UDC 669.295
DOI: 10.15587/1729-4061.2023.276746

DEVELOPMENT OF A TECHNOLOGY TO PRODUCE TITANIUM POWDER WITH A LOW CARBON FOOTPRINT

Andrii Gonchar
Corresponding author
Deputy Chief Executive Officer-Technical Director*
Director **
E-mail: andriy.gonchar@innovativetio2.com
Viktor Troshchylo
General Director*
Technical Director **
Andriy Brodskyy
President
VELTA HOLDING US INC
King str., 1226, Wilmington, New Castle, USA, 19801
Volodymyr Yarovynskyi
Innovation Director
Titanera LLC
Glinki str., 7, Dnipro, Ukraine, 49000
Oleksandr Chukhmanov
Chief Chemist *
*VELTA RD TITAN LLC
Glinki str., 7, Dnipro, Ukraine, 49000
**RD Titan Group Ltd
Stryiska str., 3, vil. Solonka, Ukraine, 81131

This paper reports the analysis of modern technologies for the production of titanium from oxide raw materials. It has been established that current industrial methods for producing titanium require the use of carbon as a reducing agent and, accordingly, cannot decrease carbon emissions without changing the technology. That is why devising a technology for producing titanium with a reduction in emissions of carbon components is a relevant task. So, the object of research is the technology of obtaining titanium from its oxide without the use of carbon components. It was found that an integrated approach to the preparation of raw materials and the separation of reduction processes with the successive use of two types of reducing agents – magnesium and calcium, made it possible to create an effective process for producing titanium without the use of carbon reducing agents. The influence of calcium and magnesium chlorides as promoters of the reduction process was revealed. Experimental studies have established that the shape and density of raw materials significantly affect the efficiency of the reduction process by streamlining the reducing agent flows and reaction products in the furnace charge. The established regularities made it possible to improve the process of reduction of titanium oxide to obtain samples of titanium powders with an oxygen content of 0.17 %, which corresponds to international standards for titanium alloys and powders. Additional plasma treatment made it possible to obtain materials that were suitable for additive processes in all respects. A systematic approach to the utilization of reaction products made it possible to devise a technological scheme in which all possible waste is either returned to the technological process after treatment or processed into marketable products. Based on the results of the study, a technological scheme for obtaining powders of titanium alloys from titanium oxide by complex reduction in two stages – magnesium and calcium – was developed. The proposed scheme involves standard metallurgical processes and is brought to standard processes and equipment of metallurgical enterprises and chemical industry.

In terms of practical significance, the results of this work could be used in the development of industrial technology to produce titanium from titanium dioxide without the use of carbon components

Keywords: titanium powders, titanium dioxide, dendrite, titanium deoxidation, carbon footprint, reduction

Received date 16.01.2023
Accepted date 26.03.2023
Published date 28.04.2023

How to Cite: *Gonchar, A., Troshchylo, V., Brodskyy, A., Yarovynskyi, V., Chukhmanov, O. (2023). Development of a technology to produce titanium powder with a low carbon footprint. Eastern-European Journal of Enterprise Technologies, 2 (6 (122)), 42–54. doi: https://doi.org/10.15587/1729-4061.2023.276746*

1. Introduction

Titanium is an important element of the periodic system of chemical elements, which in its pure form or in the form of compounds can be used both in the construction of aerospace vehicles in the form of metal alloys [1, 2], and for decorating homes, cars, equipment, and other things in the form of oxide, which is a pigment filler of paint, plastic, or paper [3–5]. Due to its exceptional properties, it is possible to use metallic titanium and its alloys in nuclear industry [6] and for medical applications [7]. Corrosion endurance and low specific density contribute to the use of titanium alloys in the construction of ships, aircraft, and chemical equipment, as well as sports equipment [8–11]. Significant use of titanium alloys is observed in the construction of military equipment [12, 13]. In the last 8 years, powder metallurgy in the form of additive processes has gained traction, for which the quality and cost of powder compositions are critically important [14–16].

The main obstacle to the wider use of titanium alloys is the complexity of the technology of obtaining primary titanium from the feedstock with the subsequent production of titanium alloys and powders [17–19].

The restrictions imposed in the world on technological processes that produce significant carbon emissions force industry to either improve existing manufacturing technologies or devise fundamentally new production schemes. Since standard titanium manufacturing schemes require the use of carbon as a reducing agent in significant volumes, the development of carbon-free titanium production technologies is an urgent issue. Thus, scientific research into the processes of reduction of titanium raw materials will contribute to the choice of effective technological solutions in the development of appropriate industrial processes.

2. Literature review and problem statement

For a long time, new methods for producing titanium have been developed and researched. According to conducting techniques, they can be divided into the following groups:

– thermochemical reduction processes that use titanium tetrachloride as a feedstock;

– thermochemical reduction processes that use titanium dioxide (TiO_2) as a feedstock;

– electrochemical processes.

Other processes are combinations of the above methods.

The basic industrial technique for producing primary titanium is the Kroll thermochemical process. According to the industrial interpretation of this method, the technological scheme for producing titanium involves the following stages: obtaining titanium slag with a high content of titanium dioxide, chlorination of titanium slag, purification of titanium tetrachloride to an acceptable level, reduction of titanium tetrachloride with magnesium, and vacuum heat treatment of sponge titanium [20].

The alternative to the use of a reducing agent, Hunter's industrial process follows a technological pathway similar to the Kroll process. In the Hunter process, sodium acts as a reducing agent, which affects some features in the management of the titanium reduction process from tetrachloride and necessitates the processing of sodium chloride salt after the reduction process.

The resulting product of both industrial processes is spongy titanium in the form of a powder or sponge with a particle size of less than 70 mm, mainly 2–25 mm.

Alloys with the addition of alloying elements are subsequently smelted from sponge titanium, or titanium powders are made by grinding.

The technological operations, most dangerous from the point of view of negative impact on the external environment, in the process of titanium production are the production of titanium slag from ore raw materials and its chlorination. The technology of ore-thermal smelting to obtain slag is used to increase the titanium content in raw materials for chlorination since it is not often common to find a high titanium content in ore materials. Suitable for effective industrial use, natural titanium (ilmenite) concentrates contain from 37 % to 75 % titanium dioxide. Economically justified for chlorination titanium materials must contain more than 72 % TiO_2. With a lower content of useful raw materials, the cost of production increases significantly due to the formation of a significant amount of chlorination waste. Ore-thermal smelting and chlorination of titanium-containing oxide materials occurs with the release of a significant amount of carbon oxides.

According to stoichiometry, in the production of titanium slag, in terms of 1 ton of TiO_2, 0.35 tons of carbon monoxide are formed, and when chlorinating titanium slag in terms of 1 ton of $TiCl_4$ – 0.29 tons of CO. Accordingly, it is these processes that significantly affect the overall carbon footprint of titanium production. An option to overcome the problem of using carbon in the reduction process may be devising a fundamentally new technology for producing titanium.

Industrial processes according to the methods of Hunter and Kroll have a proven technological cycle and consistently high product quality. The main producers of titanium according to these technologies are China, Kazakhstan, Japan, Ukraine, the United States of America, and Russia. But they practically cannot solve the issue of excluding carbon from the technological process.

Alternative techniques for producing titanium by thermochemical reduction of titanium tetrachloride have not been industrially introduced up to 2023. Vapor Phase Reduction and CSIR-Ti technologies use, as a reducing agent, magnesium in various forms – powder or vapor. In works [21, 22], powdered magnesium and titanium tetrachloride are fed into the apparatus where titanium is reduced. However, the residual content of oxygen and chlorine remains quite high (about 0.3 wt%) due to the high dispersion of the resulting product. Study [23] proposes to implement a high-temperature process in which the reaction occurs in the gas phase. The resulting product, with a particle size of 1–30 μm, requires purification from reaction products. However, the content of oxygen, magnesium, and nitrogen exceeds the permissible limits.

Since these technological advancements use $TiCl_4$ as the starting product, they do not solve the issue of reducing emissions of carbon components.

Sodium-thermal technologies are represented by Armstrong and ARC processes, which use metallic sodium as a reducing agent. A potential advantage of these methods is the ability to create continuous processes [24].

However, in comparison with conventional technologies, the quality of the resulting product obtained from the above methods is worse in terms of the content of detrimental impurities. Since oxygen has the greatest influence on the strength and ductility of titanium alloy products, its content is strictly regulated by standards. The results of the studies reported in [25], according to available data, have at least twice the oxygen content in the final product. The reason for this is the contamination of titanium with reaction products, the removal of which by chemical or thermal methods leads to the oxidation of active dispersed titanium.

The devised technologies for obtaining high-quality titanium from oxide raw materials by thermochemical methods also face the problem of obtaining a high-quality product with a low content of critical impurities. Such processes require high temperatures and pressures. One of the processes, which, according to the available data, makes it possible to obtain titanium powders with an acceptable oxygen content (<0.15 %) uses a complex reduction scheme employing explosive substances – hydrogen in large quantities [26].

