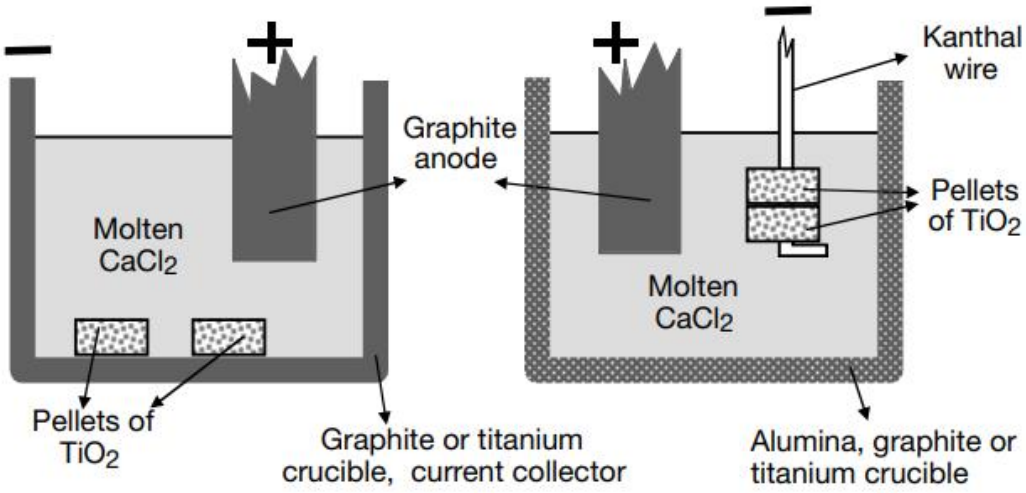


Figure 10. Schematic illustration of the FFC process [109] (Adapted from [109], with permission from Springer Nature, 2000).

Although TiO_2 is normally an insulator, it is conductive due to the formation of the Magnelli phase (TiO_{2-x}), which makes the reaction possible [111]. Schwandt et al. [112–114] studied the specific reaction mechanism, and the results showed that TiO_2 would react step by step with Ca^{2+} in the electrolyte to produce $CaTiO_3$ and a variety of titanium oxides, such as Ti_4O_7, Ti_3O_5, Ti_2O_3 and TiO, and finally deoxidize TiO to get titanium metal. According to reports [115,116], in addition to pre-formed block TiO_2, oxide powder or artificial rutile can also be used as precursors. Titanium alloys, such as Ti-Mo alloy [117], Ti-Nb alloy [118] and TiNi alloy [119] can also be produced by mixing the corresponding oxides with TiO_2 as precursors. The FFC process is a one-step process that saves costly steps such as reductant and vacuum distillation compared to the Kroll process, and in addition, there is no contamination, as no chlorine is produced throughout the process. Therefore, this process is considered to be commercially viable due to its short process, the potential for continuous production, the resulting titanium quality and lower oxygen and the environmental friendliness. However, its disadvantage is also very obvious, namely low current efficiency. The current efficiency depends on various factors, for example, the lower the oxygen content in the obtained titanium, the lower the current efficiency, which is obviously a very undesirable result. Although this process was proposed more than 20 years ago, there is no industrial production based on this process.

3.1.2. OS (Ono–Suzuki) Process

Based on the previous work [120], in 2002, Ono et al. [121] proposed an electrolytic process for preparing titanium, called the OS process. The schematic illustration of this

process is shown in Figure 11 [122]. Although molten $CaCl_2$ is also used as electrolyte and graphite as anode, the reaction mechanism is completely different from FFC process. In the electrolytic zone on the left, CaO in molten $CaCl_2$ will be electrolyzed to produce Ca, while in the reduction zone on the right, TiO_2 powder will undergo reduction reaction with Ca to produce titanium powder. The main reactions are as follows:

