IJMMM International Journal of
Minerals, Metallurgy and Materials
矿物冶金与材料学报（英文版）

Revolutionizing titanium production: A comprehensive review of thermochemical and molten salt electrolysis processes

Haohang Ji, Shenghui Guo, Lei Gao, Li Yang, Hengwei Yan, and Hongbo Zeng

Cite this article as:
Haohang Ji, Shenghui Guo, Lei Gao, Li Yang, Hengwei Yan, and Hongbo Zeng, Revolutionizing titanium production: A comprehensive review of thermochemical and molten salt electrolysis processes, *Int. J. Miner. Metall. Mater.*, 33(2026), No. 1, pp. 15-34. https://doi.org/10.1007/s12613-025-3210-y

View the article online at SpringerLink or IJMMM Webpage.

Articles you may be interested in

Yuhui Liu, Meng Tang, Shuang Zhang, Yuling Lin, Yingcai Wang, Youqun Wang, Ying Dai, Xiaohong Cao, Zhibin Zhang, and Yunhai Liu, U(VI) adsorption behavior onto polypyrrole coated 3R-MoS_2 nanosheets prepared with the molten salt electrolysis method, *Int. J. Miner. Metall. Mater.*, 29(2022), No. 3, pp. 479-489. https://doi.org/10.1007/s12613-020-2154-5

Ying Gao, Ce Zhang, Jiazhen Zhang, and Xin Lu, Microstructure evolution and strengthening mechanism of high-performance powder metallurgy TA15 titanium alloy by hot rolling, *Int. J. Miner. Metall. Mater.*, 31(2024), No. 6, pp. 1426-1436. https://doi.org/10.1007/s12613-023-2809-0

Langping Zhu, Yu Pan, Yanjun Liu, Zhiyu Sun, Xiangning Wang, Hai Nan, Muhammad-Arif Mughal, Dong Lu, and Xin Lu, Effects of microstructure characteristics on the tensile properties and fracture toughness of TA15 alloy fabricated by hot isostatic pressing, *Int. J. Miner. Metall. Mater.*, 30(2023), No. 4, pp. 697-706. https://doi.org/10.1007/s12613-021-2371-6

Shi-yuan Liu, Yu-lan Zhen, Xiao-bo He, Li-jun Wang, and Kuo-chih Chou, Recovery and separation of Fe and Mn from simulated chlorinated vanadium slag by molten salt electrolysis, *Int. J. Miner. Metall. Mater.*, 27(2020), No. 12, pp. 1678-1686. https://doi.org/10.1007/s12613-020-2140-y

Xuemeng Gan, Shaofu Li, Shunyuan Xiao, and Yafeng Yang, Integrated high-performance and accurate shaping technology of low-cost powder metallurgy titanium alloys: A comprehensive review, *Int. J. Miner. Metall. Mater.*, 31(2024), No. 3, pp. 413-426. https://doi.org/10.1007/s12613-023-2774-7

Xiao-li Xi, Ming Feng, Li-wen Zhang, and Zuo-ren Nie, Applications of molten salt and progress of molten salt electrolysis in secondary metal resource recovery, *Int. J. Miner. Metall. Mater.*, 27(2020), No. 12, pp. 1599-1617. https://doi.org/10.1007/s12613-020-2175-0

IJMMM WeChat

QQ author group

INTERNATIONAL JOURNAL OF
Minerals, Metallurgy and Materials

Volume 33, Number 1, January 2026
Page 15

Review https://doi.org/10.1007/s12613-025-3210-y

Revolutionizing titanium production: A comprehensive review of thermochemical and molten salt electrolysis processes

Haohang Ji[1], *Shenghui Guo*[1],✉, *Lei Gao*[1],✉, *Li Yang*[1], *Hengwei Yan*[1], *and Hongbo Zeng*[2],✉

1) Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming 650093, China
2) Department of Chemical and Materials Engineering, University of Alberta, Edmonton T6G 1H9, Canada

(Received: 28 April 2025; revised: 6 June 2025; accepted: 17 June 2025)

Abstract: Titanium exhibits outstanding properties, particularly, high specific strength and resistance to both high and low temperatures, earning it a reputation as the metal of the future. However, because of the highly reactive nature of titanium, metallic titanium production involves extensive procedures and high costs. Considering its advantages and limitations, the European Union has classified titanium metal as a critical raw material (CRM) of low category. The Kroll process is predominantly used to produce titanium; however, molten salt electrolysis (MSE) is currently being explored for producing metallic titanium at a low cost. Since 2000, electrolytic titanium production has undergone a wave of technological advancements. However, because of the intermediate and disproportionation reactions in the electrolytic titanium production process, the process efficiency and titanium purity according to industrial standards could not be achieved. Consequently, metallic titanium production has gradually diversified into employing technologies such as thermal reduction, MSE, and titanium alloy preparation. This study provides a comprehensive review of research advances in titanium metal preparation technologies over the past two decades, highlighting the challenges faced by the existing methods and proposing potential solutions. It offers useful insights into the development of low-cost titanium preparation technologies.

Keywords: titanium preparation; titanium alloy; thermal reduction; molten salt electrolysis

1. Introduction

Titanium is regarded as a fourth-generation metal after copper, iron, and aluminum and has remained at the forefront of materials science since its discovery by William Gregor in 1791 and subsequent naming by Martin Heinrich Klaproth after the Titans of Greek mythology [1]. Over the centuries, titanium has evolved from being a mere curiosity to a key material used in various high-end applications.

Titanium and its alloys exhibit a wide range of outstanding properties and have demonstrated their diverse applicability and irreplaceability in various engineering fields, including chemical processing, aerospace, biomedical engineering, and extraterrestrial construction. The Ti–6Al–4V alloy significantly exceed aerospace material specifications, demonstrating 14%–22% higher yield strength, 12%–19% greater tensile strength, and 40%–85% higher elongation compared with standard aerospace material specifications [2]. Owing to its outstanding performance, the Ti–6Al–4V alloys is used in aircraft structural components and jet engine parts. β-type titanium alloys hold transformative potential in biomedical engineering, combining nontoxicity with a low Young's modulus, closely resembling that of natural bone thereby reducing stress-shielding effects in orthopedic implants [3]. Moreover, the shape memory alloy, Ni–Ti, is widely used in precision surgical instruments to ensure stability and accuracy in complex surgeries. The unique adaptability of titanium and its alloys to extreme environments is also remarkable. The shape memory alloy, Ti–Al–Cr, is superelastic over the wide temperature range from –269 to +127°C; therefore, it can withstand the extreme temperature variations on the lunar surface while being a promising material for lunar rover tires [4]. As the average annual corrosion rate of Ti–5Ta alloys in boiling nitric acid is 0.1–0.2 mm/a, which is 10%–20% of the average corrosion rate of pure titanium, they find applications in nuclear fuel reprocessing where nitric acid is used [5]. Titanium and titanium alloys will be integral to the next-generation energy systems and deep-space exploration structures; thus, titanium is known as the metal of the future. To confirm the aforementioned potential of titanium, a thorough investigation of its sources and production processes has become imperative.

Titanium accounts for 0.6wt% of Earth's continental crust and is the ninth most abundant element [6]. Approximately 140 titanium-bearing minerals have been discovered. Among these, rutile (TiO_2) and ilmenite ($FeTiO_3$) are industrially utilized， as shown in Fig. 1 [7]. Rutile is the purest natural source of titanium dioxide, containing approximately

---

✉ Corresponding authors: Shenghui Guo Email: 20040051@kust.edu.cn; Lei Gao Email: glkust2013@hotmail.com; Hongbo Zeng Email: hongbo.zeng@ualberta.ca

93wt%–95wt% TiO_2 [8]. Primarily found in ancient metamorphic rocks and granites, rutile becomes concentrated in coastal sands through weathering and erosion, resulting in alluvial or placer deposits [9]. Natural rutile typically has a complete tetragonal columnar or acicular crystal form, and its aggregates are granular, dense, and massive. While rutile is commonly found in dark red, maroon, yellow, and orange colors, the iron-rich rutile is typically black. Rutile is readily extractable and can be directly used as a high-grade raw material in titanium metal preparation. However, Earth's rutile reserves are limited. In 2023, global rutile reserves were approximately 55 million tons. On the contrary, global ilmenite reserves amount to 690 million tons. Ilmenite is a principal titanium ore and a globally traded, common, titanium-bearing heavy mineral. $M(TiO_2)$ of ilmenite ore can vary from 40wt%–60wt% [9]. Ilmenite is mainly found in loose massive deposits; therefore, ilmenite mining is easy and inexpensive. However, minerals such as limonite, sphene, tremolite, magnesite, manganite, and titanomagnetite are often present alongside ilmenite, which makes ilmenite mining challenging and reduces ilmenite utilization efficiency. Although titanium resources are abundant on Earth, the continuous mining and utilization of high-grade titanium ores have led to their depletion. Owing to the gradual depletion of rutile resources, ilmenite is being increasingly used to meet the rising demand for titanium, despite its lower titanium content than rutile.

Titanium resources are also abundantly found in the space environment. The estimated titanium reserves in "Oceanus Procellarum" and "Mare Tranquillitatis" on the Moon are approximately 1.5×10^{11} t, greatly exceeding the total reserves of titanium on Earth [10]. In the absence of atmospheric protection and magnetic shielding, the lunar regolith undergoes severe space weathering, producing nanophase iron, amorphous layers, radiation tracks, surface cracks, micrometeorite craters, and sputtering features on soil particles [11]. The high concentrations of TiO_2 (5wt%–15wt%) in Apollo 11 mare basalt samples [12] suggest the potential for lunar resource exploitations, although substantial technological advancements will be required to make it a reality. Future space development will require vast amounts of titanium resources, increasing the demand for complex titanium ore metallurgical technologies [13].

The roots of titanium metallurgy can be traced back to 1910 when Hunter successfully produced titanium metal using Na as a thermal reducing agent. However, this process relies on an instantaneous exothermic reaction, which poses safety risks in its industrial applications. In 1940, Kroll developed a method for producing titanium metal by using magnesium to thermally reduce $TiCl_4$ and industrialized titanium production; this is currently the dominant titanium production process.

While rutile can be directly used in the Kroll process, low-grade ores must be first enriched before recovering titanium. For ilmenite, owing to its high density, paramagnetism, and electrical conductivity, traditional methods such as gravity

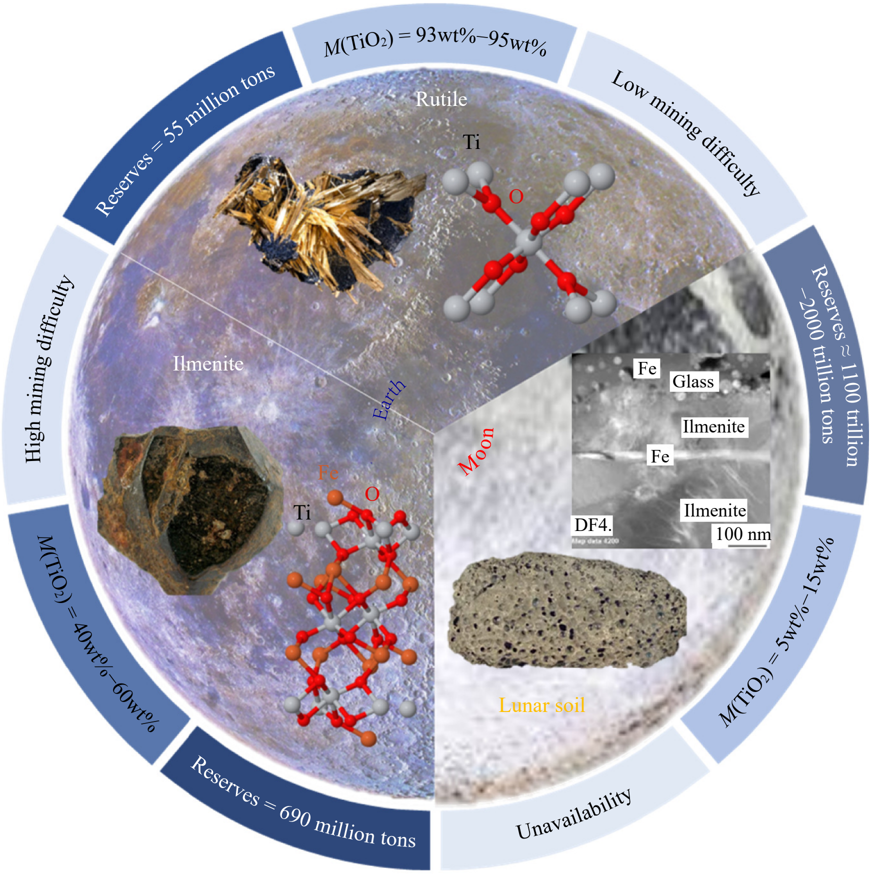

Fig. 1. Composition of the titanium sources: ilmenite, rutile, and lunar soil. ($M(TiO_2)$ denotes the TiO_2 content).

separation, high-intensity magnetic separation, and electrostatic separation are employed in its extraction [14]. Iron and titanium are then separated from this enriched titanium concentrate by smelting it in an electric arc furnace. The temperatures during arc melting reach up to 1600°C, and the energy consumption accounts for 20%–30% of the total cost of titanium metal production [15]. After completing arc melting, the high-titanium slag, with a high TiO_2 content (>80wt%), can be converted into titanium metal using the Kroll process; however, the material utilization rate of the process during high-precision material production is only 18% [16]. Thus, the titanium industry is currently characterized by complex processes, high processing challenges, and technological bottlenecks associated with raw material preparation, metal reduction, and high-level material production, leading to elevated titanium prices.

Titanium applications are rapidly expanding into cutting-edge technologies, involving energy storage, hydrogen storage, optoelectronics, and aerospace engineering. This growing demand for titanium coincides with the tightening global supply of titanium resources. Within the European Union (EU), titanium has emerged as a strategic enabler for green industrial transformation, particularly in renewable energy systems, electric vehicle technologies, and advanced manufacturing sectors. In 2020, recognizing the critical importance of titanium, the EU officially designated it as a critical raw material, following a comprehensive analysis of trade patterns of member states. This landmark decision of the EU underscores the dual role of titanium in driving sustainable industrial development and ensuring economic security while establishing mechanisms to guarantee stable supply chains for this vital material.

In this backdrop, process innovation in titanium production is particularly important. In 1959, Kroll predicted that between 1964 and 1969, molten salt electrolysis (MSE) would revolutionize titanium production by reducing costs and enabling industrial-scale applications [17]. MSE has encountered persistent technical hurdles, particularly in optimizing electrolytic efficiency. Despite the market demand that continues to drive production process innovations, previously reported MSE technologies are still limited to laboratory-scale operations. In recent years, emerging titanium production methods have mainly focused on simplifying process flow, improving cost efficiency, and achieving excellent product quality. Recent advancements in titanium production have focused on process simplification, cost reduction, and quality improvement, with comprehensive analysis of the potential of emerging technologies for overcoming the limitations of conventional methods [18–21]. In 2024, Matsanga *et al.* [18] synthesized information on all thermal reduction processes used in titanium production. Tebaldo *et al.* [19] summarized the titanium recovery methods mainly used for aerospace component production through multiple process recovery, outlining the current state of the art in the field of titanium recovery. Reddy presented an overview of the various preparation techniques for titanium and its alloys, along with the advantages and disadvantages of the techniques [20]. Khalloufi *et al.* [21] reviewed several effective processes for producing titanium from titanium–iron ores. This study quantitatively analyzes the research trends in the fields of thermal reduction, MSE, and titanium alloy production since 2000 and accurately identifies the main research focus areas and process trends in each year. The revolution in the titanium alloy synthesis process facilitated by the advancements in recycling titanium scrap are discussed in depth. In addition to an extensive literature review and mechanism analysis, the study provides a comprehensive overview of the historical evolution of titanium metallurgy and offers profound insights into and forward-looking guidance on the sustainable development of titanium production.

2. Thermal reduction of titanium

Traditional metal extraction processes typically use powerful reducing agents to replace metallic compounds. Titanium production via thermal reduction also involves metal extraction. The agents commonly used for the thermal reduction of titanium include metallic sodium, calcium, and magnesium, as well as the recently emerged aluminum and hydrogen. As shown in Fig. 2, the thermal reducing agent for titanium is marked with a yellow symbol, and the alloying elements that form with titanium are marked in blue.