Electrochemical techniques for producing titanium cause significant use of electricity; besides, they have problems with the presence of carbon materials in the process, which either pollute the resulting product or generate greenhouse gases [27, 28]. None of the electrochemical processes for producing titanium has reached the stage of industrial implementation.

The situation with the production of titanium alloy powders looks even more dramatic. Standard methods for producing powders are:

– spraying of a rotating workpiece (PREP);

– gas atomization (GA);

– plasma atomization (PA);

– hydrogenation-dehydrogenation (HDH) [29].

But all these processes require a workpiece with a given content of alloying elements. To this end, they use the methods of vacuum melting (arc or electron beam), or powder metallurgy (mixing elementary powders with subsequent heat treatment). According to this technological scheme, the cost of titanium alloy powders increases several times compared with the primary sponge titanium [14]. The reason for this is the need for multiple melts to average the chemical composition and achieve a uniform distribution of alloying elements in titanium. Also, the atomization of titanium from the melt is a high-energy and technologically complex process.

There is a group of technological advancements resulting in the production of titanium alloy powders from titanium raw materials directly, without smelting ingots. However, they all have drawbacks. When obtaining a powder according to the method from [30], it is necessary to use finely dispersed explosive powders of alloying elements, which are active metals. In the process reported in [31], the production of alloyed powders occurs through the production of titanium slag (TiO_2) with reducing additives in titanium slag to form purified TiO_2. The technique may also include the reduction of purified TiO_2 using a metal reducing agent to form a hydrogenated titanium product containing TiH_2. This product requires additional operations to bring the product to industrial quality standards. The metallothermic process of chloride reduction by a complex reducing agent in the form of magnesium and hydrogen [32] requires the production of titanium tetrachloride mixed with alloying elements, which in no way decreases the carbon footprint of the titanium production process. Patent US10316391B2 [33] describes the way in which a composition containing a source of titanium oxide is loaded into the reaction chamber along with an excess magnesium source. Such compositions may include Mg powder, Mg granules, Mg nanoparticles, or Mg/Ca eutectic mixture. It is desirable that the reduction of the composition containing the source of titanium oxide occurs without direct physical contact with the composition containing the magnesium source, in order to reduce the potential for contamination of the resulting titanium product. Then the reaction chamber is closed with a lid, saturated with noble gas, and heated to an internal temperature of 800–1000 °C. As soon as the temperature is sufficient to evaporate Mg, the reaction would begin.

The reaction is carried out for at least 30 minutes, and preferably between 30 minutes and 120 minutes. The reaction chamber is then cooled to room temperature and the resulting products are washed with one or more flushing agents. Flushing agents include dilute acids (such as HCl, HNO_3, and H_2SO_4) and water (such as deionized water) but are not limited to them. In other embodiments, the Mg^{2+} impurities can be removed by rinsing with water or dilute acid with sonication. Then the resulting product is dried.

In this technique, the reduction process is difficult or does not proceed completely. Also, the issues of oxygen content in the finished product remained unresolved. The reason for this may be the blocking of titanium oxide particles by the products of the reduction reaction and the cessation of access of fresh portions of magnesium vapors to the particles surface. Because of this, not only is the required level of reduction not achieved, but also side reactions occur that adversely affect the equipment. An option to overcome the corresponding difficulties may be the formation of a structure of the components of the reduction process, which will ensure the effectiveness of transport reactions.

During many years of research, the authors of works [34, 35], by using magnesium-thermic reduction of titanium dioxide (TiO_2), were able to achieve deep deoxidation through the use of a rotary tube reactor, which provided a heterophase reduction reaction. The minimum oxygen content was about 3 %. However, industrializing such a process and scaling equipment to achieve industrial performance will be a rather complicated process due to a high hazard level of dispersed magnesium and titanium.

Therefore, the issue of the mechanism for effective reduction of titanium without the use of carbon reducing agents remains unresolved.

All this suggests that it is expedient to conduct a study on the development of a technology for obtaining high-quality powders of titanium and its alloys with minimal greenhouse gas emissions.

3. The aim and objectives of the study

The purpose of our research is to determine the patterns and conditions of the process of titanium production without the use of carbon reducing agents, under which there is an effective reduction of titanium oxide by a metal reducing agent. This will make it possible to devise a carbon-free scheme for obtaining the finished product in the form of titanium powder with quality at the level of international standards.

To accomplish the aim, the following tasks have been set:

– to determine the influence of granulometric indicators of raw materials on the process of titanium oxide reduction;

– to determine the optimal and effective way to form the structure of raw materials for the most effective reduction;

– to determine the optimal reduction scheme;

– to determine the quality of the resulting product and compare it with commercial products available on the titanium powder market, as well as to assess compliance with the requirements of industry standards.

4. The study materials and methods

4. 1. The object and hypothesis of research

The object of research is the processes of reduction of titanium from the oxide form. The main problem of high-quality reduction of titanium dioxide is the slowing down of the process due to the blocking of the reducing agent by the reaction products. Therefore, when forming a corresponding porous or capillary structure in raw materials, it is possible to achieve conditions for effective mass transfer during the process. The reduction of titanium oxide in two stages will contribute to the more effective elimination of reaction products that block the deoxidation of titanium. The two-stage reduction will also increase the economic performance of the process through the use of different-cost reducing agents. The use of catalysts or promoters of the reduction process will make it possible to control the process of titanium formation.

4. 2. Investigated materials and equipment used in the experiment

To obtain titanium powders, titanium dioxide was used as a feedstock, both a commercial product and the synthetic titanium dioxide of our production. As a commercial product, titanium dioxide of the anatase modification Kronos 1000 and the rutile modification Pretiox R-200 were investigated. Titanium dioxide of our production was obtained by hydrolysis of titanium oxychloride, followed by calcination (i-synrutile) (Fig. 1). The use of such a titanium production scheme is due to the fact that ilmenite concentrates contain a significant amount of impurities in their composition [36]. When recovering titanium from ilmenite, most impurities will go to the final product – titanium powder, which is unacceptable.

The particle size of titanium dioxide Kronos 1000 (manufactured by Kronos), Pretiox R-200 (manufactured by Precheza) was 0.1–0.5 µm, and that of the i-synrutile sample was 10–30 µm (Fig. 1). The study of titanium dioxide microparticles was carried out on a scanning electron microscope Tescan Mira 3 LMU (Czech Republic).

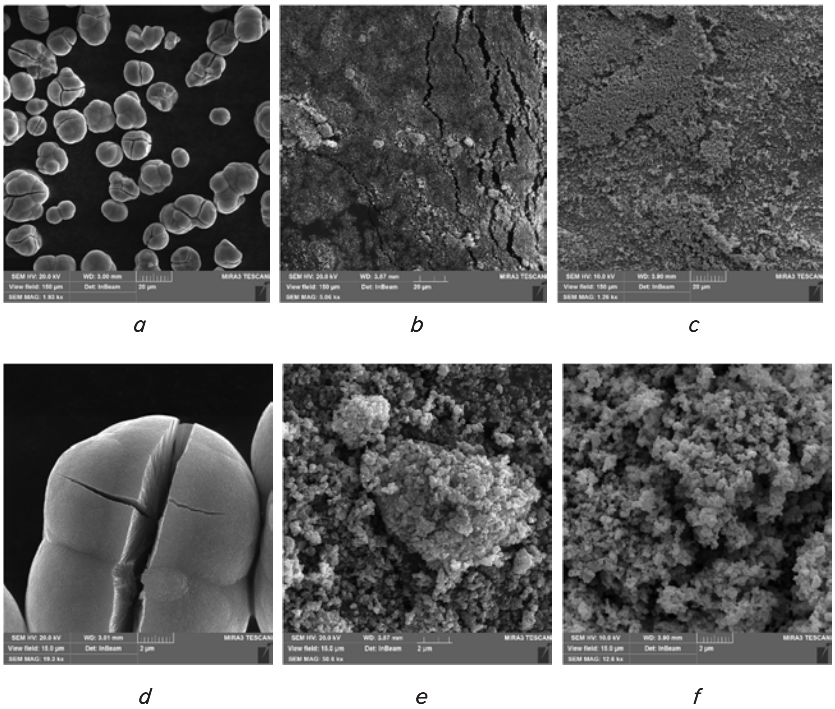


Fig. 1. Scanning electron microscopy (SEM) images of titanium dioxide samples used for research: *a* – i-synrutile; *b* – Pretiox R-200; *c* – Kronos 1000 (the area of the field for viewing all images is 22500 µm); *d* – i-synrutile; *e* – Pretiox R-200; *f* – Kronos 1000 (viewing field area – 225 µm)

The i-synrutile titanium dioxide was made from ilmenite concentrate of the Byrzulove deposit (Kirovohrad oblast, Ukraine) using a patented technology [37, 38]. The different fractional composition of samples of commercial titanium dioxide and i-synrutile is explained by the peculiarities of titanium dioxide production technologies, which contribute to the formation of titanium dioxide particles of various sizes.

The particle granulometric characteristics were determined by laser diffraction (ISO 13320:2009 Particle size analysis – Laser diffraction methods) using the CILAS 990 Particle Size Analyzer (France).

