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Promising metal-thermal technologies for titanium production

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Перспективні металотермічні технології виробництва титану

Abstract. *This review discusses existing and new titanium production technologies, their advantages and disadvantages. The current global production of titanium metal is based on the production of titanium sponge by reducing titanium tetrachloride with liquid magnesium and then purifying it by electric arc remelting (Kroll's metallothermal method). The Kroll method has some disadvantages: periodicity of the process, low speed, and high cost of raw materials. The paper analyzes a number of fundamentally new technological schemes for titanium production: magnetism in salt melts; magnetism in a liquefied layer of magnesium particles (TIRO process); sodium jet thermionic (Armstrong process); steam process. In the near future, we can expect a breakthrough in titanium technology that will reduce its cost.*
Key words: *titanium, titanium production, metallothermal technologies, Kroll method, magnesium reduction, TIRO process, Armstrong process.*

Анотація. *У цьому огляді обговорюються існуючі та нові технології виробництва титану, їхні переваги та недоліки. Сучасне світове виробництво титану базується на отриманні титанової губки шляхом відновлення тетрахлориду титану рідким магнієм з подальшим очищенням методом електродугової переплавки (металотермічний метод Кролла). Метод Кролла має низку недоліків: періодичність процесу, низьку швидкість та високу вартість сировини. У статті проаналізовано низку принципово нових технологічних схем виробництва титану: магнезієтермія у сольових розплавах; магнезієтермія у розрідженому шарі частинок магнію (процес TIRO); натрійтермічний струминний процес (процес Армстронга); парофазний процес. У найближчому майбутньому можна очікувати прориву в технології виробництва титану, що дозволить знизити його вартість.*
Ключові слова: *титан, виробництво титану, металотермічні технології, метод Кролла, магнезієтермія, TIRO процес, процес Армстронга.*

Introduction

Titanium is considered a light "new" metal that possesses a combination of unique properties: high mechanical strength, corrosion resistance, heat resistance, and low density. These properties make titanium of particular interest as a structural material in aerospace and rocket engineering, machinery, medicine, and other industries.

The raw materials for the metallurgical production of titanium can be ore concentrates and titanium slags containing titanium in the form of TiO_2. Direct reduction of titanium dioxide to metal is associated with significant challenges. The reason for these difficulties lies in titanium's high reactivity, even at elevated temperatures, particularly with respect to oxygen, nitrogen, and carbon. Even small amounts of these impurities lead to the formation of titanium oxides, nitrides, and carbides.

Therefore, at all stages of titanium production, it is necessary to prevent its contact with these elements. This is achieved by sealing the equipment and creating a neutral atmosphere or vacuum within it.

Today, the largest share of titanium produced worldwide is made through the reduction of titanium tetrachloride with magnesium, sodium, and calcium (metallothermic reduction).

Magnesiothermic process of obtaining titanium sponge (Kroll method)

The traditional and most widespread method of obtaining metallic titanium was patented by William Justin Kroll in 1940 [1]. The Kroll method involves the reduction of titanium tetrachloride ($TiCl_4$) by liquid magnesium to produce titanium sponge, which is then subjected to arc remelting into ingots [1]. The overall reaction of the process is as follows:

$$TiCl_{4(g)} + 2Mg_{(l)} = Ti_{(s)} + 2MgCl_{2(l)} \quad (1)$$

Titanium tetrachloride is obtained by carbothermic chlorination of titanium slag. The cost of titanium sponge is 8-10 USD/kg [2]. The cost of raw materials in titanium production by the Kroll method is as follows (USD/kg): titanium slag 0.37; $TiCl_4$ – 0.91; Mg – 1.0. The cost breakdown of individual stages in the Kroll process as a percentage of total cost is: preparation of titanium slag 4%, synthesis of $TiCl_4$ 9%, reduction of TiCl4 with magnesium 25%, remelting of sponge 12%.

The Kroll method has the following drawbacks [3]: 1) The process is batch-based, with component loading done in doses; 2) Low reaction kinetics of the magnesium thermic process; 3) The use of expensive raw materials (rutile or titanium slag) to obtain $TiCl_4$; 4) The need for regeneration of magnesium and chlorine from

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process products through electrolysis of molten salts; 5) To remove residual oxygen from the ingots of the obtained titanium, vacuum separation or acid leaching of the titanium sponge is required.

