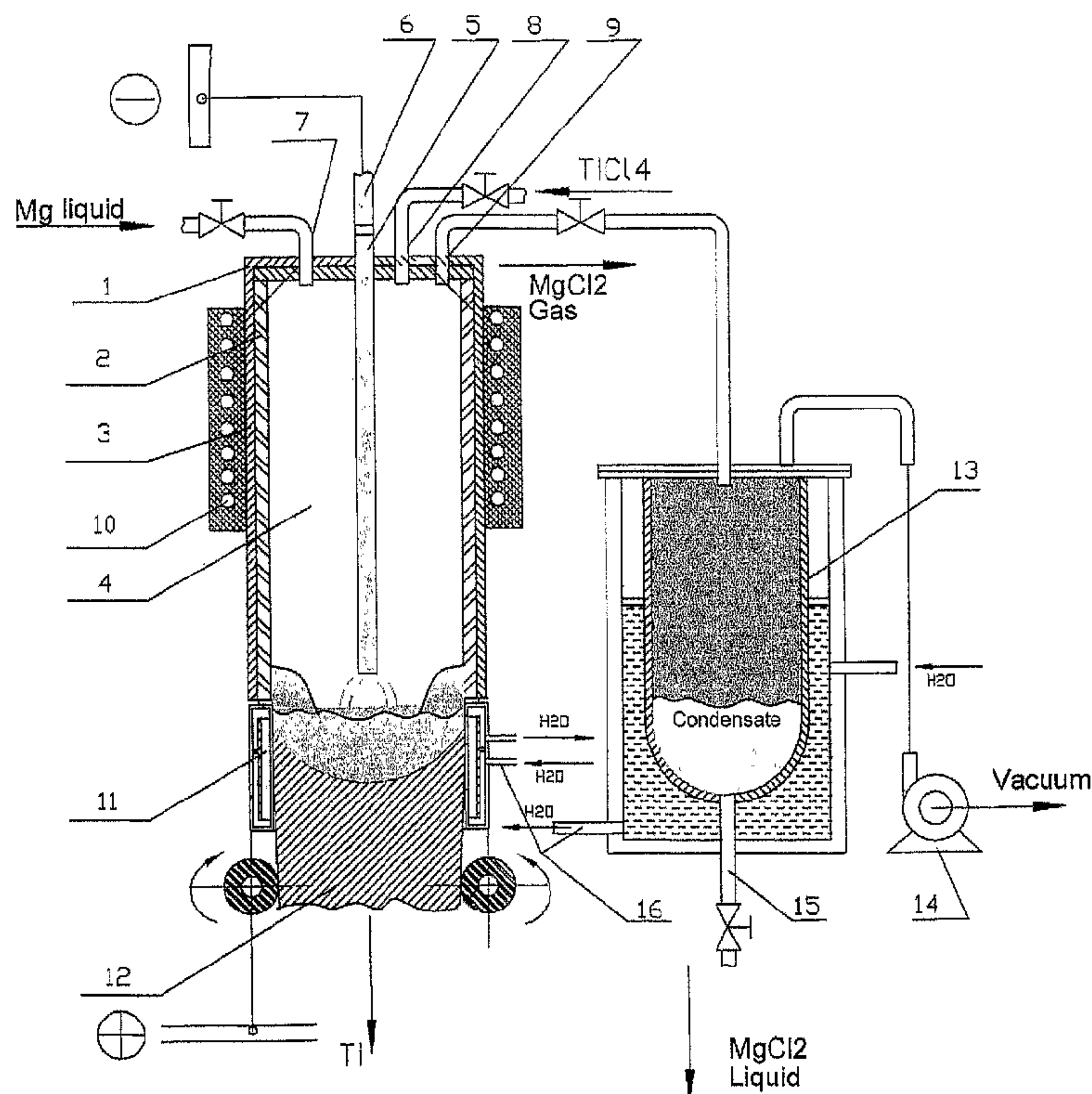




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(54) Titre : PROCEDE ET APPAREIL DE PRODUCTION CONTINUE DE TITANE METALLIQUE ET D'ALLIAGES A BASE DE TITANE
(54) Title: METHOD AND APPARATUS FOR CONTINUOUS PRODUCING OF METALLIC TITANIUM OR TITANIUM-BASED ALLOYS