4. 3. Procedure for determining the physicochemical properties of samples

The degree of sphericity of titanium powders was determined using the Hall volumeter (ASTM B988-18).

The determination of oxygen in titanium powders was carried out by the method of reducing melting in the current of inert carrier gas (ASTM E1409-13 (2021)) using ELTRA ON 900 equipment (Germany).

Nitrogen was determined using the Kjeldal method (DSTU 3083.1-95. Spongy titanium. Method for determining nitrogen). The carbon content was determined by induction heating (DSTU 3083.3-95. Spongy titanium. Methods for determining carbon) using ELTRA CS 800 equipment (Germany).

The content of iron, magnesium, and calcium impurities was determined using the ICP-AES method (ASTM E2371-21a) using Thermo Electron IRIS Intrepid II equipment (USA).

5. Results of investigating titanium dioxide reduction

5. 1. Investigation of the influence of properties and the technique of feedstock formation for the most effective reduction

The process of reducing titanium dioxide in general is as follows:

$$TiO_2+2Me=Ti+2MeO, \qquad (1)$$

where Me is a reducing metal (magnesium or calcium).

After the reduction, leaching of the reaction products – reducing agent oxides – was carried out using acid solutions.

The reduction of titanium dioxide samples in powder form was ineffective. The average oxygen content in samples after reduction was 10–19 %. It does not matter which (metallic magnesium or metallic calcium) and with what excess the reducing agents were taken since the reduction reaction did not proceed completely due to the blocking of particles of the material being reduced by the products of the reduction reaction. As a result, there was a cessation of access of fresh portions of the reducing agent to the particles surface, which is why not only the required level of reduction was not achieved but also the reducing agent was wasted.

Empirically, it has been established that the formation of feedstock elements with the specified porosity and strength allows for the reduction process with maximum efficiency (Fig. 2).

The strength of feedstock elements from ground titanium oxide powder must be at least 10 kg per 1 cm^2 since with less strength there will be a destruction of the element and a decrease in the number of capillary pathways of entry of the reducing agent to the material. Since the source titanium dioxide has a different particle size distribution, the obtained samples of feedstock elements differed significantly in characteristics (Fig. 3).

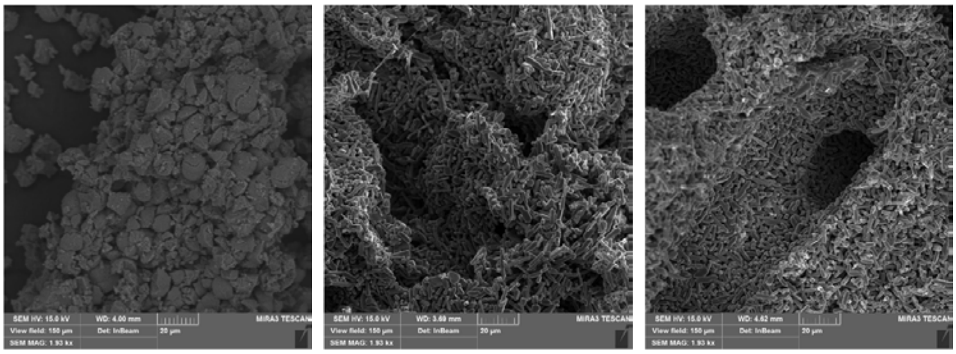
Fig. 3 demonstrates that the samples made from commercial titanium dioxide Kronos 1000 and Pretiox R-200 have both large pores formed by the voids in the material and micropores between the titanium dioxide particles. In the sample of the feedstock element made from i-synrutil, there are practically no macropores but the interparticle micropores have slightly larger sizes, which is due to the particle size.

a *b*

Fig. 2. Photographs of feedstock elements made from titanium dioxide: *a* – single feedstock elements; *b* – charge of loaded feedstock elements

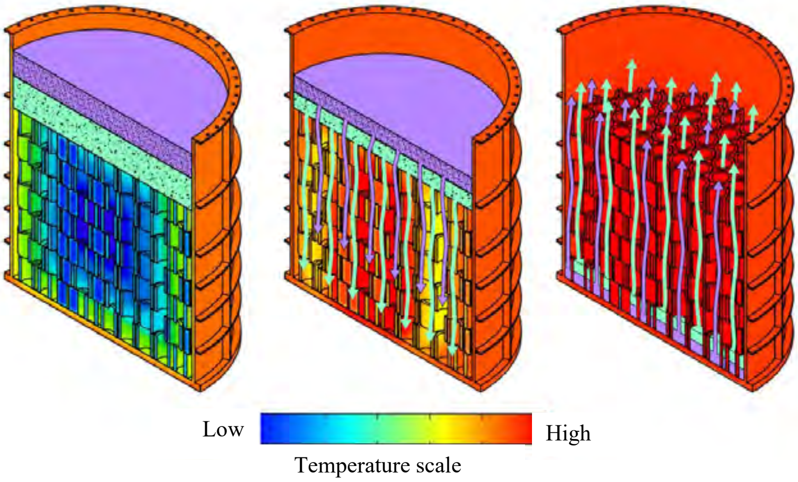
To ensure the effective course of the reduction process, the way to load feedstock elements in the 1st stage of reduction and the reducing agent is important, which allows reduction using reducing agent vapors (Fig. 4).

Properly formed stack ensures uniform distribution of the thermal field of the process during the heating stage (Fig. 4, *a*). An important aspect is the placement of feedstock elements in such a way that their holes are directed vertically. This arrangement makes it possible to organize the impregnation of the entire volume of feedstock elements by the reducing agent (light blue layer in the upper part of the charge) and its chloride (purple layer) during the melting of calcium or magnesium (Fig. 4, *b*). Also, this technique of forming the charge provides the most optimal gas dynamics for the reduction by reducing agent vapors (Fig. 4, *c*), which is a very important factor for the successful course of the process. Due to the shape and placement of feedstock elements, gases have a free flow from bottom to top and from top to bottom, which ensures a high level of circulation of gases and their penetration into all parts of the material being reduced.



a *b* *c*

Fig. 3. Microstructure of feedstock elements made from different types of titanium dioxide: *a* – i-synrutile; *b* – Kronos 1000; *c* – Pretiox R-200



a *b* *c*

Fig. 4. Scheme of loading feedstock elements into the reactor and temperature distribution scale: *a* – heating of the charge; *b* – melting of the reducing agent; *c* – reduction of titanium dioxide

This ensures a high level of heat transfer and the heat is more evenly distributed between different parts of the material being reduced. It also provides access of the required amount of reducing agent vapors to the material being reduced. Also, this process prevents excessive growth and sintering of metal titanium particles, precipitation of oxides of reducing agents on the walls and bottom of the crucible/retort.

5. 2. Investigation of the effect of particle size on reduction efficiency

Table 1 gives data on oxygen content in samples obtained after the initial reduction of feedstock elements made from the titanium dioxide Pretiox R-200, Kronos 1000, and i-synrutile. Metallic calcium was used as a reducing agent.

Table 1

Oxygen content in titanium samples after the first stage of feedstock elements reduction, depending on the starting material

Sample No.	Starting Material	Starting Material Particle Size, µm	Oxygen Content in the Sample after Reduction, %
1	Pretiox R-200	0.10–0.50	8.46
2	Kronos 1000	0.05–0.30	8.63
3	i-synrutile	10–30	3.39

Table 1 demonstrates that the oxygen content in the samples after the first stage of reduction is significantly different. Our studies have established that the efficiency of titanium oxide reduction to metallic titanium depends on the particle size of crystalline titanium oxide, from which feedstock elements are formed for reduction. So, if the particles of titanium oxide are too small, for example, if titanium oxide pigment with primary particle sizes of 0.10–0.50 µm is used, it is extremely difficult to obtain titanium metal with low oxygen values during the reduction process. This is probably associated with the blocking of the reducing agent's access to titanium dioxide due to the formation of CaO and MgO reduction reaction products.

5. 3. Determining the optimal reduction scheme

The choice of a reducing agent is primarily related to the efficiency of titanium deoxidation and the possibility of industrialization of the process. Magnesium and calcium are the main reducing agents used in the reduction of titanium. Magnesium has advantages over calcium as a reducing agent due primarily to economic issues. The cost of metallic magnesium on the market is about 2 to 4 times lower than the cost of metallic calcium; besides, the amount of magnesium used for reduction is about 1.67 times lower in terms of stoichiometry.

Another advantage of the use of magnesium is its availability on the world market (overall production is about 1 million tons per year against 35–50 ktpa of metallic calcium) [39, 40]. Also important is the high purity of magnesium, especially with regard to such impurities as nitrogen and carbon, and lower requirements in terms of storage and safety of handling. Unlike metallic calcium, metallic magnesium is quite resistant to environmental influences, including air humidity and carbon dioxide contained in the air. Metallic calcium is significantly more reactive; contact with moisture leads to a violent chemical reaction with the release of hydrogen and a large amount of heat. In addition, calcium is oxidized by atmospheric oxygen to form calcium oxide, which then, upon contact with moisture in the air, turns into calcium hydroxide. Calcium oxide and hydroxide are highly reactive against carbon dioxide and capture CO_2 from the air. This feature eventually leads to an increase in the content of carbon in calcium, which then passes into titanium during the reduction process and impairs its quality. Therefore, in the production of calcium and in all stages of further work with it, reliable protection against contact with air and moisture must be provided.

