June 2, 1959 R. H. SINGLETON 2,889,221

METHOD OF PRODUCING TITANIUM

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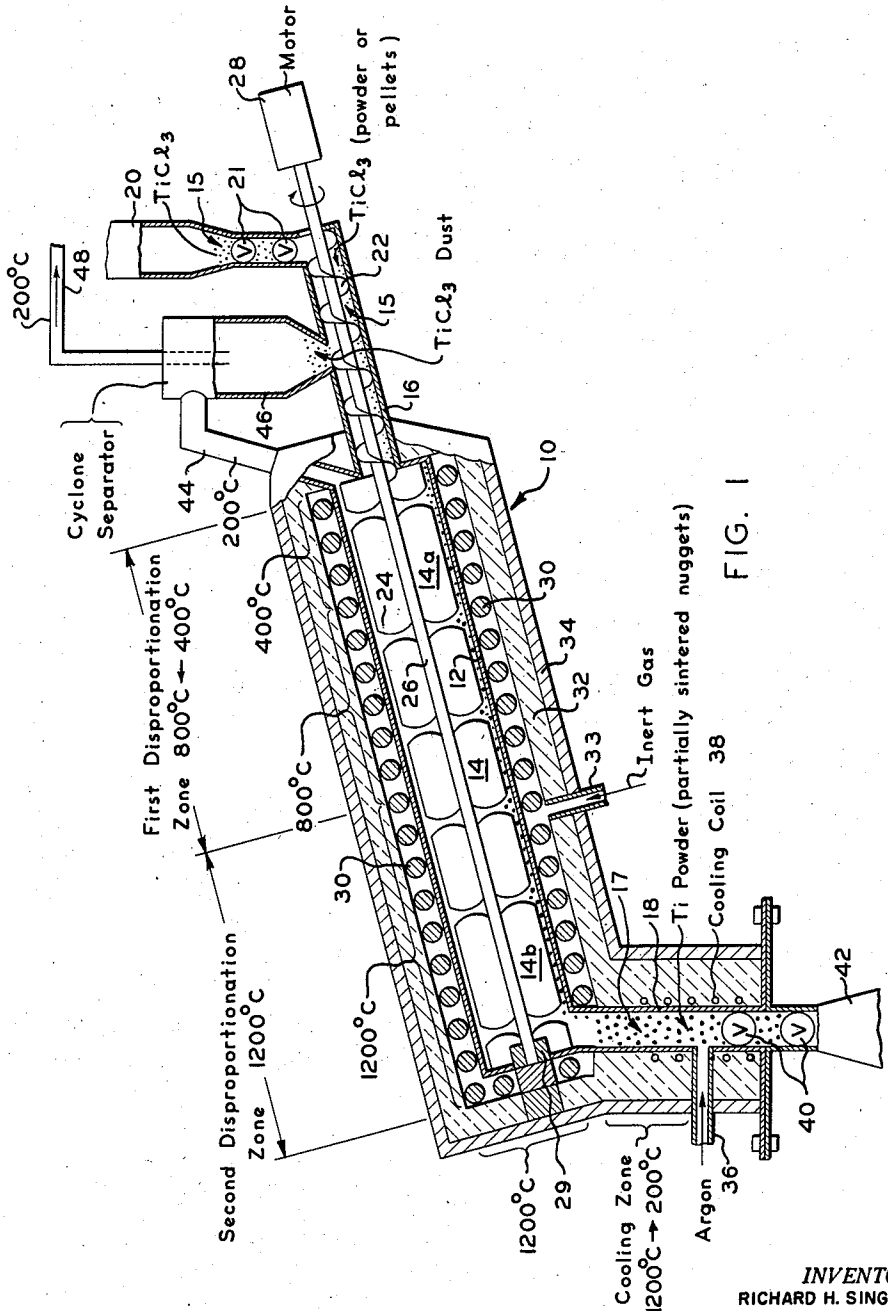