(57) Abrégé/Abstract:

This invention relates to nonferrous metallurgy, particularly, to the methods of continuous producing metallic titanium and metallic titanium alloys by the metallothermic reduction of titanium tetrachloride, and also to the devices for producing metallic titanium or its



(57) Abrégé(suite)/Abstract(continued):

alloys. The offered method of continuous producing metallic titanium and metallic titanium alloys is characterized in that the reaction of titanium tetrachloride reduction by the reducing agent and the melting of obtained spongy titanium are conducted simultaneously in vacuum in the electric-arc furnace. Device for continuous producing metallic titanium or metallic titanium alloy is characterized in that to accomplish the reaction of reduction of titanium tetrachloride by the reducing agent in vacuum with simultaneous melting of spongy titanium for producing metallic titanium or its alloy, the reactor is executed in the form of electric-arc furnace (1), which is connected with the vacuum pump (14) and is supplied with consumable electrode (6), which functions as a cathode, as an anode serves liquid bath of titanium or titanium alloy, which is located in the cooled crystallizer (11) at the upper part of dummy bar (12), to which voltage is supplied.

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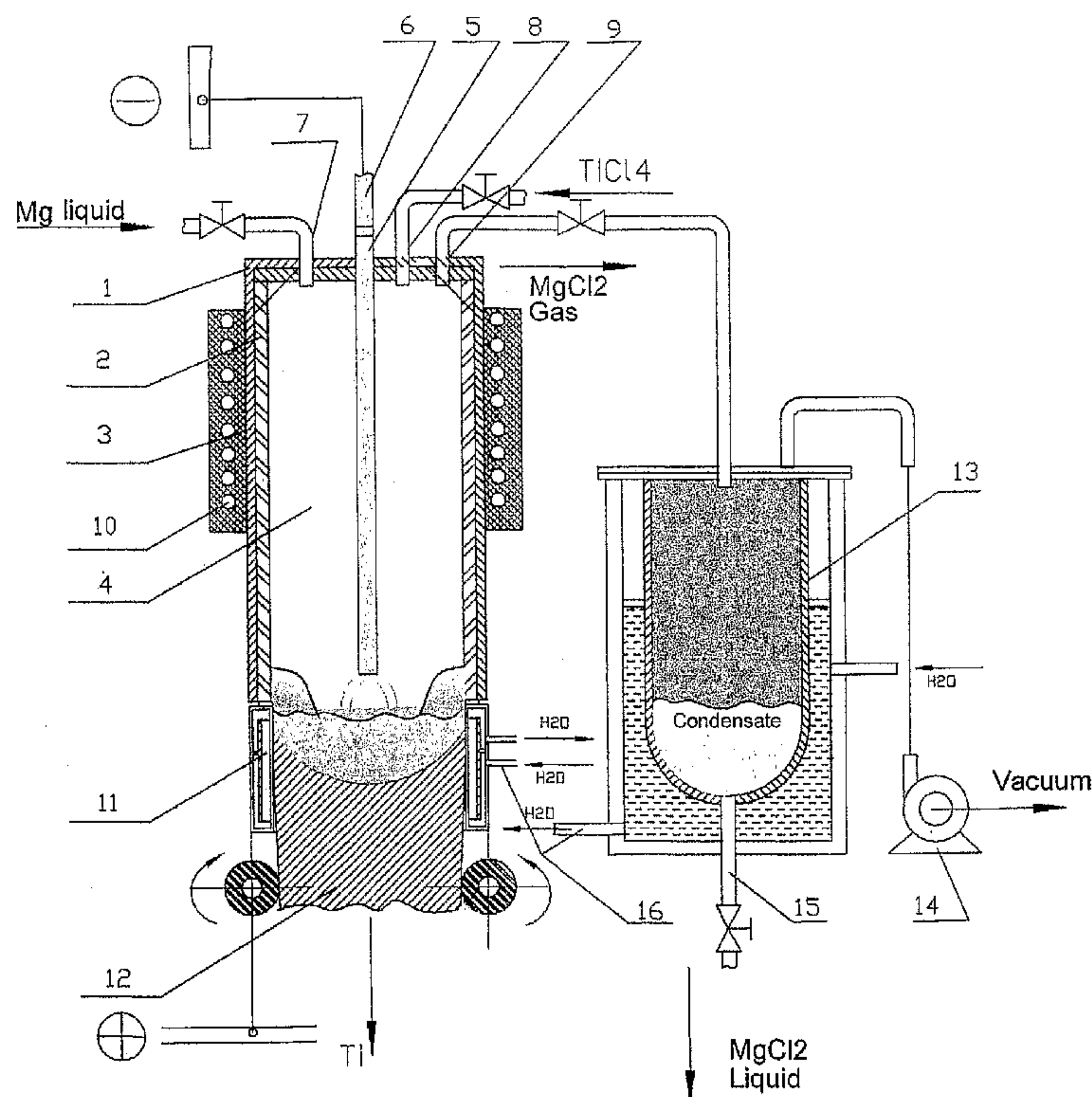
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(54) Title: METHOD AND APPARATUS FOR CONTINUOUS PRODUCING OF METALLIC TITANIUM AND TITANIUM-BASED ALLOYS