To increase the reduction efficiency, reducing agent chlorides ($MgCl_2$ and $CaCl_2$) were also used to be added as promoters of the process. In our opinion, the important functions of these salts in the first stage of reduction, when exothermic reduction reactions proceed at high speed, are the following:

1. Decreasing the temperature of the material being reduced due to the fact that part of the heat that released during the reduction reaction is spent on heating, melting, and the formation of magnesium or calcium chlorides vapors, which keeps the material being reduced from uncontrolled overheating. Overheating is highly undesirable as it can lead to the destruction of feedstock elements and deterioration of reduction results. Also, increasing the temperature too high can lead to contamination of titanium being reduced with crucible/retort material and even to destruction of the crucible/retort in which the reduction is carried out.

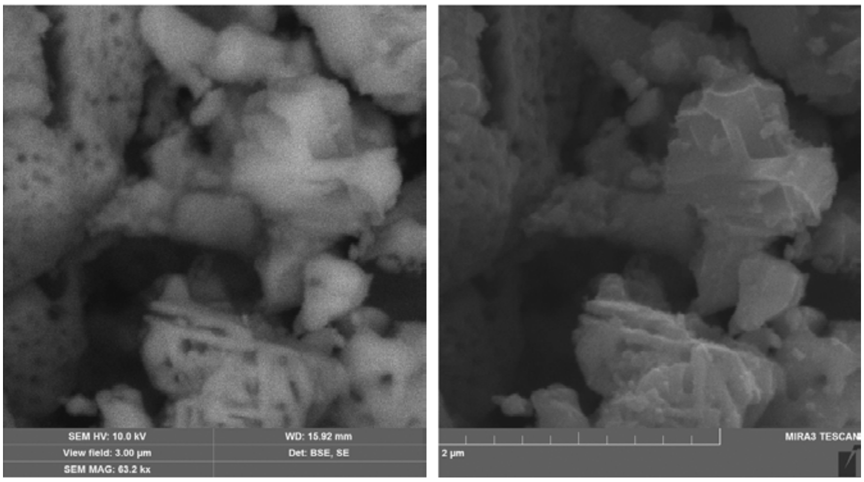
2. Promoting a more even distribution of heat between all parts of the material being reduced and the reducing agent due to the partial evaporation of magnesium and calcium chlorides and the transfer of heat by these heat vapors to other zones. This ensures the heating of the material being reduced and the reducing agent in all zones and the simultaneity of the reduction process.

Another important function of melts of reducing salts is their ability to dissolve reducing agent oxides. For example, the solubility of MgO in molten magnesium chloride ($MgCl_2$) is 0.63–2.90 mol % at 1073–1373 K and 0.24–0.63 mol **%** in pure calcium chloride ($CaCl_2$) melt at a temperature of 1223–1523 K [41]. As for calcium oxide, its solubility in the melt of calcium chloride increases significantly with increasing temperature and reaches a value of 18–22 mol % in the range of 1100–1300 K [42, 43].

So, due to this, partial dissolution of magnesium or calcium oxides in melts of magnesium or calcium chlorides occurs on the surface of the material being reduced. This ensures the access of fresh portions of the reducing agent to feedstock elements and the continuation of the reduction process, which is blocked by the corresponding oxides. It also contributes to the consolidation of titanium particles and their growth and, accordingly, to the reduction of the specific surface area. Fig. 5 shows SEM images of the particles of titanium metal after the 1st stage of reduction using magnesium without the use of promoters.

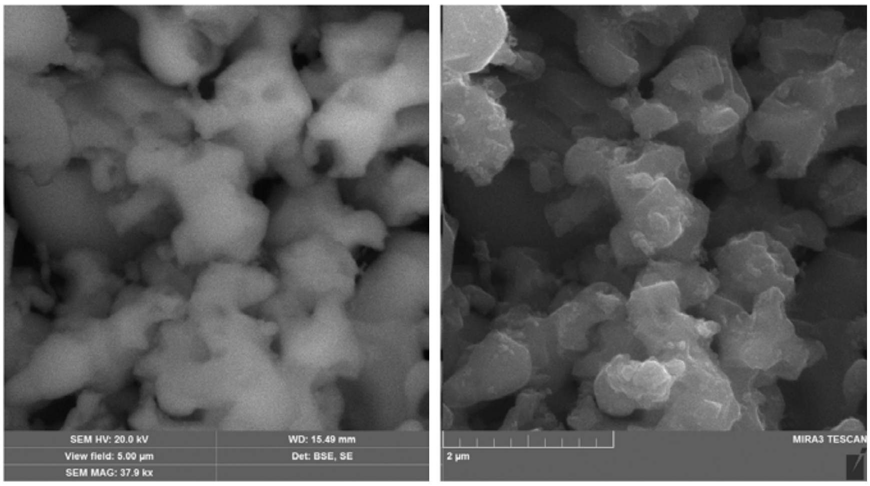
One can see that titanium particles obtained without the use of $MgCl_2$ have a smaller size and greater microporosity compared to the slightly larger titanium particles obtained using $MgCl_2$ as a process promoter. The microporosity of samples obtained using $MgCl_2$ is much smaller (Fig. 6).

Powders obtained using $MgCl_2$ in a single-stage reduction with the use of magnesium as a reducing agent consisted of dendritic particles with an extremely highly developed surface. Granulometric characteristics of the particles were determined and are given in Fig. 7.



a *b*

Fig. 5. Microstructure of the product of the reaction of single-stage reduction by metallic magnesium without using magnesium chloride as a promoter: *a* – image of a surface fragment built using a detector of elastically reflected electrons (Back Scattered Electron – BSE); *b* – image of a surface fragment built using a secondary electron detector (Secondary Electron – SE)



a *b*

Fig. 6. Microstructure of the product of the reaction of single-stage reduction by metallic magnesium using magnesium chloride as a reduction process promoter: *a* – image of a surface fragment built using a detector of elastically reflected electrons; *b* – image of a surface fragment built using a secondary electron detector

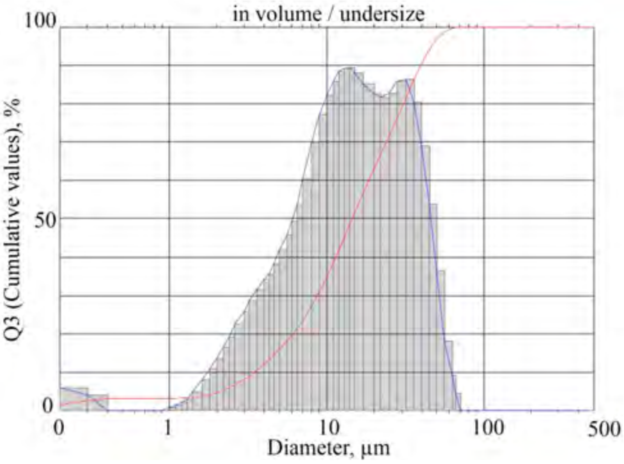


Fig. 7. Size distribution curve of titanium particles after single-stage reduction

Fig. 7 demonstrates that the titanium powder obtained during single-stage reduction has the following granulometric characteristics:

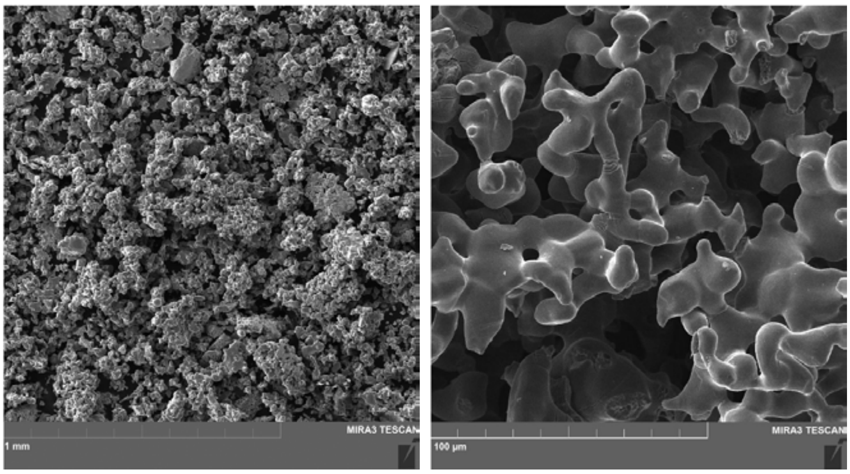
– D_{10}: 3.44 µm;
– D_{50}: 14.52 µm;
– D_{90}: 39.77 µm;
– mean diameter: 18,53 µm.