FIG. 1

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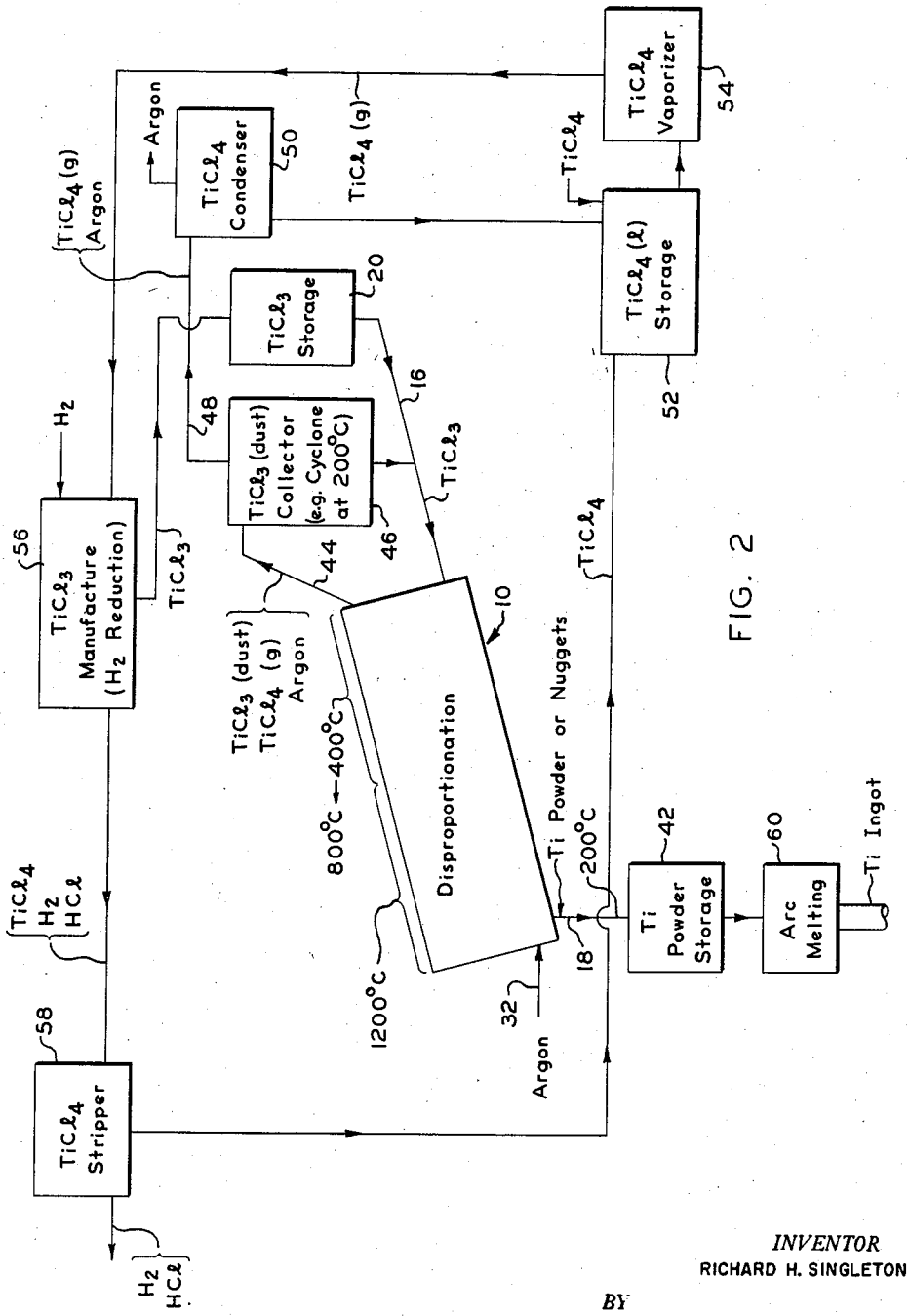


FIG. 2

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2,889,221

METHOD OF PRODUCING TITANIUM

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6 Claims. (Cl. 75—84.5)

This invention relates to the production of metals and more particularly to the production of titanium by the disproportionation of lower chlorides thereof to titanium metal.

