June 24, 1958 H. K. NAJARIAN 2,840,466

METHOD OF REDUCING METAL CHLORIDES

Filed Oct. 29, 1954 3 Sheets-Sheet 1

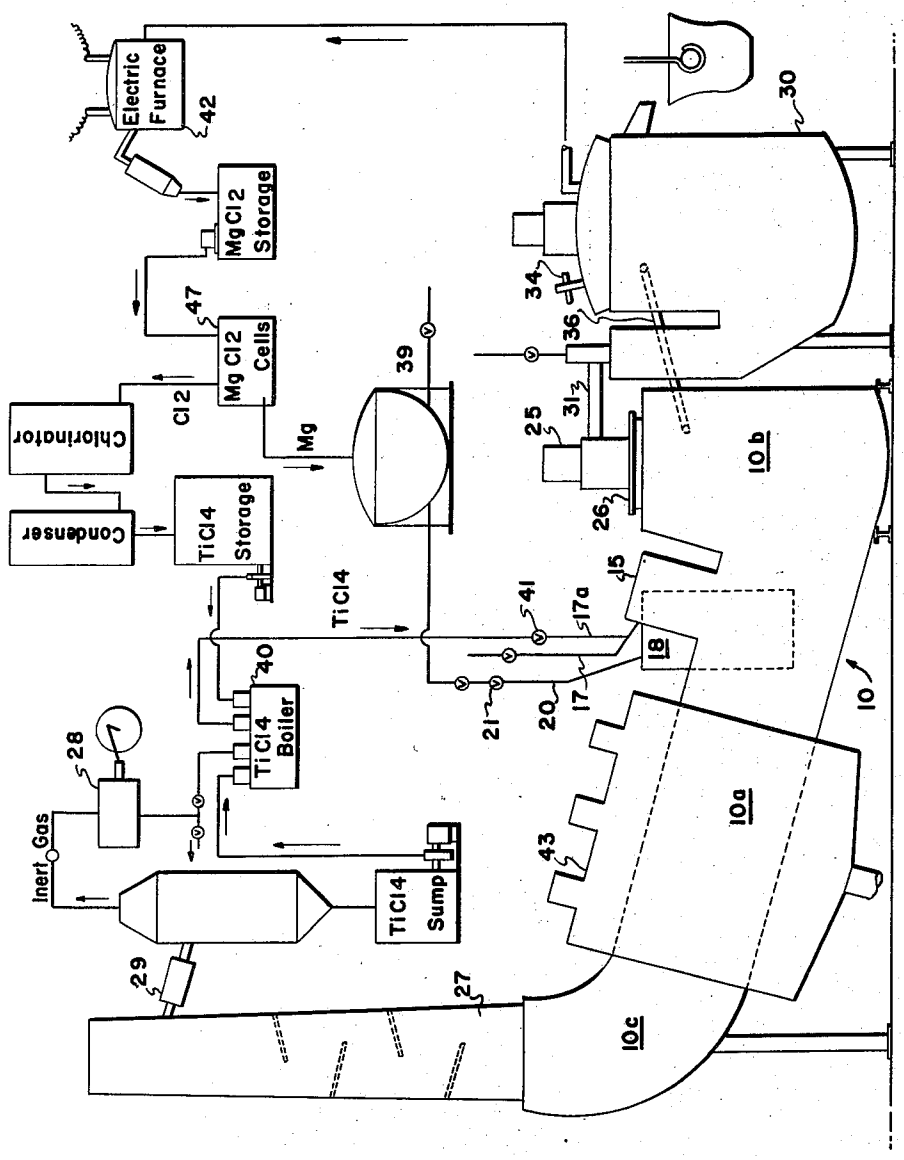


FIG. 1.

