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[54] **METHOD AND APPARATUS FOR THE PRODUCTION OF LIQUID TITANIUM FROM THE REACTION OF VAPORIZED TITANIUM TETRACHLORIDE AND A REDUCING METAL**

[75] Inventors: **Philip Douglas Johnston; James Lawton; Ian Mackison Parker,** all of Chester, England

[73] Assignee: **The Electricity Council,** London, England

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[51] **Int. Cl.** **C22b 53/00**

[58] **Field of Search** 75/84.5; 266/15, 16; 164/252, 52

[56] **References Cited**

UNITED STATES PATENTS

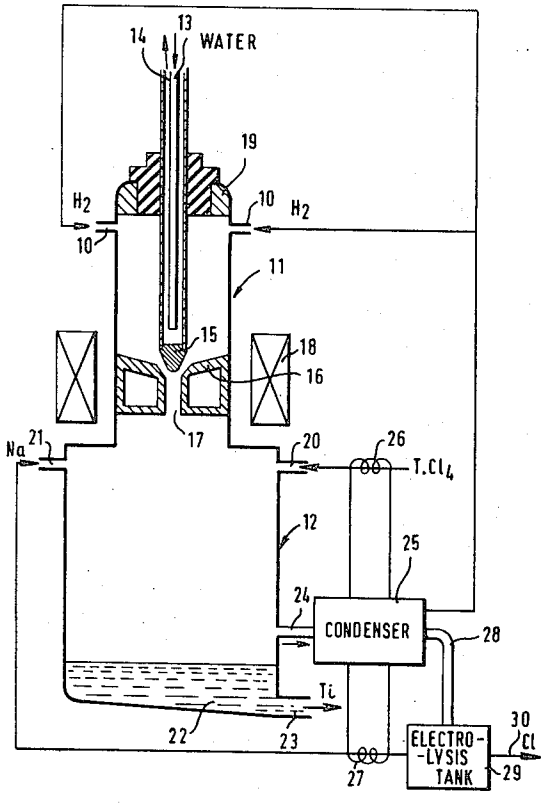
2,768,074	10/1956	Stauffer	164/52
2,816,828	12/1957	Benedict et al.	75/84.5
2,955,333	10/1960	Berry et al.	164/252