Using the proposed methods of feedstock preparation and techniques of carrying out the process in two stages of reduction with reducing agents of different types (the first stage – magnesium, the second stage – calcium), the samples of titanium powders were obtained (Fig. 8).

The powder consisted of coral-like particles with a highly developed surface but there are differences from the powder obtained in the 1st stage of reduction using magnesium as a reducing agent. In this case, there was a significant enlargement of the particle size, a significant decrease in the specific surface area, and a change in the morphology from the dendritic type to the coral-like type. Granulometric characteristics of titanium particles after two-stage reduction are:

- D_{10}:13.19 µm;
- D_{50}:46.47 µm;
- D_{90}:97.63 µm;
- mean diameter: 51.80 µm.

The curve of particle size distribution is shown in Fig. 9.



a *b*

Fig. 8. Titanium powder obtained by reducing titanium dioxide by a combined reducing agent in two stages (first stage — magnesium, second stage — calcium): *a* — viewing field area — 2250000 µm; *b* — viewing field area — 22500 µm

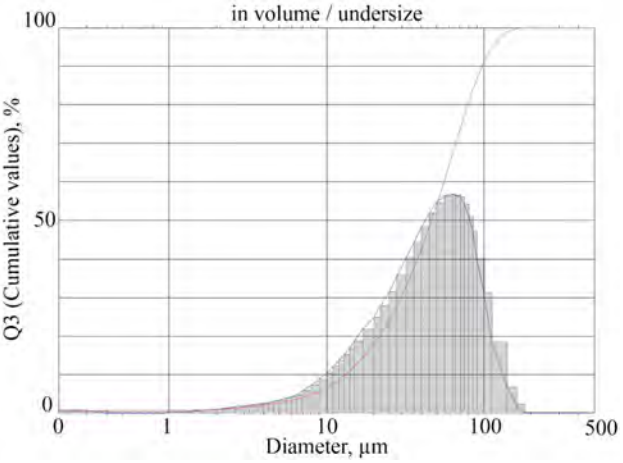
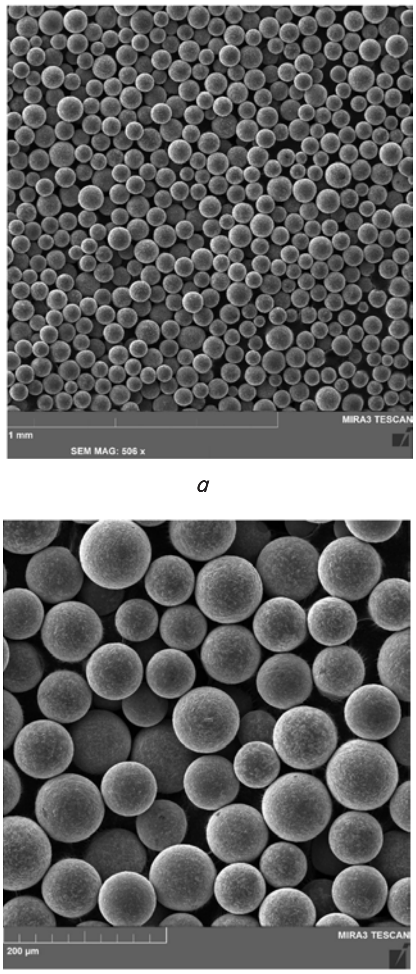


Fig. 9. The particle size distribution curve of titanium powder obtained by the reduction of titanium dioxide in two stages

Fig. 9 demonstrates that the main part of the material is made up of powder particles with a size of less than 100 µm. Compared to the single-stage process the average particle size is much larger. This is most likely due to the increase in the duration of the process and the tendency of titanium powder particles with a lower oxygen content and, accordingly, a smaller amount of reducing oxide content to consolidate on titanium particles surface. Further experiments established that it is possible to form particles of a given size by changing the reduction modes.

5. 4. Determining quality indicators of the resulting product according to various reduction schemes and post-processing

Our work also included plasma spheroidization of the resulting titanium powders using induction-plasma treatment. The introduction of this processing method allows for the production of spherical powders for use in various additive manufacturing techniques where a high degree of sphericity of particles and high fluidity are required (Fig. 10).



a

b

Fig. 10. Spheroidized titanium powder after induction-plasma treatment: *a* — viewing field area — 2250000 µm; *b* — viewing field area — 250000 µm

The content of impurities in titanium powders obtained by various methods is given in Table 2.

To determine the technical suitability of the resulting material, a comparison was made with commercial products available on the titanium powder market (Table 3).

To produce titanium powders with a lower oxygen content, further improvement of reduction technology is necessary.

Table 2 demonstrates that the effectiveness of calcium and magnesium reduction in single-stage reduction is comparable, despite the fact that in the Ellingam diagram (Fig. 11) calcium is below magnesium, indicating its greater potential for reduction.

Table 2

Chemical composition of titanium powders obtained by various methods

Sample No.	Reducing agent I/Reducing agent II	Content of Components, wt%					
		O	N	C	Fe	Mg	Ca
1	Mg/–	14.02	0.0063	0.0150	0.0067	1.8232	0.046
2	Ca/–	9.83	0.0131	0.0316	0.0510	0.0620	4.200
3	Mg+MgCl$_2$/–	3.15	0.0051	0.0143	0.0054	1.7617	0.031
4	Ca+CaCl$_2$/–	2.15	0.0145	0.0321	0.066	0.0640	2.020
5	Mg+MgCl$_2$/Ca	0.17	0.0232	0.0520	0.0243	0.0345	0.099
6	Mg+MgCl$_2$/Ca+PS*	0.17	0.0253	0.0531	0.0437	0.0002	0.007

*Note: *PS – Plasma Spheroidization*

Table 3

Impurity content and standard specifications of titanium alloy powders based on examples of products available on the market

No.	Titanium Powder Grade / Manufacturing Company	Content of Components, wt%					Powder Type/ Method of Production
		O	N	C	Fe	Mg	
1	TSP-100 (<150 μm)/Osaka Titanium technologies Co., Ltd	max 0.25	max 0.03	max 0.02	max 0.02	max 0.02	Irregular/HDH
2	TSP-350 (<45 μm)/Osaka Titanium technologies Co., Ltd	max 0.35	max 0.03	max 0.02	max 0.03	max 0.02	Irregular/HDH
3	TMP-100 (<150 μm)/Osaka Titanium technologies Co., Ltd	max 0.50	max 0.03	max 0.02	max 0.05	max 0.02	Irregular/HDH
4	TMP-350 (<45 μm)/Osaka Titanium technologies Co., Ltd	max 0.60	max 0.03	max 0.02	max 0.05	max 0.02	Irregular/HDH
5	Gr.1/Qishan Metal Titanium Co., Ltd. (MTCO)	max 0.25	max 0.03	max 0.02	max 0.08	max 0.02	Irregular/HDH
6	forAM CP-Ti G2 15–53 EG/Höganäs AB	max 0.17	max 0.03	max 0.03	max 0.08	–	Spherical/VIGA
7	forAM CP-Ti G2 45–106 EG/Höganäs AB	max 0.10	max 0.03	max 0.03	max 0.08	–	Spherical/VIGA
8	Cp-Ti Grade 2 (0–25 μm)/AP&C	max 0.21	–	–	–	–	Spherical/PA
9	Cp-Ti Grade 2 (15–45 μm)/AP&C	max 0.20	–	–	–	–	Spherical/PA
10	Cp-Ti Grade 2 (15–53 μm)/AP&C	max 0.20	–	–	–	–	Spherical/PA
11	Cp-Ti Grade 2 (20–63 μm)/AP&C	max 0.18	–	–	–	–	Spherical/PA
12	Cp-Ti Grade 2 (45–106 μm)/AP&C	max 0.16	–	–	–	–	Spherical/PA
13	Cp-Ti Grade 2 (45–150 μm)/AP&C	max 0.16	–	–	–	–	Spherical/PA
14	Cp-Ti Grade 1 (15–45 μm)/AP&C	max 0.16	–	–	–	–	Spherical/PA
15	Cp-Ti Grade 1 (15–53 μm)/AP&C	max 0.15	–	–	–	–	Spherical/PA
16	Cp-Ti Grade 1 (20–63 μm)/AP&C	max 0.12	–	–	–	–	Spherical/PA
17	Cp-Ti Grade 1 (45–106 μm)/AP&C	max 0.10	–	–	–	–	Spherical/PA
18	Cp-Ti Grade 1 (45–150 μm)/AP&C	max 0.10	–	–	–	–	Spherical/PA
19	OSPREY® Ti-6Al-4V Class 5/Sandvik AB	max 0.20	max 0.05	max 0.08	max 0.30	–	Spherical/GA
20	OSPREY® Ti-6Al-4V Class 23/Sandvik AB	max 0.13	max 0.05	max 0.08	max 0.25	–	Spherical/GA

According to theoretical calculations, when using calcium as a reducing agent, it is possible to achieve a residual oxygen content of 300–730 ppm [44, 45]. However, on a practical level, it is difficult to achieve a high degree of titanium oxide reduction in one stage due to the formation of a layer of the reaction product-calcium oxide-on the surface of metal titanium particles. This reaction product blocks access of new portions of the reducing agent to the particles, which slows down, or even completely blocks further reduction reaction.