A principal object of the present invention is to provide an improved process for the manufacture of titanium by the disproportionation of lower chlorides thereof to give high yields of the product titanium.

Still another object of the present invention is to provide such a process which can be operated on a continuous basis with high thermal efficiency and with high production of titanium per unit of volume of apparatus.

Still another object of the invention is to provide a process of the above type which produces a product of high purity on a continuous basis.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the process involving the several steps and the relation and the order of one or more of such steps with respect to each of the others which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description taken in connection with the accompanying drawings wherein:

Fig. 1 is a diagrammatic, partially sectional view of one preferred apparatus embodying the invention; and

Fig. 2 is a flow sheet showing the relationship of the equipment associated with the apparatus of Fig. 1.

Titanium metal has been produced in the past by the disproportionation of lower chlorides thereof. This past work has been limited to small bench-scale operations which have given low production rates and has provided only an impure product titanium. This past work has also been primarily directed to batch operations which have been completely unsuitable for commercial production. In the present invention high yields of high purity titanium are obtained by employing a novel combination of process steps based upon careful correlation of temperatures and pressures within the disproportionation apparatus. The present invention is also based upon an appreciation of certain aspects of the disproportionation which were not previously understood. More specifically, applicants have discovered that titanium dichloride disproportionates to titanium trichloride and titanium metal. The existence of this reaction requires that a maximum of recycling of titanium trichloride within the disproportionation apparatus be employed, preferably by using a continuous type disproportionation apparatus, in order that a maximum yield of titanium metal be obtained.

The first step of the disproportionation process (after the formation of titanium trichloride by a suitable means) involves the passing of the titanium trichloride into a first disproportionation zone. In this first zone the titanium trichloride is heated to a temperature on the order of about 400° C. to 800° C. to disproportionate a majority of the titanium trichloride to titanium dichloride and titanium tetrachloride in accordance with the following formula

$$2TiCl_3 \rightarrow TiCl_2 + TiCl_4 \qquad (A)$$

During this first disproportionation step the partial pressure of titanium tetrachloride in the first disproportionation zone is maintained below the equilibrium titanium tetrachloride pressure over titanium trichloride at the temperature thereof in the first zone. This equilibrium partial pressure of titanium tetrachloride will vary as a function of the temperature in the first zone, the various experimental values of this pressure being set forth in the following table:

Table I

Temperature, ° C., $TiCl_3$	Disproportionation Pressure ($pTiCl_4$)
529°	16.1 mm. Hg.
576°	54.1 mm. Hg.
590°	75.5 mm. Hg.
627°	182.2 mm. Hg.
655°	339.0 mm. Hg.
696° (extrapolated)	760.0 mm. Hg. (1 atm.).

In order to maintain this low disproportionation pressure the titanium tetrachloride must be removed as rapidly as possible from the disproportionation zone. This removal is preferably accomplished by operating the first disproportionation zone at a high temperature of about 700° C.–800° C. or above so that the partial pressure of titanium tetrachloride in this zone is above atmospheric pressure. As a result of this operation, the titanium tetrachloride can be readily removed as a vapor and condensed outside of the first disproportionation zone. When lower disproportionation temperatures (e.g., 500° C.–700° C.) are employed in the first zone, this low partial pressure of titanium tetrachloride may be maintained by (*a*) utilizing an inert sweeping gas or by (*b*) maintaining the system under a vacuum and condensing the evolved titanium tetrachloride in a frozen state at a point removed from the first disproportionation zone. However, it is preferred to operate the first disproportionation zone at a sufficiently high temperature so that the partial pressure of titanium tetrachloride in the first zone is above atmospheric pressure. This allows condensation of the titanium tetrachloride in liquid phase and obviates the necessity of low temperature condensation of titanium tetrachloride or the circulation of large quantities of sweeping gas through the disproportionation apparatus.

