United States Patent Office 2,804,386
Patented Aug. 27, 1957

2,804,386

METHOD OF PRODUCING TITANIUM METAL

Edward G. McMackin and John E. McMillan, Henderson, Gordon W. Miles, Boulder City, and William E. Mooz, Henderson, Nev., assignors to Titanium Metals Corporation of America, New York, N. Y., a corporation of Delaware

No Drawing. Application May 31, 1956, Serial No. 583,228

7 Claims. (Cl. 75—84.5)

This invention relates to the production of titanium metal, and more particularly to improvements in the general process wherein titanium tetrachloride is reacted with a metallic reducing agent.

The general process to which this invention relates, involves adding to a molten reducing agent, for instance, magnesium, contained in a reactor under a protective gas and at substantially atmospheric pressure, sufficient titanium tetrachloride to produce metal as a result of its reduction by the reducing metal. This process is generally referred to as the Kroll process and is described in U. S. Patent No. 2,205,854. In commercial practice of the Kroll process, however, the efficiency of utilization of the magnesium reducing metal generally is not high. This efficiency may not exceed 60–75% under ordinary conditions and rarely, if ever, reaches 80% in large commercial size reactors. Apparently, after the reaction has proceeded to a certain extent, an appreciable amount of magnesium is trapped below the titanium sponge formation and is not available to react with $TiCl_4$ fed from the top. The low efficiency of magnesium utilization results in obvious loss of this raw material, and also complicates the subsequent separation of the titanium sponge product from the excess magnesium employed and the magnesium chloride by-product. Efforts to feed additional titanium tetrachloride to the lower portion of the titanium deposit have generally proved unsuccessful due to plugging of the titanium tetrachloride introduction means by formation of titanium metal in the vicinity of the titanium tetrachloride flow into the reaction zone. Corrosion of ferrous pipes or other apparatus by reaction with the titanium metal produced has also been a serious problem.

It is therefore a principal object of this invention to provide an improved method for the production of metallic titanium. An additional object is to provide a method for production of titanium from titanium tetrachloride by reduction with a reducing metal in which the utilization efficiency of the reducing metal is substantially improved. A still further object of this invention is to provide a more efficient method for production of titanium metal by reaction of titanium tetrachloride and a reducing metal with respect to utilization of the reducing metal and subsequent separation of the titanium sponge produced from excess metallic reducing agent and chloride by-product. Yet another object of this invention is to provide a method for production of titanium metal by reaction of titanium tetrachloride with a reducing metal in which titanium tetrachloride is introduced for contact with said reducing metal both on top of the reaction mass and also from the bottom of the reaction mass to promote higher utilization of the reducing metal employed. These and other objects of this invention will be apparent from the following complete description thereof.

This invention, in its broadest aspects, contemplates reduction of titanium tetrachloride with a reducing metal in a two-step process, the reaction being carried out at