$$Anode: 2O^{2-} + C = CO_2 + 4e^- \quad (11)$$

or $O^{2-} + C = CO + 2e^-$

$$Cathode: CaO + 2e^- = Ca + O^{2-} \quad (12)$$

$$Reduction\ reaction: TiO_2 + 2Ca = Ti + 2CaO \quad (13)$$

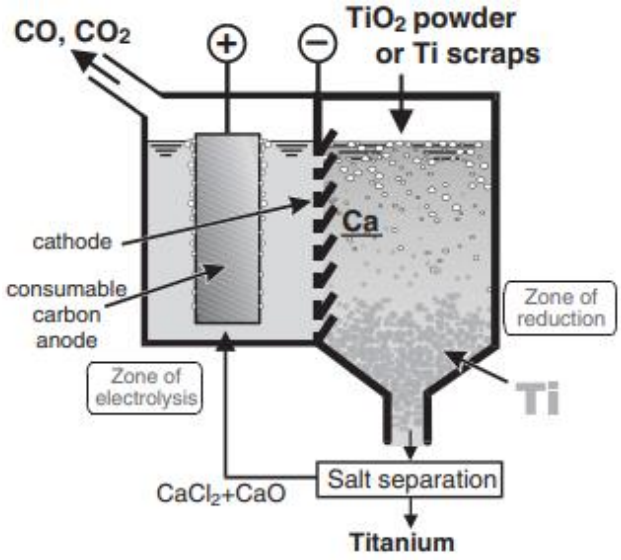


Figure 11. Schematic illustration of the OS process [122] (Adapted from [122], with permission from The Japan Institute of Metals and Materials, 2004).

The voltage difference that enables the decomposition of CaO and $CaCl_2$ makes this process feasible. It is clear that the applied voltage should be higher than the decomposition voltage of CaO and lower than $CaCl_2$. The CaO produced by reduction reaction can inhibit further reaction; however, the large amount of dissolution of CaO and Ca by $CaCl_2$ effectively overcomes this problem. The CO_2 and CO produced at the anode need to be discharged quickly and cleanly. If not, harmful reactions of Ca and CO_2 or CO may occur to form C and CaO. Obviously, the resulting C will contaminate titanium powder and $CaCl_2$.

Suzuki et al. [122,123] studied the influence of different positions of TiO_2 on the quality of titanium powder. The results showed that TiO_2 could generate titanium powder with 0.16% oxygen when placed near the cathode. However, when TiO_2 is far away from the cathode, there are low-priced oxides, such as Ti_2O_3 and TiO, in titanium powder. At the same time, they also tried to accelerate the reduction reaction by stirring, but they found that stirring would reduce the Ca concentration on the cathode surface, making the reduction of TiO_2 incomplete. Kobayashi et al. [124] studied the influence of current density and electrode distance on the experimental results, and found that a larger cathode current density could obtain titanium powder with lower oxygen and a larger electrode distance could minimize the occurrence of harmful reactions in which Ca reacts with CO_2 or CO to produce C. Suzuki et al. [125] used TiS_2 as precursor for experimental verification and found that the content of impurity S in titanium powder could be reduced to a very low level, but the oxygen content could not be guaranteed. Compared to the FFC process, the composition using $CaCl_2$ as the molten salt, the use of carbon as the anode and the applied voltage are similar, but the operating mechanism is different. The use of sintered

TiO_2 microspheres as cathodes in the FFC process requires oxygen diffusion in the titanium cathode. In contrast, TiO_2 does not need to be in contact with the cathode lead during the OS process and can be fed in powder form. In addition, the OS process shows that TiO_2 is reduced to titanium by Ca, which is a short-term reductive reduction oxidation process that does not require oxygen diffusion over long distances.

3.1.3. QIT (Quebec Iron and Titane) Process

The QIT process is a method of electrolytically producing titanium or titanium alloy from liquid titanium mixed oxide, such as molten titanium ore, molten titanium slag or molten TiO_2 [126]. In this process, molten TiO_2-containing materials are added to the reactor as cathode, the cathode is covered with a layer of molten salt or solid ionic conductor as electrolyte and carbon is used as expendable anode, and finally voltage is applied to deoxidize the cathode by electrolysis. The main reaction is as follows:

$$TiO_2 + C = Ti + CO_2 \quad (14)$$

During electrolysis, liquid titanium or titanium alloy are created at the lower interface of the electrolyte and sink to the reactor bottom as gravity pulls them down. At the same time, CO_2 is produced at the anode. Since this process was originally developed to extract titanium metal from titanium slag, the concentration of impurities such as Fe, Mn, Cr, and Si in the precursor will be high and pretreatment may be required to remove these impurities.