The nonvolatile product from the first disproportionation zone is preferably continuously passed into a second disproportionation zone where this product is heated to a considerably higher temperature. The product fed to the second disproportionation zone is primarily titanium dichloride, but may be intermixed with some titanium trichloride and some titanium metal. In the second disproportionation zone the titanium dichloride is heated to a high temperature (on the order of 1000°C.–1400° C.) to disproportionate the dichloride to titanium metal, with the evolution of either titanium trichloride or titanium tetrachloride in accordance with the following equations:

$$2TiCl_2 \rightarrow Ti + TiCl_4 \qquad (B)$$

$$3TiCl_2 \rightarrow Ti + 2TiCl_3 \qquad (C)$$

During this second disproportionation step the partial pressure of the titanium chlorides, evolved in the second disproportionation zone, is maintained below the equilibrium disproportionation pressure of the titanium dichloride at the temperature in the second zone. The equilibrium disproportionation pressures for Equations B and C have been calculated and are set forth in Table II below:

Table II

Temperature, ° C. of $TiCl_2$	Pressure, $TiCl_3$ (Equation C)	Pressure, $TiCl_4$ (Equation B)
1,100°	200 mm. Hg Abs.	40 mm. Hg Abs.
1,200°	1 atm.	200 mm. Hg Abs.
1,300°	(3 atm.)[1]	300 mm. Hg Abs.
1,400°	(10 atm.)[1]	600 mm. Hg Abs.
1,500°	(50 atm.)[1]	(3 atm.).[1]

[1] The bracketed figures are not real when the disproportionation is carried out at atmospheric pressure. They represent only a measure of the driving force of the reaction.

Since the principal partial pressure in the second zone will be due to the partial pressure of titanium trichloride, the low partial pressure of titanium trichloride may be conveniently maintained by having the second disproportionation zone in open communication with the first disproportionation zone and condensing the evolved titanium trichloride in this first disproportionation zone. This has the additional important advantage that the titanium trichloride (from the disproportionation of the dichloride) is condensed in the first disproportionation zone and is thus recycled within the disproportionation apparatus by being disproportionated in the first zone to titanium dichloride and titanium tetrachloride. This titanium dichloride is then fed back to the second disproportionation zone. This condensation pumping of the titanium trichloride vapors is a preferred embodiment of the invention and the titanium dichloride in the second disproportionation zone is preferably heated to a temperature above 1200° C. so that the partial equilibrium pressure of titanium trichloride therein is above atmospheric pressure. However, it is possible to utilize a sweeping gas or a vacuum for driving the titanium trichloride vapors from the second disproportionation zone towards the first disproportionation zone where condensation thereof takes place, thus permitting use of a lower temperature.

The titanium tetrachloride vapors from Equations A and B are continuously withdrawn from the disproportionation zones by being condensed adjacent that end of the first disproportionation zone to which the titanium trichloride is originally fed. To assist in the flow of titanium chloride vapors in countercurrent to the travel of titanium and titanium chloride solids in the disproportionation apparatus, a slight current of argon gas is preferably provided. This argon gas enters that end of the second disproportionation zone from which the titanium product is removed, passes through the two disproportionation zones, and leaves the first disproportionation zone adjacent that end thereof to which the initial titanium trichloride is fed. Since the temperature gradient in the disproportionation zones also encourages travel of the vapor phase titanium trichloride in this same direction, only a small quantity of argon is required to prevent condensation of titanium trichloride adjacent the titanium powder being removed from the apparatus. This sweep of argon also assists in carrying the titanium tetrachloride out of the first disproportionation zone and into the titanium tetrachloride condenser.