2.1. Thermal reduction of titanium using sodium

The Hunter process was the earliest laboratory process that successfully produced metallic titanium (99.9%) using Na as the thermal reducing agent [22]. During the Hunter process, $TiCl_4$ and excess Na are heated in a vacuum reactor. When the reduction reaction temperature is reached, Na rapidly undergoes a displacement reaction with $TiCl_4$ to form Ti and NaCl [23]. The purity of titanium produced by the Hunter process depends on the purity of the $TiCl_4$ used; therefore, it is necessary to strictly control impurities, such as Fe and Si present in raw materials. Building upon the concept of the Hunter process, Hurd [24] proposed the addition of $TiCl_4$, VCl_4, $AlCl_3$, and excess sodium into the reactor to produce Ti–6Al–4V alloy in argon atmosphere. The Hunter process reduces the temperature required for direct Ti reduction and shortens alloy production [25].

The Armstrong process was developed by the International Titanium Powder (ITP) Company in the United States, known as the ITP process. Similar to the Hunter process, the ITP process uses metallic Na to reduce $TiCl_4$. The differences between the two processes lie in the unique modifications made to the reactor. During the Armstrong process, gaseous $TiCl_4$ and molten Na are continuously pumped into the reactor to participate in the reaction. The resulting titanium powder and NaCl are collected as they flow out from the reactor, enabling continuous titanium production. After purifying the titanium powder, the Armstrong process yields porous particulate metallic titanium, also known as minisponge Ti [26]. As with the Hunter process, the purity of the $TiCl_4$ raw material produced by the Armstrong process significantly affects the purity of the final titanium powder and can

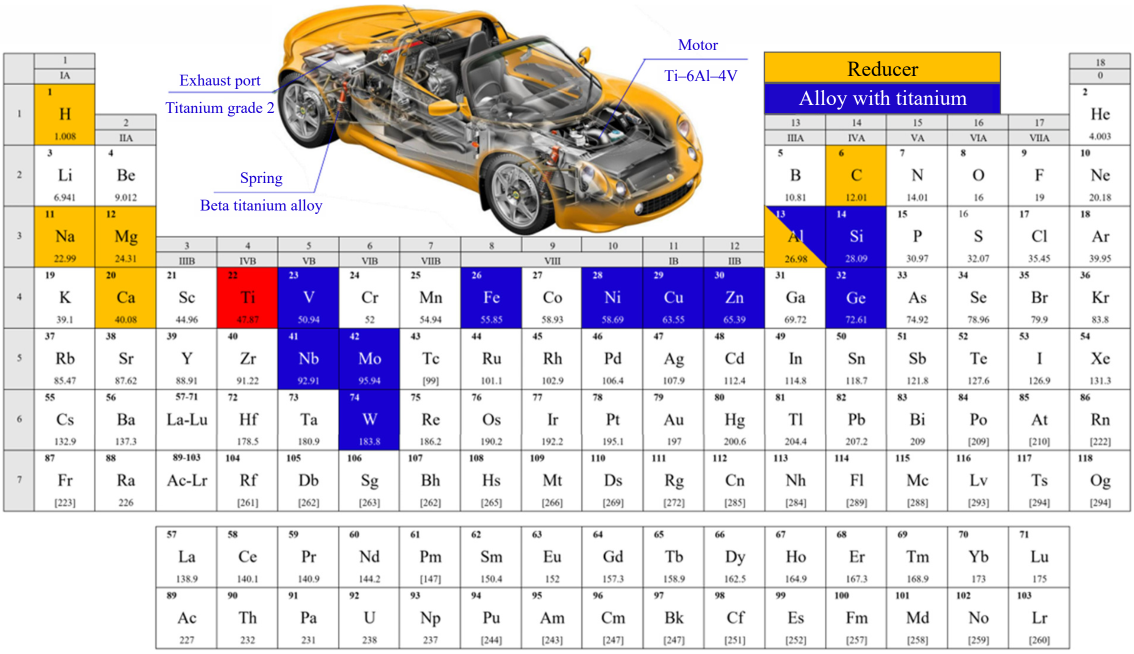

Fig. 2. Thermal reduction agents and alloying elements of titanium.

affect its subsequent sintering behavior [27–28]. Researchers have improved the Armstrong process by introducing other metal chlorides alongside $TiCl_4$ into the reaction to produce alloys such as Ti–6Al–4V [29]. The Armstrong process was commercialized in 2004. The ITP planned to produce 10 t titanium powder on a trial basis in 2005; it produced 10000 t titanium powder in 2008 for use as a substitute for titanium sponges used in the production of semi-finished titanium products, final rolled products, and near-net-formed titanium components.

Thus, the processing and analysis of titanium or titanium alloy powders produced using the Armstrong process has been the primary focus of previous research [30]. Studies have been conducted on hot mechanical processing of titanium and Ti–6Al–4V thin sheets and foils [31], consolidation of commercial pure titanium (CP-Ti) powder into compacts [32–33], net-shape component manufacturing using CP-Ti and Ti–6Al–4V alloy powder consolidation techniques [34], compaction parameters for Ti–6Al–4V powder [35], and cold-spray additive manufacturing of titanium powder parts [36–38]. The aim of the present study is to explore various processing techniques and applications of titanium or titanium- alloy powders obtained using the Armstrong process.

A process using Na as a reducing agent but distinct from the Hunter and Armstrong processes is also used to produce titanium metal. The Armstrong process involves a two-step reaction rather than a single-step reaction. It first uses Na to partially reduce $TiCl_4$ to $TiCl_2$, which thereafter is further reduced to titanium powder or fine particles [39]. The Armstrong process allows for the gradual reduction of sodium and titanium compounds to obtain the desired titanium powder or fine particles.

2.2. Thermal reduction of titanium using calcium

The high reactivity of Na causes its thermal reduction reaction to occur instantaneously, releasing a large amount of heat that will require reactors that can withstand high pressure and resist explosions. To address this issue, researchers have chosen Ca, which has a slightly lower reactivity than Na, as a substitute for Na and serve as a thermal reducing agent for metallic titanium. In 1937, Kroll attempted to reduce $TiCl_4$ using Ca. Metallic titanium was obtained via a displacement reaction by heating a mixture of $TiCl_4$ and excess calcium in Ar atmosphere [40]. Although large-scale industrial production of titanium was not made using this process, Kroll identified the critical conditions required for the thermal reduction of titanium metal using Ca. Moreover, the addition of inert gases, such as Ar, reduces the reaction rate of titanium chloride during the reduction process, preventing excessively vigorous reactions or explosions, setting the direction for subsequent research on titanium production.

The Russian Tula Chemical Metallurgical Plant used metal-hydride reduction (MHR) for producing titanium powder using TiO_2 as the raw material and calcium hydride as the thermal reducing agent. Calcium hydride decomposes into calcium and hydrogen gas between 1100 and 1200°C. Calcium reacts with TiO_2 via a displacement reaction [41]. Because no intermediate products or chlorides were involved, the resulting product was chlorine-free and the oxygen content was below 0.1%. Vacuum sintering and annealing reduced the hydrogen content of the product to 0.001%. Compared with the Kroll process, the MHR process significantly shortens the processing time and further reduces the production cost of metallic titanium through mechanical alloying and low-temperature heat treatment. The MHR process can also produce alloys, such as Ti–6Al–4V, by incorporating Al and V into TiO_2.

Okabe from the University of Tokyo developed the preformed reductive process (PRP)—a type of calcium thermal reduction process [42]. The PRP involves three main steps:

preforming TiO_2, calcium vapor reduction, and acid leaching for impurity removal. TiO_2 is mixed with flux agents, such as CaO, $CaCl_2$, and binders, and then sintered and formed between 1073 and 1273 K. Finally, TiO_2 in the sintered block is replaced with metallic titanium using calcium vapor. The resulting metallic titanium is further processed through acid leaching, followed by vacuum drying, to obtain fine titanium powder with controlled purity and uniform particle size [43]. In another process, which is similar to the PRP, $CaTiO_3$ is first prepared and then converted into Ti through calcium thermal reduction. $CaTiO_3$ is utilized in this process because it reduces to Ti more easily than TiO_2, under calcium vapor [44].

A common issue faced in calcium thermal reduction of TiO_2 is the difficult-to-remove layer of CaO formed on titanium particle surfaces during the reduction of TiO_2 by metallic calcium. The CaO layer inhibits the continuous reduction reaction. When melting the titanium powder during the PRP, CaO can enter the titanium ingot, causing excessive levels of calcium and oxygen and affecting the properties of the produced titanium material. Therefore, researchers have shifted their focus toward identifying alternative thermal reducing agents that offer advantages over calcium.

2.3. Thermal reduction of titanium using magnesium

Compared with calcium, molten magnesium has a density closer to that of molten $TiCl_4$, preventing stratification due to density differences, thereby ensuring an efficient reaction between magnesium and $TiCl_4$ during the reduction process. Calcium tends to form stable compounds with titanium, which makes the separation of titanium products from calcium challenging. However, magnesium forms unstable compounds and alloys with titanium, facilitating easier separation in the subsequent stages. Magnesium, though less reactive than calcium, possesses a sufficient affinity for chlorine (exceeding titanium) to reduce $TiCl_4$ to titanium. Furthermore, the reaction rate of magnesium is slightly slower than that of calcium, preventing excessive temperature increases caused by rapid reactions.

Based on the reasons mentioned above, Kroll process uses magnesium as the reducing agent instead of calcium. It involves the following three main steps: (1) titanium ore enrichment, chlorination, and refinement to obtain pure $TiCl_4$ [45]; (2) metallic magnesium injection into a distillation vessel filled with inert gas where it reacts with $TiCl_4$ within the range of 800–900°C to produce titanium and $MgCl_2$; (3) vacuum distillation to remove Mg and $MgCl_2$, followed by post-processing of the resulting product to obtain the final sponge titanium.

After years of refinement and modification, the Kroll reduction process has evolved into three industrial processes: magnesium reduction–vacuum distillation, magnesium reduction–leaching, and magnesium reduction–helium loop distillation. The key differences among the three industrial processes lies in the method of separating magnesium and titanium in the final reduction process. The first process is predominantly used in China and Japan, whereas the second and third processes are used in the United States. The distillation process in sponge metal production accounts for 70% of the total energy consumed and is one of the main contributors to increased production costs [30].

In 2011, Kasparov proposed a novel titanium powder purification process by introducing a hydrogen reduction step into the Kroll process. This innovative process combines magnesium thermal reduction of titanium chloride with full vacuum separation of titanium within a single production cycle, while incorporating hydrogen gas during production steps, such as reduction, phase separation, and cooling. The Kroll process effectively reduces the cost of titanium production. The average magnesium content of the produced hydrogenated porous titanium compound was within the range of 0.015wt%–0.020wt%, and the corresponding average chlorine content ranged from 0.070wt%–0.086wt%. High-purity hydrogenated titanium can be used as a product or dehydrogenated to obtain high-purity titanium via hydride dehydrogenation. In 2016, Zhang *et al*. [46–48] utilized the Kroll process to reduce the titanium content in upgraded titanium slag. Through an analysis of the reaction mechanism and kinetics of the Kroll process, high-purity titanium powder was successfully produced, meeting the specifications required for generic sponge titanium.

The $TiRO^{TM}$ process, which is based on the magnesium thermal reduction mechanism, is another process used for producing low-cost titanium metal powder [49]. It involves two main steps: reduction of $TiCl_4$ using magnesium powder in a fluidized bed reactor, followed by vacuum distillation to remove the byproducts—$MgCl_2$ and Mg. Pilot plant testing of the $TiRO^{TM}$ process is currently underway and is expected to have significantly lower capital and operating costs than those of the traditional Kroll process, while offering advantages such as continuous production, low temperatures, and low costs. However, the Ti produced by the $TiRO^{TM}$ process has higher oxygen and chlorine contents than that produced by the Kroll process [50].

The first two methods employed liquid magnesium and solid magnesium powder, respectively, as reducing agents to produce titanium. The results revealed that the entropy of the Mg directly influences the particle size of the product, suggesting an inverse relationship between the entropy of the reductant and the final particle size. The atmospheric distillation and magnesium reduction (ADMA) process uses gaseous Mg to reduce $TiCl_4$, resulting in titanium products with submicron particle sizes [51]. However, the ADMA process requires high temperatures between 1700–1900°C, leading to high energy consumption and necessitating the use of robust reaction equipment.

2.4. Use of hydrogen and aluminum as reducing agents

Stanford Research Institute International uses hydrogen gas as a thermal reducing agent to produce micron- and millimeter-sized titanium metal/alloy particles from $TiCl_4$ in a high-temperature fluidized bed reactor [52–53]. The reactor is typically designed with two reaction zones. In the first reaction zone (between 800 and 1200°C), the $TiCl_4$ vapor disproportionates into $TiCl_x$ (x = 2 and 3) using a mixed fluidized bed containing sponge titanium or titanium chips. The $TiCl_x$ (x = 2 and 3) species thereafter moves to the second reaction zone (between 1230 and 1250°C) in the presence of an inert gas, where hydrogen reduction occurs, resulting in hydrogen-containing Ti metal. Subsequent vacuum dehydrogenation yields high-purity titanium metal. Idaho technologies, similar to SRI International, utilizes the direct hydrogenation of $TiCl_4$ in a single step, producing TiH_2 that can be sold as a hydrogen storage material or further processed into metallic titanium through vacuum dehydrogenation [54].

As early as 1938, researcher mentioned that oxygen, nitrogen, and hydrogen exhibit significant solubility in titanium [55] and that reducing titanium using hydrogen is challenging. Thermodynamic calculations show that the Gibbs free energy change for the reduction of TiO_2 to Ti by hydrogen is greater than zero. Thus, the reaction cannot be performed under common conditions. At 2000°C and 13–15 MPa, hydrogen reduction of TiO_2 stops at the TiO phase, preventing the direct formation of titanium. The high oxygen potential of TiO_2 indicates that its direct reduction to its elemental form using hydrogen is challenging, as shown in Fig. 3 [56]. However, hydrogen can reduce metal impurities, such as Fe and V, present in most titanium-bearing ores. To reduce costs and expand ore sources, titanium present in low-cost titanium-bearing ores is converted into TiO_2 through hydrogen reduction [57], which is particularly useful for ilmenite [58–59], titanomagnetite [60], vanadium–titanomagnetite [61–62], and high-vanadium titanomagnetite (HVTM) ores [63]. Following hydrogen reduction and impurity separation, the ores can be used as high-quality raw materials in titanium production processes, including the Kroll process.

Aluminum is a new-generation thermal reducing agent. However, the reduction residue containing unreacted Al and Al_2O_3 obtained from the thermite reduction of titanium dioxide has a density close to that of titanium metal, making the separation of titanium metal from the byproducts challenging. Therefore, thermite reduction is commonly used to produce Ti–Al alloys or ceramics, including TiB_2–Al_2O_3 [64], TiAlC [65], $TiAl_x$ (x = 3, 0.5) [66–68], Ti–Si–Al [69], Ti–Al [70–71], Ti–Al–Fe [72], $(Ti,V)_2AlC$ [73–74], and Ti–Al–V [75–76]. To facilitate the separation of the products, the amount of the aluminum reducing agent added can be reduced to produce low-oxygen titanium (Ti_xO, where x = 1, 2, 3, and 6) with significantly different concentrations of aluminum oxide [77–78]. Alternatively, other elements with varying concentrations can be added to titanium to form alloys. These added elements can differ from the elements present in titanium reduction residues. For example, Ti_3SiC_2 [79] and Ti–Fe [80–81] can be produced this way. Thermite reduction has become the primary method of producing Ti–Fe alloys.

3. Molten salt electrolysis

Kroll predicted that MSE would eventually replace the thermal reduction processes used in the production of metallic titanium. However, the use of MSE for titanium production has become challenging because titanium undergoes multivalent state transitions during electrolysis, making the reduction mechanism complex. MSE cell includes external power supply, cathode, anode, and molten salt electrolyte. MSE involves molten electrolyte and oxidation or reduction reactions at the electrodes to reduce the high-valence titanium ions in the molten salt or electrode material to metallic titanium.

