May 15, 1956 A. C. BYRNS 2,745,735

METHOD OF PRODUCING TITANIUM

Filed April 28, 1953 3 Sheets-Sheet 1

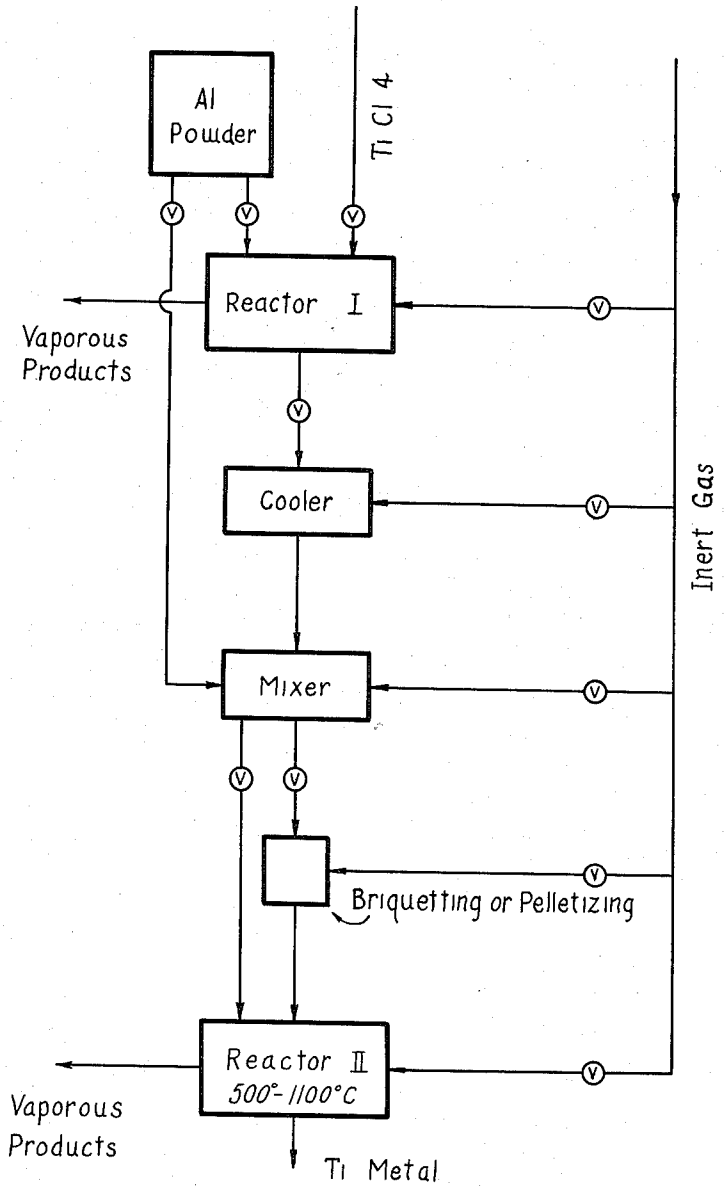



FIG. 1.