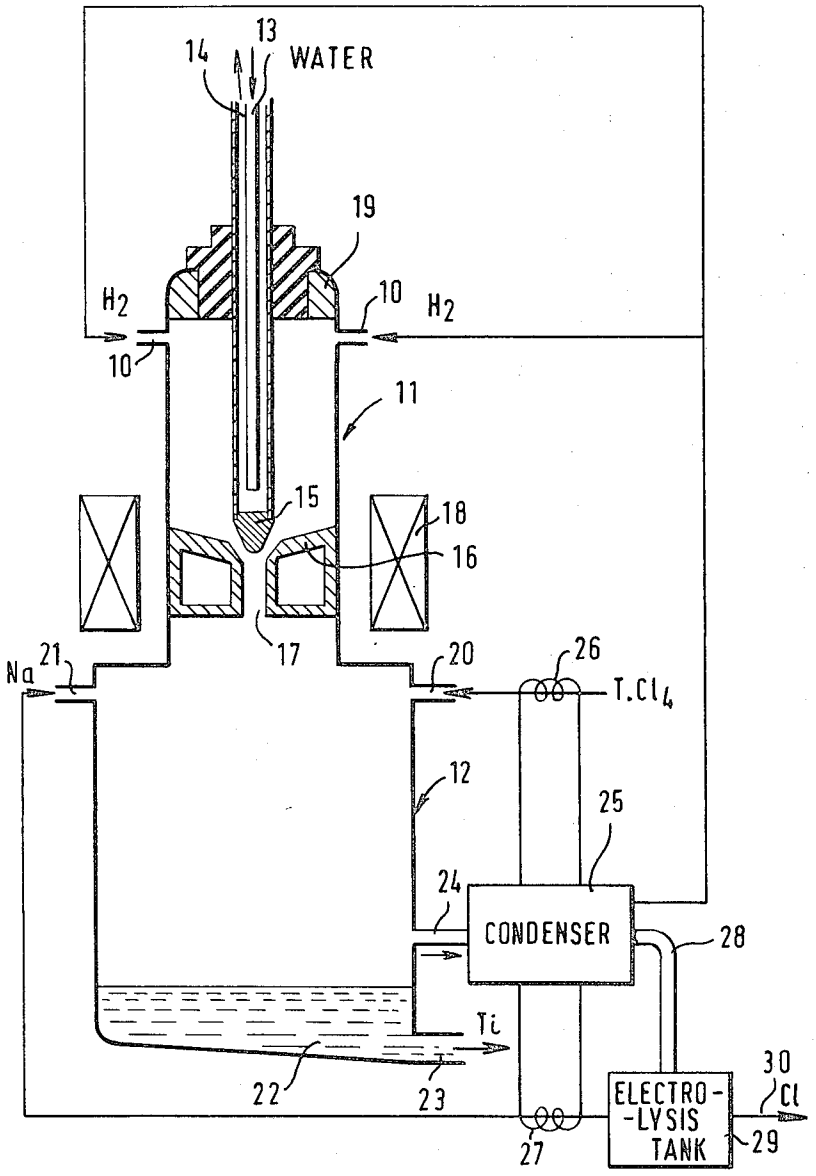
Primary Examiner—Carl D. Quarforth
Assistant Examiner—B. Hunt
Attorney, Agent, or Firm—Browne, Beveridge, DeGrandi & Kline

[57] **ABSTRACT**

Elemental titanium is produced by reducing titanium tetrachloride using an alkali or alkaline earth metal, preferably sodium. The reaction is carried out in the vapour phase, a carrier gas, preferably hydrogen, being heated by an electric arc and injected into the reaction chamber to heat the sodium and titanium tetrachloride which are injected as liquids or vapours. The reaction is carried out at a temperature above the melting point of titanium, typically between 1,800° and 2,500°C, the titanium falling as a liquid to the bottom of the reaction chamber and the chloride of the reducing metal and other unwanted products being removed in vapour form. The chloride of the reducing metal is passed through a heat exchanger for heating material passing into the chamber and is electrolysed to provide the required alkali or alkaline earth metal.

17 Claims, 1 Drawing Figure




13
14
WATER
19
H_2
10
H_2
10
11
15
18
16
17
Na
21
20
26
$T.Cl_4$
12
25
24
CONDENSER
28
Ti
22
23
30
Cl
ELECTRO-
-LYSIS
TANK
27
29

METHOD AND APPARATUS FOR THE PRODUCTION OF LIQUID TITANIUM FROM THE REACTION OF VAPORIZED TITANIUM TETRACHLORIDE AND A REDUCING METAL

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a method of and apparatus for the production of elemental titanium by the reduction of titanium tetrachloride.

2. Description of the Prior Art

The present method for large scale commercial production of titanium is by the chlorination of the impure oxide ore to produce titanium tetrachloride. This, after purification, is reduced in an inert atmosphere using for example magnesium or sodium. The titanium produced in this way is in the form of a sponge and is contaminated by excess reducing agent and by the chlorides of the reducing metal, e.g., sodium chloride or magnesium chloride. Thus to obtain the metal in a usable form for machining and working, the sponge has to be subjected to a lengthy and expensive refining process. This results in a high cost of production of titanium and the present day extent of usage of titanium metal is limited because of this high cost.

It has in particular, been proposed in Canadian Pat. No. 770,017 to reduce titanium tetrachloride using sodium or magnesium, carrying out the reaction in a liquid phase by injecting liquid reducing metal and liquid titanium tetrachloride onto the surface of a titanium ingot which surface is maintained molten by an argon or helium plasma jet.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide an improved method of and apparatus for the production of titanium metal in a usable form directly from titanium tetrachloride.