While thermal reduction still dominates titanium production, MSE is gaining research interest because of its advantages, such as low cost, low energy consumption, and high titanium purity. In the mid-19th century, aluminum was considered "noble metal", commanding prices higher than silver and gold. This status of aluminum has dramatically changed with the development of MSE for aluminum production. The electrolytic methods, with their short processing times, low costs, and high efficiency, have almost completely displaced the thermal-reduction techniques. This technological shift has caused the prices of aluminum to plummet, transforming it from a precious metal to an affordable industrial commodity. The successful transition of the aluminum industry through increased aluminum production and significant cost reduction through MSE, is driving research on the application of MSE to titanium production. The earliest MSE processes used in the preparation of titanium metal were based on the MSE of aluminum. These processes utilized titanium-containing salts, such as potassium fluorinate (K_2TiF_6) and low-valence titanium chloride, as titanium sources. Metallic titanium was thereafter electrodeposited from the electrolyte [82–84]. The inert atmosphere was provided during electrolysis to prevent the oxidation of the electrolyte and deposited titanium metal. However, the MSE process is characterized by lengthy procedures and unwelcome impurities [85–86].

MSE primarily uses electrolysis. It also encompasses electron-mediated reduction, which combines MSE with thermal reduction, as well as processes such as FFC Cambridge, solid oxide membrane (SOM), Quebec iron and titanium (QIT), Materials and Electrochemical Research (MER), University of Science and Technology Beijing (USTB), OS processes, and Electron Mediated Reduction (EMR). A schematic of the processes involved in MSE is shown in Fig. 4.

3.1. Titanium-containing materials as cathode materials

In 2000, a publication in *Nature* sparked a research boom on the use of MSE for titanium production [87]. Fray and Mohandas [88–89] at the University of Cambridge proposed a new process for titanium metal production via the electrolytic deoxygenation of bulk TiO_2 in a chloride molten salt system, using TiO_2 as the solid cathode and a carbonaceous material as the anode, under constant pressure. In this process, electrolysis is conducted at an approximate temperature of 850°C [90–91], with the voltage maintained within the range of 2.8–3.2 V [92–93]. The TiO_2 cathode, which receives electrons, is reduced to metallic titanium, while oxygen ions diffuse into the solution and migrate to the anode, oxidizing to form O_2, CO, or CO_2 gases on the carbon electrode, as illustrated in Fig. 4(a) [94–96]. In its early stages, owing to experimental limitations, the FFC Cambridge process was primarily used to deoxygenate surface oxide layers on commercially pure titanium or Ti–6Al–4V alloy [97–98]. However, in recent years, low-purity rutile has been used in electrolysis as the direct cathode [99].

However, the conversion of Ti from the +4 to 0 valence states involves a series of intermediate reactions [100]. Nie *et al.* [101] observed two distinct pairs of redox peaks in the cyclic voltammetry (CV) curves of TiO_2 electrodes in molten calcium chloride during potentiodynamic scanning from −0.45 to −1.78 V, proved that the reduction of TiO_2 in molten salts occurred in a stepwise manner. TiO_2 was first reduced to Ti_3O_5 or Ti_2O_3 and then reduced to Ti_3O, Ti_2O, TiO, or metallic Ti. X-ray diffraction (XRD) analysis of the TiO_2 particles performed subsequent to the CV tests revealed that the primary phase of TiO_2 has been transformed into stable $CaTiO_3$ and that small amounts of Ti_3O_5 were also present. The $CaTiO_3$ phase hindered the oxidation of low-valence Ti [101]. TiO_2 undergoes a series of intermediate reactions during its reduction and forms intermediate compounds, such as Ti_4O_7, Ti_3O_5, Ti_2O_3, TiO, $CaTiO_3$, and $CaTi_2O_4$ [102].

The XRD analysis of the products obtained after 1, 5, and 7 h of electrolysis showed that continuous Ca^{2+} absorption at the cathode led to the gradual blocking of its transport pores, hindering oxygen ion movement, thereby slowing down the reduction reaction rate [103–105]. Thus, a mixture of TiO_2 and CaO or $CaCO_3$ powder can be pressed into particles, heated to 1300°C to form porous $CaTiO_3$ microspheres, which are then electrochemically reduced in molten $CaCl_2$ to produce metallic titanium [106–107]. $CaTiO_3$ exhibits twice the rate of electrode oxygenation of TiO_2 and higher current efficiency and energy efficiency than TiO_2 [108]. Ongoing studies on the FFC Cambridge process primarily focus on cathode replacement, anode selection, and molten salt modification.

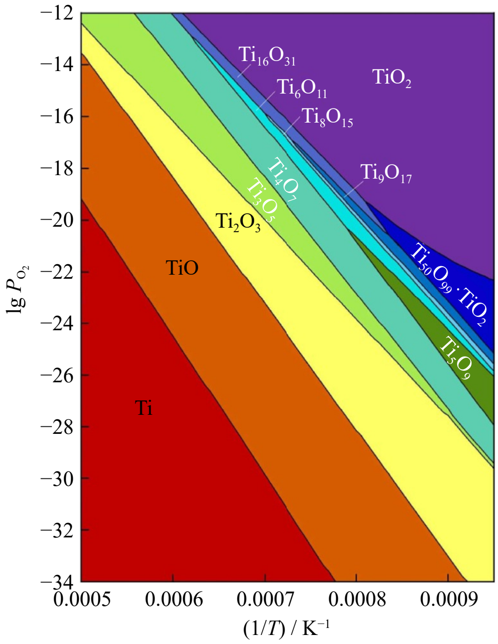

Fig. 3. Oxygen potential diagram of titanium, calculated using FactSage 5.2.

To improve the cathodic titanium source, TiO_2 is first partially reduced to conductive titanium suboxides; this overcomes the poor electronic conductivity of TiO_2 and renders the material a suitable cathode. Subsequent electrolysis of the reduced oxide in molten $CaCl_2$ yields titanium powder [109–110]. Another approach to improve the electrolytic performance of cathodes is to use titanium sulfide as a cathode material in place of TiO_2 [111–112]. The principle involves the high-temperature (1000°C) reduction of TiO_2 using carbon and sulfur to produce titanium sulfide (typically Ti_5S_8). Unlike TiO_2, titanium sulfide exhibits good conductivity, enabling rapid electrochemical reduction [113]. Using titanium sulfide for titanium production allows for improved control of the oxygen content in the produced metallic titanium. This is crucial because oxygen, with a solubility limit of 10wt% in α-titanium, will be readily dissolved in α-titanium, forming solid-state oxygen and leading to a high oxygen content in the final product. On the other hand, sulfur has a solubility limit of only 0.02wt% in α-titanium, which has a hexagonal close-packed structure, effectively mitigating the negative effects of high oxygen content [114–115]. The USTB process can be applied to sulfide-based metal ores. Minerals such as MoS_2 [116], CuS [117], and WS_2 [118] can be desulfurized into their respective metals through electrochemical desulfurization in molten salt.

The graphite anode used in the FFC Cambridge process could contaminate the product, and the formation of CO_3^{2-} ions and their subsequent reduction could significantly reduce the efficiency of process. Researchers have begun to explore potential inert metals to replace graphite as anode materials. Tian *et al.* [119] proposed the inert anode material $Ni_{0.36}Al_{0.10}Cu_{0.30}Fe_{0.24}$. Alzamani *et al.* [120–121] selected $Ni_{10}Cu_{11}Fe_6Al$ as the anode. Hu *et al.* [122] investigated the use of $TiO_2\cdot RuO_2$ as an inert anode. The SOM process, an alternative method for reducing carbon pollution, involves the use of liquid metal anodes encapsulated within SOMs [123]. The SOM is designed to separate liquid metal from the electrolyte, while allowing O^{2-} ions to pass through. Thus, contamination of the graphite anodes is effectively prevented, as shown in Fig. 4(b). SOM produces titanium metal and various alloys, such as Ti–Fe, Ti–Al, and Ti–Nb [124–125]. SOMs are expensive and have a short lifespan, limiting their industrial applications [126].

Initially, $CaCl_2$ was selected as the molten salt system owing to $CaCl_2$ attributes, such as chemical stability, low cost, high oxygen solubility, and excellent conductivity [127]. Subsequent studies involved the use of chloride electrolytes, such as LiCl [128], $MgCl_2$ [129–130], $MgCl_2$–$HoCl_3$ [131], LiCl–KCl [132–133], and KCl–LiCl–$MgCl_2$ [134], as well as fluorides in place of chlorides. Calculations have shown that the disproportionation reactions of Ti^{4+} with Ti^{2+}, Ti^{3+}, and Ti lead to an increase in the energy consumption of the titanium

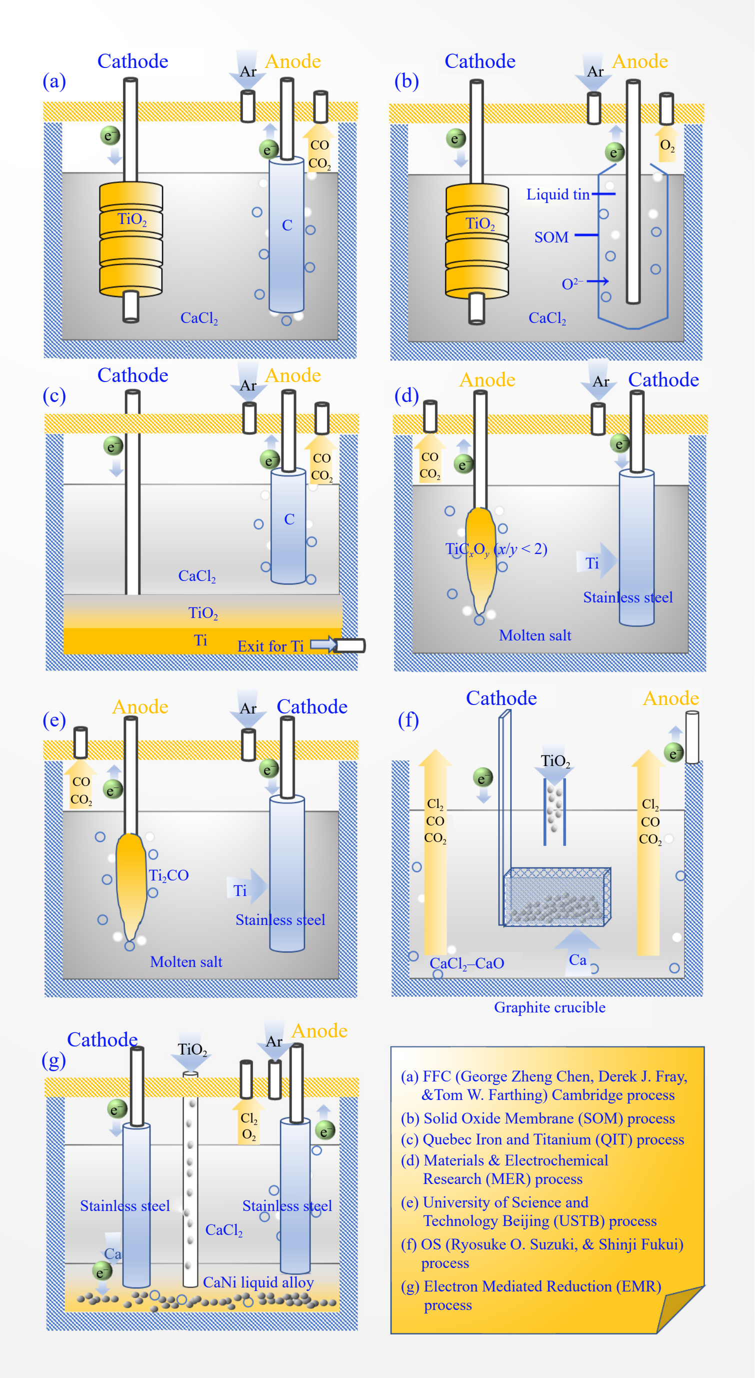

Fig. 4. Main processes involved in molten salt electrolysis for producing titanium metal: (a) FFC Cambridge process; (b) SOM process; (c) QIT process; (d) MER process; (e) USTB process; (f) OS process; (g) EMR process.

reduction process, as shown in Fig. 5 [135–136]. High-valence titanium ions in molten halide salts exist as complex ions and the complexation between titanium and fluoride ions is stronger than that between titanium and chloride ions [137–139]. Therefore, in fluoride molten salts, the chemical and electrochemical reduction reactions of titanium occur without the participation of divalent titanium ions, which can increase the electrolysis efficiency [140–143]. The FFC Cambridge process exhibits broad applicability in producing metals, such as Zr [144], Cr [145], Tb [146], Mo [116], and Nb [103] and research on titanium production has gradually shifted toward the preparation of various titanium alloys or titanium-based composite materials, including Ti–Si [147–148], Ti–W [149], TiC/SiC [150], Ti–Mo [151], Ti_3AlC_2 [152], Ti–Nb alloy [153], and Ti–Fe [154–155].

In 2003, QIT, a titanium slag production company in Canada, invented a novel titanium metal smelting process that involved melting titanium slag and its electrolytic reduction into liquid titanium metal [156]. The QIT process was performed at temperatures higher than the melting point of titanium, resulting in liquid titanium metal. The QIT process begins by placing a molten salt electrolyte, such as CaF_2, in an electrolytic reactor and adding molten titanium slag. Density differences drive the titanium slag to accumulate in

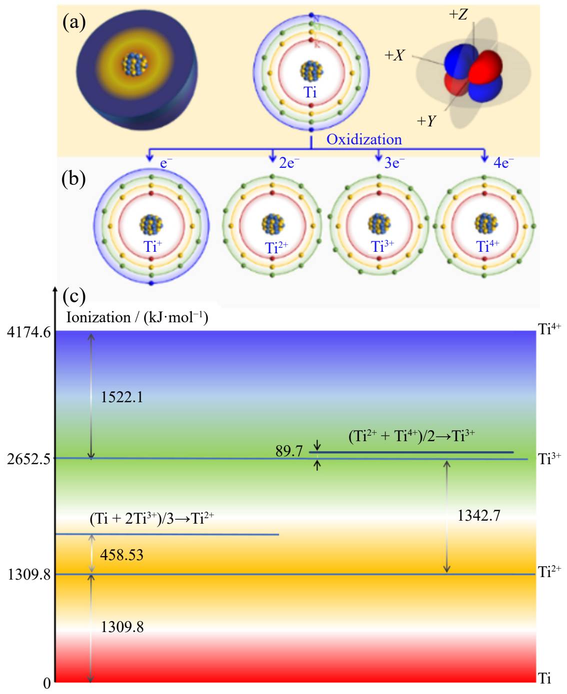

Fig. 5. (a) Schematic of the atomic cross-sectional interface, Bohr model, and three-dimensional electron cloud model of metallic titanium; (b) Bohr models of Ti^+, Ti^{2+}, Ti^{3+}, and Ti^{4+} ions; (c) potential diagrams of each titanium valence state.

the lower region of the molten salt electrolyte during electrolysis, as shown in Fig. 4(c). The electrolysis can be completed in one or two steps. In the one-step process, pure titanium slag with added metal oxides, such as Al_2O_3 and V_2O_5, is used to produce alloys, such as Ti–6Al–4V. The two-step process is suitable for titanium slag with impurities, such as Fe, Cr, Mn, and V. In the first stage, the electrolytic reduction of impurities possessing a higher reduction potential compared with titanium is favored. The metallic products are separated from the electrolyte and titanium slag owing to density differences. Impurities are deposited at the interface between the electrolyte and slag, settled at the bottom of the reaction chamber, and subsequently discharged via the bottom outlet. In the subsequent stage, the purified slag is electrolytically reduced to liquid titanium metal at elevated temperatures. The QIT process can remove impurities and has lower raw material requirements than the FFC Cambridge Process, eliminating the need for refining processes and significantly reducing raw material costs. However, the products obtained through the QIT process are in a molten state and are typically associated with molten titanium oxide inclusions, leading to a high oxygen content in the produced titanium metal. Furthermore, the reduction reaction of the QIT process occurs at the temperatures of 1700–1900°C, leading to a high energy consumption and strong corrosive effects on the equipment.