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METHOD OF REDUCING MELTAL CHLORIDES

Filed Oct. 29, 1954 3 Sheets-Sheet 2

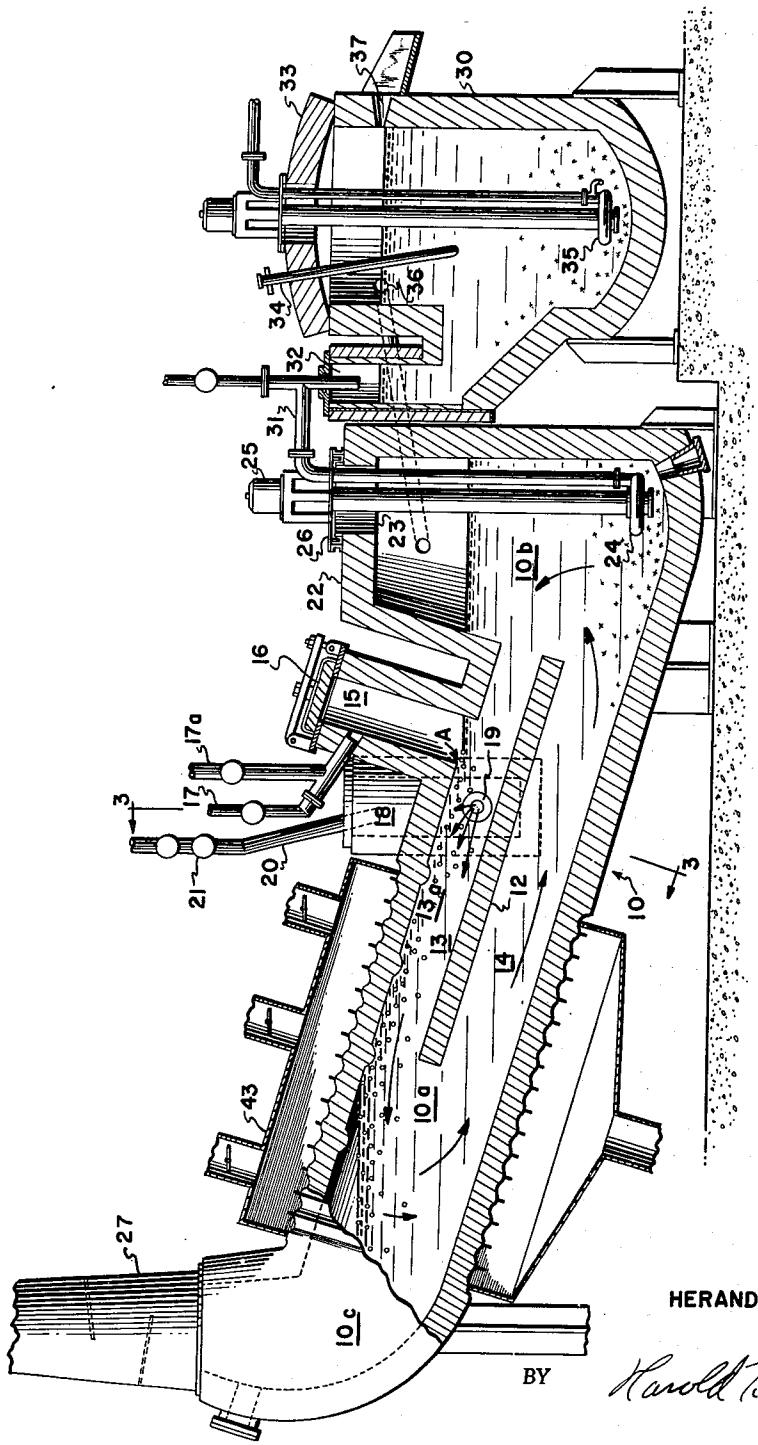


Fig. 2.

