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Preparation of Titanium Metal by Deoxygenation Under KCl-NaCl-YCl_3 System Using Soluble Anode

Tianzhu Mu [1,†], Fuxing Zhu [1], Yan Zhao [2,3,4,5,†], Haoyu Fang [2,4,5], Haohang Ji [5] and Lei Gao [5,*]

[1] State Key Laboratory of Vanadium and Titanium Resources Comprehensive Utilization, Pangang Group Research Institute Co., Ltd., Panzhihua 617000, China; mutianzhu02@163.com (T.M.); 15881293957@163.com (F.Z.)
[2] Key Laboratory for Nonferrous Vacuum Metallurgy of Yunnan Province, Kunming University of Science and Technology, Kunming 650093, China; zy15864165880@163.com (Y.Z.); fanghaoyuya1@163.com (H.F.)
[3] State Key Laboratory of Complex Non-Ferrous Metal Resources Clean Utilization, Kunming University of Science and Technology, Kunming 650093, China
[4] The National Engineering Research Center of Vacuum Metallurgy, Kunming University of Science and Technology, Kunming 650093, China
[5] Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming 650093, China; jhhkust2022@163.com
* Correspondence: glkust2013@hotmail.com
† These authors contributed equally to this work.

Abstract: Titanium metal is primarily produced via the Kroll process, which is characterized by a semi-continuous production flow and a lengthy process cycle, resulting in high production costs. Researchers have explored alternative methods for titanium production, including molten salt electrolysis, such as the Fray–Farthing–Chen (FFC), Ono Suzuki (OS), and University of Science and Technology Beijing (USTB) processes, aiming to achieve more economical production. Among these, the USTB process, a representative of soluble anode electrolysis, has shown significant promise. However, controlling oxygen concentration in titanium produced by soluble anode electrolysis remains a challenge. This study proposes a novel approach to enhance deoxidation efficiency in soluble anode electrolysis for titanium production by introducing yttrium chloride (YCl_3) into the molten salt electrolyte. Thermodynamic analysis and experimental validation demonstrate that the theoretical deoxidation limit for titanium can reach below 100 ppm under Y/YOCl/YCl_3 equilibrium. We report the successful synthesis of titanium powder with an oxygen concentration of 6000 ppm from titanium-carbon-oxygen solid solution. Under optimized conditions, the purity of the titanium powder reached 99.42%, demonstrating a new approach for producing high-purity titanium. This method, based on soluble anode electrolysis, offers a potential alternative to the conventional Kroll process. The research elucidates the fabrication process and analytical methods for titanium-carbon-oxygen solid solution, and employs a combination of analytical techniques, including XRD, SEM-EDS, and ONH Analyzer, for characterization of the electrolytic product, encompassing phase analysis, microstructure, and oxygen concentration testing.

Keywords: high-purity titanium; deoxidation; molten salt electrolysis; soluble anode; rare earth

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1. Introduction

Titanium and its alloys possess exceptional physical and chemical properties, including low density, high strength, excellent low-temperature ductility, and superior corrosion resistance, making them a promising class of structural materials. Their wide applications extend across aerospace, marine engineering, chemical industries, and medical devices [1,2]. However, compared to conventional metals such as iron, aluminum, and copper, titanium is a relatively new metal with a strong affinity for oxygen, rendering its extraction challenging and leading to high production costs. This significantly hinders its widespread adoption in commercial applications. A substantial reduction in production cost could potentially enable titanium to replace widely used materials like iron, steel, aluminum, and copper, opening up vast market demand and positioning it as a versatile metal with significant future prospects [3]. The Kroll process, a prominent method for producing high-purity titanium, relies on magnesium to remove impurities like oxygen and iron, reducing $TiCl_4$ to metallic titanium. However, the Kroll process is characterized by lengthy cycles and high energy consumption, leading to persistent high production costs and hindering significant process improvements [4,5].

The rapid development of molten salt electrochemistry has opened promising avenues for resource recycling and metal melting [6], with techniques like the Fray—Far-hing-Chen(FFC), Ono Suzuki (OS), electron-mediated response (EMR), and University of Science and Technology Beijing (USTB) processes demonstrating potential. Molten salt electrolysis presents a compelling pathway for lowering titanium production costs. The FFC process is a notable example in this domain. In 2000, Chen et al. [7] employed titanium foil coated with oxide scales (composed of TiO_2) as the cathode, $CaCl_2$ as the electrolyte, and graphite as the anode. Electrochemical reduction of TiO_2 to produce titanium metal was achieved through molten salt electrolysis [8]. Their results indicated an oxygen concentration below the detection limit of 200 ppm in the titanium foil at 1223 K. Ma et al. [9] successfully electrochemically reduced porous pellets derived from three titanium dioxide precursors (titanium dust, titanic acid, and titaniferous slag) to titanium in molten $CaCl_2$ at 1173 K, applying a constant voltage of approximately 3 V. The resulting titanium exhibited oxygen concentration ranging from 3000 ppm to 6000 ppm. S. C. Heck et al. [10] utilized natural ilmenite sand as the raw material to fabricate cathode pellets, with graphite as the anode, employing the FFC process. Titanium metal was successfully produced under conditions of 1073 K to 1323 K and a voltage of 3.1 V. L. L. Benson et al. [11] employed loose synthetic rutile powder as raw material, achieving complete reduction to low-oxygen titanium alloy within 16 h. The study emphasized the reduction behavior of iron throughout the process, a primary residual element in the raw material according to the Becher process. Ultimately, the titanium alloy powder synthesized using this method, derived from rutile, exhibited an oxygen concentration of approximately 3500 ppm. While widely adopted, the FFC process faces challenges, including low current efficiency, slow oxygen diffusion, and difficulty in separating the metal from the molten salt.