Referring now to Fig. 1 there is shown one schematic, diagrammatic, partially sectional view of one apparatus embodying the present invention. This apparatus comprises a disproportionation furnace, generally indicated at **10**, comprising an inner cylindrical gas-tight chamber **12**. This cylindrical chamber **12** defines a disproportionation space **14** which includes a first disproportionation zone **14***a* and a second disproportionation zone **14***b*, these two disproportionation zones being preferably in open communication with each other. Titanium trichloride **15** which is to be disproportionated is introduced into the first disproportionation zone **14***a* by means of a feeding mechanism **16**. The resultant titanium product, in the form of small partially sintered nuggets

17, is removed from the second disproportionation zone **14***b* through a suitable outlet pipe **18**. The titanium trichloride is fed to the introducing means **16** from a supply **20** thereof, the flow of the titanium trichloride being controlled by a pair of valves **21** which can be arranged in any well-known manner for feeding predetermined quantities into the feeding mechanism **16**.

Titanium trichloride powder is advanced down the feeding mechanism **16** by means of a screw conveyor **22** so that this titanium trichloride powder may be fed, at a carefully controlled rate, into the first disproportionation zone **14***a*. The disproportionating titanium trichloride, and the resulting titanium dichloride (and possibly titanium metal) are advanced down the disproportionation chamber **12**, from zone **14***a* to zone **14***b*, by means of scraper blades **24** supported on a shaft **26**. This shaft **26** preferably also supports the screw conveyor **22** and is driven by a motor **28**. The lower end of the shaft **26** may be supported in a suitable water-cooled bearing **29**.

For applying the heat to the two disproportionation zones **14***a* and **14***b*, there is provided a plurality of electrical heating elements **30** which may be carbon resistance elements. These heating elements may be arranged to heat the entrance part of the first disproportionation zone **14***a* to a temperature on the order of 400° C., the temperature increasing along this zone **14***a* to a temperature of about 800° C. or somewhat above. The heating elements **30** adjacent the second disproportionation **14***b* are arranged to heat the second disproportionation zone to a temperature on the order of 1200° C. and above. For preventing heat loss from the resistance heating elements **30** there is provided a layer of insulation **32**. A gas-tight steel shell **34** provides the outer casing of the disproportionation furnace. The atmosphere around the resistance elements **30** is preferably an inert gas (e.g., argon) to prevent oxidation of these resistance elements, this inert gas atmosphere being provided by means of a pipe **33** connected to a suitable supply of such a gas. The heating elements **30** are preferably spaced a slight distance away from the chamber **12** to prevent attack of chamber **12** by the hot elements **30**. A thin layer of refractory (e.g., zirconia) may be provided between the heater elements **30** and the refractory metal chamber **12** to assist in preventing this direct contact.

The partially sintered titanium nuggets, which travel from the lower end of the second disproportionation zone **14***b* into the exit pipe **18**, are at a very high temperature, on the order of 1200° C. and above. These titanium particles are partially cooled by cooled argon or other inert gas which is introduced through the pipe **36** and which flows upwardly through the pipe **18** containing the titanium particles. This pipe **18** is also cooled by cooling coils **38** so that the titanium particles are cooled to a temperature on the order of about 200° C. by the time that they reach the bottom of the exit pipe **18**. The fact that the argon passes upwardly through these particles before entering the second disproportionation zone **14***b* serves to preheat the argon to a temperature on the order of the temperature within the second disproportionation zone. This provides for economy of heat for the over-all process.

Referring now to Fig. 2, as well as Fig 1, the over-all arrangement of the steps of the process can be more fully understood. The titanium particles which leave the exit tube **18** pass through a pair of valves **40** into a titanium storage chamber **42**. The argon and titanium tetrachloride vapors leave the entrance end of the first disproportionation zone **14***a* through a pipe **44** which is connected to a cyclone separator **46**. This separator **46** serves to remove from the vapor stream any fine dust particles of titanium trichloride which have been entrained in this vapor stream. These titanium trichloride dust particles are fed back into the titanium trichloride

feeding mechanism **16** and thus are returned to the first disproportionation zone **14***a*. The argon and titanium tetrachloride vapors from the cyclone separator **46** pass through a pipe **48** to a titanium tetrachloride condenser **50** (see Fig. 2). The condensed titanium tetrachloride is fed to a titanium tetrachloride storage tank **52** to which fresh titanium tetrachloride is added.