3.2. Titanium oxide/carbon–oxygen solid as the soluble anode

In 2004, MER introduced the concept of using carbon thermal reduction to produce soluble anodes from TiO_2. During the electrolysis of TiO_x ($0 < x < 2$), the oxygen in the oxide generates CO and CO_2 at the anode, while the simultaneously generated Ti ions enter the molten salt as divalent or trivalent ions and transported to the cathode where they are reduced to metallic Ti [157–158]. Ti–6Al–4V alloys can also be produced by adding Al to the anode [159]. However, the electrolysis efficiency of the MER process can be improved by addressing the back-diffusion of low-valence titanium from the cathode to the anode where they are reoxidized to a high-valence state.

In 2005, Jiao and Zhu [160] introduced the USTB process for titanium production using TiC_xO_y as the soluble anode, as shown in Fig. 4(d). TiC and TiO in TiC_xO_y have acceptable conductivities, compensating for the low electrolysis rate caused by the nonconductive TiO_2 cathode used in the FFC Cambridge process [161]. The most common soluble anode material is Ti_2CO in which the ratio of oxygen atoms to titanium atoms is 1:1 [162]. During electrolysis, C and O combine to form CO, which is released as a gas. At the same time, titanium ions enter the molten salt as divalent ions and migrate to the cathode to generate Ti by gaining electrons [163–164]. Since then, the research team at the USTB has continued to develop high-performance soluble anode materials, including TiN [165], $TiC_xO_yN_z$ [166], and Ti–C–S [167] and further expanded the application range of the USTB process. Weng *et al.* [168] proposed the use of oxygen-containing sponge titanium as an anode and electrolyzed it in a NaCl–KCl–$TiCl_x$ molten salt solution to obtain high-purity titanium powder. In the USTB process, Ti–Cu [169], TC4 [170], TA3 [171], and other similar alloys can be used as soluble anodes for the electrolytic extraction and recovery of titanium from the alloys.

To further reduce the titanium production costs, in 2010, Fray and Jiaor proposed a process for directly extracting titanium from titanium dioxide ore [172]. The ore contained high amounts of impurities, including calcium oxide and iron oxide. Titanium oxide reacts with TiC to form Ti_2CO, which serves as a soluble anode material for MSE [173]. However, during electrolysis, the impurities in the anode can contaminate the molten salt, necessitating its replacement to ensure product purity, affecting the industrial viability of the USTB process.

The soluble anode process has advantages, such as high product purity and low production costs. However, the USTB process is complex, and a high energy consumption during anode sintering is challenging. Product collection is also cumbersome and requires the regular cooling of the molten salt and scraping of the titanium product from the cathode. Additionally, product collection must be performed in an inert gas environment to prevent reactions between metallic titanium and atmospheric oxygen or nitrogen. To address these issues, the concept of continuous MSE using a rotating cathode has been proposed [174]. In this method, following the electrolytic adsorption of metallic titanium, the cathode rotates out of the molten salt, allowing the separation of the metallic titanium using scraper plates within the electrolytic cell. The cathode then rotates back into the molten salt to continue with the electrolysis process.

3.3. Combination of thermal reduction and molten salt electrolysis

The combination of thermal reduction and MSE is advantageous for producing titanium. Therefore, researchers have proposed a process that combines thermal reduction with MSE for titanium preparation. During MSE, a reduction reaction occurs at the cathode, producing active metallic calcium. Metallic calcium is first electrodeposited at the cathode; this calcium then chemically reduces the nearby titanium dioxide to metallic titanium while itself being oxidized to CaO, which subsequently dissolves back into the molten $CaCl_2$ salt. The combination of calcium thermal reduction and its MSE simplifies the Kroll process, reducing time and cost.

At the 2002 Titanium Association Annual Meeting, Ono and Suzuki from Kyoto University presented a novel titanium reduction process that combined the thermal reduction of titanium and electrolytic recovery of the reducing agent within the same reactor, known as the OS process [175–176]. It uses a graphite rod or crucible as the anode and a titanium basket or vessel wall as the cathode. The electrolysis reaction takes place at the temperature ranging from 800–1000°C, resulting in calcium generation at the cathode and the generated calcium then reacts with the TiO_2 at the cathode displacing oxygen from TiO_2 to produce metallic titanium [177], as shown in Fig. 4(f). A metal sponge titanium-containing 0.2wt% oxygen was prepared in 0.5mol% CaO–$CaCl_2$ melt [178–179]. While the Kroll process consumes 6945 kWh of energy per ton of titanium, the OS process consumes only 3189 kWh, which is approximately half the energy consumed by the Kroll process [175]. The low current efficiency of the OS process, ranging from 8.8% to 25.5%, is a result of side and reverse reactions. Research on the OS process conducted over the past decade has mainly focused on enhancing the molten salt system and optimizing titanium source selection. Examples include using sulfurized Ti(C,N) [180], TiS_2 [181], or sulfurized Ti(C,N) as the titanium source with $CaCl_2$–CaS as the molten salt; $CaTiO_3$ as the titanium source with $CaCl_2$–CaO as the molten salt [182]; or TiO_2 as the titanium source with $SrCl_2$–KCl–SrO as the molten salt [183].

Based on the OS process, EMR has been developed to produce titanium powder [184]. The OS process uses a reducing agent, such as a calcium–nickel alloy, to isolate the molten salt from the titanium source, as shown in Fig. 4(g). Titanium oxide is reduced by the electrons released from the reducing agent. During the OS process, titanium is indirect contact with the $CaCl_2$ melt, effectively preventing titanium contamination and improving the purity of the final titanium powder produced [185–186]. The EMR process achieves the electron-mediated reduction of titanium and the electrolytic reaction of the reducing agent within the same reactor, ensuring continuous operation and improving current efficiency of titanium production. Additionally, EMR allows the selection of magnesium [187] or aluminum [188] as the reducing agents.

4. Titanium reduction processes (2000—present)

Over the past two decades, the evolution of Ti metallurgy has revealed a dynamic interplay between the established methodologies and emerging innovations. In this study, thermal reduction and MSE are systematically compared, examining their respective mechanisms, material conversions, and product properties. Recent advancements have led to a paradigm shift toward atomic-scale process optimization, with particular emphasis on interfacial reaction kinetics and cathode material design. Concurrently, growing advancements in alloy synthesis strategies are witnessed through three distinct metallurgical approaches, effectively addressing the longstanding challenges in disproportionation management. Although MSE has progressed through continuous process refinement, its widespread industrial application remains constrained by continued reliance on the century-old Kroll process and challenges faced in high-oxygen titanium scrap utilization. A comprehensive analysis of technology trajectories, complemented by an extensive literature review and mechanistic studies, provides a framework for understanding the current achievements and future directions in sustainable titanium production.

In Fig. 6(a), the left side shows the main raw materials used in electrolytic titanium production. The materials listed in the order of decreasing prices are ilmenite, rutile, titanium slag, $TiCl_4$, TiO_2, $CaTiF_6$, and TiO_xC_y. Raw materials can be thermally or electrochemically reduced using reductants, such as Na, Ca, Mg, H_2, and Al, resulting in the production of titanium powder, titanium blocks or slag, sponge titanium, and titanium alloys. Similar processes with approximate principles are indicated using the same color. In Fig. 6(b), the thermal reduction mechanism is indicated by orange boxes, while the recovery reactions of the reductants are highlighted in green. The controllability, cost-effectiveness, and recyclability of the reductants are key factors to consider in thermal reduction. The cathode and anode undergo the same reactions in electrochemical reduction processes using chloride electrolyte systems. However, avoiding intermediate and disproportionation reactions at the cathode is challenging. The oxidation state of Ti gradually decreases from +4 to lower oxidation states and the coexistence of multiple oxidation states can lead to disproportionation reactions of titanium, thereby increasing energy consumption. The processes developed by the USTB and MER address the abovementioned issue by prereducing titanium dioxide, converting Ti from tetravalent state (+4) to divalent state (+2), thereby reducing the impact of disproportionation reactions. Another approach is to directly synthesize titanium alloys as the source material to avoid disproportionation reactions. Alloying can be broadly categorized into three types. Type I alloys can be formed by selecting liquid metals (Sn, Pb, and Fe) as the cathode, which allows direct electron transfer from TiF_6^{3-} in the solution, forming titanium alloys with the liquid cathode [189–191]. Similarly, when KF–KCl–$K_2Ti_6O_{13}$ is used as the molten salt and copper powder is used as the cathode, ti-

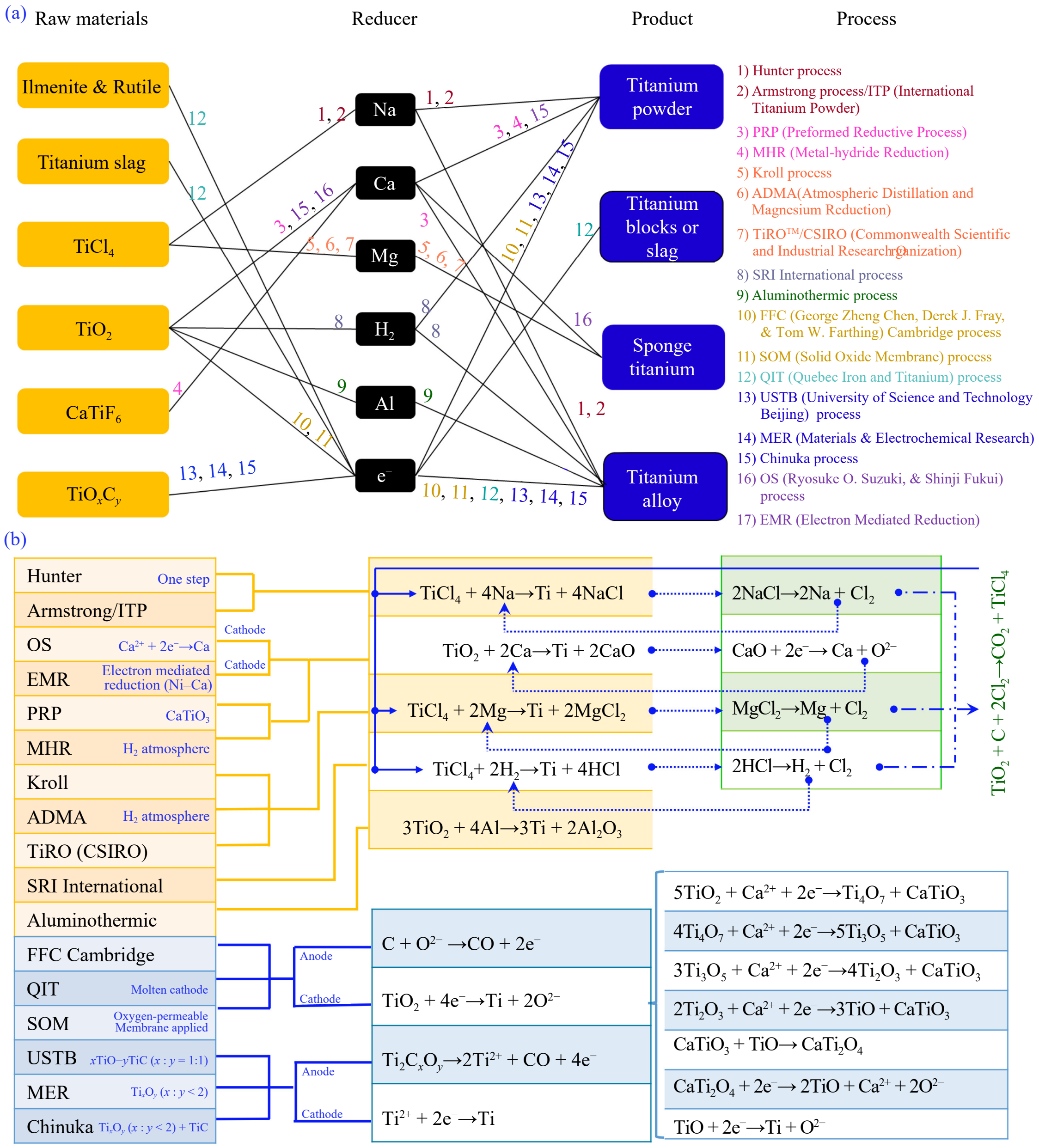

Fig. 6. **(a) Raw materials–Process–Product pathway diagram and (b) chemical mechanism diagram for producing titanium metal.**

tanium precipitates on the surface of the copper powder, forming Ti–Cu alloys [192]. Type II alloy, a molten salt containing multiple metal ions can be chosen and direct electrolysis and reduction of the metal ions in the molten salt can generate alloys. For example, using NaCl–KCl–NaF–K_2TiF_6–K_2NbF_7 as the molten salt, Ti–Nb alloys can be obtained through cathodic electrolysis [193]. Similarly, using LiCl–KCl–VCl_3–$TiCl_2$ or KCl–LiCl–$MgCl_2$–$TiCl_3$–$AlCl_3$ as the molten salt allows for the cathodic electrolysis and production of Ti–V alloys [193–194]. Type III alloys can be produced by mixing other metal oxides with titanium dioxide to form a cathode, followed by electrolysis to generate the desired alloy.

Fig. 7(a) lists the literature on titanium production processes developed over the past two decades. The FFC Cambridge process is still a significant methos used for titanium metal preparation, and recent research conducted particularly around 2020 has proposed advancements to it. The USTB process, MSE, aluminum thermal reduction, and hydrogen reduction are also methods used for titanium production, and related research is ongoing. Fig. 7(b) compares the number of publications on thermal reduction and MSE processes. MSE continues to attract significant research interest, resulting in a surge in studies since 2019, particularly in developing the FFC Cambridge and other related MSE processes. Regarding electrolysis, the focus of research remains on the enhancing the efficiency of high-purity titanium production and accumulating knowledge on replacing the Kroll process with MSE. Since 2016, research on producing titanium alloys through electrochemical and thermochemical has shown a growing trend because of the ability of alloying elements to enhance electrolysis efficiency, as shown in Fig. 7(c).

Fig. 8 summarizes the timeline of the development of titanium metal production processes and their research direc-

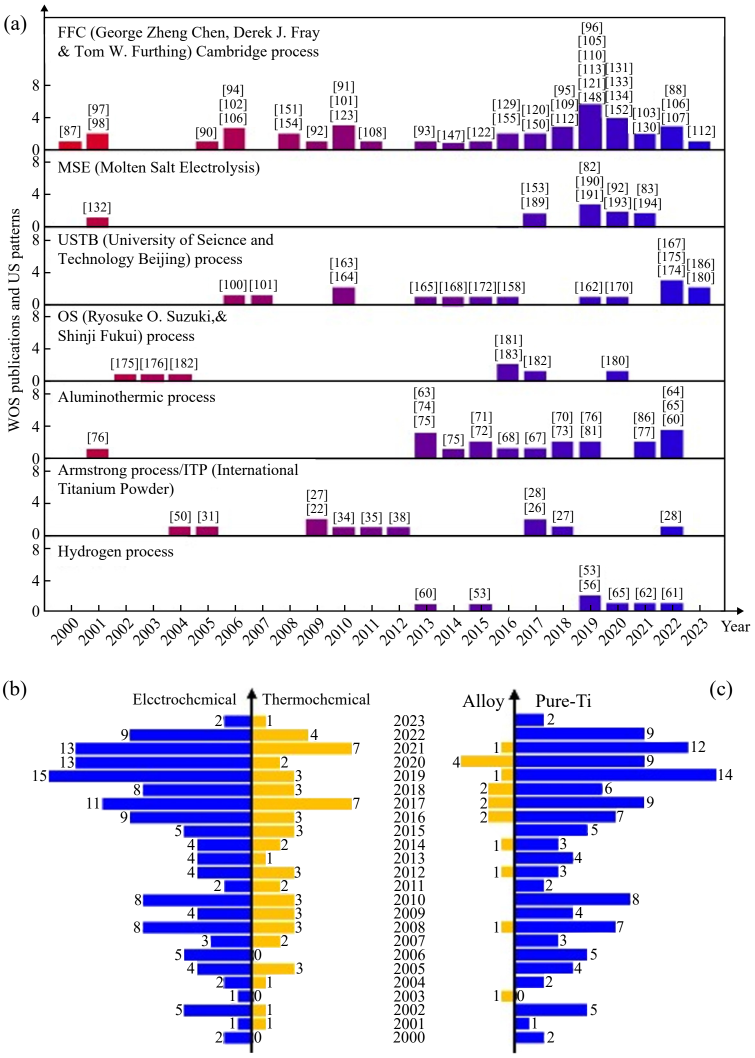

Fig. 7. (a) Research interest in different processes during the 2000—2023 period, (b) comparative of research interest between electrochemical and thermochemical process, and (c) comparative graph of research interest in titanium metal and titanium alloy production.

tions. It shows the research development of titanium and titanium alloy production as a tree structure, comprising two main parts: “root system” (1910—2005) and “research focus” (2013—2023). The root system is divided into thermal reduction and MSE roots. The thermal reduction method started with the sodium thermal reduction method in 1910 and went through the calcium thermal reduction method in 1937, hydrogen reduction method in 1938, magnesium reduction method in 1940, and aluminum thermal reduction method for titanium–aluminum alloy production in 2001. Thermal reduction has continuously explored different reducing agents to improve the efficiency of industrial production, purity, safety, and cost of titanium.