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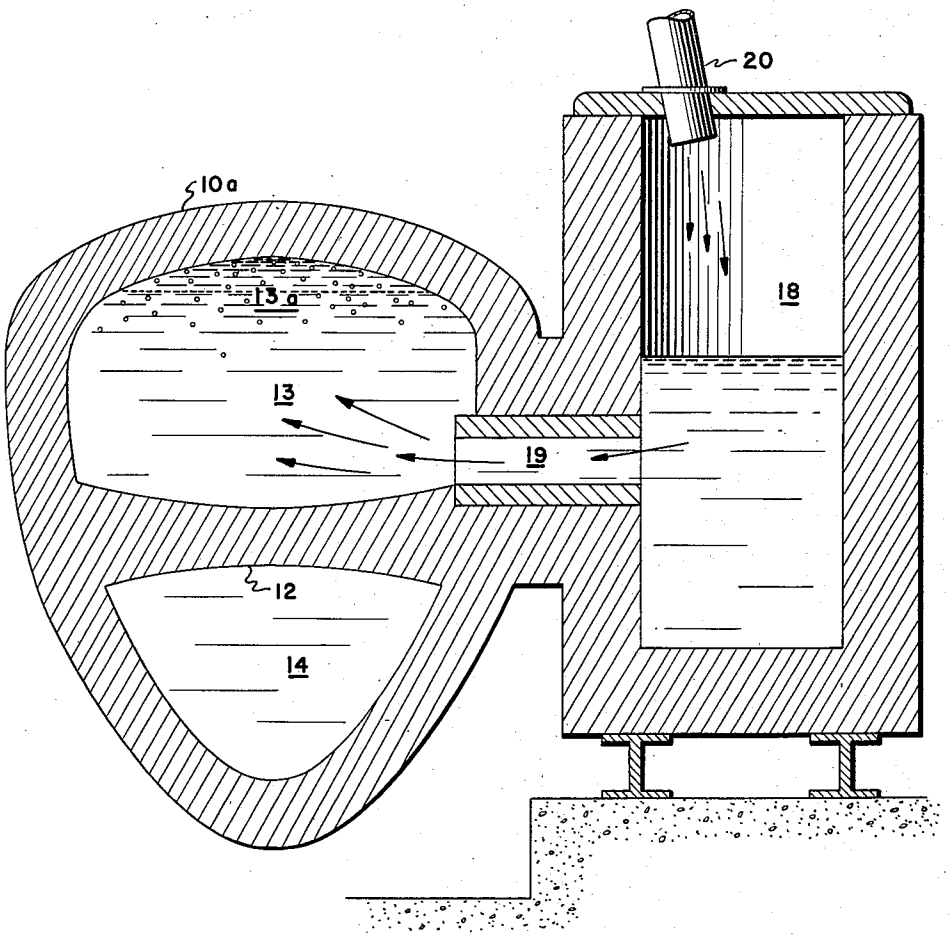
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June 24, 1958 H. K. NAJARIAN 2,840,466

METHOD OF REDUCING METAL CHLORIDES

Filed Oct. 29, 1954 3 Sheets-Sheet 3

Fig. 3.



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METHOD OF REDUCING METAL CHLORIDES

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7 Claims. (Cl. 75—84.5)

This invention relates to an improved method and apparatus for the reduction of chlorides of metals, such as titanium and zirconium to the metals.

An object of the invention is to provide means whereby titanium and zirconium metal, in either powder or ingot form and free of impurities, can be produced in substantial commercial quantities and cheaply, in apparatus permitting continuous operation, exclusion of contaminants, maintenance and control of relatively moderate operating temperatures involved and easy handling of materials used in the process and resultant products.

The following discussion will be directed more particularly to the production of titanium from titanium tetrachloride, but the method and apparatus of the invention ar also applicable to the production of zirconium which behaves very similarly to titanium in the reduction method of the invention.

The method of the invention generally comprises maintaining a stream of molten magnesium chloride at a temperature intermediate the melting point of magnesium and the boiling point of magnesium, preferably at about 775°–800° C., in continuous circulation in an inclined upward current from a lower body of magnesium chloride to an upper body of magnesium having a free surface and in a downward current from the upper body to the lower body, introducing into the lower portion of the inclined upward current molten magnesium and titanium tetrachloride in the proportion of at least two atoms of magnesium to each molecule of titanium tetrachloride, and withdrawing from the lower portion of the lower body a suspension of titanium metal in magnesium chloride. If the amount of magnesium chloride withdrawn exceeds the amount being formed by the reaction of the titanium tetrachloride and magnesium, sufficient additional magnesium chloride is introduced into the stream of magnesium chloride to maintain the volume of the stream substantially constant. The flow of the inclined upward current is advantageously maintained by introducing into the lower portion of the current, either separately or in admixture with the titanium tetrachloride being introduced, an inert gas, such as argon or helium. A suction is preferably maintained over the free surface of the upper body of magnesium chloride to remove the inert gas from the system.