According to this invention, a method for the production of elemental titanium from titanium tetrachloride comprises the step of combining titanium tetrachloride in vapour form with a vaporized alkali or alkali earth metal or metals, the vapours being heated, either by an inert or reducing carrier gas passed through an electric arc or by passing the titanium tetrachloride and/or metal vapour, possibly also with a carrier gas, through the arc, to maintain the reacting materials at a temperature at which elemental titanium is liquid but above the boiling point of the chloride formed by combining the chlorine with the alkali or alkaline earth reducing metal employed, the chloride of the reducing metal and other unwanted products being removed in vapour form. The alkali or alkaline earth employed is preferably sodium or magnesium. Other alkali or alkaline earth metals such as potassium, calcium, strontium or barium might be employed but are more expensive than sodium. If any of these materials is employed, the reaction may be carried out at temperatures just above the melting point of titanium, typically within the approximate temperature range of 1,800° to 2,500°C.

In the method of the present invention, the reaction is carried out in the vapour phase. At the reaction temperature, however, the elemental titanium is liquid and hence falls to the bottom of the reaction vessel. The impurities are in vapour form and, by carrying out the reaction well above the surface of the molten metal in the bottom of the vessel, a high degree of purity of the metal is obtained without impurities being cooled and trapped in the molten metal.

The titanium may be withdrawn in liquid form or it may be allowed partially or completely to solidify; in the latter case, the titanium is withdrawn periodically. The impurities and other products of the reaction are withdrawn as vapour.

The alkali or alkaline earth metal may be injected into the reaction vessel as a vapour or it may be injected as a liquid; in the latter case, the liquid vaporizes at the high temperature in the vessel so that the reaction is effected in the vapour phase. Similarly the titanium tetrachloride may be injected as a vapour or as a liquid which vaporizes in the vessel.

The carrier gas must be a gas suitable for transferring the heat from the electric arc discharge to the alkali or alkaline earth metal and titanium tetrachloride vapours. It is possible to heat the alkali or alkaline earth metal vapour or titanium tetrachloride vapour directly by passing it through the arc, however there are stability problems and for this reason a carrier gas is convenient. Any carrier gas may be employed which does not react in a deleterious manner with titanium and provided it has good discharge characteristics, that is to say it produces a stable arc discharge and can be conveniently matched with respect to the voltage and current characteristics. For effecting heat transfer, the gas should preferably have a high enthalpy per unit volume. Hydrogen is the most suitable gas meeting these requirements. It is advantageous as it is a reducing gas and it has good discharge characteristics producing a stable discharge. An inert gas such as argon might be employed but, to convey the required amount of heat, it is necessary to use of the order of three times as much argon as hydrogen, moreover the reactor vessel should not be flooded with unnecessary gases which would reduce the partial pressure of the reactants. For these reasons therefore preferably hydrogen is used as the aforementioned carrier gas.

The chloride produced as a reaction product, that is the alkali or alkaline earth chloride, may be electrolysed in a separate process stage to provide the alkali or alkaline earth metal for feeding into the reactor vessel in vaporized form. The titanium tetrachloride and the alkali or alkaline earth metal may be preheated or vaporized before injection into the reactor vessel using a heat exchanger extracting heat from the vaporized chloride and/or the liquid titanium passing out of the reactor vessel.

The invention also includes within its scope titanium produced by the above described method.