The MSE root started with the 1955, which was the first in the world to produce titanium–aluminum alloys. It has centered on anodic reactions, such as the electrolysis of titanium dioxide as the cathode in 2000, the electrolysis of calcium to reduce titanium dioxide in 2002, and the exploration of a soluble anode (TiC_xO_y) in 2005, which is dedicated to reducing side reactions, improving current efficiency, purity, and flexibility. This study focused on a variety of directions. In summary, we sorted out the history of titanium preparation development and the current research interests to promote the continuous progress and innovation of titanium and titanium alloy production technology.

The titanium metallurgy industry faces two critical technical challenges: (1) continued dependence on the magnesium reduction process developed by Kroll in 1940 for titanium metal production, which is characterized by elevated operational costs, extended processing durations, and strict specifications for raw material quality; (2) substantial generation of titanium scrap with elevated oxygen content during the metallurgical, casting, and machining processes. In standard metallurgical and material processing workflows, approximately 85% of the Ti mass is transformed into contaminated waste chips and residues, collectively classified as industrial Ti scrap, requiring removal [195].

5. Titanium scrap recycling technologies

Ti mining and refining are expensive. Recycling titanium scrap enables resource reuse and reduces titanium produc-

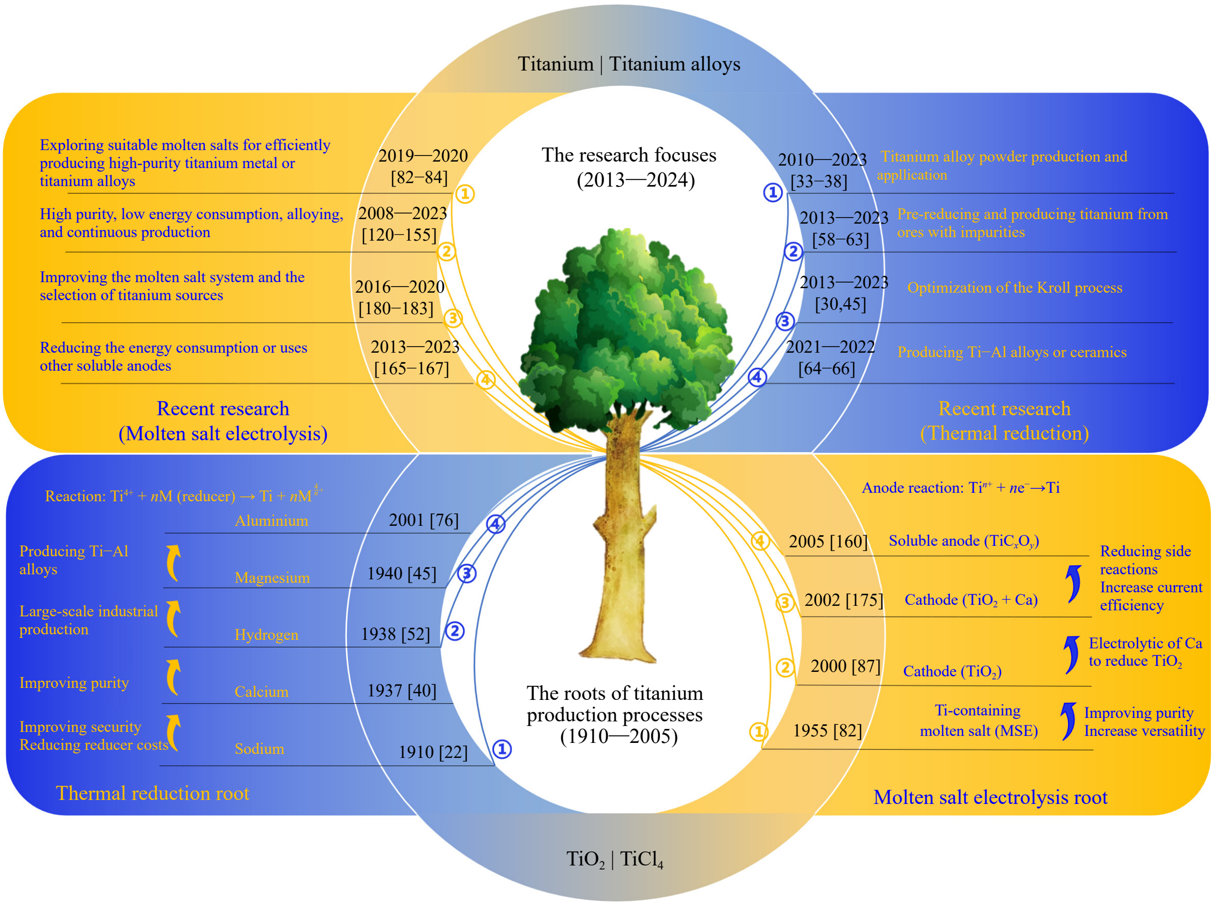

Fig. 8. **Titanium metal production process and its progress.**

tion costs. Recycling titanium from scrap parts avoids the high costs of titanium ore mining and smelting, creates value at various lifecycle stages, and boosts economic efficiency of the industry. A precision machinery company using a titanium chip briquetting system raised the titanium scrap recovery rate from 42% to 89%, saving over 1.68 million dollar annually in raw material procurement.

Industrial titanium scrap primarily comprises substandard metallic titanium generated during sponge titanium production, melting operations, and material processing, as shown in Fig. 9. Titanium scrap comes under four principal categories: (i) iron-contaminated surfaces of magnesium-reduced sponge titanium resulting from reactor wall interactions, particularly affecting the bottom and lateral sections, with scrap rates typically reaching 10%–20%, (ii) ingot head sections removed during melt-casting operations and machining swarf generated during surface defect elimination, collectively representing 4%–5% of the total ingot mass, (iii) residual material from downstream titanium product manufacturing, including trimmings from hot/cold rolling processes, accounting for 30%–35% of the total mass, and (iv) scarp arising from precision machining limitations due to inherent properties of titanium. The combination of high hardness and low thermal conductivity induces cutting zone temperatures in the range of 800–1000°C, promoting oxygen/nitrogen interactions that form brittle oxide layers. This phenomenon restricts the material utilization rate to 18% in high-precision applications. Fig. 9 presents the material flow dynamics and oxygen concentration variations during a titanium scrap recycling process. Multiple sources of scrap Ti, each with distinct properties and challenges, underscore the need for effective recycling and reprocessing strategies to fully leverage the valuable secondary resources.

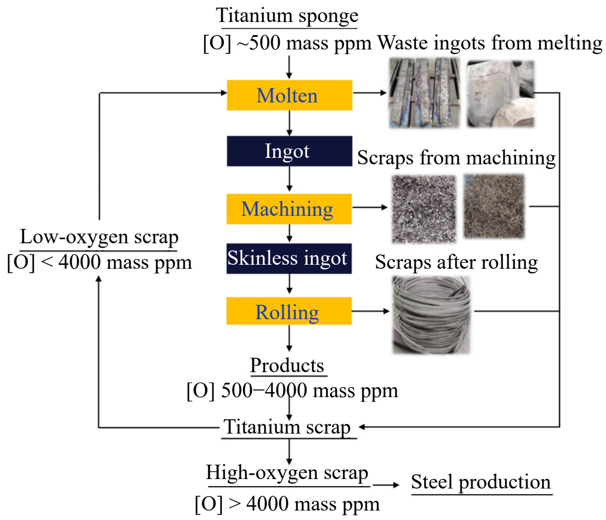

Fig. 9. **Material flow and oxygen concentration of titanium production process.**

Implementing the cascaded utilization or closed-loop recycling of titanium scrap is crucial for enhancing the utilization efficiency of titanium metal. The removal of iron from titanium scrap is particularly challenging. Typically, sponge titanium with a high iron content is directly used as a raw material for producing iron–titanium alloys. Titanium with low iron and oxygen contents below 0.4wt% is directly fed into the remelting stage for ingot production. When the oxygen content exceeds 0.4wt%, a mix of high-purity titanium sponge (0.05wt%) is required in proportion to the oxygen content, which is then recovered by vacuum arc remelting (VAR), electron beam cold heater melting (EBCHM), or plasma arc melting (PAM). Although remelting is performed in a vacuum environment, it does not effectively deoxidize and remove iron, and thus the remelting process may even increase the oxygen content. Given the limited production of high-purity sponge Ti, methods such as VAR and EBCHM struggle to efficiently process large quantities of industrial titanium scrap [196]. Stored titanium scrap forms a thicker oxide layer on the titanium scrap surface when exposed to air for extended periods, further complicating the recycling of titanium scrap. A significant amount of titanium scrap with high oxygen contents cannot be fully recycled through remelting processes, and the current practice of stockpiling represents a waste of space and resources. The challenges of treating and recycling titanium scrap highlight the need to consider alternative methods that effectively address the unique properties of titanium scrap compared with traditional raw materials.

The composition and morphology of titanium scrap significantly differ from those of the typical raw material, titanium dioxide, commonly used in titanium metal production. Titanium scrap contains impurities, such as oxygen, calcium, magnesium, and iron. In contrast to powdered raw materials, such as titanium dioxide or titanium tetrachloride, used for titanium metal production, titanium scrap often exists as shaped metal pieces or high-density blocks. The traditional industrial process, such as Kroll process, requires scrap to be processed into $TiCl_4$ for recycling. However, the chlorination process requires the pulverization of titanium scrap into pellets. Impurities, such as calcium and magnesium, in the titanium scrap have to be below 1.0% to prevent the accumulation of low-volatile impurity chlorides ($CaCl_2$ and $MgCl_2$) in the fluidized bed, which can lead to agglomeration in the fluidized bed. Thus, titanium scrap cannot be recovered using conventional industrial fluids. The inherent differences between spent titanium material and TiO_2 cause many processes suitable for treating titanium dioxide or titanium tetrachloride to encounter problems, such as poor reaction kinetics, when treating titanium scrap. Therefore, recycling titanium scrap has become a popular research topic in recent years.

Zheng and Okabe [197] mixed crushed titanium scrap (31 μm) with $FeCl_x$ at the temperature from 900 to 1200 K, converting 99% of the titanium in the scrap into $TiCl_4$. $TiCl_4$ serves as raw material for recycling processes, such as the Kroll process. Moon *et al*. [198] achieved the reduction of pure metallic titanium through the heat reduction of titanium machining waste in a cold crucible using calcium as the reducing agent. Hur *et al*. [199] utilized hydrogen thermal reduction to convert shredded titanium scrap (30 mm × 80 mm) into TiH_2 and then recovered metallic titanium via vacuum heating to remove H_2.

All the aforementioned processes utilized powdered titanium scrap as the primary raw material. However, the experimental results revealed the sintering phenomenon of titanium scrap during high-temperature thermal reduction processes, which reduced the deoxidation efficiency. Additionally, continuous attention is required to monitor the consumption of deoxidizers and the influence of byproduct concentration on the reaction process. Combining thermal reduction methods with MSE, the OS process can also be applied to the treatment and recovery of titanium scrap [200]. Based on the OS process, Kong *et al*. [201] utilized $MgCl_2$–$HoCl_2$ as molten salt to reduce titanium scrap. The oxygen ions in the molten salt reacted with $HoCl_2$ to form rare-earth oxyhalides, reducing the oxygen concentration in the titanium product to the ppm level. Using MSE with NaCl–KCl eutectic system for purifying titanium scrap, Jiao *et al*. [170] conducted anodic electrolysis digestion of titanium scrap, resulting in the deposition of high-purity titanium on the cathode. To understand the deoxidation purification mechanism, direct 3D visualization techniques using computed tomography were used to comprehensively analyze the MSE process, an approach aimed at regulating the titanium ion concentration in the molten salt and enhancing the reaction efficiency. Nevertheless, the electrolytic treatment of titanium scrap in molten salt encounters pressing issues, which include (1) optimizing mass-transfer conditions for highly dense titanium scrap during electrolysis and (2) preventing oxidation during the collection of products after electrolytic purification.

Effective recycling of titanium scrap requires addressing the aforementioned challenges. However, the recycling of titanium scrap is a critical constraint in the development of the titanium industry. Recycling titanium scrap can bring significant benefits, such as lowering the price of titanium, increasing the efficiency of resource utilization, and minimizing waste. Therefore, the development of an efficient and low-energy recycling process for titanium scrap is necessary for the future development of the titanium industry.

6. Conclusions

Metallic titanium is predominantly produced using the Kroll process. However, driven by the increasing demand, it has become critical to develop low-cost titanium production technologies. Since 2000, titanium production technologies have focused on thermal reduction and MSE, gradually forming distinct technological clusters. Research efforts have been directed toward improving product purity, achieving continuous production, and reducing energy consumption in titanium production.

The Armstrong process can continuously produce titanium via thermal reduction of sodium. The aluminum thermal reduction process involves a spontaneous reaction, and the heat released during the reaction can effectively reduce energy consumption during the preparation of titanium alloys. The use of hydrogen gas as a thermal reducing agent in the production of titanium metal does not introduce impurities; therefore, the resulting product is a clean and environmentally friendly titanium-iron alloy with excellent development potential.

When using MSE, various intermediate and disproportionation reactions occur during the titanium reduction. Processes using titanium-containing materials as cathodes further improve the efficiency or product purity of electrolytic titanium production. Processes using soluble anodic electrolysis have high current efficiency. Thus, studies are focused on developing high-performance soluble anodes that are difficult to detach, exhibit high conductivity, and uniform valence states. These processes combine thermal reduction with MSE, effectively avoiding the problem of multiple intermediate reactions/disproportionation reactions in MSE and reducing energy consumption in relation to single thermal reduction.

This study provides a comprehensive overview of the developmental trajectory of titanium metal production technology, offering insights into the technical bottlenecks, challenges, and prospective solutions embedded in currently processes. We also discuss the potential approaches for the recovery of scrap titanium and its applications. The aim was to instill new perspectives within the industry, fostering a renewed focus on research and development in titanium metal production. By expediting the progress of industrial-scale processes poised to replace the Kroll process, the application domains of titanium as a high-performance metal can be redefined.

Acknowledgements

The authors acknowledge the financial support from the Yunnan Province Key Industries Science and Technology Special Project for Colleges and Universities, China (No. FWCY-QYCT2024006), National Natural Science Foundation of China (Nos. 52104351 and 52364051), Science and Technology Major Project of Yunnan Province, China (No. 202202AG050007), the Yunnan Fundamental Research Projects, China (No. 202401AT070314), the Key Technology Research and Development Program of Shandong Province, China (No. 2023CXGC010903), and Central Guidance Local Scientific and Technological Development Funds, China (No. 202407AB110022). The authors would like to acknowledge Yunnan Province Xingdian Talent Support Plan Project, China.

Conflict of Interest

Hongbo Zeng is an advisory member for this journal and was not involved in the editorial review or the decision to publish this article. The authors declare that there are no competing interests.

References

[1] Fink, G, Encyclopedia of the elements, *Angew. Chem. Int. Ed.*, 44(2005), p. 3174.

[2] F. Weng, G.J. Bi, Y. Chew, *et al.*, Robust interface and excellent as-built mechanical properties of Ti–6Al–4V fabricated through laser-aided additive manufacturing with powder and wire, *Int. J. Miner. Metall. Mater.*, 32(2025), No. 1, p. 154.