In 2002, Ono and Suzuki et al. [12] introduced the OS process, a novel method for producing titanium powder by reducing TiO_2 with calcium metal generated by electrolyzing CaO in a $CaCl_2$ (or $CaCl_2$ + CaO) molten salt. Unlike the FFC process, the OS process utilizes TiO_2 powder directly as the raw material, simplifying the operation. Additionally, the shorter diffusion path of oxygen within TiO_2 powder compared to sintered materials leads to enhanced reduction efficiency. This method has successfully produced titanium metal with an oxygen concentration of 2000 ppm [13]. Subsequently, Suzuki et al. [14] investigated the impact of the distribution of calcium deposited in molten $CaCl_2$ on the reduction efficiency during electrolysis to enhance the OS process. Experimental results demonstrated that both deposited and dissolved calcium can reduce TiO_2 in molten $CaCl_2$. Calcium exhibits a stronger reducing power near the cathode, leading to preferential reduction of TiO_2 samples placed on the cathode surface. When the TiO_2 samples are separated from the cathode, the reduction process is delayed. Therefore, the geometrical arrangement of the electrodes and the sample is crucial for suppressing parasitic reactions and enhancing the efficiency of the OS process. However, the OS method faces challenges, including low current efficiency and susceptibility of the titanium powder to contamination by elements like carbon and iron, hindering its industrialization. The Electron Mediated Reaction (EMR) process, a variant of the OS process, employs calcium as a reducing agent to directly produce titanium powder from TiO_2 via an electron-mediated reaction. This semi-continuous production process offers effective control over the location and morphology of the metal deposits. Okabe and Park et al. [15] successfully reduced contamination of titanium powder by carbon and iron using this method, opening a new path for continuous production of titanium metal or powder. Nevertheless, the EMR method presents complexities in the electrolytic cell structure and suffers from low current efficiency. While several deoxidation methods for molten salt electrolysis have been developed, existing electrolytic approaches continue to face challenges, including intricate oxide electrode fabrication, low current efficiency, and difficulties in separating metal from the molten salt.

Further removal of dissolved oxygen from titanium metal is crucial. In 2006, Zhu Hongmin et al. [16] from the University of Science and Technology Beijing proposed a new electrolytic method for titanium production, termed the USTB process, successfully producing high-purity titanium (>99.9%) on the cathode. This method utilizes TiC_xO_y solid solution as the anode and a steel rod as the cathode in a KCl-NaCl molten salt. During the anodic reaction, titanium ions dissolve into the molten salt, simultaneously releasing CO/CO_2 gas on the anode surface. Under the influence of the electric field, titanium ions migrate to the vicinity of the cathode and deposit as metallic titanium [17]. Zhu Hongmin et al. achieved low-oxygen titanium metal with an oxygen concentration below 210 ppm through the USTB electrolysis of TiC_xO_y. Subsequently, Wang et al. [18] successfully produced titanium with an oxygen concentration less than 300 ppm using $TiC_{0.25}O_{0.25}N_{0.5}$ as the anode for electrolysis. Tian et al. [19] proposed a liquid zinc cathode for the electrolysis of Ti-Zn alloys in KCl-NaCl molten salt using cast $TiC_{0.5}O_{0.5}$ as the anode material. The results showed that Ti^{2+} from the cast $TiC_{0.5}O_{0.5}$ anode was directly reduced to Ti on the liquid Zn cathode. This method successfully yielded Ti-Zn alloy. Jiao et al. [20] employed molten salt electrolysis to recover titanium from waste titanium alloy, using a TC4 alloy plate as the anode and a nickel plate as the cathode. At 1023 K, titanium with a purity of 99.94% was successfully collected on the cathode. The USTB process exhibits advantages such as short process flow, high reduction efficiency, cleanliness, and direct extraction of high-purity titanium metal, currently recognized as the most promising new method for titanium metallurgy.

The USTB process demonstrates unique potential in molten salt electrolysis, minimizing disproportionation reactions and overcoming the drawbacks of low current efficiency encountered in FFC and OS methods. However, the USTB method still faces challenges related to impurities in the product and difficulties in deoxygenating large-scale electrolytic products. Therefore, optimization is still required for the production of low-oxygen, high-purity titanium using the USTB process. Oxygen is a detrimental element in titanium, and its high solubility in titanium (9000 mass ppm of O in β-Ti at 1300 K) and strong affinity for titanium make deoxidation a significant challenge [21]. Excess oxygen concentration in titanium products negatively impacts the physical, chemical, and mechanical properties of titanium and its alloys, reducing ductility and significantly affecting mechanical performance, fracture toughness, and fatigue resistance [22]. Therefore, efficient deoxidation is crucial. There is an urgent need for an economical, efficient, and environmentally friendly method for directly removing oxygen from titanium. Reducing oxygen concentration helps improve titanium's mechanical and processing properties, mitigating potential brittleness issues during usage. Titanium with a purity exceeding 99% is classified as pure titanium, where a higher purity signifies lower impurity concentration in the metal. Compared to regular titanium, pure titanium exhibits superior mechanical performance and biocompatibility, making it highly valuable in aerospace, biomedical, and other fields. Consequently, reducing the oxygen concentration and enhancing titanium purity is of paramount importance.

Rare earth elements exhibit unique physical and chemical properties, making their deoxidation processes a subject of extensive research. Rare earth chlorides are commonly employed as deoxidants in this domain. Yttrium (Y), a relatively abundant element in the Earth's crust even exceeding lithium or lead [23], stands out as a particularly effective deoxidant compared to other rare earth metals like La, Ce, Pr, and Nd. Okabe et al. [24] from the University of Tokyo conducted thermodynamic analyses of deoxidation of titanium (Ti) by rare earth metals, including yttrium (Y) and light rare earth metals (La, Ce, Pr, and Nd). Their findings revealed that under Y/Y_2O_3 equilibrium at 1300 K, a highly reducing atmosphere with an oxygen partial pressure of 10^{-41} atm is achieved, resulting in an oxygen concentration in Ti as low as 200 ppm by mass. Under Y/YOCl/YCl_3 equilibrium at 1300 K, a lower oxygen partial pressure can be achieved compared to Y/Y_2O_3 equilibrium, theoretically reducing the oxygen concentration in Ti to 10 ppm or even lower. Iizuka et al. [25] developed a novel sintering process, involving the placement of titanium sponge and yttrium (Y) in a molten salt, to remove oxygen from titanium. At 1300 K, oxygen removal from titanium using metallic Y in the molten salt enabled sintering of titanium powder and precise oxygen concentration control, achieving oxygen concentrations ranging from 30 to 2000 ppm. Zheng et al. [26] proposed a novel electrochemical deoxidation process for titanium using a mixture of magnesium chloride and yttrium chloride ($MgCl_2$-YCl_3) as a flux. In this new process, titanium and carbon serve as the cathode and anode, respectively. Experimental results indicated that under conditions of 1200 to 1300 K, the process produced Ti with an oxygen concentration of less than 500 ppm (sometimes around 100 ppm O by mass). Kamimura et al. [27] conducted deoxidation experiments at 1200 K using cerium chloride as the deoxidant. Under Ce/CeOCl/$CeCl_3$ equilibrium, the oxygen concentration in Ti could be reduced to less than 100 ppm O by mass. So far, the deoxygenation of titanium has been studied by many scholars (Table 1).