Furthermore within the scope of the invention is apparatus for the production of titanium from titanium tetrachloride comprising a reactor vessel for containing vapours and molten metal at a temperature at which titanium is liquid but above the boiling point of an alkali or alkaline earth chloride, means for injecting liquid or vaporized alkali or alkaline earthmetal and liquid or vaporized titanium tetrachloride into said reactor vessel, electrodes for an electric arc, means for passing a carrier gas, preferably hydrogen, into the reactor vessel through the arc between the electrodes to heat the carrier gas and thereby heat the titanium tetrachloride and alkali or alkaline earth metal, means for drawing off vaporized alkali chloride from the vessel and means

for drawing off liquid or partially or completely solidified titanium from said vessel.

Preferable the apparatus has an arc chamber containing said electrodes, which electrodes are concentric and shaped to form a nozzle leading into the reactor vessel, ports, preferably tangential, being porvided in the arc chamber for the injection of the carrier gas.

BRIEF DESCRIPTION OF THE DRAWING

The accompanying drawing illustrates diagrammatically a reactor vessel with the associated equipment for producing titanium metal from vaporized titanium tetrachloride.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring to the drawing, hydrogen gas is fed via pipes **10** into tangential inlet ports of a cylindrical enclosure **11** for an arc heater within a reactor vessel **12.** The arc heater comprises a water cooled cathode formed of concentric pipes **13, 14** carrying a tungsten tip **15,** the water flowing in through the inner pipe **13** and back through the outer pipe **14.** The arc is struck between this tungsten tip **15** and a cylindrical water-cooled copper anode **16** shaped to provide, in conjunction with the tip **15,** a nozzle **17** through which the gas flows downwardly out of the enclosure **11** into the reaction chamber. An electrically energised coil **18,** producing an axial magnetic field, causes the arc to rotate generating swirl and turbulence in the gas stream emerging from the nozzle. Insulation between the anode and cathode is provided by an insulating block **19** through which the cathode structure passes. The arc heater is arranged to heat the hydrogen gas to a temperature such that after mixing with the principal reactants the temperature of the mixture lies between about 1,800° and 2,500°C. Liquid or vaporized titanium tetrachloride is injected into the vessel at **20** and liquid or vaporized sodium is injected into the reactor vessel at **21.** If the materials are injected in liquid form, they vaporize in the vessel. The hot hydrogen gas stream from the nozzle **17** intersects and interacts with the vaporized titanium tetrachloride and the reducing metal to raise the temperature of these materials so that the titanium tetrachloride is reduced by the sodium in accordance with the following reaction:

$$TiCl_4 + 4\ Na \rightarrow Ti + 4NaCl$$

The reaction takes place in the vapour phase, the sodium and titanium tetrachloride being injected through the side walls near the top of the reaction chamber. The titanium metal condenses and collects at **22** to be withdrawn at **23.** The sodium chloride vapour, hydrogen and any titanium subchlorides are extracted at **24** and the sodium chloride is condensed out in a heat exchanger **25.** The heat from this heat exchanger is used as indicated diagramatically at **26, 27** to preheat and vaporize the titanium tetrachloride and sodium metal for injection into the reactor vessel. This condensed sodium chloride is run out via a pipe **28** into an electrolytic tank **29** where it is electrolysed to produce sodium for feeding through pipe **21** into the reactor vessel. The chlorine from the electrolytic tank **29** is removed at **30.** The hydrogen and other remaining gaseous products passing out of the condenser are fed back through pipes **10** as the carrier gas in the reactor vessel.

Instead of using a copper anode, a water-cooled titanium anode may be employed to minimise the risk of impurities in the titanium metal produced in the reactor vessel. Similarly a titanium tip can be used for the cathode instead of the tungsten tip **15.**

We claim:

1. A method for the production of elemental titanium from titanium tetrachloride comprising the setp of injecting into a reaction chamber titanium tetrachloride in vapor form and a vaporized reducing metal selected from the group consisting of alkali and alkaline earth metals, heating the vapors in said reaction chamber by injecting into said chamber hydrogen heated by being passed through an electric arc to maintain the reacting materials at a temperature at which the elemental titanium is liquid but above the boiling point of the chloride formed by combining the chloride with the reducing metal employed, the chloride of the reducing metal and other unwanted products being removed in vapor form.