In Ukraine, titanium sponge and ingots produced by the Kroll method are manufactured at the Zaporizhzhya Titanium and Magnesium Plant with a capacity of 500 tons per month [4].

The drawbacks of titanium production worldwide and in Ukraine stimulate the search for new technologies for metallothermic production of pure titanium.

Comparison of metallothermy and electrochemistry for titanium production

Metallothermy of titanium is characterized by high specific productivity of the reactor and the release of a large amount of thermal energy, which serves as potential energy in the reducing metal (Mg, Na). The pure alkali and alkaline earth metals used for reduction can only be obtained through the electrochemical decomposition of their salts. Therefore, the process of obtaining titanium is complicated by the stage of regenerating the reducing metal. As a result, the total electricity consumption per unit of product for metallothermy is higher than for electrochemical processes. In this respect, metallothermy falls behind electrochemistry.

The metallothermic process is most efficiently carried out at temperatures above the melting point of titanium (1668°C). At this temperature, the reduced titanium is able to leave the reaction zone without interfering with the reduction process. At relatively low temperatures (<1000°C), titanium chloride reduction does not yield satisfactory productivity.

However, the reducing metal (Na, Mg) is in liquid form at 1000°C, and the electrolysis of their chlorides does not present significant difficulties. From this point of view, the technological scheme of metallothermy includes both the electrochemical regeneration stage of the reducing metal and the titanium reduction process itself.

The initial reagent for titanium metallothermy is always its chlorides. The reduction of titanium dioxide with an alkali metal is not possible, as they do not form stable oxide compounds and, during reduction, a solid mixture of titanium particles and alkali metal oxide is formed. Separating them is difficult, and heating this mixture to temperatures above the melting point of titanium leads to the oxidation of titanium (TiO) – at such a high temperature, titanium has an oxygen affinity comparable to calcium and magnesium.

During the reduction of chlorides, the equilibrium constant of the metallothermic reaction is very large. Reducing metals form strong salts with chlorine. Leaching these salts from titanium sponge or powder, or their vacuum distillation, can yield a sufficiently pure product. There is another argument in favor of chloride metallothermy. The intermediate product, titanium tetrachloride, is relatively easy to purify from most impurities through rare-phase reactions and distillation, so any reaction for obtaining high-purity metallic titanium or its dioxide involves the synthesis and purification of $TiCl_4$. Additionally, reducing the chloride or its subchlorides requires much lower energy costs than regenerating the reducing metal in the process.

New metallothermic processes in titanium metallurgy

New technologies for obtaining pure metallic titanium can be divided into two groups: metallothermic and electrochemical. Metallothermic processes for titanium reduction include the following: reduction of titanium from chlorides ($TiCl_4$) using magnesium or sodium; reduction of titanium from oxides (TiO_2) using calcium. Depending on the reduction method, titanium is obtained in the form of sponge or powder, which are then used to produce compact billets by electrosmelting and powder metallurgy methods [5]. Below is a critical review of new metallothermic methods for obtaining metallic titanium.

Magnesium thermite in molten salts

A serious disadvantage of the Kroll process is the heterogeneity of the titanium reduction reaction. In the Kroll method, gaseous $TiCl_4$ interacts with the surface of molten magnesium. The strong exothermic reduction reaction is localized at the interface. The release of a large amount of heat in a relatively small volume of space leads to a disturbance in the optimal thermal regime when the reactant supply rate is high. Reducing this rate causes low reactor productivity [3].

To improve the process, it is necessary to move toward homogeneity in the reduction process. This can be achieved by converting all the reactants into gas or liquid phases. In this case, there are no diffusion limitations, and the reaction takes place throughout the entire reaction volume, which allows for an even distribution of thermal load throughout the reactor and a significant increase in its productivity.