Several other processes have been reported based on similar principles to the QIT process. Zhao et al. [127] proposed a new process for preparing titanium in molten NaCl-$CaCl_2$ by carbon-chlorination and electrolysis. Using carbon-doped TiO_2 as the precursor at 1123 K and electrolyzing at 4.0 V for 5 h, titanium powder with a purity of 98.7% can be obtained in the cathode. Mohanty et al. [128] pretreated TiO_2 into low-priced titanium oxide and compacted it, and then electrolyzed it in molten $CaCl_2$ at 1273 K for 1–5 h. The results show that the longer the electrolysis time, the purer the titanium powder. Calcium is the main impurity and can be removed by pickling. In addition, by comparing the current-time graphs of electrolytically pre-treated TiO_2 and unpretreated TiO_2, it can be seen that the current consumption of electrolytically pre-treated TiO_2 is significantly lower than that unpretreated TiO_2.

3.2. Electrolysis with Titanium-Containing Materials as the Anode

In the electrolysis process, neither TiO_2 nor $TiCl_4$ can be used as anodes directly because their solubility in the electrolyte is almost zero, but they can be used as consumable anodes after carbonization because carbides conduct electricity. In 1955, Wainer et al. [129] first used TiC-TiO as consumable anode to produce titanium by electrolysis. Several typical electrolytic processes with titanium-containing materials as anode are analyzed and discussed below.

3.2.1. USTB (University of Science and Technology Beijing) Process

TiC is used as the anode, and pure titanium can be obtained at the cathode through electrolysis [130]. The disadvantage is that the carbon after electrolysis will remain in the electrolyte, causing pollution. Jiao et al. [131], of the University of Science and Technology Beijing (USTB), developed an electrolytic process called the USTB process that avoids carbon contamination. A schematic illustration of this process is shown in Figure 12 [132]. Carbon pollution is avoided because the anode material is modified to use TiC_xO_{1-x} solid solutions obtained by carbothermic reduction of TiO_2 in vacuum at 1500–1700 °C as the consumable anode [133]. In electrolysis, CO and CO_2 are formed at the anode instead of carbon, while pure titanium is formed at the cathode. The anode and cathode reactions are listed as follows:

$$Anode: TiC_xO_{1-x} - ne^- = Ti^{n+} + (3x-1)CO + (1-2x)CO_2 \quad (15)$$

$$Cathode: Ti^{n+} + ne^{-} = Ti \quad (16)$$

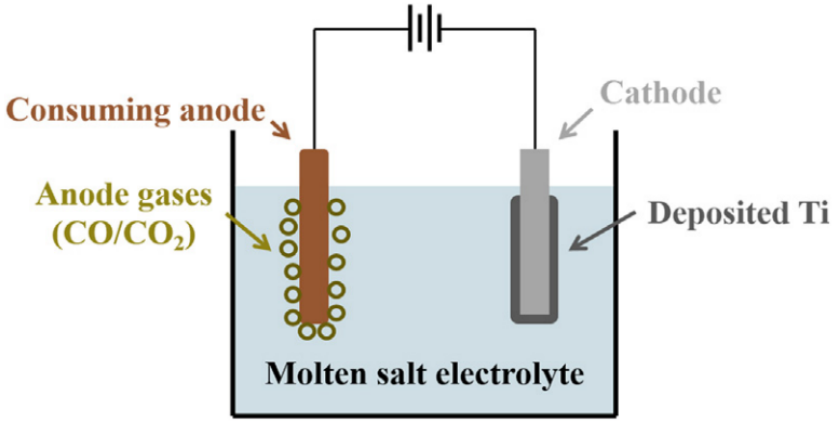


Figure 12. Schematic illustration of the USTB process [132] (Adapted from [132], with permission from Elsevier, 2020).