Use of molten magnesium as reducing agent for tetrachloride of titanium and carrying out the reduction continuously at the relatively moderate temperature range of 775°–800° C. as the method contemplates, has many advantages over the methods disclosed in the prior art. Most of the prior methods are small-scale batch-wise operations and are unsuitable for large-scale, continuous operation.

Some of the prior methods involve the use of alkali metals, such as sodium and potassium, as the reducing agent for titanium compounds. These alkali metals are effective reducing agents, particularly for tetrachloride of titanium. However, in processes designed for continuous operation where it is necessary to maintain in the

reaction apparatus temperatures 75° to 100° above the melting points of the metallic salt products of reaction, metallic sodium and potassium tend to vaporize actively due to local high temperatures produced at the reaction zone. These metallic vapors evolved react with gaseous titanium tetrachloride and form titanium mist which tends to build up as spongy masses on interior walls and passages of the reaction apparatus, making continuous operation difficult and often impossible.

Conceivably, metallic calcium can be used for reduction of titanium tetrachloride in a continuous process. However, much higher reaction vessel temperatures have to be maintained as the melting point of calcium is considerably higher than the melting point of magnesium. Furthermore, production of calcium is much more costly, and the amount of metallic titanium produced per unit weight of calcium is substantially less than is produced by unit weight of magnesium. Separation of metallic titanium from the calcium chloride resulting from the reaction also involves costlier processes.

The prior art also discloses methods wherein vapors of magnesium and vapors of titanium tetrachloride are passed into a bath of molten salt maintained at temperatures above the boiling point of magnesium. Operations involving such high temperatures in the apparatus are hard to control and apparatus are much more costly. Completion of reaction by gas to gas contact within a molten salt bath is difficult to realize, resulting in gas to gas reaction above the surface of the molten salt bath and formation of spongy metal accumulations within the reaction vessel and passageways therein, making continuous operation difficult and impractical.

In the preferred method of the invention, a continuous stream of titanium tetrachloride vapor is brought into intimate contact with molten magnesium in a long, relatively shallow, channel-like reaction zone, inclined preferably at about 30° from the horizontal, and confined to a space between the inclined roof portion of a reaction vessel and upper surfaces of a stream of molten magnesium chloride flowing upwardly through the reaction zone.

The inclined reaction zone may be substantially rectilinear as is shown in the apparatus more particularly described below, or it may be of zig-zag or spiral configuration.

Due to novel features of the apparatus of the invention and novel method of operation thereof, the titanium tetrachloride vapors and molten magnesium flow concurrently in the long shallow turbuent reaction zone until the reaction between the reactants is substantially complete. The rate of flow of titanium tetrachloride and molten magnesium into said reaction zone is under control at all times during operation insuring completion of reaction within the prescribed reaction zone. The apparatus is so designed that titanium tetrachloride vapors cannot disperse, as such, to other zones of the reaction vessel. The reaction between titanium tetrachloride and molten magnesium is complete in said reaction zone resulting in production of metallic titanium particles and molten magnesium chloride salt.

With the novel method of the invention, the reaction between titanium tetrachloride vapors and molten magnesium occurs substantially entirely at liquid-gas interfaces as individual bubbles of tetrachloride of titanium are more or less enveloped by molten magnesium throughout their entire passage through the reaction zone, as more fully explained hereinafter. Provision is made to have excess of molten magnesium within the inclined reaction zone at all times. Because of its relatively low specific gravity, the excess of molten magnesium accumulates in the upper portion of the reaction zone, thus insuring substantially complete reaction of the titanium

tetrachloride vapors passed into the reaction zone. Furthermore, provision is made to dissipate the heat of reaction and maintain in the reaction zone a temperature range substantially below the boiling point of the metallic reducing agent, thus making sure that substantially all the reaction between the magnesium and tetrachloride of titanium vapors occurs while the magnesium is in liquid phase, thus preventing the formation of spongy metal accumulations within the reaction vessel or reducing them to a minimum.