Predetermined quantities of the titanium tetrachloride in the storage tank **52** are fed to a titanium tetrachloride vaporizer **54**, these vapors being fed into a hydrogen reduction apparatus **56** where the titanium tetrachloride is reduced to titanium trichloride. This partial reduction of the titanium tetrachloride is preferably achieved by passing titanium tetrachloride vapors and hydrogen in close proximity to a surface heated to a temperature on the order of 1200° C. and above, the resultant titanium trichloride being condensed on a surface maintained at a temperature of approximately 200° C. to 400° C. In a preferred embodiment of the invention, the number of moles of titanium tetrachloride fed to the reactor is more than twice the number of moles of hydrogen fed to the reactor. This method of operating the hydrogen reduction step has the decided advantage that the small amount of hydrogen leaving the reactor can be discarded, thus obviating the necessity for expensive hydrogen recycling systems. While not shown on the drawings, the titanium tetrachloride vapors may be preheated to a temperature on the order of 500° C. prior to introduction into the hydrogen reduction apparatus. This preheating appears to increase the percent conversion per pass. The solid titanium trichloride is scraped from the condensing surface and fed by suitable mechanical means to the titanium trichloride storage chamber **20**.

In some cases it is desirable to compress the titanium trichloride into small pellets before feeding into the disproportionation apparatus. This is particularly true when the titanium trichloride is rapidly heated to a relatively high temperature, the pellet form preventing undue entrainment of the titanium trichloride powder.

The excess titanium tetrachloride vapors, excess hydrogen and hydrogen chloride gas leaving the hydrogen reduction apparatus **56** pass through a stripper **58** where the excess titanium tetrachloride is removed from the gas stream. This excess titanium tetrachloride is then returned to the titanium tetrachloride storage tank **52**. The hydrogen chloride gas may be condensed or may be fed to a plant for recovering the chlorine which may be used to chlorinate titanium-bearing ores to produce titanium tetrachloride, thus preserving the chlorine content of the gases leaving the titanium tetrachloride stripper.

In a preferred embodiment of the invention the disproportionation chamber **12** is preferably formed of molybdenum or tungsten as are the scrapers **24** and their supporting shaft **26**. The inner portion of the bearing **29** is also formed of molybdenum or tungsten, all of these portions of the apparatus being subjected to titanium tetrachloride vapors at relatively high temperature. The other portions of the apparatus may be formed of stainless steel or mild steel to the extent that they are not subjected to high temperatures. The resistance heating elements **30**, as mentioned previously, preferably are carbon resistance elements, but other suitable elements may be equally employed. While it is preferred that resistance heating be utilized, other types of heating can be employed. However, the high temperatures required and the possibility of corrosion make resistance heating by the use of carbon resistance elements most desirable.

In the operation of the embodiment of the invention illustrated in Figs. 1 and 2, the supply of titanium trichloride is generated in hydrogen reduction apparatus **56**, the resultant titanium trichloride being fed to the titanium trichloride storage tank **20**. The disproportionation zones **14***a* and **14***b* are then brought up to their indicated operating temperatures by the use of the heating elements **30** and a slight flow of argon is started through the pipe **36** so that argon sweeps, at a slow rate, from the exit end of the second disproportionation zone to the entrance end of the first disproportionation zone **14***a* and out through the vapor exit pipe **44**.