[3] R. Wang, X. Song, L. Wang, *et al.*, New role of α phase in the fracture behavior and fracture toughness of a β-type bio-titanium alloy, *Int. J. Miner. Metall. Mater.*, 30(2023), No. 9, p. 1756.

[4] Y.X. Song, S. Xu, S. Sato, *et al.*, A lightweight shape-memory alloy with superior temperature-fluctuation resistance, *Nature*, 638(2025), No. 8052, p. 965.

[5] J. Sure, D.S.M. Vishnu, R.V. Kumar, U.K. Mudali, and C. Schwandt, Corrosion performance of electrochemically prepared Ti–5Ta–2Nb alloy in concentrated nitric acid, *Mater. Today Commun.*, 26(2021), art. No. 101786.

[6] G.K. Das, Y. Pranolo, Z. Zhu, and C.Y. Cheng, Leaching of ilmenite ores by acidic chloride solutions, *Hydrometallurgy*, 133(2013), p. 94.

[7] G.Z. Qiu and Y.F. Guo, Current situation and development trend of titanium metal industry in China, *Int. J. Miner. Metall. Mater.*, 29(2022), No. 4, p. 599.

[8] H. G. Dill, The "chessboard" classification scheme of mineral deposits: Mineralogy and geology from aluminum to zirconium. *Earth Sci. Rev.*, 100(2010), No. 1-4, p. 1.

[9] Global Titanium Mining—Statistics & facts, [2025–04–25], https://www.statista.com/topics/11141/titanium-industry-worldwide/.

[10] O. Turchinskaya and E.N. Slyuta, Titanium and iron probable reserves in the lunar soil, [in] *52nd Lunar and Planetary Science Conference 2021*, 2021.

[11] C. Li, W.H. Ma, Y. Li, and K.X. Wei, Metallurgical performance evaluation of space-weathered Chang'e-5 lunar soil, *Int. J. Miner. Metall. Mater.*, 31(2024), No. 6, p. 1241.

[12] W.J. Zhang, Estimate of lunar TiO_2 and FeO with M3 data, [in] B. Cudnik, ed., *Encyclopedia of Lunar Science*, Springer, Cham, 2023, p. 262.

[13] R. Merle, M. Höök, V. Troll, and A. Giegling, Assessing the plausibility of mining lunar titanium, *Eur. Geol.*, 57(2024), p. 43.

[14] J.Z. Cai, J.S. Deng, L. Wang, *et al.*, Reagent types and action mechanisms in ilmenite flotation: A review, *Int. J. Miner. Metall. Mater.*, 29(2022), No. 9, p. 1656.

[15] Y.F. Cai, N.N. Song, Y.F. Yang, L.M. Sun, P. Hu, and J.S. Wang, Recent progress of efficient utilization of titanium-bearing blast furnace slag, *Int. J. Miner. Metall. Mater.*, 29(2022), No. 1, p. 22.

[16] W.H. Wang, Material flows and waste management of titanium products in China from 2005 to 2020, *J. Sustain. Metall.*, 9(2023), No. 2, p. 564.

[17] D. Koreček, P. Solfronk, and J. Sobotka, A deformational analysis of a titanium alloy supported by the mathematical modelling of the sheet metal forming process via numerical simulation, *Materials*, 18(2025), No. 7, p. 1598.

[18] N. Matsanga, M. Wa Kalenga, and W. Nheta, An overview of thermochemical reduction processes for titanium production, *Minerals*, 15(2025), No. 1, art. No. 17.

[19] V. Tebaldo, G. Gautier di Confiengo, D. Duraccio, and M.G. Faga, Sustainable recovery of titanium alloy: From waste to feedstock for additive manufacturing, *Sustainability*, 16(2024), No. 1, art. No. 330.

[20] R.G. Reddy, P.S. Shinde, and A.M. Liu, Review: The emerging technologies for producing low-cost titanium, *J. Electrochem. Soc.*, 168(2021), No. 4, art. No. 042502.

[21] M. El Khalloufi, O. Drevelle, and G. Soucy, Titanium: An overview of resources and production methods, *Minerals*, 11(2021), No. 12, art. No. 1425.

[22] M.A. Hunter, Metallic titanium, *J. Am. Chem. Soc.*, 32(1910), No. 3, p. 330.

[23] M.A. Hunter and A. Jones, Titanium in metallurgy, *Trans. Electrochem. Soc.*, 66(1934), No. 1, p. 21.

[24] F.W. Hurd, *Metal Reduction Process Employing Metal Subhalides*, Google Patents, Appl. 4032329, 1977.

[25] F.W. Hurd, *Metal or Alloy Forming Reduction Process and Apparatus*, Google Patents, Appl. 4687632, 1987.

[26] W. Chen, Y. Yamamoto, and W.H. Peter, Investigation of pressing and sintering processes of CP-Ti powder made by Armstrong process, *Key Eng. Mater.*, 436(2010), p. 123.

[27] K.S. Weil, Y. Hovanski, and C.A. Lavender, Effects of $TiCl_4$ purity on the sinterability of Armstrong-processed Ti powder, *J. Alloy. Compd.*, 473(2009), No. 1-2, p. L39.

[28] X.Y. Xu, P. Nash, and D. Mangabhai, Characterization and sintering of Armstrong process titanium powder, *JOM*, 69(2017), No. 4, p. 770.

[29] R. Liu, S.X. Hui, W.J. Ye, *et al.*, Dynamic stress–strain properties of Ti–Al–V titanium alloys with various element contents, *Rare Met.*, 32(2013), No. 6, p. 555.

[30] R. Anderson, W. Ernst, L. Jacobsen, D. Kogut, and J. Steed, Commercialization of the Armstrong process for producing titanium alloy powder, [in] *Cost-Affordable Titanium: A Symposium Dedicated to Professor Harvey Flower as held at the 2004 TMS Annual Meeting*, Charlotte, 2004, p. 121.

[31] J.D.K. Rivard, C.A. Blue, D.C. Harper, *et al.*, The thermomechanical processing of titanium and Ti–6Al–4V thin gage sheet and plate, *JOM*, 57(2005), No. 11, p. 58.

[32] D. Eylon, W.A. Ernst, and D.P. Kramer, Development of ultrafine microstructure in titanium via powder metallurgy for improved ductility and strength, *Mater. Sci. Forum*, 604-605(2008), p. 223.

[33] M.A. Imam, P.S. Pao, and R.A. Bayles, Stress-corrosion cracking and fatigue crack growth behavior of Ti–6Al–4V plates consolidated from low cost powders, [in] T.S. Srivatsan, M.A. Imam, R. Srinivasan, eds., *Fatigue of Materials II*, Springer, Cham, 2013, p. 105.

[34] Y. Yamamoto, J.O. Kiggans, M.B. Clark, S.D. Nunn, A.S. Sabau, and W.H. Peter, Consolidation process in near net shape manufacturing of Armstrong CP-Ti/Ti–6Al–4V powders, *Key Eng. Mater.*, 436(2010), p. 103.

[35] W. Chen, Y. Yamamoto, W.H. Peter, *et al.*, Cold compaction study of Armstrong Process® Ti–6Al–4V powders, *Powder Technol.*, 214(2011), No. 2, p. 194.

[36] D. MacDonald, R. Fernández, F. Delloro, and B. Jodoin, Cold spraying of Armstrong process titanium powder for additive manufacturing, *J. Therm. Spray Technol.*, 26(2017), No. 4, p. 598.

[37] D. Montonera and P. Nash, Sinter bonding titanium and Ti–6Al–4V, *Int. J. Adv. Manuf. Technol.*, 96(2018), No. 5-8, p. 2907.

[38] L.I. Perez-Andrade, V.S. Bhattiprolu, W.M. Schuette, and L.N. Brewer, Influence of powder properties and processing gas on the microstructural evolution of Armstrong CP-titanium and Ti_6Al_4V powders processed by cold spray, *Surf. Coat. Technol.*, 431(2022), art. No. 128011.

[39] W. Kroll, The production of ductile titanium, *Trans. Electrochem. Soc.*, 78(1940), No. 1, p. 35.

[40] W.J. Kroll, How commercial titanium and zirconium were born, *J. Frankl. Inst.*, 260(1955), No. 3, p. 169.

[41] F.H. Froes, The production of low-cost titanium powders, *JOM*, 50(1998), No. 9, p. 41.

[42] H.Y. Zheng, H. Ito, and T.H. Okabe, Production of titanium powder by the calciothermic reduction of titanium concentrates or ore using the preform reduction process, *Mater. Trans.*, 48(2007), No. 8, p. 2244.

[43] T.H. Okabe, T. Oda, and Y. Mitsuda, Titanium powder production by preform reduction process (PRP), *J. Alloy. Compd.*, 364(2004), No. 1-2, p. 156.

[44] J.G. Jia, B.Q. Xu, B. Yang, D.S. Wang, H. Xiong, and D.C. Liu, Behavior of intermediate $CaTiO_3$ in reduction process of TiO_2 by calcium vapor, *Key Eng. Mater.*, 551(2013), p. 25.

[45] A.D. Hartman, S.J. Gerdemann, and J.S. Hansen, Producing lower-cost titanium for automotive applications, *JOM*, 50(1998), No. 9, p. 16.

[46] Y. Zhang, Z.Z. Fang, P. Sun, *et al.*, Kinetically enhanced metallothermic redox of TiO_2 by Mg in molten salt, *Chem. Eng. J.*, 327(2017), p. 169.

[47] Y. Zhang, Z.Z. Fang, Y. Xia, *et al.*, A novel chemical pathway for energy efficient production of Ti metal from upgraded titanium slag, *Chem. Eng. J.*, 286(2016), p. 517.

[48] Y. Zhang, Z.Z. Fang, Y. Xia, *et al.*, Hydrogen assisted magnesiothermic reduction of TiO_2, *Chem. Eng. J.*, 308(2017), p. 299.

[49] G. Brooks, M. Cooksey, G. Wellwood, and C. Goodes, Challenges in light metals production, *Miner. Process. Extr. Metall.*, 116(2007), No. 1, p. 25.

[50] K. Ono, T. Okabe, M. Ogawa, and R. Suzuki, Production of titanium powders by the calciothermic reduction of TiO_2, *Tetsu Hagane*, 76(1990), No. 4, p. 568.

[51] D.A. Hansen and S.J. Gerdemann, Producing titanium powder by continuous vapor-phase reduction, *JOM*, 50(1998), No. 11, p. 56.

[52] B. Wang, C.Y. Chen, J.Q. Li, L.Z. Wang, Y.P. Lan, and S.Y. Wang, Production of Fe–Ti alloys from mixed slag containing titanium and Fe_2O_3 via direct electrochemical reduction in molten calcium chloride, *Metals*, 10(2020), No. 12, art. No. 1611.

[53] B.O. Duisebaev, K.M. Baitasov, and A.S. Mukusheva, Theoretical basis for using hydrogen reduction in titanium production, *At. Energy*, 127(2019), No. 2, p. 127.

[54] F.H. Froes, S.J. Mashl, J.C. Hebeisen, V.S. Moxson, and V.A. Duz, The technologies of titanium powder metallurgy, *JOM*, 56(2004), No. 11, p. 46.

[55] S.K. Nayak, C.J. Hung, V. Sharma, *et al.*, Insight into point defects and impurities in titanium from first principles, *NPJ Comput. Mater.*, 4(2018), art. No. 11.

[56] D.E. Bullard and D.C. Lynch, Reduction of titanium dioxide in a nonequilibrium hydrogen plasma, *Metall. Mater. Trans. B*, 28(1997), No. 6, p. 1069.

[57] K. Choi, H.S. Jeon, S. Lee, Y. Kim, and H. Park, Gaseous reduction behavior of primary ilmenite at temperatures between 1273 K and 1473 K, *Metall. Mater. Trans. B*, 53(2022), No. 1, p. 334.

[58] W. Lv, X.W. Lv, J.Y. Xiang, *et al.*, Effect of preoxidation on the reduction of ilmenite concentrate powder by hydrogen, *Int. J. Hydrogen Energy*, 44(2019), No. 8, p. 4031.

[59] Y.F. Guo, P.F. Li, T. Jiang, A.Y. Travyanov, F.Q. Zheng, and G.Z. Qiu, Control of the forming behavior of anosovite in the reduction of ilmenite by hydrogen, [in] T. Jiang, ed., *6th International Symposium on High-Temperature Metallurgical Processing*, Springer, Cham, 2015, p. 611.

[60] J. Dang, X.J. Hu, G.H. Zhang, X.M. Hou, X.B. Yang, and K. Chou, Kinetics of reduction of titano-magnetite powder by H_2, *High Temp. Mater. Process.*, 32(2013), No. 3, p. 229.

[61] J.W. Yu, Y. Ou, Y.S. Sun, Y.J. Li, and Y.X. Han, Hydrogen reduction behaviors and mechanisms of vanadium titanomagnetite ore under fluidized bed conditions, *Powder Technol.*, 402(2022), art. No. 117340.

[62] J.W. Yu, N. Hu, H.X. Xiao, P. Gao, and Y.S. Sun, Reduction behaviors of vanadium–titanium magnetite with H_2 *via* a fluidized bed, *Powder Technol.*, 385(2021), p. 83.

[63] W. Li, G.Q. Fu, M.S. Chu, and M.Y. Zhu, An effective and cleaner process to recovery iron, titanium, vanadium, and chromium from Hongge vanadium titanomagnetite with hydrogen-

rich gases, *Ironmaking Steelmaking*, 48(2021), No. 1, p. 33.

[64] C.L. Yeh and R.F. Li, Formation of TiB_2–Al_2O_3 and NbB_2–Al_2O_3 composites by combustion synthesis involving thermite reactions, *Chem. Eng. J.*, 147(2009), No. 2-3, p. 405.

[65] G.F. Liu, Y.W. Li, L.X. Fan, M. Nath, Y.B. Xu, and J. Liu, Formation mechanism of Ti_3AlC_2 in TiO_2–Al–C/TiC systems at high temperatures, *Ceram. Int.*, 48(2022), No. 2, p. 2614.

[66] V.F. Balakirev, T.V. Osinkina, S.A. Krasikov, E.M. Zhilina, L.B. Vedmid', and S.V. Zhidovinova, Joint metallothermic reduction of titanium and rare refractory metals of group V, *Russ. J. Non-Ferrous Metals*, 62(2021), No. 2, p. 190.

[67] K. Zhao and N.X. Feng, A new two-stage aluminothermic reduction process for preparation of Ti/Ti–Al alloys, [in] H. Kim, S. Alam, N.Neelameggham, eds., *Rare Metal Technology 2017*, Springer, Cham, 2017, p. 167.

[68] R.A. de Brito, K.K.P. Gomes, O. Chiavone-Filho, and C. Alves, Reducción aluminotérmica del óxido de titanio (TiO_2) por plasma de Cátodo hueco, *Inf. Tecnol.*, 24(2013), No. 6, p. 23.

[69] Q.Y. Huang, X.W. Lv, R. Huang, and J.J. Song, Preparation of Ti–Si–Al alloy by aluminothermic reduction of TiO_2 bearing blast furnace slag, *Can. Metall. Q.*, 52(2013), No. 4, p. 413.

[70] C.L. Yeh and C.Y. Ke, *In situ* formation of TiB_2/Al_2O_3-reinforced Fe_3Al by combustion synthesis with thermite reduction, *Metals*, 8(2018), No. 4, art. No. 288.

[71] A.M. Liu, K.Y. Xie, L.X. Li, *et al.*, Preparation of Al–Ti master alloys by aluminothermic reduction of TiO_2 in cryolite melts at 960°C, [in] T. Jiang, ed., *6th International Symposium on High-Temperature Metallurgical Processing*, Springer, Cham, 2015, p. 239.

[72] S.S. Razavi and M. Soltanieh, The investigation of the aluminothermic reduction of dissolved ilmenite in molten cryolite, *Can. Metall. Q.*, 54(2015), No. 4, p. 460.

[73] C.L. Yeh and W.J. Yang, Combustion Synthesis of $(Ti, V)_2AlC$ Solid Solutions, *Adv. Mater. Res.*, 909(2014), p. 19.