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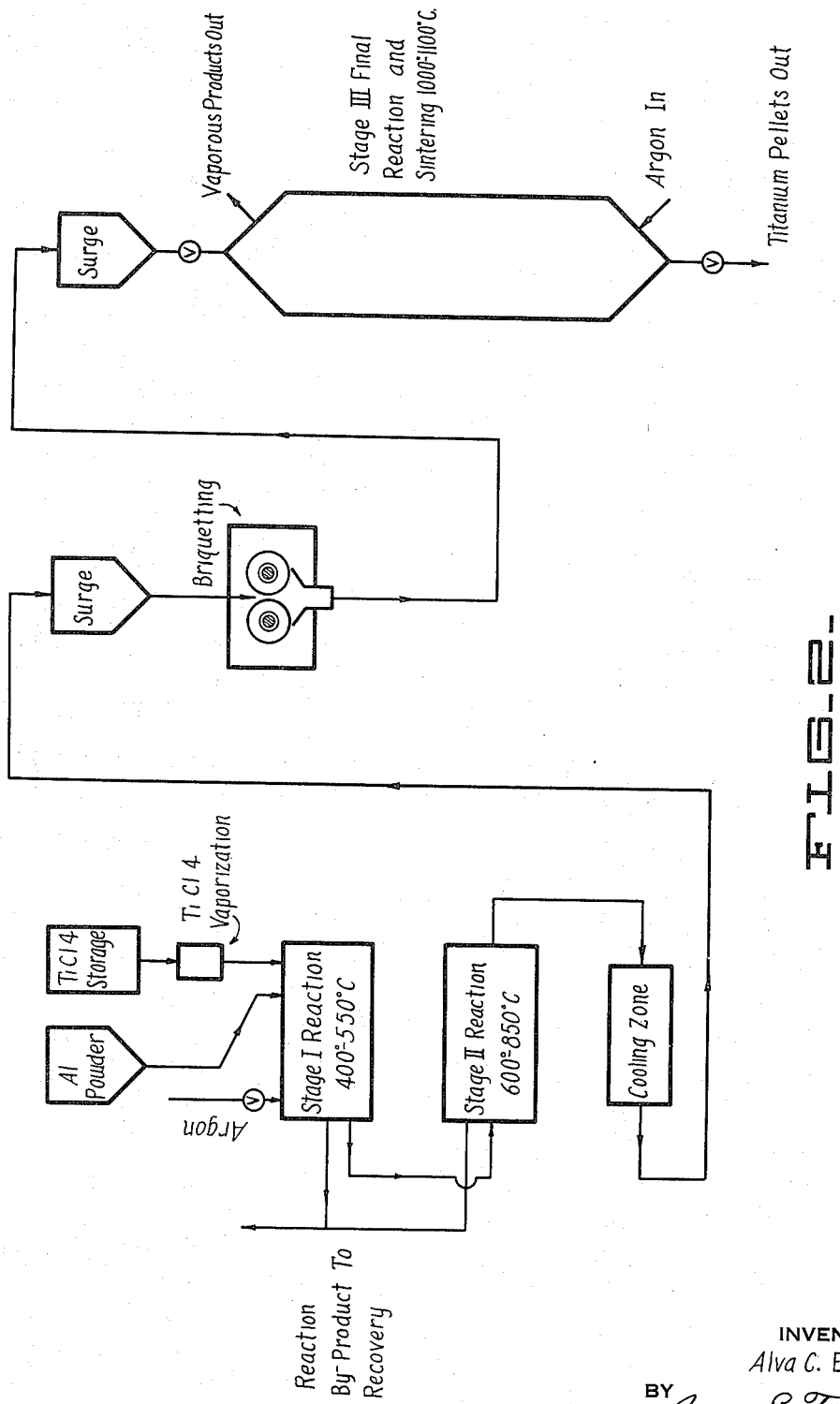



FIG. 2.