2. A method as claimed in claim **1** wherein the reducing metal employed is sodium.

3. A method as claimed in claim **1** wherein the reducing metal employed is magnesium.

4. A method as claimed in claim **1** wherein the reducing metal employed is potassium or calcium or strontium or barium.

5. A method as claimed in claim **1** wherein the reaction is carried out at a temperature between 1,800° and 2,500°C.

6. A method as claimed in claim **1,** wherein the chloride of the reducing metal produced as a reaction product is electrolyzed in a separate process to provide the reducing metal for feeding into the reactor vessel in vaporized form.

7. A method as claimed in claim **1** wherein the titanium tetrachloride and the reducing metal are vaporized before injection into the reactor vessel using a heat exchanger extracting heat from the vaporized chloride and from the liquid titanium passing out of the reactor vessel.

8. A method as claimed in claim **1** wherein the titanium is withdrawn in liquid form from a reactor vessel in which the reaction is carried out and wherein the impurities and other reaction products are withdrawn in vapor form with the hydrogen.

9. A method as claimed in claim **1** wherein the titanium is at least partially solidified in a reactor vessel in which the reaction is carried out before being withdrawn and wherein the impurities and other reaction products are withdrawn in vapor form with the hydrogen.

10. A method for the production of elemental titanium from titanium tetrachloride comprising the steps of passing hydrogen gas through an electric arc to heat the gas, injecting the hydrogen gas through a nozzle constituted by the arc electrodes into the top of a reaction chamber, passing an electric current through a coil around the nozzle to cause the gas stream to swirl, injecting sodium and titanium tetrachloride in vapor form into said chamber near the top thereof in a direction to intersect the hydrogen gas stream to effect a chemical reaction in the vapor phase, the arc discharge being such as to maintain a temperature between 1,800° and 2,500°C. in the reaction chamber, collecting the titanium in liquid form in the bottom of said chamber, withdrawing the sodium chloride, produced

by the reaction, in vapor form from said chamber, passing the sodium chloride through a heat exchanger to heat the sodium and titanium tetrachloride before the injection into said chamber, and electrolysing the sodium chloride to produce metallic sodium for injection into said chamber.

11. An apparatus for the production of titanium from titanium tetrachloride comprising a reaction chamber, a nozzle including electrodes for an electric arc in the top of said chamber, means for injecting hydrogen as a carrier gas through said nozzles between said electrodes to be heated by an arc between the electrodes, means for injecting a vaporized reducing metal selected from the group comprising alkali and alkaline earth metals and vaporized titanium tetrachloride into the top of said chamber in directions to intersect the hot hydrogen stream emerging from said nozzle, means for drawing off the vaporized chloride of the reducing metal from said chamber and means for withdrawing titanium from said chamber.

12. An apparatus as claimed in claim **11** wherein said nozzle is arranged to direct the hot carrier gas downwardly into the top of a reaction chamber and wherein the titanium tetrachloride and the reducing metal are injected inwardly through the side wall near the top of said chamber.

13. An apparatus as claimed in claim **11** wherein heat exchanger means are provided for transferring heat from the materials leaving the reactor vessel to the materials injected into the reactor vessel.

14. An apparatus as claimed in claim **11** and having means for electrolysing the chloride of the reducing metal taken from the reactor vessel to produce the reducing metal for injecting into the reactor vessel.

15. An apparatus as claimed in claim **11** and having an arc chamber containing said electrodes, which electrodes are concentric and shaped to form said nozzle leading into said reactor vessel, ports being provided in said arc chamber for the injection of the hydrogen gas.

16. An apparatus as claimed in claim **15** wherein said arc chamber is cylindrical and wherein said ports are arranged tangentially.

17. An apparatus as claimed in claim **15** wherein an electrically energized coil surrounds the electrodes to cause the arc to swirl.

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