Table 1. Existing processes related to research.

Year	Author	Experimental Program	Ref.
2000	Chen et al.	Electrochemical experiments using TiO_2 as raw material and $CaCl_2$ as electrolyte.	[7]
2002	Ono and Suzuki et al.	Electrochemical experiments using TiO_2 as raw material and Ca as electrolyte.	[12]
2005	Okabe and Park et al.	Calcium as electrolyte for direct preparation of titanium powder from TiO_2 via electron-mediated reactions.	[15]
2006	Hongmin Zhu et al.	Titanium metal obtained electrochemically by using TiC_xO_y as raw material and NaCl-KCl as electrolyte.	[16]
2014	Wang et al.	Electrochemistry using $TiC_{0.25}O_{0.25}N_{0.5}$ as raw material in NaCl-KCl.	[18]
2020	Tian et al.	Electrochemical experiments using $TiC_{0.5}O_{0.5}$ as raw material in NaCl-KCl.	[19]
2019	Zheng et al.	Electrochemical deoxygenation using YCl_3 as deoxidizer.	[26]
2020	Iizuka et al.	Thermochemical deoxidation with Y as deoxidizer.	[25]
2022	Kamimura et al.	Thermochemical deoxygenation using Ce as deoxidizer.	[27]

This research initially examines the potential advantageous regions of rare earth elements in deoxidation through thermodynamic calculations. Subsequently, experiments were conducted based on deoxidation theory, employing various analytical techniques such as XRD, SEM-EDS, and ONH Analyzer for characterizing the electrolytic products, including the process of phase reconstruction, the microstructure and morphology of the product, and its elemental composition. Thermodynamic analysis indicates that yttrium chloride (YCl_3) exhibits exceptional deoxidation efficiency among rare earth chlorides, leading to its selection as the primary focus of this study. At 1073 K, the theoretical Y/YOCl/YCl_3 equilibrium achieves a lower oxygen partial pressure compared to Y/Y_2O_3 equilibrium [28,29]. Simultaneously, soluble anode electrolysis for titanium production has garnered significant research interest due to its promising potential. This study combines thermodynamic research with soluble anode electrolysis for titanium production and deoxidation technology using rare earth yttrium chloride. The addition of yttrium chloride as a deoxidant to the molten salt further enhances the deoxidation efficiency of soluble anode electrolysis for titanium production. This research investigates the impact of yttrium chloride as a deoxidant on the purity and oxygen concentration of the electrolytic products obtained from titanium-carbon-oxygen solid solutions. This work advances the progress of molten salt electrolysis for titanium production and provides theoretical foundations and research insights for the production of high-purity titanium via soluble anode electrolysis.

2. Experimental

2.1. Experimental Materials

This study employed commercially available TiO_2 powder (white powder, mass fraction ≥99.00%, Shanghai Aladdin Biochemical Technology Co., Ltd., Shanghai, China) and high-purity graphite as raw materials. The reagents used were NaCl (mass fraction ≥99.5%, white particles, Tianjin Zhonglian Chemical Reagent Co., Ltd., Tianjin, China), KCl (mass fraction ≥99.5%, white particles, Sichuan Longxi Science Co., Ltd., Chengdu, China), and anhydrous YCl_3 (mass fraction ≥99.9%, white powder, Suzhou Kang peng Chemical Co., Ltd., Gao chun Chemical Co., Ltd., Suzhou, China). The gasses used include Ar (≥99.999 vol%, Kunming Peng Yi Da Gas Products Co., Ltd., Kunming, China). A graphite crucible was used for the experiments. Table 2 provides a comprehensive list of the materials and chemical reagents used in this study.

Table 2. The materials and chemicals used in the experiment.

Materials/Chemicals	Morphological	Purity/Model	Supplier
TiO_2	White powder	≥99.00%	Shanghai Aladdin Biochemical Technology Co., Shanghai, China
C	Black powder	≥99.99%	Ivana Tianwang Graphite Products Co., Dongguan, China
NaCl	white granule	≥99.5%	Tianjin Zhonglian Chemical Reagent Co., Tianjin, China
KCl	white granule	≥99.5%	Sichuan Longxi Science Co., Chengdu, China
YCl_3	White powder	≥99.9%	High Pure Chemical Co. Suzhou Compon Chemical Co., Suzhou, China
Graphite Crucible			Henan Xinwang Special Graphite Products Co., Zhengzhou, China
High purity Ar		≥99.999 vol%	Kunming Pengyida Gas Products Co., Kunming, China