(57) Abstract: This invention relates to nonferrous metallurgy, particularly, to the methods of continuous producing metallic titanium and metallic titanium alloys by the metallothermic reduction of titanium tetrachloride, and also to the devices for producing metallic titanium or its alloys. The offered method of continuous producing metallic titanium and metallic titanium alloys is characterized in that the reaction of titanium tetrachloride reduction by the reducing agent and the melting of obtained spongy titanium are conducted simultaneously in vacuum in the electric-arc furnace. Device for continuous producing metallic titanium or metallic titanium alloy is characterized in that to accomplish the reaction of reduction of titanium tetrachloride by the reducing agent in vacuum with simultaneous melting of spongy titanium for producing metallic titanium or its alloy, the reactor is executed in the form of electric-arc furnace (1), which is connected with the vacuum pump (14) and is supplied with consumable

electrode (6), which functions as a cathode, as an anode serves liquid bath of titanium or titanium alloy, which is located in the cooled crystallizer (11) at the upper part of dummy bar (12), to which voltage is supplied.

METHOD AND APPARATUS FOR CONTINUOUS PRODUCING OF METALLIC TITANIUM OR TITANIUM-BASED ALLOYS

5 Technical Field

The present invention relates to nonferrous metallurgy, and more particularly, to the methods of continuous producing metallic titanium and metallic titanium alloys by the metallothemic reduction of titanium tetrachloride, and also to the devices for producing
10 metallic titanium or its alloys.

Background Art

15 There are known methods of producing metallic titanium by reduction the titanium tetrachloride by magnesium or by sodium with subsequent crushing and melting of spongy titanium in the vacuum arc furnaces to the ingots (variations of the Kroll's method). With any version of the technological process of metallothemic reduction by the Kroll's method a purified titanium tetrachloride is being entered into the sealed reactor, which is filled
20 with argon, and into which the reducing agent is being fed preliminarily or simultaneously with titanium tetrachloride. The upper limit of the temperature of the process is limited by durability of steel equipment, and the lower limit is determined by the melting point of chlorides obtained as a result of reduction. After the completion of the process of titanium tetrachloride reduction by the reducing agent and vacuum separation of the products of
25 reaction (usually in magnesium-thermic process), titanium sponge is extracted from the reactor by drilling or by pressing out. Then titanium sponge is crushed. After that, titanium sponge is melted down to the ingots (Титан. Свойства, сырьевая база, физико-химические основы и способы получения. М.: Metallurgy, 1983. С.339-342 [Titanium. Properties, Source Of Raw Materials, Physicochemical Fundamentals And
30 Method Of Obtaining Thereof. Moscow: Metallurgy, 1983, p. 339-342]). Traditionally the melting of titanium sponge is conducted in vacuum-arc furnaces or in the atmosphere of inert gas. However, melting in vacuum has essential advantage - during the melting in vacuum the bath of metal boils; therefore the removal of volatile impurities (hydrogen,