As for the use of magnesium for reduction, it is precisely because of thermodynamic constraints that the theoretically possible oxygen content in the finished product will be at the level of 2–3 **%** [46, 47]. This figure is significantly higher than the standard requirements for the quality of titanium, so it is not suitable as a reducing agent for the second stage of reduction.

Thus, a technological scheme has been devised for obtaining metal titanium powder with the content of impurities at the level of international standards. Also, potentially, the technology makes it possible to obtain the full range of existing or prospective titanium alloys by joint reduction of titanium dioxide and oxides of alloying elements. This process excludes the use of carbon materials for reducing processes, that is, it significantly decreases emissions of carbon components into the atmosphere (carbon footprint).

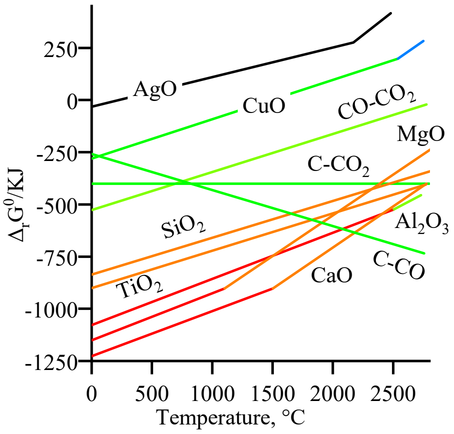


Fig. 11. Dependence of standard free energies of CO formation and oxides of different metals on temperature (Ellingam diagram)

Technological scheme includes:

– production of titanium dioxide with the predefined chemical and granulometric composition;

– formation of feedstock elements from ground titanium oxide powder with a strength of at least 10 kg per 1 cm^2;

– carrying out the first stage of feedstock elements reduction using a reducing agent (magnesium or calcium), the oxygen content in reduced titanium is typically ≥2 %;

– purification of metal titanium powder obtained after the first stage of reduction from the reaction products formed, reducing agent chlorides and unreacted reducing agent residues;

– carrying out the second stage of metal titanium powder reduction using a reducing agent (calcium), the oxygen content in the reduced titanium is in the range of ≤0.18–0.40 % depending on the desired grade;

– purification of metal titanium powder obtained after the second stage of reduction from the reaction products formed, reducing agent chlorides and unreacted reducing agent residues;

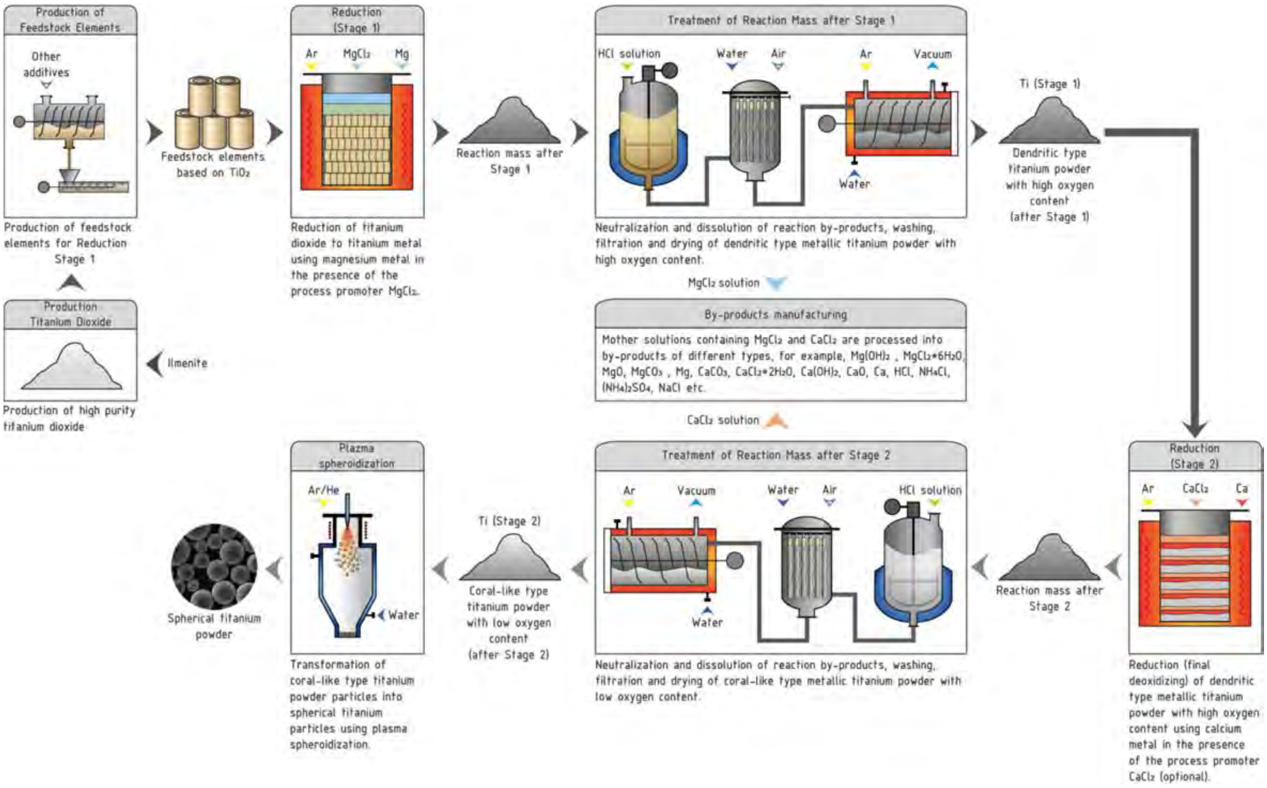
– plasma spheroidization of metal titanium powder obtained after the second stage of reduction (optional);

– classification by size;

– processing of reaction products after purification of the reduced titanium powder after the 1st and 2nd stages of reduction containing $MgCl_2$ and $CaCl_2$ into by-products of various types, for example, $Mg(OH)_2$, $MgCl_2{\cdot}6H_2O$, MgO, $MgCO_3$, Mg, $CaCO_3$, $CaCl_2{\cdot}2H_2O$, $Ca(OH)_2$, CaO, Ca, HCl, NH_4Cl, $(NH_4)_2SO_4$, NaCl, etc.

In general, the production scheme is shown in Fig. 12.

The technology of obtaining metal titanium powder of standard quality from titanium dioxide by the method of two-stage reduction has been developed. It is proposed to use magnesium as a reducing agent in the first stage of reduction, and calcium in the second stage. This approach increases the economic attractiveness of the developed technology and makes it possible to obtain high quality metal titanium powders.



Production of feedstock elements for Reduction Stage 1

Production of high purity titanium dioxide

Reduction of titanium dioxide to titanium metal using magnesium metal in the presence of the process promoter $MgCl_2$.

Neutralization and dissolution of reaction by-products, washing, filtration and drying of dendritic type metallic titanium powder with high oxygen content.

Mother solutions containing $MgCl_2$ and $CaCl_2$ are processed into by-products of different types, for example, $Mg(OH)_2$, $MgCl_2{*}6H_2O$, MgO, $MgCO_3$, Mg, $CaCO_3$, $CaCl_2{*}2H_2O$, $Ca(OH)_2$, CaO, Ca, HCl, NH_4Cl, $(NH_4)_2SO_4$, NaCl etc.

Reduction (final deoxidizing) of dendritic type metallic titanium powder with high oxygen content using calcium metal in the presence of the process promoter $CaCl_2$ (optional).

Neutralization and dissolution of reaction by-products, washing, filtration and drying of coral-like type metallic titanium powder with low oxygen content.

Transformation of coral-like type titanium powder particles into spherical titanium particles using plasma spheroidization.

Fig. 12. Technological scheme to produce titanium alloy powders from titanium dioxide

6. Discussion of results of the study on the development of carbon-free technology to produce metallic titanium from dioxide

With the help of our research, it was established that the particle size distribution of feedstock affects mainly the oxygen content in titanium (Table 1) and the porosity of feedstock elements (Fig. 3). Obviously, the developed technology, tested on individual samples, can be modified for the use of other similar raw materials.

It is determined that the main effect on the degree of titanium dioxide reduction is exerted by the effective heat transfer and transportation of the reducing agent and reaction products in the reactor volume. To ensure the necessary conditions for the process, the form and characteristics of the feedstock elements were determined (Fig. 2), as well as the technique to form the charge in the reactor (Fig. 4).

In contrast to [34], the task to obtain an oxygen content of less than 0.20 % by the reduction method was solved through a two-stage process (Table 2). However, in this case, it is desirable to use magnesium in the first stage, and calcium in the second one. This is primarily due to the economic benefits of using a cheaper reducing agent.

The use of magnesium chloride as a promoter of the process makes it possible not only to increase the efficiency of the reduction process but also creates conditions under which it is possible to additionally control the formation of titanium particles to the required size (Fig. 5–9).