2.2. Experimental Procedure

2.2.1. Preparation of Titanium Oxy Carbonitride

TiC_xO_y (where $y = 1 - x$) was prepared by carbothermal reduction method in a high temperature tube furnace (JF22090028-02, Hangzhou Jiayue Intelligent Equipment Co., Ltd., Hangzhou, China) using titanium dioxide and graphite as raw materials. In order to observe the deposition of the cathode after electrolysis of soluble anode, different molar ratios were set for small scale exploration. The corresponding reaction formula is shown in Equation (1) as follows:

$$TiO_2 + (1 + 2x)\cdot C = TiC_xO_{1-x} + (1 + x)\cdot CO \quad (1)$$

To obtain $TiC_{0.45}O_{0.55}$, $TiC_{0.5}O_{0.5}$, $TiC_{0.55}O_{0.45}$, $TiC_{0.6}O_{0.4}$, and $TiC_{0.65}O_{0.35}$, we varied the value of x in reaction (1) to 0.45, 0.5, 0.55, 0.6, and 0.65, respectively. This resulted in theoretical molar ratios of TiO_2 to graphite of 1:1.9, 1:2, 1:2.1, 1:2.2, and 1:2.3, respectively. Raw materials were weighed according to these molar ratios at room temperature and thoroughly mixed. To enhance the shaping of the sintered titanium-carbon-oxygen solid solution, 2 wt% to 4 wt% ethyl cellulose was added as a binder. The well-mixed raw materials were then pressed into 10 mm diameter and approximately 4 mm thick disks weighing 1.8 ± 0.05 g using a YP-24T manual powder press (Tianjin Jin Fu run Technology Co., Ltd. Tianjing, China) under a pressure of 10 MPa. The pressed samples were subsequently placed in alumina crucibles and sintered using a high-temperature tube furnace. The sintering process was conducted at 2873 K for 4 h. The entire sintering process was carried out under an argon protective atmosphere, as illustrated in the experimental flow diagram shown in Figure 1. After sintering, the reaction products were characterized using X-ray diffraction (X'pert3powoer).

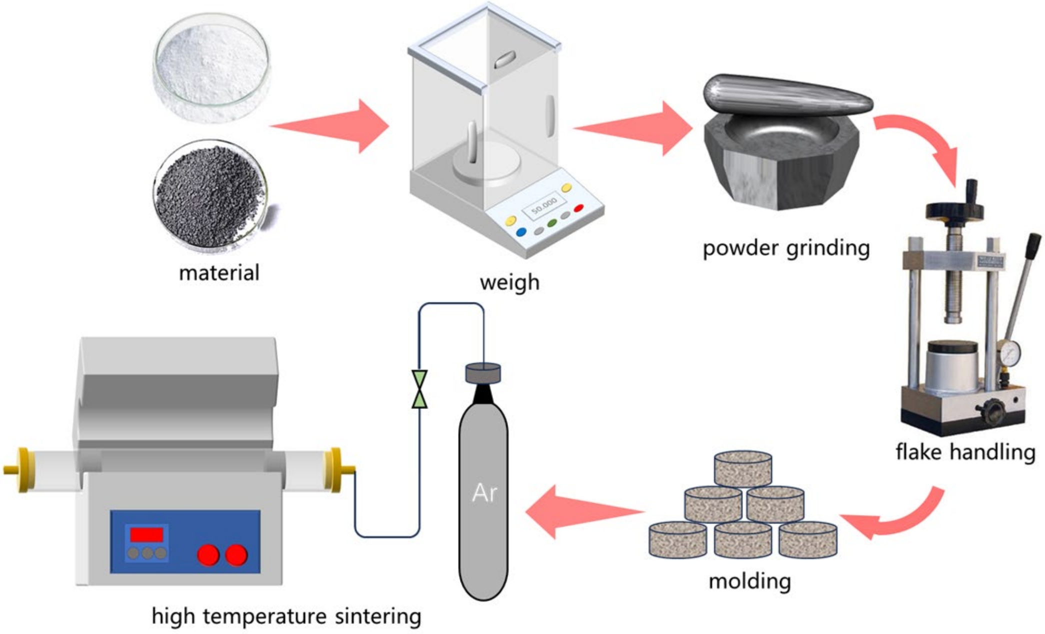

Figure 1. Experimental preparation at high temperature of 1600 °C.

2.2.2. Titanium Metal Preparation

The electrolyte was prepared by mixing equimolar amounts of KCl, NaCl, and YCl_3. The mixture was then vacuum-dried at 473 K for 24 h to remove moisture, followed by drying at 673 K for 48 h. The pre-melted salt was cooled under high-purity argon and then transferred to a glovebox for storage. The prepared sample was used as the anode for titanium deposition experiments conducted using an electrolytic cell (JF22090028-01, Hangzhou Jiayue Intelligent Equipment Co., Ltd., Hangzhou, China). The sample was placed at the bottom of a graphite crucible, serving as a consumable anode, with a molybdenum rod as the cathode. The titanium deposition experiment was conducted in a KCl-NaCl-YCl_3 molten salt bath. A mixture of KCl and NaCl (molar ratio 1:1) was weighed and homogenized before being added to the graphite crucible. YCl_3 was added to the mixture at a concentration of 0.5 wt%. The crucible was then placed in a molten salt electrolysis furnace(Hangzhou Jiayue intelligent equipment Co., LTD., Hangzhou, China). Under an argon atmosphere, the temperature was raised to 800 °C; all electrolysis experiments were conducted at this temperature. Constant voltage electrolysis was performed at 2.85 V for 48 h. During electrolysis, the anode was continuously consumed, with carbon monoxide (CO) being the primary gaseous product. Upon dissolution, titanium ions diffused to the cathode, where they deposited to form low-oxygen titanium. After the experiment, the cathode product was chemically etched with dilute hydrochloric acid (volume ratio 1:10) to remove residual salts and Y_2O_3. The etched product was then sequentially washed with deionized water and anhydrous ethanol. Finally, the cathode product was dried under vacuum at 60 °C for 2 h. X-ray diffraction (XRD, Rigaku Smart L ab SE, Tokyo, Japan) was used to identify the phase composition of the cathode product. Microstructural analysis was performed using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) (ZEISS Sigma 300, German). A schematic representation of the electrolysis experiment is shown in Figure 2.