Further studies by Jiao et al. [134] showed that titanium powder with a grain size of more than 40 μm and an oxygen content of less than 0.3% could be obtained using this process. It is worth mentioning that not only TiC_xO_{1-x} can be used as anode material, but also TiN [135] and $TiC_{0.25}O_{0.25}N_{0.5}$ [136]. The low-cost anode material, stable dissolution of the anode during electrolysis and stable deposition of titanium on the cathode all indicate the feasibility of the USTB process. The developers argue that this process is energy-efficient, environmentally friendly, and cost-effective, with the potential to bring the cost of producing titanium close to that of aluminum.

3.2.2. MER (Materials and Electrochemical Research) Process and Chinuka Process

The MER process and the Chinuka process, developed by Withers et al. [137] and Fray et al. [138], are similar in principle to the USTB process except that the anode material is different.

The MER process uses Ti_xO_yC prepared by carbothermal reduction of titanium oxide and carbon as anode material [139]. Titanium oxide can be TiO, Ti_2O_3, Ti_3O_5, Ti_4O_7 or their mixture. During electrolysis, the anode releases Ti^{2+} or Ti^{3+}, which forms titanium at the cathode and CO_2 or CO at the anode. It has been reported that this process can produce titanium powder with oxygen content of 0.04–0.08 wt%.

The Chinuka process is designed to produce titanium metals from titanite with low TiO_2 content. Ti_2CO powder is prepared by mixing TiO_2 containing impurities with carbon in vacuum at 1500–1600 °C. After compaction and sintering, The Ti_2CO consumable anode obtained. Pure titanium can be produced at the cathode by electrolysis of Ti_2CO in molten NaCl-KCl. Although Ti_2CO contains impurities, such as Al, Ca, Fe, etc., they will enter the electrolyte during the electrolysis process and will not affect the formation of pure titanium. However, it is still necessary to monitor whether the impurities accumulate during the electrolysis process to ensure the purity of titanium powder. It has been reported that this process can produce titanium powder with impurities of 0.5 wt%.

3.3. Electrolysis with Titanium-Containing Materials in Electrolyte

Titanium-containing materials can not only be used as cathode and anode, but can also be dissolved in electrolyte instead of electrode, a typical example is solid oxide membrane (SOM) process.

SOM Process

Pal et al. [140,141] demonstrated that the SOM process can efficiently prepare pure metals directly from oxide ores, producing not only magnesium but also titanium. In SOM process, MgF_2-CaF_2-TiO_2 is added to the reactor as flux, inert metal or carbon as cathode,

and yttrium-stabilized zirconia (YSZ) film containing liquid metal or ionic flux is connected to the anode. During electrolysis, titanium ions are reduced to titanium at the cathode, while oxygen ions pass through the YSZ film to form water vapor or CO at the anode [142]. In addition, titanium alloys, such as Ti-Si alloy [143], Ti-Fe alloy [144,145], Ti-Al alloy [146] and Fe-Ti-Si alloy [147], can also be prepared directly using the SOM process. However, at present, this process is mainly used to produce magnesium metal, and more research is needed to produce titanium metal.