In comparison with conventional methods, the developed two-stage reduction scheme makes it possible to implement the technological scheme of the process without the use of carbon reducing agents.

In contrast to the powder reduction system, the use of feedstock elements with the predefined porosity, which were formed from titanium dioxide with the predefined granulometric composition, made it possible to ensure active mass transfer during the reduction process.

According to the procedure devised, tests were carried out using titanium dioxide from various commercial manufacturers (Precheza, Kronos) as feedstock. Taking into account the comparable results, we believe that the developed technology is universal and suitable for the production of metal titanium from industrial titanium dioxide of various origins.

The proposed technological scheme (Fig. 12), in contrast to regular technologies according to the Kroll or Hunter methods, makes it possible to directly obtain metal titanium powders from oxide raw materials. At the same time, carbon reducing agents are not used, which contributes to a significant decrease in carbon footprint. Also, this scheme makes it possible to achieve a level of quality that corresponds to international (ASTM B348/B348M-21, ASTM B988-18, and GB/T 2524-2019), national (GOST 19807-91. Titanium and deformed titanium alloys), and industry standards. Comparison of the particle size distribution (Fig. 9) and the content of the main components with commercial samples (Table 3) shows that the developed technology makes it possible to obtain a competitive product. In addition, the proposed technological scheme, in addition to the grades of pure metal titanium (Grades 1–4), makes it possible to obtain various alloys of metallic titanium by joint reduction of titanium dioxide and oxides of alloying additives. At the same time, in the Kroll and Hunter processes only pure metal titanium is obtained, and the production of alloys requires additional stages of smelting titanium sponge with alloying additives.

The hardware and technological scheme of the two-stage reduction process involves standard operations of the chemical and metallurgical industry and mainly requires standard equipment. Consequently, it has every opportunity for industrialization.

It is worth paying attention to the fact that the achievement of stable indicators of oxygen content, or a further decrease in the oxygen content in titanium powders and its alloys faces a certain limitation. The fact is that part of the oxygen in the powder is associated with the surface of titanium powders. This surface is an oxide film – a thin layer of titanium dioxide with a thickness of ~3–10 nm [48–50]. Therefore, the achievement of these indicators will require the development of techniques for managing the specific surface area and its reduction. This is a challenge for future research.

It is impossible not to note that the results of research on the development of the technology are tied to a certain raw material – i-synrutile – with specified granulometric characteristics, which obviously imposes some restrictions on the industrialization of the process. This may be a potential limitation of the developed technology, namely, dependence on the content of detrimental impurities in the feedstock. The presence of a significant amount of impurities affects not only the quality of the final product but also the amount of waste generated.

At the same time, our results (Table 2) indicate that further improvement of the technology will expand the range of raw materials for commercial titanium dioxide products with a different range of physicochemical properties.

Further development of research should include the refinement of technology, industrial tests to improve the reduction processes in order to obtain a stable quality of titanium with an oxygen content at the level of 0.10–0.20 %. This oxygen content is a requirement of international standards for Grade 1 titanium powders and titanium alloys such as Grade 5, Grade 20, Grade 23, Ti-48Al-2Cr-2Nb, and others. Also, a promising direction is the research on the production of titanium alloy powders. The main purpose of these works is to determine the influence of a large-scale factor on the efficiency of the process from the point of view of technology industrialization.

7. Conclusions

1. Our studies have established the influence of particle size distribution characteristics of titanium dioxide on the reduction efficiency. The particle size affects the formation of the predefined structure of feedstock elements. The use of titanium dioxide particles less than 10 μm leads to a slowdown in reduction processes, due to the complexity of removal of reaction products.

2. The optimal parameters and structures of feedstock elements for the efficiency of the reduction process have been determined. The peculiarity of feedstock elements formation lies in the creation of a uniform thermal field and a branched capillary system for efficient mass transfer. This ensures a high level of heat transfer and the heat is more evenly distributed between different parts of the material being reduced. Also, this process prevents excessive growth and sintering of titanium metal particles, deposition of reducing agents oxides on the walls and bottom of the crucible/retort.

3. The optimal scheme of the process of titanium dioxide reduction in two stages, using magnesium in the first stage and calcium in the second one, has been determined. The influence of $CaCl_2$ and $MgCl_2$ as process promoters has been established. Promoters contribute to a more even heat distribution between

all parts of the material being reduced and the reducing agent due to partial evaporation of magnesium and calcium chlorides and the transfer of heat by these vapors to other zones. Also, their effect lies in the dissolution of reaction products formed on the surface of titanium being reduced and blocking the reduction. This improves access for reducing agents (magnesium, calcium) into the reaction zone and also contributes to the growth of particles and a decrease in the specific surface area of reduced titanium.

4. It has been established that the quality of products obtained as a result of our research meets the requirements of most industry standards and is not inferior to commercial products available in the market.

Conflicts of interest

The authors declare that they have no conflicts of interest in relation to the current study, including financial, personal, authorship, or any other, that could affect the study and the results reported in this paper.

This paper is a result of research conducted with the participation of several authors (co-authors), including inventors named in the patent. The use of concepts, definitions, and descriptions of technologies that make up the patent matter, in this paper does not cause a conflict of interest regarding the joint work (co-authorship) and application of patented objects and is not considered as a violation of the patent owner rights.

Funding

The authors express their gratitude to VELTA RD TITAN LLC for funding the research and the opportunity to publish the results for future fundamental changes in the global titanium industry.

Data availability

All data are available in the main text of the manuscript.

References

1. Williams, J. C., Boyer, R. R. (2020). Opportunities and Issues in the Application of Titanium Alloys for Aerospace Components. Metals, 10 (6), 705. doi: https://doi.org/10.3390/met10060705
2. Liu, S., Song, X., Xue, T., Ma, N., Wang, Y., Wang, L. (2020). Application and development of titanium alloy and titanium matrix composites in aerospace field. Journal of Aeronautical Materials, 2020, 40 (3), 77–94. doi: https://doi.org/10.11868/j.issn.1005-5053.2020.000061
3. Haider, A. J., Jameel, Z. N., Al-Hussaini, I. H. M. (2019). Review on: Titanium Dioxide Applications. Energy Procedia, 157, 17–29. doi: https://doi.org/10.1016/j.egypro.2018.11.159
4. Chen, M. C., Koh, P. W., Ponnusamy, V. K., Lee, S. L. (2022). Titanium dioxide and other nanomaterials based antimicrobial additives in functional paints and coatings: Review. Progress in Organic Coatings, 163, 106660. doi: https://doi.org/10.1016/j.porgcoat.2021.106660
5. Adams, R. (2022). Thirtieth anniversary conference: TiO2 & colour pigments in amsterdam. Focus on Pigments, 2022 (11), 1–4. doi: https://doi.org/10.1016/j.fop.2022.10.001
6. Kapustyan, A. Y., Ovchinnikov, A. V., Yanko, T. B. (2018). Syntered titanium alloys for nuclear industry. Questions of atomic science and technology, 1 (113), 134–141. Available at: https://vant.kipt.kharkov.ua/ARTICLE/VANT_2018_1/article_2018_1_134.pdf
7. Baltatu, M. S., Tugui, C. A., Perju, M. C., Benchea, M., Spataru, M. C., Sandu, A. V., Vizureanu, P. (2019). Biocompatible titanium alloys used in medical applications. Revista de Chimie, 70 (4), 1302–1306. doi: https://doi.org/10.37358/RC.19.4.7114
8. Taşdemir, A., Nohut, S. (2021). An overview of wire arc additive manufacturing (WAAM) in shipbuilding industry. Ships and Offshore Structures, 16 (7), 797–814. doi: https://doi.org/10.1080/17445302.2020.1786232
9. Li, M., Pan, Y., Zou, Y. (2021). Application and optimization design of Titanium alloy in sports equipment. Journal of Physics: Conference Series, 1820. doi: https://doi.org/10.1088/1742-6596/1820/1/012011
10. Zhang, L.-C., Chen, L.-Y. (2019). A review on biomedical titanium alloys: recent progress and prospect. Advanced Engineering Materials, 21 (4), 1801215. doi: https://doi.org/10.1002/adem.201801215
11. Froes, F. H., Qian, M., Niinomi, M. (Eds.) (2019). Titanium for Consumer Applications: Real-World Use of Titanium. Elsevier.
12. Mohr, W. (2010). Assessment of Structural Integrity of Titanium Weldments for U.S. Navy Applications. Singapore. doi: https://doi.org/10.3850/978-981-08-5118-7_070
13. Yimeng, F., Wenhua, W., Xun, G., Yadong, L., Xiaozhou, Z., Qingyan, M. et al. (2021). Characteristics, Connotation and Military Application of Additive Remanufacturing Technology. Journal of Physics: Conference Series, 1948 (1), 012118. doi: https://doi.org/10.1088/1742-6596/1948/1/012118
14. Fang, Z. Z., Paramore, J. D., Sun, P., Chandran, K. R., Zhang, Y., Xia, Y. et al. (2018). Powder metallurgy of titanium – past, present, and future. International Materials Reviews, 63 (7), 407–459. doi: https://doi.org/10.1080/09506608.2017.1366003
15. Behera, M. P., Dougherty, T., Singamneni, S. (2019). Conventional and Additive Manufacturing with Metal Matrix Composites: A Perspective. Procedia Manufacturing, 30, 159–166. doi: https://doi.org/10.1016/j.promfg.2019.02.023
16. Zhang, T., Liu, C.-T. (2021). Design of titanium alloys by additive manufacturing: A critical review. Advanced Powder Materials, 1 (1), 100014. doi: https://doi.org/10.1016/j.apmate.2021.11.001
17. Denkena, B., Jacob, S. (2015). Approach for increasing the resource efficiency for the production process of titanium structural components. Procedia CIRP, 35, 45–49. doi: https://doi.org/10.1016/j.procir.2015.08.054
18. Xin, S., Zhang, J., Mao, X., Zhao, Y., Hong, Q. (2019). Research and Development of Low-cost Titanium Alloys. Journal of Physics: Conference Series, 1347 (1), 012022. doi: https://doi.org/10.1088/1742-6596/1347/1/012022
19. Reddy, R. G., Shinde, P. S., Liu, A. (2021). Review – The Emerging Technologies for Producing Low-Cost Titanium. Journal of The Electrochemical Society, 168 (4), 042502. doi: https://doi.org/10.1149/1945-7111/abe50d