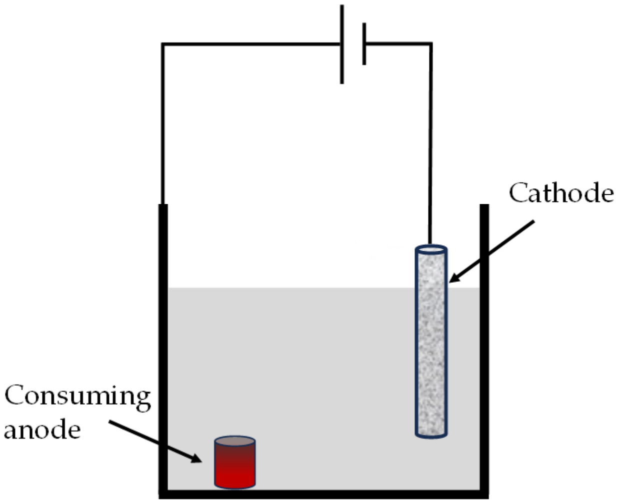

Figure 2. The schematic diagram of the electrolysis experiment.

3. Results and Discussion

3.1. Characterization of TiC_xO_y

The prepared samples were characterized using XRD analysis. The powdered samples were loaded into a sample holder and gently pressed against the sample holder surface using a frosted glass slide to ensure a flat surface. The holder was then placed in a sample tower and inserted into the diffractometer for analysis. The testing range was 2θ: 5–90°, with a scan rate of 10°/min. The radiation source employed was Cu-Kα, with a tube voltage of 40 kV and a current of 40 mA. Figure 3 presents the XRD patterns of the titanium-carbon-oxygen solid solutions synthesized via high-temperature sintering in a tube furnace. Comparing the obtained patterns with the standard card database [30], the peaks corresponding to PDF #86-2352 and PDF #32-1383 can be clearly identified as TiO and TiC, respectively. The appearance of these new peaks suggests a chemical reaction between TiO and TiC during high-temperature sintering at 1600 °C, leading to the formation of a new crystalline structure, the titanium-carbon-oxygen solid solution. XRD analysis conclusively confirms the synthesis of the titanium-carbon-oxygen solid solution, as opposed to a simple mixture of TiO and TiC [2,16,29,31].

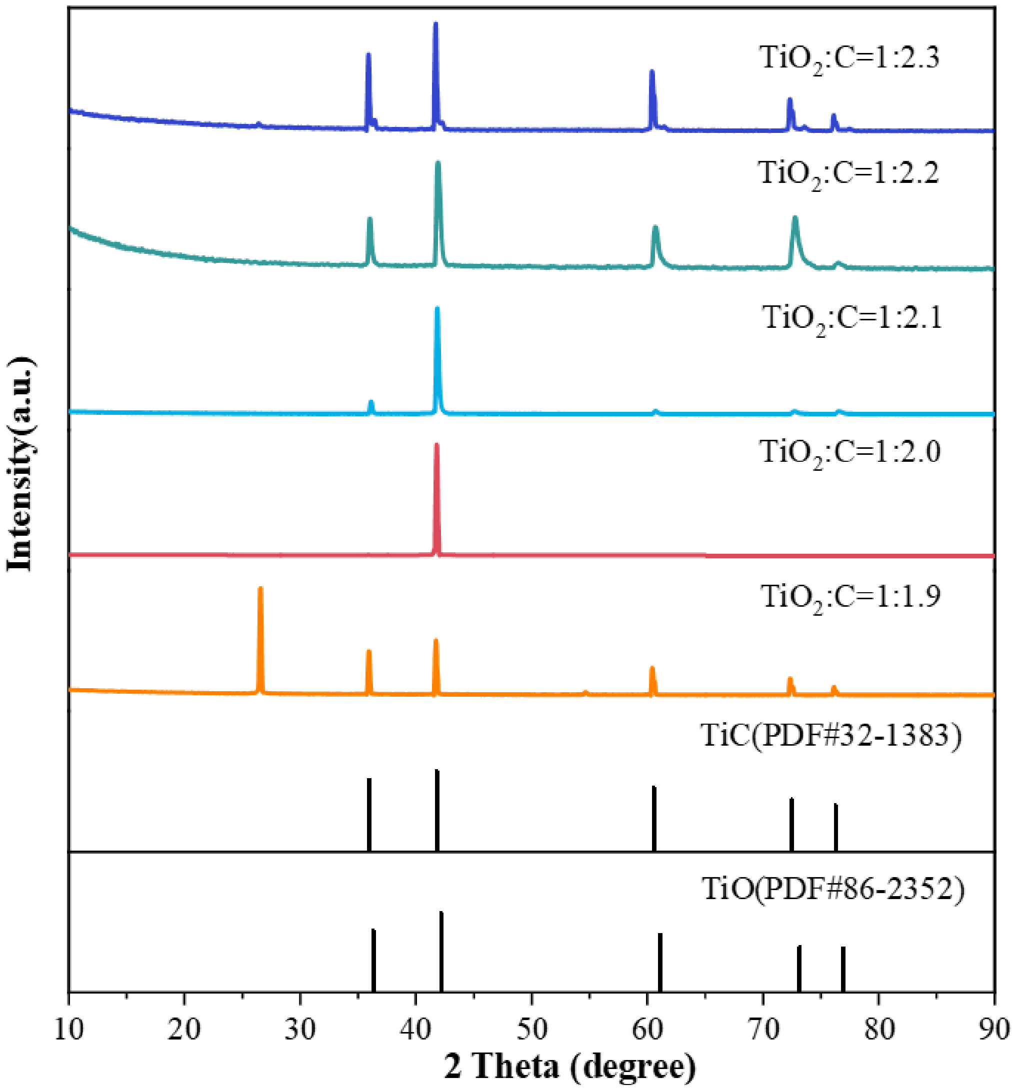

Figure 3. XRD patterns of samples with different molar ratios of TiO_2 and graphite mixtures after holding at 1600 °C for 4 h in argon atmosphere.