4. Comprehensive Analysis of Various Processes

The above processes are summarized in Table 1, including the precursors, core reactions, advantages and disadvantages. Although the Kroll process became the only process for titanium production after the Hunter process, its high cost has also limited the large-scale development of the titanium industry. It is well known that the high cost of producing titanium using the Kroll process is not only due to the precursors and reductants, but also the recycling of by-products accounts for a large portion of the energy consumption. According to the evaluation of Xia et al. [148], it takes 257.78 MJ of energy to produce 1 kg of titanium using the Kroll process. As the demand for titanium continues to grow in various fields, a variety of new processes are being developed to reduce the cost of producing titanium metal. New processes using $TiCl_4$ as precursor, for example, Armstrong process and ARC process are based on the improvement of Hunter process, and Vapor-phase reduction process, CSIR-Ti process and TiRO process are based on the improvement of Kroll process. They are all trying to reduce costs through continuous production, but they are not as effective as they could be because they are not free from the high energy consumption steps. The Armstrong process, which is the most promising, can reduce energy consumption by about 50% compared to the Kroll process. With the consideration of omitting energy-consuming steps such as chlorination and vacuum distillation, some new processes have been developed using TiO_2 as precursor, such as PRP process, MHR process, EMR process, HAMR process and SHS process. However, the HAMR process, for example, claim to reduce the total energy consumption compared to the Kroll process, but it also has a total energy consumption of 211.53 MJ to produce 1 kg of titanium, which is only about 18% lower than the Kroll process [148]. A large part of the reason for this may be attributed to the use of expensive Ca reductant. Although many improvements have been made to the thermal reduction process, the prospects for significant cost reductions in the production of titanium metals are uncertain. With reference to the development of the aluminum industry, the production of titanium using the electrolytic process seems to be the most promising, since electricity is considered to be the cheapest reductant. The development of FFC process, OS process, QIT process, USTB process, MER process and SOM process are all in progress. The production of 1 kg of titanium using the FFC process requires only 1.66 kg of TiO_2, while the Kroll process requires 4 kg of $TiCl_4$, and the total energy consumption of the FFC process has indeed been evaluated to be significantly reduced compared to the Kroll process [149]. If upgraded titanium minerals are used as precursors, it is expected that the energy consumption of the USTB process can be reduced to about 40% of that of the Kroll process [136]. Although the electrolytic preparation of titanium metals with homogeneous composition seems to be the most promising route, it presupposes that the technical problems identified, including the continuity of production, the stability of the electrolyte composition and the current efficiency, must be solved. In fact, with the exception of a few processes such as the HAMR process, there is very limited data in the open literature on the purity of the titanium metal produced by the various processes. The authors believe that the potential to replace the Kroll process can be judged only when it is produced commercially with these processes.

Table 1. Summary of titanium production processes.

Classification	Processes	Precursors	Core Reactions	Advantages	Disadvantages	Development Date	Refs.
Thermal reduction	Hunter process	$TiCl_4$	$TiCl_4 + 4Na = 4NaCl + Ti$	Titanium powder with low oxygen content and metallic impurities	Low productivity; expensive reductant; high energy consumption	1910	[23]
	Kroll process	$TiCl_4$	$TiCl_4 + 2Mg = 2MgCl_2 + Ti$	Titanium powder with low oxygen content and metallic impurities	Low productivity; high energy consumption	1940	[24]
	ARC process	$TiCl_4$	$TiCl_4 + 2Na = TiCl_2 + 2NaCl$ $TiCl_2 + 2Na = Ti + 2NaCl$	Continuous production; controllable reaction speed	Expensive reductant	1997	[44]
	Vapor-phase reduction process	$TiCl_4$	$TiCl_4 + 2Mg = 2MgCl_2 + Ti$	Continuous production	High temperature; titanium powder with high oxygen content or high magnesium and chlorine content	1998	[45]
	Armstrong process	$TiCl_4$	$TiCl_4 + 4Na = 4NaCl + Ti$	Continuous production; titanium powder with excellent compressibility and denseness	Expensive reductant; residual impurities	2003	[38]
	CSIR-Ti process	$TiCl_4$	$TiCl_4 + Mg = TiCl_2 + MgCl_2$ $TiCl_2 + Mg = Ti + MgCl_2$	Continuous production; CP 4 Grade titanium powder	Oxygen content is difficult to control	2011	[48]
	TiRO process	$TiCl_4$	$TiCl_4 + 2Mg = 2MgCl_2 + Ti$	Continuous production; CP 2 Grade titanium powder	Titanium powder with high oxygen content	2011	[51]
	EMR process	TiO_2	$TiO_2 + 4e^- = Ti + 2O^{2-}$ $2Ca = 2Ca^{2+} + 4e^-$	Continuous production; titanium powder with high purity	Complicated process; difficult separation of metal and salt	1997	[71]
	MHR process	TiO_2	$TiO_2 + 2CaH_2 = Ti + 2CaO + 2H_2$	Single-step reaction	High energy consumption and pollution	1998	[68]
	PRP process	TiO_2	$TiO_2(s) + 2Ca(g) = Ti(s) + 2CaO(s)$	High reduction efficiency; titanium powder with high purity	Expensive reductant	2004	[61]
	HAMR process	TiO_2	$TiO_2 + 2Mg + H_2 = TiH_2 + 2MgO$ $TiH_2 = H_2 + Ti$	Titanium powder with low oxygen content	High temperature; high energy consumption	2016	[73]
	SHS process	TiO_2	$TiO_2 + 2Mg(Ca) = Ti + 2MgO(CaO)$	Low demand for raw materials; high efficiency	Uncontrollable process	2019	[80]