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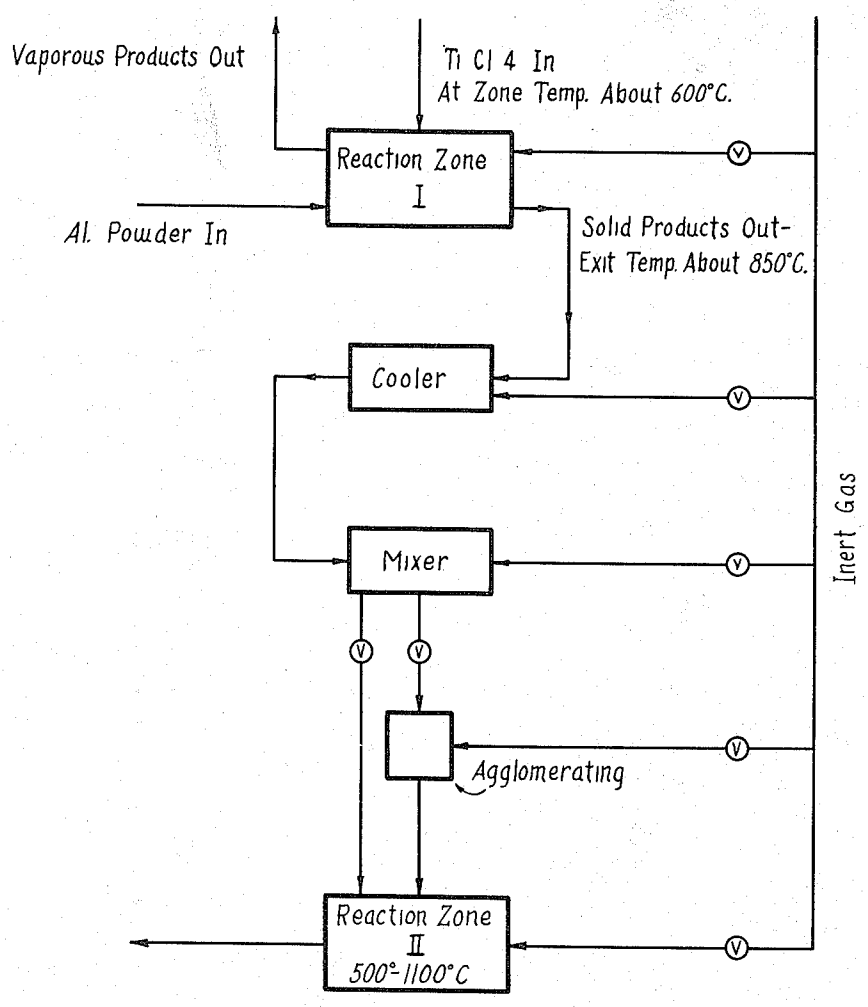



FIG. 3.

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United States Patent Office 2,745,735 Patented May 15, 1956



2,745,735

# METHOD OF PRODUCING TITANIUM

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Application April 28, 1953, Serial No. 351,664

12 Claims. (Cl. 75—84)

This invention relates to a process for producing ductile titanium metal; and, more particularly, to such process wherein titanium chlorides are reduced by a reducing metal to yield high purity titanium metal and volatile chlorides.

Titanium is known to be a metal of great strength and light weight and to be very desirable in construction where these qualities are of particular importance, for instance, in aircraft manufacture. Various methods have been proposed for preparing the pure metal inasmuch as it occurs principally as the oxide, in rocks and ores, those methods including reduction of the oxide with aluminum, electrolysis of the oxide dissolved in fused calcium chloride, and conversion of the Ti values to tetrachloride, followed by direct reduction of titanium chlorides to the metal by reaction with hydrogen or with alkali or alkaline earth metals. The direct reduction of titanium tetrachloride to titanium by reaction with a metal such as magnesium, sodium, potassium or calcium has been so successful commercially as to clearly demonstrate the above advantageous uses for titanium metal.

However, it is a particular problem in this art to make ductile metal of high purity. Some of the known processes yield titanium which contains impurities that render the metal brittle and unworkable; whereas, in other processses, the principal disadvantage is that the impurities, though not so harmful with regard to ductility, are present in substantial and objectionable amounts and are extremely difficult to remove, requiring, for example, comminution of a mass of titanium product, followed by leaching and/or treatment at higher temperatures to volatilize off the undesired contaminants, such as the halides of the reducing metal. These treatment steps are expensive and time-consuming, resulting in increased costs of production and a high-priced metal. For instance, the grinding step alone is expensive and difficult because titanium is extremely tough, requiring special grinding devices.

It is an object of the present invention to provide a process for producing high purity ductile titanium. It is a further object to provide a process for producing such titanium which is relatively simple and inexpensive, requiring only minimal amounts of an inert gas and which can be carried out under more moderate and easily controlled operating conditions than have hitherto been known. It is a specific object of this invention further to provide a process for producing high purity ductile titanium, free of impurities which would render the metal brittle and nonworkable; and for producing such titanium in compact form which is especially suitable for further melting and fabricating operations.