moisture, reducing agent, reducing agent chloride and other) from metallic titanium is conducted considerably more faster than during the melting under pressure of inert gas. Metal is obtained of the better quality. One of the known technological schemes of the producing metallic ingots of titanium by melting in the vacuum-arc furnaces consists of the primary melting on the consumable electrode, which is made of the pressed titanium sponge. Electric arc burns between the bath of liquid metal and the consumable electrode, and the melting metal flows down to the bath. The second melting is conducted in the casting mold of the bigger diameter than was used under the primary melting. The consumable electrodes for the second melting produce by welding of several electrodes obtained after the primary melting (Металлургия титана. М.: Металлургия, 1964. С. 182-184 [Titanium Metallurgy. Moscow: Metallurgy, 1964, p.182-184]).

The main disadvantage of the known methods is that the process of producing metallic titanium is divided into several stages, which leads to a great duration of the process of producing metallic titanium and low productivity of devices for the implementation of these methods.

There is also known the method of metals' reduction from their chlorides with a reducing metal (patent US 3,847,596, publ. 12.11.1974, "Process of obtaining metals from metal halides", IPC C22B 5/00), the essence of which is that the reducing metal's compound (e.g. titanium tetrachloride in a gaseous form) and reducing agent (e.g. liquid magnesium) are entered into the vacuumed and previously heated reactor, in which an exothermic reaction occurs. The reduction reaction is achieved at the temperature higher than the melting point of the metal to be produced and at the pressure not lower than the pressure of evaporating gases of reducing agent chloride. Originally titanium is formed in a solid form. As a result of reduction reaction the reducing agent chloride is heated under atmospheric pressure to a vaporization temperature and is formed in a gaseous state until the pressure of gases (pressure of molten reducing agent chloride, pressure of molten titanium and pressure of inert gas introduced into reactor) reaches the pressure, which corresponds to the temperature of substitution in the reaction. From this point on, the reducing agent chloride appears only in a liquid state. The subsequent substitution occurs at the pressure of obtained flux and at the temperature higher than melting point of titanium. In that process the formed titanium is melted and as a result, liquid titanium is produced in the reactor.

Liquid reducing agent's chloride forms a layer and floats on the surface of liquid titanium. The liquid titanium is removed continuously from the reactor through the cooled copper ingot mold under an argon atmosphere or in a vacuum.

5 The disadvantage of this method is a heavy saturation of the obtained metallic titanium by residual chlorine, metallic magnesium, magnesium chloride, and also by hydrogen and other gases, which are generated from the admixtures of titanium tetrachloride and reducing agent. Furthermore, the industrial application of this method is complicated by the problem of selecting the material for the reactor, which would resist the temperature
10 higher than melting point of titanium.

There is also known the method of continuous producing metallic titanium and apparatus therefor (patent EP 0 299 791, 21.10.1992, "Method for producing metallic titanium and apparatus therefor", IPC⁵ C22B 34/12), chosen as the closest analogue, which provides for
15 reduction of titanium tetrachloride by the reducing agent. This method is characterized by the following features: maintenance of temperature and pressure in a reaction zone in a reactor, which exceeds the melting point of titanium and the pressure of gaseous reducing agent; supply of titanium tetrachloride and the reducing agent (e.g. magnesium) into the reactor to react and produce a metallic titanium and by-product – reducing agent chloride
20 while maintaining the metallic titanium and by-product in a molten form; separation of metallic titanium and by-product – reducing agent chloride, using the difference of their densities; collection of metallic titanium at the bottom part of the reactor, and continuous extraction of metallic titanium from the bottom part of the reactor. Device for realization of this method consists of the reactor, which has the reaction zone for defining there the
25 temperature higher than melting point of titanium and maintaining the pressure sufficient for the prevention of any boiling of the reducing agent (e.g. magnesium) and its chloride; pipe for supplying the reducing agent in a liquid state into the reaction zone through the reactor's lateral side or upper part; pipe for supplying titanium tetrachloride into reaction zone through the reactor's upper part; discharge pipe to discharge the by-product –
30 reducing agent chloride from the reactor's lateral side; heating elements, mounted on the reactor's outer side at the level of the reaction zone; device for continuous extraction metallic titanium from the bottom part of the reactor.