To implement this idea, the work [6] proposed magnesium thermite in a molten salt. The process is based on the reduction of a molten double salt $TiCl_2$ - $MgCl_2$ by liquid magnesium according to the reaction:

$$TiCl_2 \cdot MgCl_2 + Mg = Ti + 2MgCl_2 \qquad (2)$$

The feature of the process is that all the reactants are in the liquid phase. $MgCl_2$ acts as an inert diluent-thermostat, which protects the reaction zone from overheating during the heat release of the reaction.

$TiCl_2$ is obtained in the same reduction reactor but in a different reaction zone by passing $TiCl_4$ through titanium powder (sponge) according to the reaction:

$$0{,}5Ti + MgCl_2 + 0{,}5TiCl_4 = TiCl_2 \cdot MgCl_2 \qquad (3)$$

Unlike reaction (2), in reaction (3) the initial charge mixture is heterogeneous. Reaction (3) is endothermic and does not cause local overheating. The heat of the reaction is supplied by the liquid $MgCl_2$. The double salt is the product of the titanium sponge synthesis with the $MgCl_2$ thermostat. The titanium sponge acts as a reducer for $TiCl_4$ to $TiCl_2$ in the reaction:

$$TiCl_4 + Ti = 2TiCl_2 \qquad (4)$$

Pieces of titanium sponge are placed in a basket made of corrosion-resistant steel, where they surround a tube for the supply of $TiCl_4$. After loading a specific amount of $MgCl_2$, the temperature in the reaction zone rises to 850-900°C, and $TiCl_4$ is blown through the titanium sponge via the tube until the molar concentration of $TiCl_2$ in the double salt melt reaches 18-24%.

Figure 1 shows a diagram of the combined reactor for the magnesium thermal reduction of $TiCl_4$ in the salt melt $TiCl_2$ - $MgCl_2$.

The reduced titanium is obtained in the reduction reactor in the form of dispersed metal droplets, which partially combine into a sponge upon cooling. Non-consolidated titanium droplets can be continuously removed from the reactor, which is a significant advantage of the proposed method for obtaining titanium over the traditional one.

The magnesium-thermic scheme for obtaining metallic titanium by reducing the molten double salt $TiCl_2$ - $MgCl_2$, which is mixed with liquid magnesium, has an advantage over the Kroll process – better macrokinetics of the reduction reaction, manifested in a shorter time for filling the reactor with sponge.

However, molten magnesium and its chloride do not form a homogeneous solution, which provokes metal coagulation in the salt melt into large droplets due to differences in surface tension. This leads to the formation of interfacial boundaries and a decrease in the volumetric productivity of the reactor.

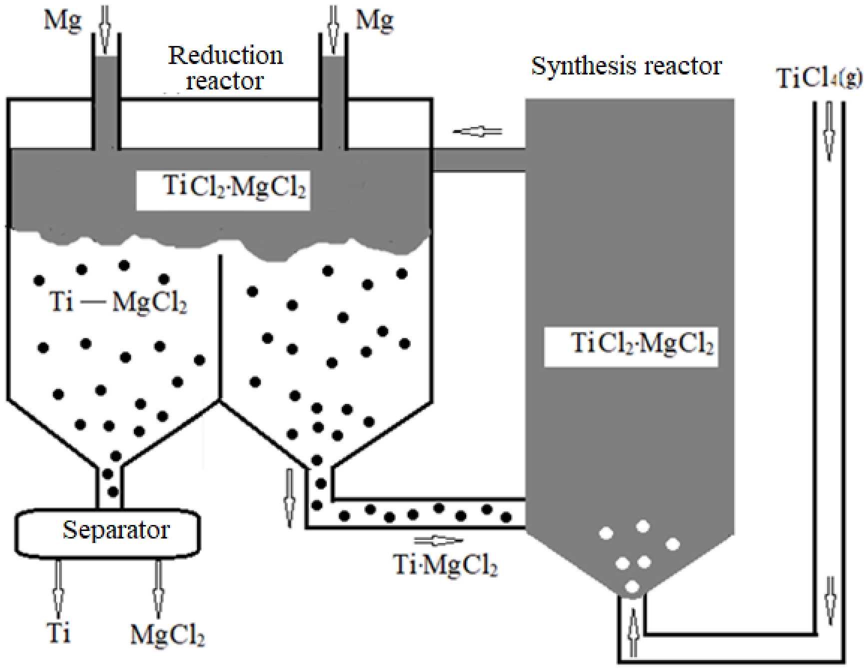

Figure 1. Diagram of the combined reactor for magnesium-thermic reduction of $TiCl_4$ in the molten salt mixture $TiCl_2$ - $MgCl_2$.