According to the present invention, ductile titanium metal is produced by heating finely divided aluminum metal and titanium tetrachloride, in the absence of a reactive gas, such as air or other reactive gas, at a temperature of from 400° C. to 600° C., preferably from 400° C. to 550° C., to form vaporous or gaseous aluminum chloride and a lower chloride of titanium, or a mixture of lower



chlorides of titanium, in solid form. The vaporous aluminum chloride is separately withdrawn. The titanium lower chloride is then intimately mixed with finely divided aluminum metal and the mixture is heated in an inert atmosphere at a temperature which gradually increases from about 500° C. to about 1100° C., whereby there are formed titanium metal and vaporous or gaseous aluminum chloride. The finely divided aluminum with which the lower chloride or chlorides of titanium is admixed can be freshly added aluminum but preferably, as will be further explained below, it is unreacted aluminum present in the solid product from the first heating stage; and it can comprise both such unreacted aluminum and a portion of freshly added aluminum. The aluminum chloride in vapor state formed in this second heating step is withdrawn and the titanium metal is separately recovered. The metal which is so produced is in powdered form if the starting materials are powdered or, when agglomerates of the admixed titanium lower chloride and finely divided aluminum metal are heated as described, the titanium metal product is in compact form and is especially adapted to further handling and subjection to melting processes; it is free of contaminants which if present would have caused brittleness and nonworkability. In another embodiment, the final temperature in the first reaction zone can be increased to about 850° C., as will be further described below, which causes the formation of a small amount or minor portion of finely divided titanium metal at that stage of the process. This is sometimes advantageous as, for instance, if the material is to be pelleted or otherwise agglomerated under pressure prior to the final heating stage, because the presence of finely divided titanium metal enables the production of much stronger and denser pellets or agglomerates.

The aluminum metal which is employed herein is substantially free of oxygen, nitrogen or other contaminants which would render the final titanium product brittle and unworkable. The aluminum is finely divided and is preferably of a particle size substantially entirely passing through a No. 200 screen; and advantageously is of particle size substantially entirely passing a No. 325 screen.

An amount of an inert gas, preferably a noble gas, for example, argon, neon, krypton, xenon or helium or mixtures of these gases, can be introduced into the first reduction zone where titanium tetrachloride is reduced to titanium lower chloride. This introduction of inert gas lowers the partial pressure of titanium tetrachloride, thereby enhancing or increasing the proportion of titanium dichloride, and effecting the formation of small amounts of titanium metal. At any rate, the reaction is carried on in a hermetically sealed zone and in the absence of air or other reactive gas. The titanium lower chloride produced in this step can be, for example, predominantly trichloride or predominantly dichloride. Usually it is a mixture of the two chlorides and the relative proportions of the two can be varied, for example, as indicated above. An especially advantageous product contains predominantly dichloride with a minor portion of trichloride, wherein the trichloride will probably be converted to dichloride in the next heating step.

The reaction in the first heating step is carried out at a temperature of not over 600° C., preferably not over 550° C., to maintain the powdered aluminum in solid and finely divided state and to avoid any substantial liquefaction of the aluminum, because such liquefaction (which would occur at higher temperatures) has been found to result in the formation of large particles of an intermetallic compound with titanium and/or the agglomeration of the aluminum powder into large particles. The solid aluminum which may remain in the zone is apparently in segregated particles surrounded

and insulated from each other by coatings of the titanium lower chloride, so that agglomeration of the aluminum into larger particles or formation of the larger particles of intermetallic compound is substantially prevented. After the desired lower chlorides or chloride has been formed, the solid reaction product can be heated to a higher temperature, that is, up to 850° C., in the absence of titanium tetrachloride, to effect formation of a small amount of titanium metal. In a batch operation, in this variation of the process, the reactants are heated in a reaction zone at the temperatures described to form the lower chlorides, after which the flow of $TiCl_4$ is stopped and the temperature of the reaction zone gradually increased to form a small amount of Ti metal. Likewise, in a variation in a continuous operation, the temperature of the first-stage reaction zone through which the reacting mass flows can be suitably maintained at the range shown, and the product can then be moved through a second reaction stage, in an inert atmosphere, wherein the temperature is varied from 600° C. at the inlet to 850° C. at the exit, to form Ti metal, as desired, as the reaction mass flows to the outlet. The aluminum chloride formed in the reaction, being in vapor state at the temperature employed, is separately withdrawn and can be cooled and condensed and sent to storage or it can be electrolyzed to recover the aluminum therefrom, and the recovered aluminum when in or reduced to suitable particle size can be again employed in the reaction.