The invention will be more fully described with reference to the accompanying drawings in which:

Fig. 1 is a diagrammatic flow chart showing an illustrative method and apparatus embodying the principles of the invention;

Fig. 2 is an enlarged elevational view, mostly in section of the reaction vessel of the invention; and

Fig. 3 is a transverse section on line 3—3 of Fig. 2.

The reaction vessel **10** comprises three principal communicating parts, a middle inclined tubular section **10***a*, a lower enclosed chamber **10***b* communicating with the lower end of the middle tubular inclined section and an upper elbow-shaped gas outlet chamber **10***c* communicating with the upper end of the middle inclined tubular section.

The reaction vessel comprises a gas tight metal outer shell, preferably of steel plate construction, and is lined with refractory materials not wetted by the reactants and reaction products within the vessel at the operating temperatures, such as carbon, graphite or silicon carbide. An insulating compressible interlining, such as asbestos sheets, is provided between the steel and refractory lining to allow for expansion of refractory within the steel shell without causing undue stresses in the steel casing.

A refractory baffle **12** running for a substantial length of the middle inclined section of the reaction vessel, from the lower end towards the upper end thereof, and paralleling the roof thereof, divides the tubular inclined middle section of the reaction vessel into two parallel passageways, one upper passageway **13** directly under the roof of the reaction vessel, and a lower passageway **14** underneath the upper passageway. A refractory lined pipe or dome **15** opening into the roof of upper passageway **13** at or near its lower end, and having a gas-tight cover **16**, provides means for passing of inert gas and titanium tetrachloride, preferably in vapor form, into the reaction vessel through pipes **17** and **17***a*, respectively, and directly below the roof of the middle incline section about its lower end. A refractory lined, insulated, standpipe **18** vertically disposed and located on one side and near the lower end of the middle inclined section of the reaction vessel, and communicating with the lower end of the middle inclined section through a conduit **19** opening into the lower end of the upper passageway **13** provides means for passing molten magnesium reducing agent into the reaction vessel. Molten magnesium is allowed to flow into the covered standpipe **18** through pipe **20** and its rate of flow is regulated by valve **21**.

The lower chamber **10***b* has a gas-tight roof **22** with a sealed opening **23**. Through the roof cover opening, a pump **24** having an encased driving shaft and a discharge pipe projects downwardly into the chamber **10***b*, the pump positioned near the lowest part at the bottom part of the chamber. The driving mechanism **25** of the pump rests on the cover plate **26** over the roof opening. The cover plate is made gas-tight with an adequate seal.

Upper chamber **10***c* is provided with a gas outlet pipe **27**, preferably insulated to maintain temperature permitting condensation of small quantities of metallic vapors that may escape out of the reaction vessel. Any small quantity of metal condensed runs downwardly into the reaction vessel by gravity. Gas outlet pipe **27**, in turn, is connected to a suction producing device, such as a vacuum pump **28**. Intermediate the vacuum pump and the gas outlet pipe, cooler **29** is provided to cool the inert gas, if desirable.

Auxiliary to the reaction vessel, an external settling chamber **30** is provided to receive reaction products transported out of the bottom of the lower chamber **10***b* by pump **24** to allow the reaction product to separate into a clear molten salt and a sludge containing the reduced metal.

Insulated pipe **31** extends from the discharge opening of pump **24** to sealed inlet opening **32** of the settling chamber **30** and serves to transport molten $MgCl_2$ from the bottom of lower chamber **10***b* of the reaction vessel **10** to the settling chamber **30**. The settling chamber **30** has a gas-tight cover **33** through which cooling pipe **34** and pump **35** extend into the body of molten $MgCl_2$ within the settling chamber. An overflow pipe **36** serves to convey cooled molten $MgCl_2$ from the settling chamber back to the lower chamber **10***a* of the reatcion vessel. Settling chamber **30** is also provided with a tap hole **37** through which excess of molten $MgCl_2$ may be withdrawn as desired, preferably continuously.