substantially atmospheric pressure in a closed reactor under a non-contaminating atmosphere of, for example, helium or argon. Titanium tetrachloride is initially introduced at or near the top of a reaction zone and instilled onto metallic magnesium until from about 60% to 75% of the stoichiometric amount required to react with the magnesium in the reactor has been added. During this first step an elongated body is maintained in the reaction zone to form in the reaction mass, which will comprise titanium sponge, metallic magnesium and magnesium chloride by-product, an elongated vertical cavity. The elongated body may conveniently be in the form of a pipe reaching from above the top of the reactor to a point near or at the bottom of the reactor. It is a feature of this invention that the external surface of this body is maintained at a temperature above the freezing point of magnesium chloride, about 710° C. but below about 920° C. The tendency for metallic titanium to attack and alloy with the ferrous metal pipe is noticeable above 950° C., and the maximum of 920° C. insures a condition under which the pipe will be free from attack. Under these critical conditions the titanium sponge product will not adhere to the pipe surface nor will the pipe itself, which is preferably composed of a ferrous metal, be corroded by the reaction products and raw materials, and thereby contaminate the titanium metal being produced. After about 60% to 75% of the tetrachloride has been introduced, the reaction generally slows down, as is evidenced by a pressure rise in the reaction zone caused by inability of the remaining magnesium metal to absorb and react with the added titanium tetrachloride. Instillation of titanium tetrachloride is, according to this invention, thereupon discontinued and the remainder of the titanium tetrachloride is introduced into the bottom or lower portion of the reaction mass to react with the residual magnesium metal which cannot be utilized by titanium tetrachloride being instilled onto the reaction mass from the top. This is accomplished by providing in the cavity maintained during the first step of the process a titanium tetrachloride feed pipe whose open lower extremity extends to a point near the bottom of the reactor. During introduction of titanium tetrachloride through this bottom feed pipe, titanium metal may form in the vicinity of the pipe open end and partially or wholly obstruct the flow of titanium tetrachloride therefrom. At intervals during the titanium tetrachloride addition, if and when this occurs, the feed pipe is raised sufficiently, generally one to three inches, to provide open unobstructed efflux of titanium tetrachloride from the feed pipe. Titanium tetrachloride is introduced in the second bottom feeding step until a total, including that added in the first step, of up to about 95% of that stoichiometrically required to react with all the magnesium metal present has been introduced. It is preferred not to attempt to introduce more than 95% since, due to dispersal of the raw materials and inability to reach the last remaining few percent of magnesium metal, the possibility of formation of objectionable titanium lower chlorides would be increased. After all the titanium tetrachloride has been introduced, the titanium sponge product is removed from the reactor and separated from the residual small amount of metallic magnesium and magnesium chloride by-product by conventional methods. These may include distillation to remove such by-products in volatile form or may comprise leaching with dilute acid to separate these as soluble compounds. It will be appreciated that the substantial reduction in the amount of residual unreacted magnesium considerably promotes efficiency of the subsequent purification steps.

The elongated body maintained in the reaction mass during the top instillation of $TiCl_4$ may be cooled to the desired temperature by any suitable means. Preferably

the body is formed of iron or steel pipe partially filled with metallic sodium under an inert gas atmosphere at a pressure of between 3 and 50 mm. of mercury absolute, at room temperature, and sealed. At operating temperature in the reactor the helium pressure will rise to about three times the room temperature pressure or between about 10 and 150 mm. to provide the required temperature control. The top of the pipe, protruding externally of the reactor, is cooled by suitable means such as a water jacket or air flow. The sodium metal boils at a constant temperature depending on the pressure. The rising vapors are condensed in the top, cooled portion of the pipe and act as an effective heat transfer medium to transfer heat and to maintain the desired pipe temperature in the reaction mass. It will be obvious that the temperature of the pipe outer wall will always be higher than the controlled temperature inside the pipe and the pressure and corresponding temperature inside the pipe should be such that the outside of the pipe is normally maintained at a temperature slightly above the freezing point of magnesium chloride and within the range 710° to 920° C. A helium or argon atmosphere at a pressure at operating temperature of 20 to 50 mm. of mercury absolute above the sodium will result in a controlled temperature of about 750–800° C. on the outside of a two inch, one-fourth inch wall mild steel pipe.

If desired, the elongated body employed to maintain the cavity in the sponge during the first $TiCl_4$ introduction step may contain the feed pipe employed for bottom feeding $TiCl_4$ during the second $TiCl_4$ introduction step. This may be accomplished by provision of a pair of concentric pipes with the inner pipe open at the bottom for $TiCl_4$ feeding and the annular space between the pipes being sealed and containing sodium heat transfer medium. $TiCl_4$ is fed through the center pipe only during the second introduction, and the whole assembly may be raised periodically to provide unobstructed flow.

During the first $TiCl_4$ introduction step the pipe operates at relatively high temperature but during the second step it is adequaely cooled by passage of liquid $TiCl_4$ therethrough. Employment of the integrated assembly involves, therefore, more complex design of sealing means where the pipe passes through the reactor cover since this must operate both at the high temperature involved during the first step and also with sliding motion when the pipe is intermittently raised during the second step. Problems arising from the two conditions may be solved individually by providing a separate sodium cooled pipe for the first step which is sealed at the reactor cover by a simple tight fitting metallic collar, or flange, provided with a heat resisting gasket and a second open pipe for the second step which is provided with a sliding seal of resilient material such as rubber, or a bellows seal, where it passes through the same hole in the cover. At completion of the first $TiCl_4$ top feed step the sodium pipe may readily be removed and the second bottom feed pipe substituted by sliding it down into the cavity left by removal of the first pipe. Contamination of the titanium metal by atmospheric gases is avoided by providing a substantial outflow of inert gas from the reactor through the temporarily open cover hole during the changeover period.