Titanium trichloride is then fed into the entrance end of the first disproportionation zone **14***a* by suitably manipulating the valves **21** and rotating the screw conveyor **22**. As the titanium trichloride enters this first disproportionation zone **14***a*, it is immediately heated to a temperature between 400° C. and 800° C., reaching a temperature in excess of 800° C. before it leaves this first disproportionation zone **14***a*. In this first zone **14***a* the titanium trichloride disproportionates to titanium dichloride (a solid) and titanium tetrachloride (a vapor). The titanium tetrachloride escapes through the pipe **44**, through the cyclone separator **46**, through the pipe **48**, and is condensed in the titanium tetrachloride condenser **50**. The argon leaving condenser **50** is preferably recycled through the system. The scrapers **24** continually agitate the titanium trichloride and the resultant titanium dichloride in the first zone **14***a*, and advance this solid powder down the disproportionation chamber to the second disproportionation zone **14***b*. In this connection the speed of rotation of the scrapers is preferably so adjusted that the titanium chloride is not advanced into the second disproportionation zone until such time as substantially all of the product has been disproportionated at least to the titanium dichloride.

As the product from the first disproportionation zone passes into the second disproportionation zone, it is heated to a higher temperature, on the order of 1200° C. and above, the titanium dichloride in this zone disproportionating to titanium metal and to titanium trichloride vapor (plus some titanium tetrachloride vapor).

While the melting point of titanium dichloride has not been definitely established, it seems certain that it, or the melting point of the mixed di- and trichlorides, lies somewhere in the range of temperatures encountered in operation of the second step. Consequently, the titanium dichloride in the second disproportionation zone **14***b* is heated above this melting point and thus forms a sludgy mass including considerable titanium metal. This sludgy mass, due to the agitation in the second zone, tends to agglomerate into balls which contain titanium dichloride and titanium metal. As these balls move down the second zone they are continually losing chlorine content (due to evolution of titanium trichloride and titanium tetrachloride). The simultaneous operation of the molten titanium dichloride and the formation of more titanium in the balls seems to encourage growth of sintered nuggets of titanium, although the mechanism involved is not completely understood. The agitation of the titanium dichloride and titanium trichloride during their movement down the disproportionation furnace, along with the maintenance of a thin layer (preferably less than about 1 inch) of the nonvolatile titanium chlorides in the disproportionation zones, considerably increases the speed of the disproportionation. This is due to the fact that escape of the volatile titanium chlorides from the mass is considerably enhanced. Additionally, the thin agitated layer permits uniform and rapid transfer of heat into the disproportionating titanium chlorides. Since the disproportionation is an endothermic reaction, this high heat transfer is essential to high production rates.

The argon flow and the temperature gradient in the chamber **12** both encourage movement of titanium trichloride vapors from the second disproportionation zone **14***b* to the first disproportionation zone **14***a*. Since this first zone **14***a* is at a temperature below the condensation temperature of titanium trichloride, this titanium trichloride will condense on the walls of the chamber **12** in the first disproportionation zone **14***a*. The scrapers **24** scrape this titanium trichloride from the walls of chamber **12** and continue to feed it down the disproportionation chamber. A considerable quantity of the tita-

nium trichloride condensing on the walls of the chamber **12** in the first disproportionation zone **14***a* will almost immediately disproportionate to titanium dichloride and titanium tetrachloride. Thus, as this product is scraped from the walls it is fed back down to the second disproportionation zone **14***b*. As can be seen, the above arrangement provides for internal recycling of the by-product of the second disproportionation zone into the first disproportionation zone where it can be condensed and disproportionated to a lower chloride which is fed back to the second disproportionation zone.