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The disadvantage of this method is the need to hold a high pressure (about 50 atmospheres) in the reaction zone to prevent boiling of reducing agent and its chloride, and also the necessity to maintain in the reaction zone the temperature, which exceeds the melting point of titanium, that is connected with problems of the reactor's outburst and gas escape, i.e., insufficient level of safety of the process of producing metallic titanium. Furthermore, the producing metallic titanium at a high pressure in the reactor leads to a heavy saturation of obtained metallic titanium by chlorine residua, metallic magnesium, magnesium chloride, hydrogen and other gases, generated from titanium tetrachloride's admixtures and reducing agent, which in its turn leads to producing metallic titanium of insufficient quality.

Brief Summary of the Invention

According to one aspect of the present invention, there is provided a method comprising: evacuating all gases from a reaction zone of an electric-arc furnace until the reaction zone has a pressure sufficiently low to vaporize all of a titanium reducing agent later added to the reaction zone at the temperature of the reaction zone; wherein the titanium reducing agent has a boiling point; increasing the temperature of the reaction zone above the boiling point of the titanium reducing agent; adding titanium tetrachloride to the reaction zone; forming metallic titanium by reducing the titanium tetrachloride in the reaction zone at a temperature above the boiling point of the titanium reducing agent and below the melting point of the metallic titanium; melting the metallic titanium in the reaction zone as the metallic titanium is formed to form molten metallic titanium; cooling the molten metallic titanium; and extracting solidified metallic titanium that has solidified in the electric-arc furnace beneath the molten metallic titanium as a result of the cooling step.

According to another aspect of the present invention, there is provided a method as described herein, wherein the metallic titanium has a melting point, and wherein the forming the metallic titanium by reducing is performed at a temperature above the boiling point of the titanium reducing agent and below the melting point of the metallic titanium.

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Disclosure of Invention

Technical result is directed toward the elimination of deficiencies of the prototype and comprises raising safety level of the process of producing metallic titanium, improvement of the quality of obtained metallic titanium and increasing the
5 productivity of device for continuous producing metallic titanium and metallic titanium alloy.

Technical result is achieved by the offered method of continuous producing metallic titanium or metallic titanium alloy, which includes carrying out the reaction of reduction of titanium tetrachloride by the reducing agent in vacuum and simultaneous
10 melting of obtained spongy titanium in the electric-arc furnace of direct current (reactor), supplied with the consumed electrode of titanium or titanium alloy and by necessity filled with additional chemical elements for obtaining titanium alloys. The separation of metallic titanium and reducing agent's chloride occurs due to the difference in densities of metallic titanium or its alloy and reducing agent chloride, and
15 also due to a periodic exhaustion of reducing agents chloride to the condenser.

Realization of reaction of reduction of titanium tetrachloride by the reducing agent in vacuum makes it possible to increase safety level of the process of producing metallic titanium, but combination of the process of reduction of titanium tetrachloride by reducing agent and the process of melting of the spongy titanium produced in the
20 vacuum-arc furnace allows to increase the quality of obtained metallic titanium and to increase the

productivity of the device for continuous producing metallic titanium and metallic titanium alloy.

The device for continuous producing metallic titanium or metallic titanium alloy is described in attached drawing.

It consists of:

- electric-arc furnace 1, walls 2 of which are made of the material that can resist high temperatures (e.g. niobium or tantalum) and casing 3 (e.g. stainless steel), which prevents the absorption of oxygen and other gases, having reaction zone 4 for setting temperature higher than the boiling point of reducing agent and maintenance of vacuum for the removal of reducing agent residua (e.g. magnesium) and its chloride from the reaction zone 4; electric holder 5 for the installation of consumable electrode 6; aperture 7 in the wall of electric-arc furnace 1 for supplying a liquid reducing agent into the reaction zone 4; aperture 8 in the wall of electric-arc furnace 1 for supplying titanium tetrachloride into reaction zone 4; aperture 9 in the wall of electric-arc furnace 1 for removal the boiling reducing agent chloride from the reaction zone 4; heating elements 10, mounted on the outer side of electric-arc furnace 1 at the level of reaction zone 4; crystallizer 11 for installation of a dummy bar 12 and formation of metallic titanium or metallic titanium alloy at the electric-arc furnace's bottom 1;
- condenser 13 for collection of boiling reducing agent chloride from electric-arc furnace 1, which is connected with vacuum pump 14 and tube 15 for discharge of a cooled reducing agent chloride;
- cooling system 16 of crystallizer 11, installed in electric-arc furnace 1 and condenser 13 for collection of reducing agent chloride from electric-arc furnace 1.