The following examples are presented to illustrate embodiments of the process of this invention.

Example 1

A charge of 1300 lbs. of metallic magnesium was placed in a reactor pot around a two inch vertical steel pipe sealed at the bottom and top, containing 5 lbs. of metallic sodium under a pressure of 13 mm. (at room temperature) of mercury absolute of helium. The bottom of the pipe extended substantially to the bottom of the inside of the reactor. The pipe passed through a seal on the reactor cover and the protruding top was provided with a jacket through which air could be passed for cooling. A short titanium tetrachloride feed pipe extending just through the cover and a helium feed pipe were also provided in the cover. The cover was sealed in place and the reactor evacuated and back filled with helium. The reactor was heated to 700° C., the heat shut off, and then titanium tetrachloride introduced through the short top feed pipe at a rate of 500 lbs. per hour until 3500 lbs. had been introduced. At this point about 68% of the stoichiometric amount to react with the magnesium had been added and the reaction slowed down. The top $TiCl_4$ was then shut off. The sodium-containing pipe was then removed and replaced with a one inch steel pipe open at the bottom and connected to the $TiCl_4$ feed supply. Helium was introduced into the reactor to provide an out flow of this gas from the reactor hole during the changeover to prevent contamination of the product by entry of air. The one inch pipe was readily inserted into the cavity in the titanium sponge left by withdrawal of the sodium-containing pipe. An additional 1000 lbs. of liquid $TiCl_4$ was then fed through the bottom feed pipe over a period of 1⅔ hours to bring the total introduced into the reactor to 4600 lbs., or 89.5% of the theoretical amount to react with the 1300 lbs. of magnesium charged. At the end of the reaction the bottom feed pipe was readily removed with its surface clean and uncorroded. Magnesium chloride was then drained from the sponge through a tap hole in the bottom of the reactor, which was then cooled, opened, and the titanium sponge removed, ground and leached with a dilute HCl solution to remove $MgCl_2$ and residual magnesium. The titanium metal when melted into an ingot was found to be of good quality, of hardness 125 Brinell and contained 0.05% iron, which is considered a normal content of this impurity.

Example 2

The operating procedure was essentially the same as that employed in Example 1 except that the sodium cooled pipe consisted of a two inch steel pipe with a one inch steel pipe inside it. The central pipe was opened and the sealed annular space between the two pipes contained 3 lbs. of metallic sodium under 30 mm. of mercury absolute pressure of helium at room temperature. An expanding bellows seal was provided where this assembly passed through the reactor cover.

Thirty-five hundred pounds of $TiCl_4$ was introduced, as before by means of the top feed pipe over a period of seven hours. At the end of the third and fifth hours magnesium chloride was tapped from the charge and a total of about 20 lbs. of magnesium was unavoidably removed with the $MgCl_2$.

After the 3500 lbs. of $TiCl_4$ had been introduced the top feed was shut off and $TiCl_4$ introduced into the bottom of the reaction mass through the central pipe of the double pipe assembly at a rate of 550 lbs. per hour.

After one-half hour of $TiCl_4$ addition, the flow of $TiCl_4$ through the bottom feed pipe became low and irregular. The pipe was then raised 1½ inches to provide an open space around the bottom of the pipe and flow recommenced at full rate. This was repeated after 1¾ hours when the flow again became obstructed and full normal flow again reobtained.

The amount of $TiCl_4$ introduced in the bottom feeding step was 1210 lbs., this being adjusted for the magnesium lost to the reaction during tapping and providing a total amount of $TiCl_4$ added (both top and bottom) of 93% of stoichiometric.

After introduction of $TiCl_4$ was complete the feed pipe assembly was readily removed and found to be clean and uncorroded. The sponge was drained, cooled, ground and leached as in Example 1. The product metal was determined to be of good quality, of hardness 128 Brinell and contained 0.045% iron.