Magnesiothermal reduction in a fluidized bed of magnesium particles (TIRO process)

A new method for obtaining titanium has been developed in Australia with the aim of halving the cost of titanium products, known as the TIRO process [7]. This is proposed to be done in two ways: 1) replacing the periodic Kroll method with continuous reduction of titanium tetrachloride in a fluidized bed of magnesium particles; 2) producing titanium powder directly, bypassing several expensive stages in the traditional titanium production technology.

The TIRO process includes two stages: 1) in a reactor with a pseudofluidized bed, $TiCl_4$ interacts with magnesium powder, forming solid magnesium chloride particles approximately 350 μm in diameter, in which micron-sized titanium particles are dispersed; 2) titanium is extracted in the form of needles from the $MgCl_2$ granules. Figure 2 shows the product of the process as titanium needles mixed with $MgCl_2$ granules. The resulting titanium crystals can be given any shape, including needle-like, which is optimal for producing titanium rolling products. The features of the reactor's design and operating conditions are outlined in the work.

Jet sodium thermic (Armstrong process)

The Armstrong process is jet sodium thermic, where a continuous process of reduction of gaseous $TiCl_4$ by liquid sodium takes place, followed by leaching of sodium chloride (NaCl) that forms, from the titanium powder by the reaction:

$$TiCl_4 + 4Na = Ti + 4NaCl \quad (5)$$

The technological diagram of the Armstrong process is shown in Figure 3 [8].

Liquid sodium flows through the chamber. $TiCl_4$ vapors are injected into the sodium through a nozzle. The reduction reaction begins immediately after the nozzle. The resulting titanium powder is carried out of the chamber by the liquid sodium. The NaCl salt is separated from the titanium by aqueous leaching. The initial reduction of several metal chlorides allows the production of almost any required alloy. The titanium powders and its alloys obtained in the Armstrong process are subjected to hot vacuum pressing and wave rolling to produce large sheets. The cost of titanium powder is 5-10 times lower than the cost of powder obtained by the Kroll process.

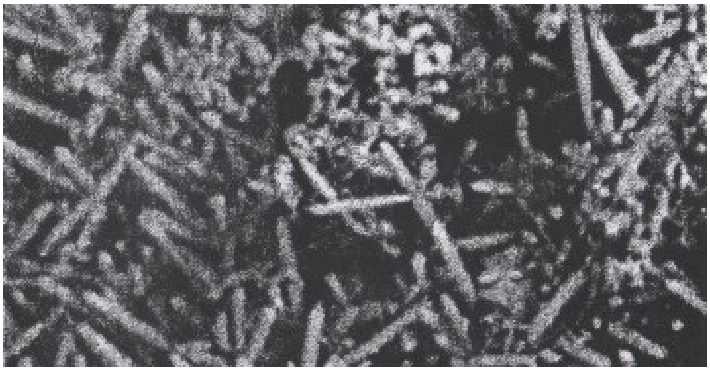

Figure 2. Product of the TIRO process – titanium needles in a mixture with $MgCl_2$ granules.

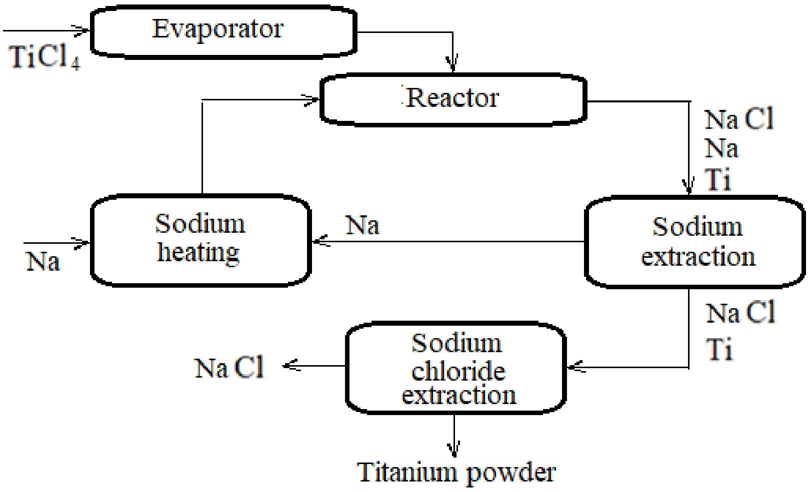

Figure 3. Diagram of the Armstrong process for obtaining titanium powder.