When the ratios of TiO_2 and graphite powder were 1:1.9, 1:2, and 1:2.1, SEM was used to test the micro-morphology of the sample surface and the phase distribution after holding at 1600 °C for 4 h to analyze the evolution pattern. As can be seen from the figure, the sample contains many micron-sized grains, which are connected together to form a coral-like structure with many holes. By zooming in on the coral-like structure in the figure, it can be seen that the surface of the grains has a layer-like microstructure similar to steps, which indicates that the formation mechanism of titanium-carbon-oxygen solid solution is layer-by-layer growth. The enlarged diagrams in Figure 4a–c show that the atomic size shows a gradually decreasing trend, which is due to the gradual decrease in the carbon concentration in the sample, and the decrease in the amount of substituted oxygen in the reaction with TiO_2, resulting in the high oxygen concentration in the sample, and thus the gradual decrease in the grain size.

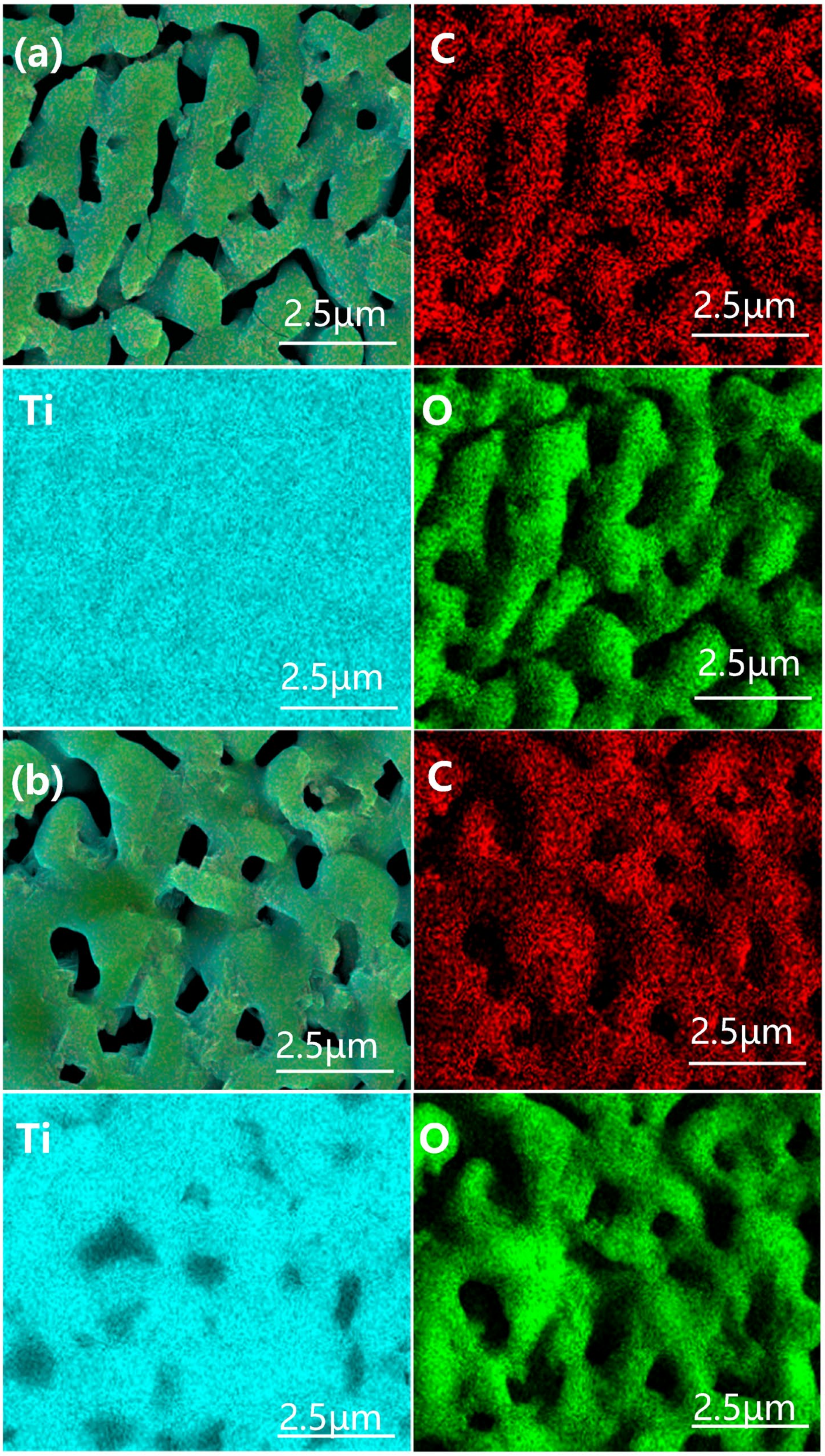

Figure 4. *Cont.*

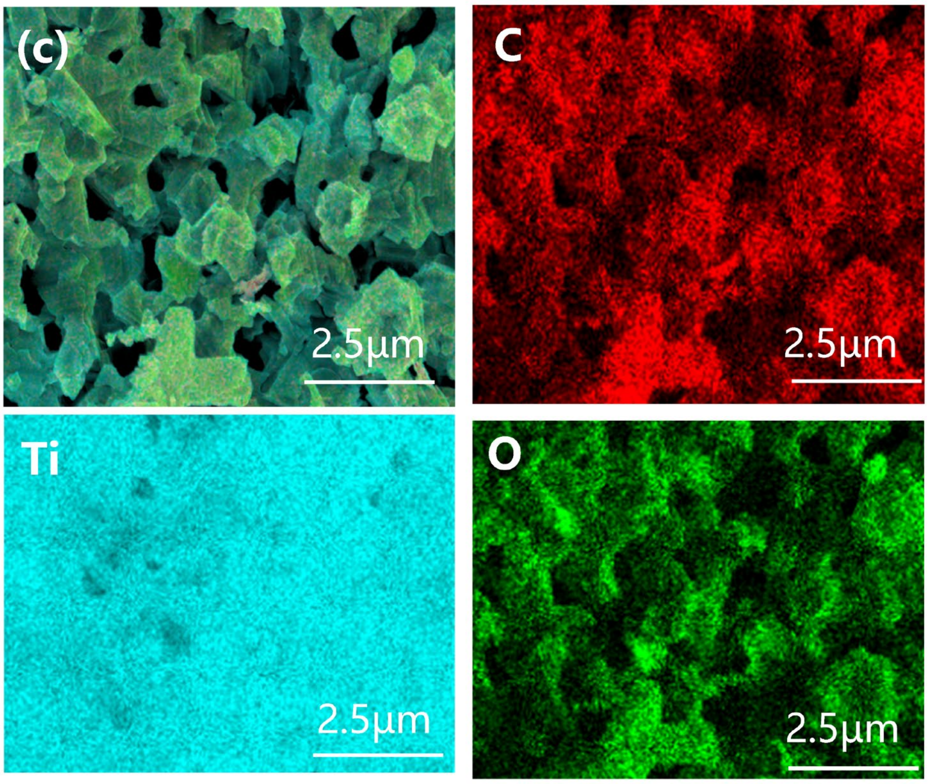

Figure 4. Microscopic morphology of samples with different molar ratios of TiO_2 and graphite mixtures after holding at 1600 °C for 4 h in argon atmosphere and results of compositional detection. (**a**) 1:1.9; (**b**) 1:2.0; (**c**) 1:2.1.

3.2. Electrolyte Product Analysis

3.2.1. Phase Analysis

In this study, we investigated the phase composition and crystal structure of the cathode deposits obtained through soluble anode electrolysis using various molar ratios of reactants. Five different anode materials with varying TiO_2:C ratios were prepared. The cathode deposits were subjected to XRD analysis to determine their phase composition. Figure 