The process of this invention makes possible efficient operation of the Kroll type of method for production of metallic titanium. Provision of the cooled body to maintain a cavity in the sponge is an important feature which

allows the bottom feed pipe to be inserted, raised periodically and removed at the end of the run. The temperature of the pipe or body is important to prevent metallic titanium from plugging the pipe and/or adhering to or corroding its surface. Apparently when the pipe or body is safely below the temperature at which alloying of Ti and Fe may start, there is no tendency for the reaction to proceed on the pipe surface, and the advantages of increased efficiency from utilization of a substantial amount of magnesium reducing agent which has heretofore been lost may be realized.

We claim:

1. In a method for production of metallic titanium wherein $TiCl_4$ is added to and reacted with metallic magnesium in a closed reactor under a non-contaminating atmosphere, the steps in combination which comprise; charging metallic magnesium into said reactor, instilling onto the top of said magnesium between about 60% and 75% of the amount of $TiCl_4$ stoichiometrically required to produce metallic titanium by reaction therewith, maintaining during such top addition of $TiCl_4$ a vertical elongated body, whose outer surface temperature is between about 710° C. and 920° C., in the reaction mass to form a vertical elongated cavity in the titanium sponge formed during such $TiCl_4$ addition, discontinuing instillation of $TiCl_4$ onto the top of the reaction mass, and introducing additional $TiCl_4$ into said reactor through a feed pipe disposed in said cavity formed in the titanium sponge and having its lower open extremity near the bottom of said reactor in amount so that the top fed and bottom fed $TiCl_4$ is between 85% and 95% of that stoichiometrically required to form metallic titanium with the metallic magnesium in the reactor.

2. In a method for production of metallic titanium wherein $TiCl_4$ is added to and reacted with metallic magnesium in a closed reactor under a non-contaminating atmosphere, the steps in combination which comprise; charging metallic magnesium into said reactor, instilling onto the top of said magnesium between about 60% and 75% of the amount of $TiCl_4$ stoichiometrically required to produce metallic titanium by reaction therewith, maintaining during such top addition of $TiCl_4$ a vertical elongated body, whose outer surface temperature is between about 710° C. and 920° C., in the reaction mass to form a vertical elongated cavity in the titanium sponge formed during such $TiCl_4$ addition, discontinuing instillation of $TiCl_4$ onto the top of the reaction mass, introducing additional $TiCl_4$ into said reactor through a feed pipe disposed in said cavity formed in the titanium sponge and having its lower open extremity near the bottom of said reactor in amount so that the total of the top fed and bottom fed $TiCl_4$ is between 85% and 95% of that stoichiometrically required to form metallic titanium with the metallic magnesium in the reactor, and periodically during such bottom addition raising said feed pipe to provide unobstructed efflux of $TiCl_4$ therefrom.

3. In a method for production of metallic titanium wherein $TiCl_4$ is added to and reacted with metallic magnesium in a closed reactor under a non-contaminating atmosphere, the steps in combination which comprise; charging metallic magnesium into said reactor, instilling onto the top of said magnesium between about 60% and 75% of the amount of $TiCl_4$ stoichiometrically required to produce metallic titanium by reaction therewith, maintaining during such top addition of $TiCl_4$ a vertical elongated body containing a feed pipe, whose outer surface temperature is between about 710° C. and 920° C., in the reaction mass to form a vertical elongated cavity in the titanium sponge formed during such $TiCl_4$ addition, discontinuing instillation of $TiCl_4$ onto the top of the reaction mass, and introducing additional $TiCl_4$ into said reactor through the feed pipe in said elongated body which has its lower open extremity near the bottom of said reactor in amount so that the total of the top fed and bottom fed $TiCl_4$ is between 85% and 95% of that stoichiometrically required to form metallic titanium with the metallic magnesium in the reactor.