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The method of continuous producing metallic titanium or metallic titanium alloy consists of the following. In cooled crystallizer 11, which is a casting mold, located at the bottom part of electric-arc furnace 1 (reactor), a dummy bar 12 of metallic titanium or metallic titanium alloy is put and sealed hermetically. In the electric holder 5, located on the wall of electric-arc furnace 1, put a consumable electrode 6 of titanium or titanium alloy, which is filled, if necessary, with additional chemical elements (e.g. aluminum, silicon, molybdenum, chromium, vanadium, manganese, iron, nickel, bismuth, silver, niobium, tantalum, polonium, tungsten, zirconium, cobalt) and seal hermetically. The electric-arc

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furnace 1 is vacuumed and its body is simultaneously heated by heating elements 10 (inductor or resistance furnace) to the temperature, which exceeds the boiling point of reducing agent. After that the heating stop. Further heating of the body of the electric-arc furnace 1 is not required, since the reaction of reduction of titanium tetrachloride occurs with the heat emission. Voltage is supplied according to the selected electric power supply diagram of vacuum-arc furnace 1 (for example "+" on the dummy bar 12, "-" on the consumable electrode 6). As a result, the upper part of dummy bar 12 is melted down, and the liquid bath of titanium is formed in the cooled crystallizer 11. Electric-arc furnace 1 is set with aim to maintain the liquid bath of titanium in the cooled crystallizer 11 during the entire process of producing titanium or titanium alloy. Further, into the reaction zone 4 of electric-arc furnace 1 the reducing agent (e.g. magnesium) in a liquid state is entered. After a certain time, sufficient for the evaporation of reducing agent, or simultaneously, a liquid titanium tetrachloride and a reducing agent in the stoichiometric ratio is added into the reaction zone 4 of electric-arc furnace 1. As a result, the reaction of titanium reduction and obtaining by-product – reducing agent chloride - with a heat emission occurs in the electric-arc furnace 1. Titanium is condensing partially on the consumable electrode 6 (cathode). Also, the part of titanium is draining to the liquid bath (anode) in the cooled crystallizer 11. Electric arc is burning between the bath of molten titanium or its alloy and consumable electrode 6, which is titanium or titanium alloy made. The molten metal is draining to the liquid bath. The reducing agent chloride is boiling. The fixed pressure and temperature of the electric-arc furnace 1 give a signal that the reaction of titanium reduction is over. Upon the completion of the reaction of reduction the vacuum pump 14, which is located on the side of condenser 13 serving for the collection of a reducing agent chloride, is engaged. The boiling reducing agent chloride is pumped out of electric-arc furnace 1 to the condenser 13. The pumping-out of the reducing agent chloride and the evacuation of electric-arc furnace 1 are to be kept on till the creation of vacuum. After that the reducing agent and titanium tetrachloride, both in a liquid state, are entered into the reaction zone 4 of electric-arc furnace 1 and the process is repeated. The process of producing metallic titanium or metallic titanium alloy is a continuous process. Then, the following is to be made, as needed: heightening of the consumable electrode 6, entering of the reducing agent in a liquid state and titanium tetrachloride into the reaction zone 4 of the electric-arc furnace, removing of the reducing agent chloride from the electric-arc furnace

1, drawing out the ingot of metallic titanium or its alloy, which is formed on the dummy bar 12 in the cooled crystallizer 11.