By the preferred method of the invention, reduction of titanium tetrachloride by means of molten magnesium is carried out within the apparatus as described above in a continuous manner, producing metallic titanium in the form of metallic particles or crystals suspended in molten magnesium and in suitable form for further processing for production of titanium powder or ingots.

Briefly, the operation of the process is as follows: The reaction vessel **10** is preheated internally to a temperature of 800° C. or thereabouts. Molten anhydrous magnesium chloride, preferably at a temperature of about 800° C., is passed into the reaction vessel through standpipe **18** by means of a temporarily installed pipe, not shown. The molten magnesium chloride is allowed to fill the reaction vessel to a level some distance (12–18 inches) above point A where inert gas and titanium tetrachloride vapors enter into the reaction zone during regular operation. All oxidizing gases above the level of molten magnesium chloride in the reaction vessel, including dome **15**, are exhausted by means of vacuum pumps or any other appropriate means. Inert gas, such as helium, is allowed to enter the lower chamber **10***b*, dome **15**, upper chamber **10***c*, and gas outlet pipes to insure that no oxidizing agents are left in the entire apparatus where they may come in contact with reactants or reaction products.

Suction is applied above the level of molten magnesium chloride in the upper chamber **10***c* through gas outlet pipe **27** by means of vacuum pump **28** or any other suction producing device. The suction in upper chamber raises the level of molten magnesium chloride in the upper chamber **10***c* and lowers the surface of the molten magnesium chloride in the dome **15** and lower chamber **10***b*. Inert gas is allowed to enter the dome **15** through pipe **17** and as soon as the level of molten magnesium chloride is lowered by suction below point A at the bottom of dome **15**, inert gas begins to bubble through the body of molten magnesium chloride in upper passageway **13** and directly under the roof of the middle tubular portion of the reaction vessel. As the inert gas bubbles through the molten magnesium chloride in the upper passageway **13**, the "air-lift" action of the gas bubbling upwardly through its incline path, begins to move the body of molten magnesium chloride within passageway **13** from the bottom region of the upper passageway **13** towards the upper chamber **10***c*. At the same time an amount of molten magnesium chloride equivalent to the amount of molten magnesium chloride being transported upwardly in upper passageway **13** flows downwardly through lower passageway **14** towards the lower chamber **10***b*. Thus substantially all of the molten magnesium chloride within the reaction vessel flows in inclined paths upwardly in upper passageway **13** and downwardly in the lower passageway **14**. The rate of flow of

molten magnesium chloride is dependent on the rate of gas passage. In general, in apparatus of the type described, a volume of 30 cubic feet of gas and vapor supplied to the lower end of passageway **13** will cause about one cubic foot of molten magnesium chloride to flow upwards through the passageway.

Into this upwardly flowing segment of the stream of molten magnesium chloride in the upper passageway **13** and at about the lower end thereof below the lower free surface of molten magnesium chloride in the gas inlet dome **15**, molten magnesium is allowed to enter from standpipe **18** and through conduit **19**. Initially the standpipe **18** holds molten magnesium chloride allowed to run into said standpipe when the reaction vessel is being supplied with the initial charge of molten magnesium chloride. When valve **21** is opened to alow molten magnesium to run from molten magnesium storage **39** through pipe **20**, the level of molten magnesium chloride in the standpipe is depressed toward conduit **19** and as soon as sufficient molten magnesium accumulates on top of the magnesium chloride, the molten magnesium begins to run through conduit **19** into the stream of molten magnesium chloride in the upper passageway **13** as shown. The molten magnesium, having lower specific gravity than molten magnesium chloride, rises towards the upper surface of the stream of molten magnesium chloride to a zone directly under the inclined roof of the inclined tubular section of the reaction vessel, as shown by the arrows. Thus, molten magnesium enters the shallow path of bubbling inert gas and is carried upwardly by the bubbling inert gas towards the gas outlet chamber and over and about the upper boundary of the stream of molten magnesium chloride.