[74] C.L. Yeh and W.J. Yang, Formation of MAX solid solutions $(Ti, V)_2AlC$ and $(Cr, V)_2AlC$ with Al_2O_3 addition by SHS involving aluminothermic reduction, *Ceram. Int.*, 39(2013), No. 7, p. 7537.

[75] Z.J. Gao and H.M. Lu, Preparation of Ti–Al–V alloys by aluminothermic reaction, [in] L. Li, D.P. Guillen, N.R. Neelameggham, eds., *Energy Technology 2016*, Springer, Cham, 2016, p. 65.

[76] O. Yücel and F.Ç. Şahin, Production of aluminum–titanium–boron master alloy by aluminothermic process, *High Temp. Mater. Process.*, 20(2001), No. 2, p. 137.

[77] J.H. Lee, H. Nersisyan, K.S. Lim, W.B. Kim, and W.S. Choi, Combustion-aluminothermic reduction of TiO_2 to produce titanium low oxygen suboxides, *Metall. Mater. Trans. B*, 52(2021), No. 6, p. 4012.

[78] X.F. Zhu, S.L. Zheng, Y. Zhang, *et al.*, Potentially more eco-friendly chemical pathway for production of high-purity TiO_2 from titanium slag, *ACS Sustainable Chem. Eng.*, 7(2019), No. 5, p. 4821.

[79] A. Atasoy, Reaction mechanism and kinetics in Ti_3SiC_2 synthesised from oxides, *J. Therm. Anal. Calorim.*, 134(2018), No. 1, p. 363.

[80] J.Z. Yang, Y.W. Wang, J.P. Peng, and Y.Z. Di, Reaction mechanism and kinetics of ferrotitanium preparation by aluminothermic reduction of $CaTiO_3$, *Mater. Today Commun.*, 30(2022), art. No. 102995.

[81] Z.Y. Wang, J.L. Zhang, Z.J. Liu, *et al.*, Production of ferrotitanium alloy from titania slag based on aluminothermic reduction, *J. Alloy. Compd.*, 810(2019), art. No. 151969.

[82] K. Zhao, Y.W. Wang, and F. Gao, Electrochemical extraction of titanium from carbon-doped titanium dioxide precursors by electrolysis in chloride molten salt, *Ionics*, 25(2019), No. 12, p. 6107.

[83] B.L. Yan, J. Wang, T. Yang, *et al.*, Synthesis of Ti powders with different morphologies *via* controlling the valence state of the titanium ion in KCl–NaCl molten salt, *J. Electroanal. Chem.*, 876(2020), art. No. 114496.

[84] K. Kumamoto, A. Kishimoto, and T. Uda, Low temperature electrodeposition of titanium in fluoride-added LiCl–KCl–CsCl molten salt, *Mater. Trans.*, 61(2020), No. 8, p. 1651.

[85] H. Sekimoto, Y. Nose, T. Uda, and H. Sugimura, Quantitative analysis of titanium ions in the equilibrium with metallic titanium in NaCl–KCl equimolar molten salt, *Mater. Trans.*, 51(2010), No. 11, p. 2121.

[86] M.A. Steinberg, S.S. Carlton, M.E. Sibert, and E. Wainer, Preparation of titanium by fluoride electrolysis, *J. Electrochem. Soc.*, 102(1955), No. 6, art. No. 332.

[87] G. Chen, D. Fray, and T. Farthing, Direct electrochemical reduction of titanium dioxide to titanium in molten calcium chloride, *Nature*, 407(2000), No. 6802, p. 361.

[88] D.J. Fray, *Removal of Oxygen from Metal oxides and Solid solutions by Electrolysis in a Fused Salt*, International Patent, WO 99/64638, 1999.

[89] K.S. Mohandas and D.J. Fray, FFC cambridge process and removal of oxygen from metal-oxygen systems by molten salt electrolysis: An overview, *Trans. Indian Inst. Met.*, 57(2004), No. 6, p. 579.

[90] C. Schwandt and D.J. Fray, Determination of the kinetic pathway in the electrochemical reduction of titanium dioxide in molten calcium chloride, *Electrochim. Acta*, 51(2005), No. 1, p. 66.

[91] Z.Q. Li, N. Zhang, C.G. Bai, X.L. Chen, and C.Y. Tao, Study on formation and transportation process of O^{2-} in TiO_2 electrode, *Rare Met. Mater. Eng.*, 39(2010), No. 3, p. 473.

[92] K. Kobayashi, Y. Oka, and R.O. Suzuki, Influence of current density on the reduction of TiO_2 in molten salt ($CaCl_2$ + CaO), *Mater. Trans.*, 50(2009), No. 12, p. 2704.

[93] G.Q. Ma, M. Zou, and Q.L. Wang, Research on effect factors of current efficiency in the process of sponge titanium production by electrolytic method, *Adv. Mater. Res.*, 873(2013), p. 72.

[94] M.F. Liu, S.G. Lu, S.R. Kan, and G.X. Li, Effect of electrolysis voltage on electrochemical reduction of titanium oxide to titanium in molten calcium chloride, *Rare Met.*, 26(2007), No. 6, p. 547.

[95] P.S. Lai, M.L. Hu, L.Z. Gao, Z.F. Qu, and C.G. Bai, The anodic behavior of electro-deoxidation of titanium dioxide in calcium chloride molten salt, [in] B. Li, ed., *Characterization of Minerals, Metals, and Materials 2018*, Springer, Cham, 2018, p. 409.

[96] Y. Haraguchi, R. Shibuya, S. Natsui, T. Kikuchi, and R.O. Suzuki, Gas generation reactions during TiO_2 reduction using molten salt, *J. Japan Inst. Metals*, 83(2019), No. 11, p. 441.

[97] G.Z. Chen, D.J. Fray, and T.W. Farthing, Cathodic deoxygenation of the alpha case on titanium and alloys in molten calcium chloride, *Metall. Mater. Trans. B*, 32(2001), No. 6, p. 1041.

[98] D.J. Fray, Emerging molten salt technologies for metals production, *JOM*, 53(2001), No. 10, p. 27.

[99] S.C. Heck, M.F. de Oliveira, and E. Radovanovic, Ti production from natural rutile sand by the FFC process: Experimental and mathematical modelling study, *J. Electroanal. Chem.*, 905(2022), art. No. 115996.

[100] B.X. Wang, X.Z. Lan, X.C. Zhao, and J. Zhang, Reaction mechanism on electrochemical reduction of TiO_2 to titanium, *Chin. J. Rare Met.*, 34(2010), No. 4, p. 618.

[101] X.M. Nie, L.Y. Dong, C.G. Bai, D.F. Chen, and G.B. Qiu, Preparation of Ti by direct electrochemical reduction of solid TiO_2 and its reaction mechanism, *Trans. Nonferrous Met. Soc.*

China, 16(2006), p. s723.

[102] B. Wang, K.R. Liu, and J.S. Chen, Reaction mechanism of preparation of titanium by electro-deoxidation in molten salt, *Trans. Nonferrous Met. Soc. China*, 21(2011), No. 10, p. 2327.

[103] S.C. Heck and E. Radovanovic, Determination of kinetic parameters for TiO_2 and Nb_2O_5 molten salt FFC reduction by modelling experimental sweep voltammograms, *J. Electroanal. Chem.*, 889(2021), art. No. 115233.

[104] K. Jiang, X.H. Hu, M. Ma, *et al.*, "Perovskitization"-assisted electrochemical reduction of solid TiO_2 in molten $CaCl_2$, *Angew. Chem. Int. Ed.*, 118(2006), No. 3, p. 442.

[105] S. Natsui, T. Sudo, R. Shibuya, H. Nogami, T. Kikuchi, and R.O. Suzuki, Visualization of TiO_2 reduction behavior in molten salt electrolysis, *Metall. Mater. Trans. B*, 51(2020), No. 1, p. 11.

[106] K. Zhao and K.J. Liu, Investigation of the electrochemical reduction of porous $CaTiO_3$ pellets in $CaCl_2$%–0.5%CaO molten salt, *J. Electrochem. Soc.*, 169(2022), No. 5, art. No. 052504.

[107] G.L. Zhao, Y. Xu, and Y.Q. Cai, Effect of sintering temperature and porosity on electro-deoxidation of calcium titanate in $CaCl_2$–NaCl molten salt, *Int. J. Electrochem. Sci.*, 17(2022), No. 2, art. No. 220245.

[108] X.C. Lang, H.W. Xie, X.Y. Zou, P.H. Kim, and Y.C. Zhai, Investigation on direct electrolytic Reduction of the $CaTiO_3$ compounds in molten $CaCl_2$–NaCl for the production of Ti, *Adv. Mater. Res.*, 284-286(2011), p. 2082.

[109] F. Yang, Y. Liu, J.W. Ye, G.R. Wang, and W. He, Preparation of titanium through the electrochemical reducing Ti_4O_7 in molten calcium chloride, *Mater. Lett.*, 233(2018), p. 28.

[110] J. Mohanty and P.K. Behera, Use of pre-treated TiO_2 as cathode material to produce Ti metal through molten salt electrolysis, *Trans. Indian Inst. Met.*, 72(2019), No. 4, p. 859.

[111] T.X. Ma, M.J. Hu, P.S. Lai, L.Y. Wen, and M.L. Hu, Preparation of titanium metal using titanium suboxides in molten salt, *Mater. Trans.*, 60(2019), No. 3, p. 400.

[112] J.J. Liu, S.L. Li, Z.P. Lv, Y. Fan, J.L. He, and J.X. Song, Electro-desulfurization of metal sulfides in molten salts, *Sep. Purif. Technol.*, 310(2023), art. No. 123109.

[113] C.S. Wu, M.S. Tan, G.Z. Ye, D.J. Fray, and X.B. Jin, High-efficiency preparation of titanium through electrolysis of carbo-sulfurized titanium dioxide, *ACS Sustainable Chem. Eng.*, 7(2019), No. 9, p. 8340.

[114] N. Suzuki, M. Tanaka, H. Noguchi, S. Natsui, T. Kikuchi, and R.O. Suzuki, Calcium reduction of TiS_2 in $CaCl_2$ melt, *Mater. Trans.*, 58(2017), No. 3, p. 367.

[115] M. Ohta, S. Satoh, T. Kuzuya, S. Hirai, M. Kunii, and A. Yamamoto, Thermoelectric properties of $Ti_{1+x}S_2$ prepared by CS_2 sulfurization, *Acta Mater.*, 60(2012), No. 20, p. 7232.

[116] G.M. Li, D.H. Wang, X.B. Jin, and G.Z. Chen, Electrolysis of solid MoS_2 in molten $CaCl_2$ for Mo extraction without CO_2 emission, *Electrochem. Commun.*, 9(2007), No. 8, p. 1951.

[117] X.L. Ge, X.D. Wang, and S. Seetharaman, Copper extraction from copper ore by electro-reduction in molten $CaCl_2$–NaCl, *Electrochim. Acta*, 54(2009), No. 18, p. 4397.

[118] T. Wang, H.P. Gao, X.B. Jin, H.L. Chen, J.J. Peng, and G.Z. Chen, Electrolysis of solid metal sulfide to metal and sulfur in molten NaCl–KCl, *Electrochem. Commun.*, 13(2011), No. 12, p. 1492.

[119] D.H. Tian, M.Y. Wang, Y.P. Zhou, *et al.*, $Ni_{0.36}Al_{0.10}Cu_{0.30}Fe_{0.24}$ metallic inert anode for the electrochemical production of Fe–Ni alloy in molten K_2CO_3–Na_2CO_3, *Metall. Mater. Trans. B*, 49(2018), No. 6, p. 3424.

[120] M. Alzamani and K. Jafarzadeh, The effect of pre-oxidation treatment on corrosion behavior of Ni–Cu–Fe–Al anode in molten $CaCl_2$ salt, *Oxid. Met.*, 89(2018), No. 5-6, p. 623.

[121] M. Alzamani, K. Jafarzadeh, and A. Fattah-Alhosseini, EIS study of oxidation heat-treatment effects on corrosion behavior of $Ni_{10}Cu_{11}Fe_6Al$ metallic inert anode inside molten calcium chloride salt, *Mater. Corros.*, 70(2019), No. 4, p. 605.

[122] L.W. Hu, Y. Song, J.B. Ge, S.Q. Jiao, and J. Cheng, Electrochemical metallurgy in $CaCl_2$–CaO melts on the basis of $TiO_2 \cdot RuO_2$ inert anode, *J. Electrochem. Soc.*, 163(2016), No. 3, p. E33.

[123] M. Suput, R. Delucas, S. Pati, G. Ye, U. Pal, and A.C. Powell IV, Solid oxide membrane technology for environmentally sound production of titanium, *Miner. Process. Extr. Metall.*, 117(2008), No. 2, p. 118.

[124] S.S. Li, X.L. Zou, K. Zheng, *et al.*, Direct production of $TiAl_3$ from Ti/Al-containing oxides precursors by solid oxide membrane (SOM) process, *J. Alloy. Compd.*, 727(2017), p. 1243.

[125] X.G. Lu, X.L. Zou, C.H. Li, Q.D. Zhong, W.Z. Ding, and Z.F. Zhou, Green electrochemical process solid-oxide oxygen-ion-conducting membrane (SOM): Direct extraction of Ti–Fe alloys from natural ilmenite, *Metall. Mater. Trans. B*, 43(2012), No. 3, p. 503.

[126] X.S. Ye, X.G. Lu, C.H. Li, *et al.*, Preparation of Ti–Fe based hydrogen storage alloy by SOM method, *Int. J. Hydrogen Energy*, 36(2011), No. 7, p. 4573.

[127] K. Otake, H. Kinoshita, T. Kikuchi, and R.O. Suzuki, CO_2 gas decomposition to carbon by electro-reduction in molten salts, *Electrochim. Acta*, 100(2013), p. 293.

[128] K. Dring, Direct electrochemical reduction of titanium dioxide in molten salts, *Key Eng. Mater.*, 436(2010), p. 27.

[129] T.H. Okabe and Y.K. Taninouchi, Recycling titanium and its alloys by utilizing molten salt, [in] R.G. Reddy, P. Chaubal, P.C. Pistorius, eds., *Advances in Molten Slags*, *Fluxes*, *and Salts*: *Proceedings of the 10th International Conference on Molten Slags*, *Fluxes and Salts 2016*, Springer, Cham, 2016, p. 751.

[130] N. Kwon, J.S. Byeon, H.C. Kim, *et al.*, Effective deoxidation process of titanium scrap using $MgCl_2$ molten salt electrolytic, *Metals*, 11(2021), No. 12, art. No. 1981.

[131] L.X. Kong, T. Ouchi, and T.H. Okabe, Electrochemical deoxidation of titanium in molten $MgCl_2$–$HoCl_3$, *MATEC Web Conf.*, 321(2020), art. No. 07006.

[132] R. Abdulaziz, L.D. Brown, D. Inman, S. Simons, P.R. Shearing, and D.J.L. Brett, Novel fluidised cathode approach for the electrochemical reduction of tungsten oxide in molten LiCl–KCl eutectic, *Electrochem. Commun.*, 41(2014), p. 44.

[133] K. Zhao and F. Gao, Electrochemical evaluation of titanium production from porous Ti_2O_3 in LiCl–KCl–Li_2O eutectic melt, *Int. J. Electrochem. Sci.*, 15(2020), No. 7, p. 6109.

[134] F.X. Zhu, L. Li, X.Z. Cheng, S.R. Ma, L.W. Jiang, and K.H. Qiu, Direct electrochemical reduction of low titanium chlorides into titanium aluminide alloy powders from molten eutectic KCl–LiCl–$MgCl_2$, *Electrochim. Acta*, 357(2020), art. No. 136867.

[135] G.S. Chen, M. Okido, and T. Oki, Electrochemical studies of the reaction between titanium metal and titanium ions in the KCl–NaCl molten salt system at 973 K, *J. Appl. Electrochem.*, 17(1987), No. 4, p. 849.

[136] M. Dayah, Ptable® is a registered trademark of Michael Dayah, (2022–10–12) [2025–04–25], https://ptable.com/lang=zh-hans#.

[137] J.X. Song, Q.Y. Wang, J.Y. Wu, S.Q. Jiao, and H.M. Zhu, The influence of fluoride ions on the equilibrium between titanium ions and titanium metal in fused alkali chloride melts, *Faraday Discuss.*, 190(2016), p. 421.