Table 1. *Cont.*

Classification	Processes	Precursors	Core Reactions	Advantages	Disadvantages	Development Date	Refs.
Electrolysis	FFC process	TiO_2	$2O^{2-} + C = CO_2 + 4e^-$ $TiO_2 + 4e^- = Ti + 2O^{2-}$	Semi-continuous production; titanium powder with low oxygen content	Low current efficiency; slow oxygen diffusion; difficult separation of metal and salt	2000	[109]
	SOM process	TiO_2-containing flux	$H_2 + O^{2-} = H_2O + 2e^-$ $Ti^{2+} + 2e^- = Ti$	Oxygen or water vapor as the major by-product	Low production efficiency	2001	[142]
	OS process	TiO_2	$2O^{2-} + C = CO_2 + 4e^-$ $CaO + 2e^- = Ca + O^{2-}$ $TiO_2 + 2Ca = Ti + 2CaO$	Semi-continuous production; titanium powder with low oxygen content	Low current efficiency; titanium powder is easily contaminated	2002	[121]
	USTB process	TiC_xO_{1-x} $(0 < x < 1)$	$TiC_xO_{1-x} - ne^- =$ $Ti^{n+} + (3x-1)CO + (1-2x)CO_2$ $Ti^{n+} + ne^- = Ti$	Semi-continuous production; titanium powder with high purity	Low current efficiency	2006	[131]
	MER process	Ti_xO_yC	$2TiO + C = 2Ti^{2+} + 4e^- + CO_2$ $Ti^{2+} + 2e^- = Ti$	Semi-continuous production; titanium powder with high purity	Carbon contamination; low current efficiency	2008	[137]
	QIT process	TiO_2	$TiO_2 + C = Ti + CO_2$	Titanite can be used as raw materials	High impurities content	2009	[126]
	Chinuka process	Ti_2CO	$Ti_2CO = 2Ti^{n+} + 2ne^- + CO$ $Ti^{n+} + ne^- = Ti$	Titanite can be used as raw materials	High impurities content	2015	[138]

5. Concluding Remarks

The widespread use of titanium and titanium alloys in different fields is driving the advancement of low-cost production processes for titanium. Although many new processes for producing titanium have been successful in the laboratory or even in pilot-scale, none has so far been able to replace the Kroll process commercially. If a new process is to replace the Kroll process, it must first be able to produce titanium of equal or better quality than the Kroll process. The purity of the titanium produced by new process mentioned in this paper is limited to laboratory levels, and little information can be found on the quality of the titanium produced after its industrialization. In addition, the production costs of new process had to be much lower than the Kroll process while still producing titanium of acceptable quality on industrial scale. A new process can only be considered as an alternative to the Kroll process if both product quality and production costs are met, and obviously none of the processes mentioned in this paper can currently meet this requirement. The thermal reduction method is basically an improvement of the Kroll process, so it seems that electrolysis is the most promising method to replace the Kroll process, represented by the FCC process and the OS process. First of all, electrolysis is less polluting to the environment, so it is suggested that the next step should be to develop electrolysis vigorously to solve the problems of its low efficiency and continuous production. Keep exploring and innovating to find new processes to reduce the cost of titanium production, when the titanium industry will also enter a new generation.

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