Simultaneously with the passage of molten magnesium into the shallow bubbling zone, titanium tetrachloride valve **41** is opened and titanium tetrachloride, preferably in vapor form from boiler **40**, is allowed to enter dome **15** and to bubble together with inert gas upwardly through the shallow bubbling zone **13***a* which, in effect, constitutes the reaction zone within the reaction vessel. Throughout the length of the above shallow long inclined reaction zone, the upwardly bubbling titanium tetrachloride gas comes in intimate contact with molten magnesium surfaces. In fact, individual bubbles of titanium tetrachloride are continuously enveloped by molten magnesium surfaces, until gas is completely consumed by the reducing agent. The feed rate of reactants is designed to give ample time for all of the tetrachloride to be consumed during the time the bubbles of tetrachloride gas pass through the reaction zone. Furthermore, the flow of reactants into the reaction vessel is so adjusted as to have at all times some excess of molten magnesium in the reaction zone flowing concurrently with the titanium tetrachloride vapors.

The products of the reaction in accordance with the well known formula, $TiCl_4+2Mg \rightarrow 2MgCl_2+Ti$, comprising small particles or crystals of metallic titanium and molten anhydrous magnesium chloride are dispersed within the stream of molten magnesium chloride circulating within the reaction vessel. At the lower extremity of the lower passageway **14**, the stream of molten magnesium chloride flowing downwardly into the lower chamber **10***b* and carrying in suspension the particles or crystals of metallic titanium, begins to flow in upwardly direction within the lower chamber. Small amounts of molten magnesium that may have been entrained in the magnesium chloride stream begin, at this point, to rise somewhat more rapidly towards the lower opening of the upper passageway and, in turn, towards the gas entrance point A of the reaction zone **13***a*. Magnesium chloride likewise gradually reverses its direction of flow and flows upwardly in the upper passageway, running continuously in its closed path. The relatively heavy particles or crystals of metallic titanium gravitate towards the bottom part of the lower chamber **10***b* and collect at this lower zone in the form of sludge of solid metallic particles suspended in molten magnesium chloride.

The heat released by the above reaction of titanium tetrachloride with molten magnesium, in the reaction zone, is quickly absorbed as released within the stream of molten magnesium chloride circulating in its unidirectional path within the reaction vessel, and is, therefore, dissipated within the entire mass of molten magnesium chloride within the reaction vessel. As the body of molten magnesium chloride in the reaction vessel is continuously cooled, as hereinafter explained, the temperature of the reaction zone wherein the entire heat of reaction is released remains within moderate limits and no excessively high temperatures are built up in any zone of the reaction vessel.

Additional temperature control can be obtained when desirable by supplying cooling or heating fluids, such as cool or hot gases, to the jacket **43** of the reaction vessel.

The titanium metal particles gravitating to the bottom zone of lower chamber **10***b* are withdrawn, preferably continuously, in the form of sludge by pump **24** through pipe **31** and transported into the external settling chamber **30**. The amount of molten magnesium chloride withdrawn from the bottom zone of lower chamber **10***b* is normally in considerable excess of the amount being produced by the reactant at any time interval. The body of molten magnesium chloride within the settling chamber **30** is in a state of comparative quiescence to allow the heavier metallic titanium particles to settle to the bottom zone thereof in the form of sludge while the lighter molten magnesium chloride rises to the top portion. There the molten magnesium chloride is cooled, for example, by contact with water cooled pipe **34** and the excess returned to the lower chamber through conduit **36** mixes with hotter magnesium chloride in lower chamber **10***b* and thus maintains the temperature of the entire body of magnesium chloride in the reaction vessel at any desired operating range. This operating temperature range is preferably 775°–800° C.

An amount of molten magnesium chloride substantially equal to the amount being produced by the reactants is withdrawn preferably continuously, from the top portion of the settling chamber **30** and is electrolyzed in well known magnesium cells **47** to produce metallic magnesium and chlorine gas. The metallic magnesium is returned to molten magnesium storage kettle **39** and used again as reducing agent in the reaction vessel. The chlorine gas from magnesium cells may be used to manufacture additional titanium tetrachloride by well known process of chlorinating ores and concentrates of titanium compounds.

The sludge at the bottom of the settling chamber comprising titanium metal particles or crystals suspended in molten magnesium chloride is withdrawn at intervals or continuously as desired and is processed further to obtain pure titanium metal powder by well developed metallurgical methods or it may be transported to an electric furnace **42** operating under vacuum and at a temperature to vaporize the magnesium chloride and subsequently melt the metallic titanium which, in turn, is cast into ingots.