The products of the process – Ti, Na, NaCl are separated by filtration, distillation, and washing. A disadvantage of the Armstrong process is the use of expensive liquid sodium. Returning sodium and chlorine to the technological process requires the use of NaCl electrolysis in a melt and demands high energy costs and complex equipment design.

Vapor-phase process of titanium production

The goal of the vapor-phase process is the continuous production of titanium powder in the gas phase using magnesium or sodium vapor. Titanium tetrachloride and the metal reducer interact in the gas phase at high speed at 850°C.

The separation of the produced powder from $MgCl_2$ is accompanied by significant difficulties, and the solution in titanium has an unacceptably high level of impurities – oxygen. This is because, at the specified temperature, magnesium chloride has a low vapor pressure, condenses on the surface of the forming titanium particles, and prevents their further growth. Due to the high dispersion of the powder, the salt process is used for sodium thermite. The molten salt serves as an inert ballast medium.

Ballasting the reaction mixture ($TiCl_4$ + Na) with salt allows for better control of the reduction reaction. During mixing, the reagents in the solution are homogenized. In this process, the growth of titanium particles is not hindered as long as they remain within the reaction zone. Intensive mixing prevents small particles from falling out of the reactive zone and allows only large particles to be removed.

Conclusions and recommendations

The current global production of metallic titanium is based on the production of titanium sponge using the Kroll method. The process consists of the metal-thermic reduction of titanium tetrachloride with liquid magnesium, followed by purification of the resulting titanium sponge through electric arc remelting.

The Kroll method has the following disadvantages:

The process is periodic with a dosed loading of components;

Low reaction kinetics of magnesium thermite;

The use of expensive rutile or titanium slag to obtain $TiCl_4$;

The need to regenerate magnesium and chlorine from the process products through the electrolysis of molten salts;

Vacuum separation or acid leaching of the titanium sponge is required to remove residual oxygen in the titanium ingots.

New metal-thermic titanium production processes include magnesium thermite in molten salts, magnesium thermite in a fluidized bed of magnesium particles, and jet sodium thermite.

Magnesium thermite in molten salts is proposed for obtaining metallic titanium by reducing a double salt melt of $TiCl_2$ - $MgCl_2$ with liquid magnesium. Unlike the Kroll process, where TiC_{l4} vapor is introduced to the surface of liquid magnesium, in the proposed process, all reactants are in the liquid phase.

$MgCl_2$ acts as an inert diluent, protecting the reaction zone from overheating. $TiCl_2$ is obtained by passing $TiCl_4$ through titanium powder (sponge) until the molar concentration of $TiCl_4$ in the double salt melt reaches 18–24%. This reaction is endothermic.

The steel reduction reactor can be used in two variants: the double salt is introduced into the molten magnesium, and magnesium granules are introduced into the slurry melt. Titanium sponge forms in about 30 minutes, filling the reactor. Unbound titanium particles can be continuously removed from the reactor.

Magnesium thermite in a fluidized bed of magnesium particles (TIRO process) produces titanium embedded in $MgCl_2$ granules. This eliminates the formation of titanium sponge. The resulting titanium crystals can be given any shape, including needle-like, which is optimal for titanium rolling.

The Armstrong process is a jet sodium thermite process, where continuous reduction of gaseous titanium tetrachloride ($TiCl_4$) with liquid sodium takes place, followed by leaching of the formed sodium chloride from the titanium powder.

The vapor (salt) process is sodium-thermic, where a salt melt ($TiCl_4$ + Na) is used as an inert ballast medium, allowing better control of the reduction reaction. Intensive mixing removes only large particles from the melt.

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