20. Titanium Manufacturing Process. Available at: https://www.osaka-ti.co.jp/e/e_product/titan/
21. Doblin, C., Chryss, A., Monch, A. (2012). Titanium powder from the TiRO™ process. Key Engineering Materials, 520, 95–100. doi: https://doi.org/10.4028/www.scientific.net/KEM.520.95
22. van Vuuren, D. S. (2015). Direct titanium powder production by metallothermic processes. Titanium Powder Metallurgy, 69–93. doi: https://doi.org/10.1016/B978-0-12-800054-0.00005-8
23. Hansen, D. A., Gerdemann, S. J. (1998). Producing titanium powder by continuous vapor-phase reduction. JOM, 50 (11), 56–58. doi: https://doi.org/10.1007/s11837-998-0289-3
24. Chen, W., Yamamoto, Y., Peter, W. H. (2010). Investigation of pressing and sintering processes of CP-Ti powder made by Armstrong Process. Key Engineering Materials, 436, 123–130. doi: https://doi.org/10.4028/www.scientific.net/KEM.436.123
25. El Khalloufi, M., Drevelle, O., Soucy, G. (2021). Titanium: An Overview of Resources and Production Methods. Minerals, 11, 1425. doi: https://doi.org/10.3390/min11121425
26. Zhang, Y., Fang, Z. Z., Xia, Y., Huang, Z., Lefler, H., Zhang, T. et al. (2016). A novel chemical pathway for energy efficient production of Ti metal from upgraded titanium slag. Chemical Engineering Journal, 286, 517–527. doi: https://doi.org/10.1016/j.cej.2015.10.090
27. Zhang, Y., Fang, Z. Z., Sun, P., Zheng, S., Xia, Y., Free, M. (2017). A perspective on thermochemical and electrochemical processes for titanium metal production. JOM, 69, 1861–1868. doi: https://doi.org/10.1007/s11837-017-2481-9
28. Noguchi, H., Natsui, S., Kikuchi, T., Suzuki, R. O. (2018). Reduction of $CaTiO_3$ by electrolysis in the molten salt $CaCl_2$-CaO. Electrochemistry, 86 (2), 82–87. doi: https://doi.org/10.5796/electrochemistry.17-00078
29. Yanko, T. B., Ovchinnikov, A. V., Lyutyk, N. P., Korzhyk, V. N. (2018). Technology for obtaining of plasma spheroidised HDH titanium alloy powders used in 3D printing. Technological systems, 85/4. doi: https://doi.org/10.29010/085.7
30. Karaca, A., Sermond, B., Wilfing, G. (2008). Pat. No. US UA102387C2. Method for manufacturing alloy powders based on titanium, zirconium and hafnium, alloyed with elements Ni, Cu, Ta, W, Re, Os, and Ir. Available at: https://patents.google.com/patent/UA102387C2/en
31. Buttner, G., Domazer, H.-G., Eggert, H. (1980). Pat. No. US 4373947A. Process for the preparation of alloy powders which can be sintered and which are based on titanium. Available at: https://patents.google.com/patent/US4373947A/de
32. Moxson, V. S., Duz, V. A., Klevtsov, A. G., Sukhoplyuyev, V. D., Sopka, M. D., Shuvalov, Y. V., Matviychuk, M. (2012). Pat. No. US9067264B2. Method of manufacturing pure titanium hydride powder and alloyed titanium hydride powders by combined hydrogen-magnesium reduction of metal halides.
33. Abayaweera, G., Amaratunga, G., Fernando, N., Karunaratne, V., Kottegoda, N., Ekanayake, R. (2016). Pat. No. US 10316391B2. Method of producing titanium from titanium oxides through magnesium vapour reduction. Available at: https://patents.google.com/patent/US10316391B2/en
34. Bolivar, R., Friedrich, B. (2019). Magnesiothermic Reduction from Titanium Dioxide to Produce Titanium Powder. Journal of Sustainable Metallurgy, 5 (2), 219–229. doi: https://doi.org/10.1007/s40831-019-00215-z
35. Bolívar, R., Friedrich, B. (2009). Synthesis of titanium via magnesiothermic reduction of TiO_2 (Pigment). Proceedings - European Metallurgical Conference. doi: https://doi.org/10.13140/RG.2.2.11374.61760
36. Kharytonov, V. M., Kharytonov, V. N., Kharytonov, D. V. (2020). Osoblyvosti khimichnoho skladu ilmenitu.
37. Brodskyy, A., Troshchylo, V., Gonchar, A., Chukhmanov, O., Romanov, R. (2022). US Pat. No. 11440096 B2.
38. Brodskyy, A., Troshchylo, V., Gonchar, A., Chukhmanov, O., Romanov, R. (2022). WO 2022/046020/A1.
39. Mineral commodity summaries 2020. doi: https://doi.org/10.3133/mcs2020
40. Cardarelli, F. (2008). Materials handbook: a concise desktop reference. Springer. doi: https://doi.org/10.1007/978-1-84628-669-8
41. Ito, M., Morita, K. (2004). The solubility of MgO in molten MgCl2-CaCl2 salt. Materials transactions, 45 (8), 2712–2718. doi: https://doi.org/10.2320/matertrans.45.2712
42. Chen, G. Z., Fray, D. J., Farthing, T. W. (2000). Direct electrochemical reduction of titanium dioxide to titanium in molten calcium chloride. Nature, 407 (6802), 361–364. https://doi.org/10.1038/35030069
43. Dring, K. (2006). Electrochemical Reduction of Titanium Dioxide in Molten Calcium Chloride. Available at: http://hdl.handle.net/10044/1/8135
44. Suzuki, R. O., Natsui, S., Kikuchi, T. (2020). OS process. Extractive Metallurgy of Titanium, 287–313. doi: https://doi.org/10.1016/b978-0-12-817200-1.00012-0
45. Suzuki, R. O. (2005). Calciothermic reduction of TiO2 and in situ electrolysis of CaO in the molten $CaCl_2$. Journal of Physics and Chemistry of Solids, 66 (2-4), 461–465. doi: https://doi.org/10.1016/j.jpcs.2004.06.041
46. Fray, D. J., Chen, G. Z. (2001). The use of electro-deoxidation to reduce titanium dioxide and other metal oxides. Proceedings of the Fourth International Conference on Materials Engineering for Resources. Available at: https://nottingham-repository.worktribe.com/output/3214612
47. Ono, K., Okabe, T., Ogawa, M., Suzuki, R. (1990). Production of titanium powders by the calciothermic reduction of TiO_2. Tetsu-to-Hagane, 76 (4), 568–575. doi: https://doi.org/10.2355/tetsutohagane1955.76.4_568
48. Sittig, C., Textor, M., Spencer, N. D., Wieland, M., Vallotton, P. H. (1999). Surface characterization. Journal of Materials Science: Materials in Medicine, 10 (1), 35–46. doi: https://doi.org/10.1023/a:1008840026907
49. Prando, D., Brenna, A., Diamanti, M. V., Beretta, S., Bolzoni, F., Ormellese, M., Pedeferri, M. (2017). Corrosion of titanium: Part 2: Effects of surface treatments. Journal of Applied Biomaterials & Functional Materials, 16 (1), 3–13. doi: https://doi.org/10.5301/jabfm.5000396
50. Fuentes, E., Alves, S., López-Ortega, A., Mendizabal, L., Sáenz de Viteri, V. (2019). Advanced Surface Treatments on Titanium and Titanium Alloys Focused on Electrochemical and Physical Technologies for Biomedical Applications. Biomaterial-Supported Tissue Reconstruction or Regeneration. doi: https://doi.org/10.5772/intechopen.85095