Since some of the titanium trichloride vapors condensing in the first zone **14***a* may condense as a fog or as very small particles on the wall of the chamber **12**, the flow of titanium tetrachloride vapors and argon passing out of the disproportionation apparatus will entrain a portion of these fine particles of titanium trichloride. These entrained particles are separated in the cyclone separator **46** and are fed back into the titanium trichloride feeding mechanism **16**. As is apparent from the drawings, all of the disproportionation apparatus, including the cyclone separator, is maintained at a temperature slightly above the boiling point of titanium tetrachloride so that this titanium tetrachloride does not condense within the disproportionation apparatus. In this connection it should also be pointed out that the flow of argon **36** up through the titanium particles, which are gradually fed from the lower end of the second disproportionation zone **14***b* into the exit pipe **18**, serves the useful function of preventing condensation of titanium trichloride within the cooling titanium particles in the exit pipe **18**. The topmost particles in this exit pipe **18** are preferably at a relatively high temperature, on the order of the temperature at which they leave the disproportionation zone **14***b*. Thus, these particles are at temperatures on the order of 1200° C. The particles of titanium at a lower level in the exit pipe **18** are being cooled, however, both by conduction to the cooled walls of the pipe **18** and by heat exchange with the entering cool argon gas. The flow of argon gas, however, up through these titanium particles prevents diffusion of titanium trichloride vapors down through the titanium particles in the pipe **18** to a point where these vapors can condense. As a result of this countercurrent flow of argon through the titanium particles in the pipe **18**, these particles are collected at a low temperature, on the order of 200° C., at the bottom of the pipe and are substantially free of any condensed titanium trichloride.

Since certain changes may be made in the above process without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description, or shown in the accompanying drawings, shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. The process of forming titanium which comprises passing titanium trichloride through a first disproportionation zone while heating said titanium trichloride to a temperature sufficient to disproportionate a substantial amount of said trichloride to the dichloride, continuously removing titanium tetrachloride from the first disproportionation zone so as to maintain the partial pressure of titanium tetrachloride below the equilibrium disproportionation pressure of titanium trichloride at the temperature of the trichloride in the first disproportionation zone, passing the nonvolatile product from the first disproportionation zone into and through a second disproportionation zone wherein the said nonvolatile product is heated to a temperature on the order of 1000° C. to 1400° C. to obtain titanium metal, maintaining the partial pressure of the gaseous titanium chlorides in the second disproportionation zone below the equilibrium disproportionation pressure of titanium dichloride at the temperature of titanium dichloride in the second disproportionation zone, continuously withdrawing the titanium chloride vapors generated in the second zone, passing said vapors countercurrent to the flow of, and in contact with, the solid titanium chlorides advancing through the two disproportionation zones, and condensing titanium trichloride from these counterflowing titanium chloride vapors in the first zone.

2. The process of claim 1 wherein said titanium trichloride is maintained in a layer less than about one inch thick while in said first disproportionation zone.

3. The process of claim 1 wherein said nonvolatile material in said second disproportionation zone is continuously agitated to cause said product to form into small balls.

4. The process of claim 1 wherein said titanium trichloride is consolidated into pellets prior to feeding into the first disproportionation zone.

5. The process of claim 1 wherein the movement of vapors through and from the disproportionation zones is aided by passing a stream of argon in countercurrent to the movement of the solid titanium chlorides.

6. The process of forming titanium which comprises passing titanium trichloride through a first disproportionation zone while heating said titanium trichloride to a temperature sufficient to disproportionate a substantial amount of said trichloride to the dichloride, continuously removing titanium tetrachloride from the first disproportionation zone so as to maintain the partial pressure of titanium tetrachloride below the equilibrium disproportionation pressure of titanium trichloride at the temperature of the trichloride in the first disproportionation zone, passing the nonvolatile product from the first disproportionation zone into and through a second disproportionation zone wherein the said nonvolatile product is heated to a temperature on the order of 1000° C. to 1100° C. to obtain titanium metal, maintaining the partial pressure of the gaseous titanium chlorides in the second disproportionation zone below the equilibrium disproportionation pressure of titanium dichloride at the temperature of titanium dichloride in the second disproportionation zone, continuously withdrawing the titanium chloride vapors generated in the second zone, passing said vapors countercurrent to the flow of, and in contact with, the solid titanium chlorides advancing through the two disproportionation zones, and condensing titanium trichloride from these counterflowing titanium chloride vapors in the first zone.

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