Example

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Melting of the titanium ingot was conducted in the electric-arc furnace 1 which has niobium walls 2. The inner diameter of the walls 2 of electric-arc furnace 1 is 36 mm, the height - 450 mm. The dummy bar 12 of metallic titanium with a diameter of 36 mm was inserted into the cooled crystallizer 11 of electric-arc furnace 1. The consumed titanium electrode 6 with a diameter of 10 mm was put into the electric holder 5. After the evacuation of electric-arc furnace to 1×10^{-3} mmHg of mercury and simultaneous heating of the electric-arc furnace 1 by heating elements 10 to the temperature of 1200°C, the electric-arc furnace 1 was turned on and the bath of liquid titanium was induced. The consumable electrode 6 was dropped down by 1 mm each minute. Further, liquid magnesium of 50 g was entered into the reaction zone 4 of electric-arc furnace 1. Then, with delay of 2 seconds, titanium tetrachloride of 192 g was added to the reaction zone 4 of electric-arc furnace 1. Temperature in the reaction zone increased to 1500°C. When the pressure and temperature in the electric-arc furnace 1 was stabilized, the vacuum pump 14 was engaged and the boiling reducing agent chloride was pumped out to the condenser 13.

20 The pumping-out of reducing agent chloride and the evacuation of electric-arc furnace 1 continued till the moment when the vacuum reached the level of 1×10^{-3} mmHg of mercury. After that liquid magnesium of 50 g and with a delay of 2 seconds - 192 grams of titanium tetrachloride were added into the reaction zone 4 of electric-arc furnace 1 repeatedly. The metallic titanium ingot was formed on the dummy bar 12. It was drawn up with velocity of

25 1 mm/sec. The entire process lasted 1 hour 30 minutes. The ingot of metallic titanium with a weight of 20 kg was obtained at that time.

Thus, the method and device for producing metallic titanium and metallic titanium alloy allow to increase the quality of obtained metallic titanium and also to increase safety level and productivity of the process for continuous producing metallic titanium and metallic titanium alloy.

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CLAIMS:

1. A method comprising:

evacuating all gases from a reaction zone of an electric-arc furnace until the reaction zone has a pressure sufficiently low to vaporize all of a titanium reducing agent later added to the reaction zone at the temperature of the reaction zone;

wherein the titanium reducing agent has a boiling point;

increasing the temperature of the reaction zone above the boiling point of the titanium reducing agent;

adding titanium tetrachloride to the reaction zone;

forming metallic titanium by reducing the titanium tetrachloride in the reaction zone at a temperature above the boiling point of the titanium reducing agent and below the melting point of the metallic titanium;

melting the metallic titanium in the reaction zone as the metallic titanium is formed to form molten metallic titanium;

cooling the molten metallic titanium; and

extracting solidified metallic titanium that has solidified in the electric-arc furnace beneath the molten metallic titanium as a result of the cooling step.

2. The method of claim 1, wherein the adding the titanium tetrachloride is performed before the adding the titanium reducing agent.

3. The method of claim 1, wherein the forming the metallic titanium by reducing generates a reducing agent chloride, further comprising:

evacuating the reducing agent chloride from the reaction zone using a vacuum pump.

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4. The method of claim 3, further comprising:

adding additional titanium reducing agent to the reaction zone;

adding additional titanium tetrachloride to the reaction zone; and

forming additional metallic titanium by reducing the additional titanium

5 tetrachloride with the additional titanium reducing agent.

5. The method of claim 4, further comprising:

crystallizing the molten titanium before the extracting the solidified

metallic titanium, wherein the crystallizing the molten titanium occurs continuously

from the forming the metallic titanium through the forming the additional metallic

10 titanium.

6. The method of claim 5, wherein the reducing agent chloride is gaseous,
further comprising:

condensing the evacuated reducing agent chloride in a condenser.

7. The method of claim 1, wherein the increasing the temperature of the

15 reaction zone is performed before addition of the titanium reducing agent.

8. The method of claim 1, wherein the cooling step comprises solidifying
the molten metallic titanium on top of a dummy bar, and wherein the extracting of the
solidified metallic titanium involves drawing down the dummy bar as additional
metallic titanium is formed, melted and solidified.

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