4. In a method for production of metallic titanium wherein $TiCl_4$ is added to and reacted with metallic magnesium in a closed reactor under a non-contaminating atmosphere, the steps in combination which comprise; charging metallic magnesium into said reactor, instilling onto the top of said magnesium between about 60% and 75% of the amount of $TiCl_4$ stoichiometrically required to produce metallic titanium by reaction therewith, maintaining during such top addition of $TiCl_4$ a vertical elongated body, whose outer surface temperature is between about 710° C. and 920° C., in the reaction mass to form a vertical elongated cavity in the titanium sponge formed during such $TiCl_4$ addition, discontinuing instillation of $TiCl_4$ onto the top of the reaction mass, removing said vertical elongated body and inserting into the cavity in the titanium sponge left by removal of said body a feed pipe having its open lower extremity near the bottom of said reactor and introducing additional $TiCl_4$ into said reactor through said feed pipe in amount so that the total of the top fed and bottom fed $TiCl_4$ is between 85% and 95% of that stoichiometrically required to form metallic titanium with the metallic magnesium in the reactor.

5. In a method for production of metallic titanium wherein $TiCl_4$ is added to and reacted with metallic magnesium in a closed reactor under a non-contaminating atmosphere, the steps in combination which comprise; charging metallic magnesium into said reactor, instilling onto the top of said magnesium between about 60% and 75% of the amount of $TiCl_4$ stoichiometrically required to produce metallic titanium by reaction therewith, maintaining during such top addition of $TiCl_4$ a vertical elongated body in the reaction mass in said reactor, cooling said elongated body to maintain its outer surface temperature between about 710° C. and 920° C. thereby to form a vertical elongated cavity in the titanium sponge formed during such $TiCl_4$ addition, discontinuing instillation of $TiCl_4$ onto the top of the reaction mass, and introducing additional $TiCl_4$ into said reactor through a feed pipe disposed in said cavity formed in the titanium sponge and having its lower open extremity near the bottom of said reactor in amount so that the total of the top fed and bottom fed $TiCl_4$ is between 85% and 95% of that stoichiometrically required to form metallic titanium with the metallic magnesium in the reactor.

6. In a method for production of metallic titanium wherein $TiCl_4$ is added to and reacted with metallic magnesium in a closed reactor under a non-contaminating atmosphere, the steps in combination which comprise; charging metallic magnesium into said reactor, instilling onto the top of said magnesium between about 60% and 75% of the amount of $TiCl_4$ stoichiometrically required to produce metallic titanium by reaction therewith, maintaining during such top addition of $TiCl_4$ a vertical elongated body in the reaction mass in said reactor, cooling said elongated body by means of a metallic sodium heat transfer medium to maintain its outer surface temperature between about 710° C. and 920° C. thereby to form a vertical elongated cavity in the titanium sponge formed during such $TiCl_4$ addition, discontinuing instillation of $TiCl_4$ onto the top of the metallic magnesium, and introducing additional $TiCl_4$ into said reactor through a feed pipe disposed in said cavity formed in the titanium sponge and having its lower open extremity near the bottom of said reactor in amount so that the total of the top fed and bottom fed $TiCl_4$ is between 85% and 95% of that stoichiometrically required to form metallic titanium with the metallic magnesium in the reactor.

7. In a method for production of metallic titanium wherein $TiCl_4$ is added to and reacted with metallic magnesium in a closed reactor under a non-contaminating atmosphere, the steps in combination which comprise; charging metallic magnesium into said reactor, instilling

onto the top of said magnesium between about 60% and 75% of the amount of $TiCl_4$ stoichiometrically required to produce metallic tianium by reaction therewith, maintaining during such top addition of $TiCl_4$ a vertical elongated body in the reaction mass in said reactor, cooling said elongated body by means of a metallic sodium heat transfer agent maintained under an atmosphere of inert gas at a pressure of between 10 mm. and 150 mm. of mercury absolute to maintain its outer surface temperature between about 710° C. and 920° C. thereby to form a vertical elongated cavity in the titanium sponge

formed during such $TiCl_4$ addition, discontinuing instillation of $TiCl_4$ onto the top of the metallic magnesium, and introducing additional $TiCl_4$ into said reactor through a feed pipe disposed in said cavity formed in the titanium sponge and having its lower open extremity near the bottom of said reactor in amount so that the total of the top fed and bottom fed $TiCl_4$ is between 85% and 95% of that stoichiometrically required to form metallic titanium with the metallic magnesium in the reactor.

No references cited.