I claim:

1. A method of producing a refractory metal of the group consisting of titanium and zirconium which comprises maintaining a stream of molten magnesium chloride at a temperature intermediate the melting point of magnesium and the boiling point of magnesium in continuous circulation in an inclined upward current from a lower body of magnesium chloride to an upper body of magnesium chloride having a free surface and in a downward current from said upper body to said lower body, introducing into the lower portion of the inclined upward current molten magnesium and a refractory metal chloride of the group consisting of ti-

tanium tetrachloride and zirconium tetrachloride in the proportion of at least two atoms of magnesium to each molecule of the refractory metal chloride, and withdrawing from the lower portion of the lower body a suspension of the refractory metal in magnesium chloride.

2. A method of producing metallic titanium which comprises maintaining a stream of molten magnesium chloride at a temperature intermediate the melting point of magnesium and the boiling point of magnesium in continuous circulation in an inclined upward current from a lower body of magnesium chloride to an upper body of magnesium chloride having a free surface and in a downward current from said upper body to said lower body, introducing into the lower portion of the inclined upward current molten magnesium and titanium tetrachloride in the proportion of at least two atoms of magnesium to each molecule of titanium tetrachloride, and withdrawing from the lower portion of the lower body a suspension of titanium in magnesium chloride.

3. A method of producing metallic titanium which comprises maintaining a stream of molten magnesium chloride at a temperature intermediate the melting point of magnesium and the boiling point of magnesium in continuous circulation in an inclined upward current from a lower body of magnesium chloride to an upper body of magnesium chloride having a free surface and in a downward current from said upper body to said lower body, introducing into the lower portion of the inclined upward current molten magnesium and titanium tetrachloride in the proportion of at least two atoms of magnesium to each molecule of titanium tetrachloride, withdrawing from the lower portion of the lower body a suspension of titanium in magnesium chloride, and introducing into said stream of magnesium chloride additional magnesium chloride in an amount sufficient to maintain the volume of said stream substantially constant.

4. A method of producing metallic titanium which comprises maintaining a stream of molten magnesium chloride at a temperature of from about 775° to about 800° C. in continuous circulation in an inclined upward current from a lower body of magnesium chloride to an upper body of magnesium chloride having a free surface and in a downward current from said upper body to said lower body, introducing into the lower portion of the inclined upward current molten magnesium and titanium tetrachloride in the proportion of at least two atoms of magnesium to each molecule of titanium tetrachloride, and withdrawing from the lower portion of the lower body a suspension of titanium in magnesium chloride.

5. The method as defined in claim 2 wherein the stream of magnesium chloride is maintained in circulation by introducing an inert gas into the lower portion of the inclined upward current.

6. The method as defined in claim 2 wherein a subatmospheric pressure is maintained above the free surface of said upper body of magnesium chloride.

7. A method of producing metallic titanium which comprises maintaining a stream of molten magnesium chloride at a temperature intermediate the melting point of magnesium and the boiling point of magnesium in continuous circulation in an inclined upward current from a lower body of magnesium chloride to an upper body of magnesium chloride having a free surface and in a downward current from said upper body to said lower body by introducing an inert gas into the lower portion of the inclined upward current and maintaining a subatmospheric pressure above the free surface of said upper body, introducing into the lower portion of the inclined upward current molten magnesium and titanium tetrachloride in the proportion of at least two atoms of magnesium to each molecule of titanium tetrachloride, withdrawing from the lower portion of the lower body a suspensin of titanium in magnesium chloride, and introducing into said stream additional magnesium chloride in an amount sufficient to maintain the volume of said stream substantially constant.

References Cited in the file of this patent

UNITED STATES PATENTS

2,205,854	Kroll	June 25, 1940
2,564,337	Maddex	Aug. 14, 1951
2,607,674	Winter	Aug. 19, 1952
2,647,826	Jordan	Aug. 4, 1953
2,766,034	Najarian	Oct. 9, 1956