5 presents the XRD patterns of the cathode deposits obtained after electrolysis. Bulk/thin film (thickness $\geq$ 0.1 cm) samples were mounted on glass/aluminum sample holders and analyzed using an X-ray diffractometer. The scan range was 2–135°, with a scan rate of 1–10°/min. The radiation source was Cu-Kα, with a tube voltage of 40 kV and a current of 40 mA. The prominent diffraction peak corresponding to PDF#04-004-9042 in the XRD patterns indicates the presence of titanium (Ti), as confirmed by comparison with the standard card database [16]. These XRD peaks reveal that the electrolytic products obtained from the five different anode materials predominantly consist of titanium (Ti). The varying proportions of the anode materials significantly affect the phase composition and deposition amount of the cathode deposits.

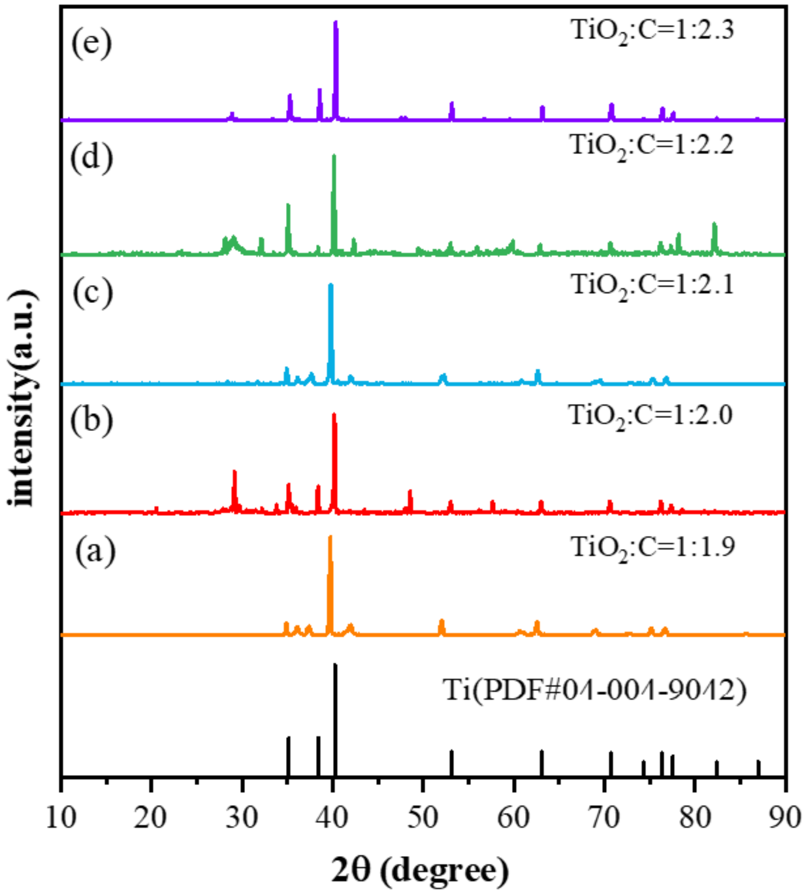

Figure 5. XRD images of electrodeposited products on cathode at 800 °C for different molar ratios of soluble anodes. (**a**) 1:1.9; (**b**) 1:2.0; (**c**) 1:2.1; (**d**) 1:2.2; (**e**) 1:2.3.

3.2.2. Microscopic Topography Analysis

The SEM-EDS point scan analysis in the Figure 6 revealed subtle differences in the elemental composition of the titanium metal produced using different TiO_2:C ratios. When TiO_2:C ratios were 1:1.9, 1:2, 1:2.1, 1:2.2, and 1:2.3, the oxygen concentration was measured as 0.64%, 0.57%, 0.61%, 0.65%, and 0.49%, respectively. The chlorine concentration was 0.01%, 0.01%, 0.01%, 0.00%, and 0.12%, respectively, while the titanium concentration was 99.35%, 99.36%, 99.38%, 99.39%, and 99.42%, respectively. The oxygen concentration of 6000 ppm after testing by the ONH analyzer further shows that yttrium chloride has a significant effect on electrolytic deoxygenation.