[138] J.X. Song, Q.Y. Wang, X.B. Zhu, J.G. Hou, S.Q. Jiao, and H.M. Zhu, The influence of fluoride anion on the equilibrium between titanium ions and electrodeposition of titanium in molten fluoride–chloride salt, *Mater. Trans.*, 55(2014), No. 8, p. 1299.

[139] X. Song, S.L. Li, S.S. Liu, Y. Fan, J.L. He, and J.X. Song, Co-

ordination states of metal ions in molten salts and their characterization methods, *Int. J. Miner. Metall. Mater.*, 30(2023), No. 7, p. 1261.

[140] S.S. Liu, S.L. Li, C.H. Liu, J.L. He, and J.X. Song, Effect of fluoride ions on coordination structure of titanium in molten NaCl–KCl, *Int. J. Miner. Metall. Mater.*, 30(2023), No. 5, p. 868.

[141] F. Lantelme, K. Kuroda, and A. Barhoun, Electrochemical and thermodynamic properties of titanium chloride solutions in various alkali chloride mixtures, *Electrochim. Acta*, 44(1998), No. 2-3, p. 421.

[142] F. Lantelme and Y. Berghoute, Transient electrochemical techniques for studying electrodeposition of niobium in fused NaCl–KCl, *J. Electrochem. Soc.*, 141(1994), No. 12, p. 3306.

[143] F. Lantelme, A. Barhoun, and K. Kuroda, Role of the oxoacidity and ligand effect in the electrowinning of titanium in fused salts, [in] D.H. Kerridge and E.G. Polyakov, eds., *Refractory Metals in Molten Salts*, Springer, Netherlands, 1998, p. 159.

[144] J.J. Peng, G.M. Li, H.L. Chen, D.H. Wang, X.B. Jin, and G.Z. Chen, Cyclic voltammetry of ZrO_2 powder in the metallic cavity electrode in molten $CaCl_2$, *J. Electrochem. Soc.*, 157(2010), No. 1, art. No. F1.

[145] G.Z. Chen, E. Gordo, and D.J. Fray, Direct electrolytic preparation of chromium powder, *Metall. Mater. Trans. B*, 35(2004), No. 2, p. 223.

[146] D.H. Wang, G.H. Qiu, X.B. Jin, X.H. Hu, and G.Z. Chen, Electrochemical metallization of solid terbium oxide, *Angew. Chem. Int. Ed.*, 45(2006), No. 15, p. 2384.

[147] H.D. Jiao, Q.Y. Wang, J.B. Ge, H.B. Sun, and S.Q. Jiao, Electrochemical synthesis of Ti_5Si_3 in $CaCl_2$ melt, *J. Alloy. Compd.*, 582(2014), p. 146.

[148] Z.R. Zhou, P. Dong, D.Y. Wang, *et al.*, Silicon–titanium nanocomposite synthesized via the direct electrolysis of SiO_2/TiO_2 precursor in molten salt and their performance as the anode material for lithium ion batteries, *J. Alloy. Compd.*, 781(2019), p. 362.

[149] R. Bhagat, M. Jackson, D. Inman, and R. Dashwood, Production of Ti–W alloys from mixed oxide precursors via the FFC Cambridge process, *J. Electrochem. Soc.*, 156(2009), No. 1, art. No. E1.

[150] Z.R. Zhou, Y.J. Zhang, P. Dong, *et al.*, Electrolytic synthesis of TiC/SiC nanocomposites from high titanium slag in molten salt, *Ceram. Int.*, 44(2018), No. 4, p. 3596.

[151] R. Bhagat, M. Jackson, D. Inman, and R. Dashwood, The production of Ti–Mo alloys from mixed oxide precursors via the FFC Cambridge process, *J. Electrochem. Soc.*, 155(2008), No. 6, art. No. E63.

[152] Z.Y. Pang, X.L. Zou, S.S. Li, W. Tang, Q. Xu, and X.G. Lu, Molten salt electrochemical synthesis of ternary carbide Ti_3AlC_2 from titanium-rich slag, *Adv. Eng. Mater.*, 22(2020), No. 5, art. No. 1901300.

[153] L.P. Polyakova, P. Taxil, and E.G. Polyakov, Electrochemical behaviour and codeposition of titanium and niobium in chloride–fluoride melts, *J. Alloy. Compd.*, 359(2003), No. 1-2, p. 244.

[154] S.P. Padhee, U.K. Chanda, R. Singh, A. Roy, B. Mishra, and S. Pati, Electro-deoxidation process for producing FeTi from low-grade ilmenite: Tailoring precursor composition for hydrogen storage, *J. Sustain. Metall.*, 7(2021), No. 3, p. 1178.

[155] L. Xiong, Y.X. Hua, C.Y. Xu, *et al.*, Effect of CaO addition on preparation of ferrotitanium from ilmenite by electrochemical reduction in $CaCl_2$–NaCl molten salt, *J. Alloy. Compd.*, 676(2016), p. 383.

[156] F. Cardarellir, *Electrochemical Deoxidation of Titanium and its Alloy Process*, US Patent, 7504017, 2009.

[157] J.C. Withers and R.O. Loutfy, *Thermal and Electrochemical Process for Metal Production*, US Patent, 7410562, 2008.

[158] J.C. Withers, R.O. Loutfy, and J.P. Laughlin, Electrolytic process to produce titanium from TiO_2 feed, *Mater. Technol.*, 22(2007), No. 2, p. 66.

[159] P.S. Bains, M. Bahraminasab, S.S. Sidhu, and G. Singh, On the machinability and properties of Ti–6Al–4V biomaterial with n-HAp powder-mixed ED machining, *Proc. Inst. Mech. Eng. H*, 234(2020), No. 2, p. 232.

[160] S.Q. Jiao and H.M. Zhu, Novel metallurgical process for titanium production, *J. Mater. Res.*, 21(2006), No. 9, p. 2172.

[161] S.Q. Jiao and H.M. Zhu, Electrolysis of Ti_2CO solid solution prepared by TiC and TiO_2, *J. Alloy. Compd.*, 438(2007), No. 1-2, p. 243.

[162] X.H. Ning, J.S. Xiao, S.Q. Jiao, and H.M. Zhu, Anodic dissolution of titanium oxycarbide TiC_xO_{1-x} with different O/C ratio, *J. Electrochem. Soc.*, 166(2019), No. 2, p. E22.

[163] X.H. Ning, H.Y. Liu, and H.M. Zhu, Anodic dissolution behavior of TiC_xO_y in NaCl–KCl melt, *Electrochemistry*, 78(2010), No. 6, p. 513.

[164] S.Q. Jiao, X.H. Ning, K. Huang, and H.M. Zhu, Electrochemical dissolution behavior of conductive TiC_xO_{1-x} solid solutions, *Pure Appl. Chem.*, 82(2010), No. 8, p. 1691.

[165] Q.Y. Wang, Y. Li, S.Q. Jiao, and H.M. Zhu, Producing metallic titanium through electro-refining of titanium nitride anode, *Electrochem. Commun.*, 35(2013), p. 135.

[166] J.X. Wang, Z. Wang, J.G. Tu, J. Zhu, M.Y. Wang, and S.Q. Jiao, Purification of titanium oxycarbonitride by leaching from titanium slag with carbothermal reduction, *Hydrometallurgy*, 215(2023), art. No. 105984.

[167] S. Jiao, T. Donghua, and J. Handongr, *Preparing Process for Titanium of Ti–C–S Anode by Carbonized/sulfurized Ilmenite*, US Patents, 11473207, 2022.

[168] Q.G. Weng, R.D. Li, T.C. Yuan, J. Li, and Y.H. He, Valence states, impurities and electrocrystallization behaviors during molten salt electrorefining for preparation of high-purity titanium powder from sponge titanium, *Trans. Nonferrous Met. Soc. China*, 24(2014), No. 2, p. 553.

[169] V.E. Ri, B.U. Yoo, H. Nersisyan, and J.H. Lee, Carbon-free recovery route for pure Ti: CuTi-alloy electrorefining in a K-free molten salt, *ACS Sustainable Chem. Eng.*, 11(2023), No. 4, p. 1414.

[170] H.D. Jiao, W.L. Song, H.S. Chen, M.Y. Wang, S.Q. Jiao, and D.N. Fang, Sustainable recycling of titanium scraps and purity titanium production via molten salt electrolysis, *J. Cleaner Prod.*, 261(2020), art. No. 121314.

[171] J.X. Liu, J.C. Liu, D.W. Long, and K. Zhan, Electroplating titanium film on 316L stainless steel in LiCl–KCl–Ti^{x+} ($2 < x < 3$) molten salts, *Nucl. Sci. Tech.*, 31(2020), No. 5, art. No. 43.

[172] D.J. Fray and S. Jiaor, *Treatment of Titanium Ores*, US Patents, 9181604, 2015.

[173] W.Y. Long, B.S. Zou, H. Li, T. Fujita, W.Z. Li, and F. Gao, Fabrication of a $TiC_{0.5}O_{0.5}$ anode using the carbothermal method under a non-vacuum atmosphere and its application in metal titanium electrolysis, *J. Mater. Sci. Mater. Electron.*, 33(2022), No. 6, p. 3045.

[174] C. Haixian and J. Caor, *Device and Process for Preparing High-purity Titanium Powder by Continuous Electrolysis*, US Patents, 17/422453, 2022.

[175] K. Ono and R.O. Suzuki, A new concept for producing Ti sponge: Calciothermic reduction, *JOM*, 54(2002), No. 2, p. 59.

[176] R.O. Suzuki, K. Ono, and K. Teranuma, Calciothermic reduction of titanium oxide and *in-situ* electrolysis in molten $CaCl_2$, *Metall. Mater. Trans. B*, 34(2003), No. 3, p. 287.

[177] T. Oki and H. Inoue, Reduction of titanium dioxide by calcium in hot cathode spot, *Memoirs of the Faculty of Engineering, Nagoya University.*, 19(1968), No. 1, p. 164.

[178] T.H. Okabe, M. Nakamura, T. Oishi, and K. Ono, Electrochemical deoxidation of titanium, *Metall. Trans. B*, 24(1993),

No. 3, p. 449.

[179] Y. Ohno, H. Suzuki, H. Yamakawa, M. Nakamura, K. Otsuka, and T. Saruta, Impaired insulin sensitivity in young, lean normotensive offspring of essential hypertensives: Possible role of disturbed calcium metabolism, *J. Hypertens.*, 11(1993), No. 4, p. 421.

[180] E. Ahmadi, R.O. Suzuki, T. Kikuchi, T. Kaneko, and Y. Yashima, Towards a sustainable technology for production of extra-pure Ti metal: Electrolysis of sulfurized Ti(C,N) in molten $CaCl_2$, *Int. J. Miner. Metall. Mater.*, 27(2020), No. 12, p. 1635.

[181] N. Suzuki, M. Tanaka, H. Noguchi, S. Natsui, T. Kikuchi, and R.O. Suzuki, Reduction of TiS_2 by OS process in $CaCl_2$ melt, *ECS Trans.*, 75(2016), No. 15, p. 507.

[182] D. Wang, S. Pang, C.Y. Zhou, Y. Peng, Z. Wang, and X.Z. Gong, Improve titanate reduction by electro-deoxidation of $Ca_3Ti_2O_7$ precursor in molten $CaCl_2$, *Int. J. Miner. Metall. Mater.*, 27(2020), No. 12, p. 1618.

[183] C.C. Tang, X.J. Yu, J.S. Chen, Q. Han, and K.R. Liu, Preparation of titanium by electrochemical reduction of titanium dioxide powder in molten $SrCl_2$–KCl, *J. Alloy. Compd.*, 684(2016), p. 699.

[184] I. Park, T. Abiko, and T.H. Okabe, Production of titanium powder directly from TiO_2 in $CaCl_2$ through an electronically mediated reaction (EMR), *J. Phys. Chem. Solids*, 66(2005), No. 2-4, p. 410.

[185] T.H. Okabe and Y. Waseda, Producing titanium through an electronically mediated reaction, *JOM*, 49(1997), No. 6, p. 28.

[186] T.H. Okabe, New smelting process of titanium, *J. Jpn. Inst. Light Met.*, 55(2005), No. 11, p. 537.

[187] T.H. Okabe, T. Uda, E. Kasai, and Y. Waseda, Mechanism of magnesiothermic reduction of $TiCl_4$ by an electronically mediated reaction (EMR), [in] *Proceedings of the 1997 126th TMS Annual Meeting*, Orlando, 1997.

[188] T. Uda, T.H. Okabe, Y. Waseda, and K.T. Jacob, Contactless electrochemical reduction of titanium (II) chloride by aluminum, *Metall. Mater. Trans. B*, 31(2000), No. 4, p. 713.

[189] H.D. Jiao, D.H. Tian, S. Wang, J. Zhu, and S.Q. Jiao, Direct preparation of titanium alloys from Ti-bearing blast furnace slag, *J. Electrochem. Soc.*, 164(2017), No. 7, p. D511.

[190] H.D. Jiao, S.Q. Jiao, W.L. Song, *et al.*, Depolarization behavior of Ti deposition at liquid metal cathodes in a NaCl–KCl–KF melt, *J. Electrochem. Soc.*, 166(2019), No. 13, p. E401.

[191] H.D. Jiao, J.X. Wang, D.H. Tian, and S.Q. Jiao, Electrochemical behaviour of K_2TiF_6 at liquid metal cathodes in the LiF–NaF–KF eutectic melt, *Electrochemistry*, 87(2019), No. 3, p. 142.

[192] K. Zhao, Y.W. Wang, J.P. Peng, Y.Z. Di, X.Z. Deng, and N.X. Feng, Electrochemical preparation of titanium and titanium–copper alloys with $K_2Ti_6O_{13}$ in KF–KCl melts, *Rare Met.*, 36(2017), No. 6, p. 527.

[193] J. Gussone, C.R.Y. Vijay, P. Watermeyer, K. Milicevic, B. Friedrich, and J. Haubrich, Electrodeposition of titanium–vanadium alloys from chloride-based molten salts: Influence of electrolyte chemistry and deposition potential on composition, morphology and microstructure, *J. Appl. Electrochem.*, 50(2020), No. 3, p. 355.

[194] F.X. Zhua, K.H. Li, W.C. Song, L. Li, D.F. Zhang, and K.H. Qiu, Composition and structure of Ti–Al alloy powders formed by electrochemical co-deposition in KCl–LiCl–$MgCl_2$–$TiCl_3$–$AlCl_3$ molten salt, *Intermetallics*, 139(2021), art. No. 107341.

[195] Z.Z. Fang, J.D. Paramore, P. Sun, *et al.*, Powder metallurgy of titanium–past, present, and future, *Int. Mater. Rev.*, 63(2018), No. 7, p. 407.

[196] Y.C. Xin, Y. Liu, L. Gao, *et al.*, The numerical simulation of element segregation control during the electron beam cold hearth melting process of large-sized Ti–6wt%Al–4wt%V titanium alloy slab, *J. Mater. Res. Technol.*, 36(2025), p. 8671.

[197] H.Y. Zheng and T.H. Okabe, Recovery of titanium metal scrap by utilizing chloride wastes, *J. Alloy. Compd.*, 461(2008), No. 1-2, p. 459.

[198] B.M. Moon, S. Hyun, H.J. Lee, J. Ho, P. Hyun, and H.D. Jung, Method of recycling titanium scraps *via* the electromagnetic cold crucible technique coupled with calcium treatment, *J. Alloy. Compd.*, 727(2017), p. 931.

[199] B.Y. Hur, D.K. Ahn, S.Y. Kim, Y.S. Um, and A. Hiroshi, Hydrogen treatment of Ti scrap, *Mater. Sci. Forum*, 439(2003), p. 143.

[200] T.H. Okabe, Y. Hamanaka, and Y.K. Taninouchi, Direct oxygen removal technique for recycling titanium using molten $MgCl_2$ salt, *Faraday Discuss.*, 190(2016), p. 109.

[201] L.X. Kong, T. Ouchi, C.Y. Zheng, and T.H. Okabe, Electrochemical deoxidation of titanium scrap in $MgCl_2$–$HoCl_3$ system, *J. Electrochem. Soc.*, 166(2019), No. 13, p. E429.