A decreasing trend in oxygen concentration was observed with increasing TiO_2:C ratios. This can be attributed to the reduced carbon concentration, leading to a decrease in its oxygen reduction capability. On the other hand, higher TiO_2:C ratios might lead to increased oxygen concentration due to the higher proportion of TiO_2 in the solid solution, which inherently contains a higher oxygen concentration. Moreover, variations in the solid solution structure and composition could influence their stability during electrolysis, ultimately affecting the final oxygen concentration in the titanium metal. Importantly, the titanium concentration remained consistently high within the range of 99.35% to 99.42% across all TiO_2:C ratios, indicating that the obtained titanium metal was close to pure titanium, as shown in Table 3.

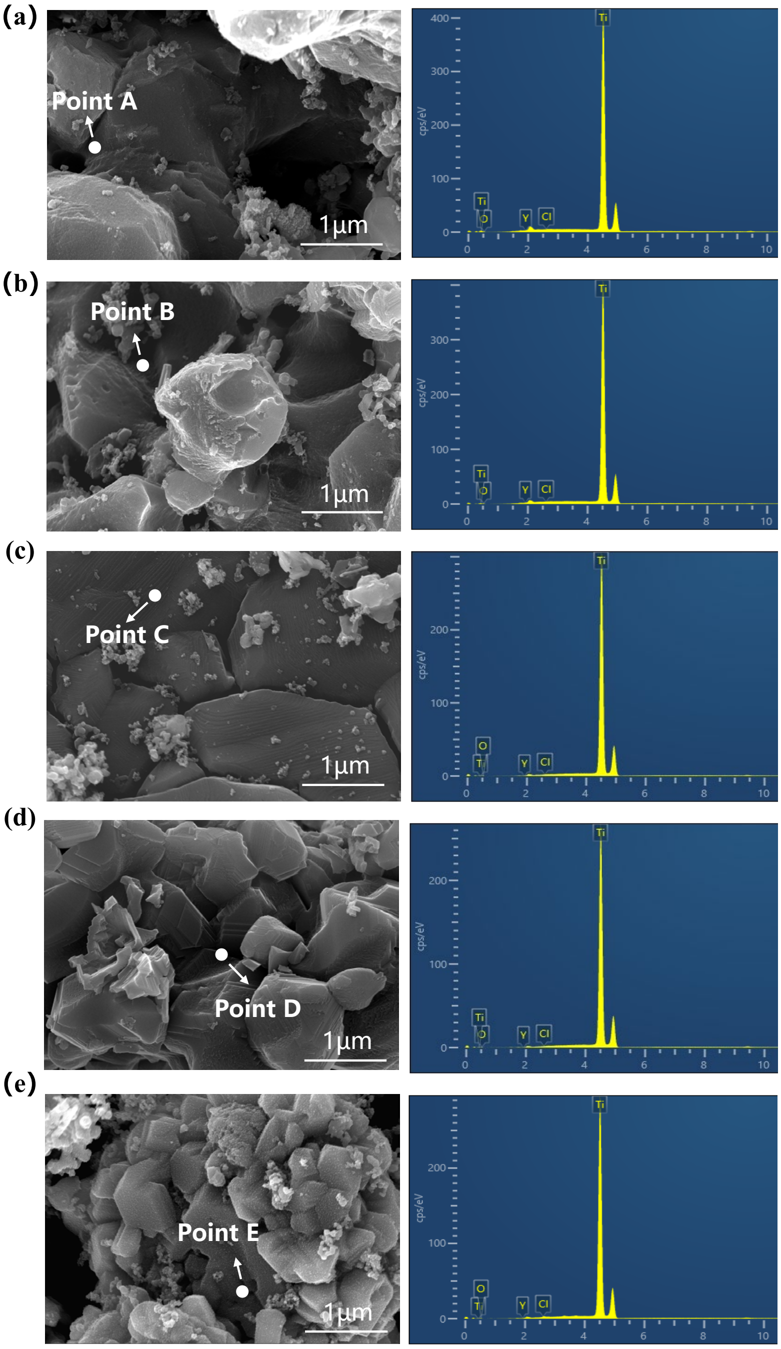

Figure 6. SEM images of electrodeposited products on the cathode at 800 °C for different molar ratios of soluble anodes. (**a**) 1:1.9; (**b**) 1:2.0; (**c**) 1:2.1; (**d**) 1:2.2; (**e**) 1:2.3.

Table 3. The EDS component detection results for the corresponding regions in Figure 6.

TiO_2:C (Molar Ratio)	Ti (wt.%)	O (wt.%)	Cl (wt.%)	Y (wt.%)
1:1.9	99.36	0.64	0.01	0.00
1:2.0	99.42	0.57	0.01	0.00
1:2.1	99.38	0.61	0.01	0.00
1:2.2	99.35	0.65	0.00	0.00
1:2.3	99.39	0.49	0.12	0.00

In summary, our findings demonstrate a significant correlation between the TiO_2:C ratio in titanium-carbon-oxygen solid solutions and the oxygen concentration of the resulting titanium metal, while the titanium concentration remains relatively stable. This suggests that controlling the TiO_2:C ratio can effectively modulate the purity of titanium metal, offering a novel approach for producing titanium with specific desired properties.

4. Conclusions

Soluble anode electrolysis for titanium production offers significant advantages in terms of enhancing titanium purity, reducing production costs, minimizing the environmental impact, and meeting market demands. This research utilizes the carbothermal reduction method to synthesize titanium-carbon-oxygen solid solution with varying molar ratios by heating at 1600 °C for 4 h in a high-temperature tube furnace. These titanium-carbon-oxygen solid solutions are then employed as anodes for the electrochemical production of low-oxygen titanium metal in a KCl-NaCl-YCl_3 molten salt bath. Thermodynamic calculations confirm the deoxidation capabilities of yttrium during the electrolysis process. At 1073 K, constant voltage electrolysis at 2.85 V results in the deposition of a substantial amount of black titanium product on the cathode, with an oxygen concentration of 6000 ppm. Notably, microstructural analysis using SEM-EDS revealed that the titanium metal obtained under different TiO_2:C molar ratios exhibits exceptionally high purity, ranging from 99.35% to 99.42%. This approach offers a novel perspective and theoretical foundation for research on the production of low-oxygen, high-purity titanium via molten salt electrolysis.

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