In this first reduction step it is advantageous to control the extent of the reaction, so that the product is a mixture of finely divided aluminum and titanium lower chlorides. It is advantageous, therefore, to employ an excess of finely divided aluminum with respect to the $TiCl_4$ to be reacted according to one or both of the following equations:

$$3TiCl_4+2Al\rightarrow 3TiCl_2+2AlCl_3$$

$$3TiCl_4+Al\rightarrow 3TiCl_3+AlCl_3$$

Conversely, it is advantageous to react slightly more than 50%, stoichiometrically, of the aluminum employed in this step. Stated in another manner, in order to ensure the removal of aluminum in the final stage, the ratio of titanium salts to aluminum in the reaction product of the first stage is such that the quantity of chlorine is at least slightly in excess of the amount stoichiometrically required to combine with the aluminum.

The titanium lower chloride produced in the first heating step is intimately mixed with powdered aluminum prior to introduction into the final heating stage or step. As stated above, for best results this aluminum is that remaining after the first stage heating, the particles thereof being coated and substantially insulated from each other by the lower chloride product. However, if desired, some additional fresh aluminum of the particle size shown above can be added at this mixing step. In the preferred mode of operation, the titanium lower chloride and powdered aluminum from the first heating step are thoroughly mixed together and are then heated in a second heating step at a temperature gradually increasing from about 500° C. to about 1100° C. It is preferred to agglomerate the mixture prior to this heating step, preferably by briquetting or pelleting under pressure. In this manner a compact metal product is obtained which is more convenient to handle and to subject to further treatment, such as melting. It is particularly advantageous to briquette titanium dichloride containing among other components a smaller amount of finely divided titanium metal, produced as described above, because it has been found that this produces a stronger briquette and results in a very dense, compact titanium metal agglomerate at the conclusion of the second heating step. The temperature in this heating step is increased gradually from 500° C. to at least 1000° C. or to 1100° C., in order to allow reaction to proceed progressively to substantial completion. The final heating temperature can be higher than 1000° C. to promote sintering or macrocrystallization and formation of larger, more stable particles of Ti metal. The range of 500° C. to 1100° C. has been found useful in this stage. The reaction is believed to be a reduction of the Ti lower chloride by aluminum to form aluminum trichloride and Ti metal. However, if any Ti trichloride is present, it probably in part disproportionates to form $TiCl_2$ and $TiCl_4$, and a small amount of Ti dichloride may also disproportionate to form Ti and $TiCl_4$. Any excess $TiCl_2$ disproportionates at the higher portions of this temperature range (500° C. to 1100° C.); and the final temperature is at least 1000° C., in order also to ensure breakdown of excess $TiCl_2$ and to remove or vaporize off all chlorides, thereby producing a highly purified titanium metal.



It is an advantage of the present process that aluminum is efficiently employed as a reducing agent in the first heating step; and also in the second heating step. It is a further advantage that only minor amounts of titanium tetrachloride are formed, resulting in fewer problems of recovery and recycle. It is a particular advantage that the aluminum chloride formed in the reactions is volatile at the temperatures of operation, whereas the other products of reaction are not volatile thereat, and therefore the aluminum chloride is efficiently separated from the end product of each reaction.

The annexed drawings represent flowsheets of modes of carrying out the present process.

In Figure 1 there is provided a source of aluminum powder of the purity described herein. It is introduced into reactor I, which is the first or primary reaction zone, and there is also introduced a flow of titanium tetrachloride as shown. This reaction zone is maintained at a temperature of from 400° C. to 550° C. to effect reaction to form a lower chloride of titanium and aluminum chloride. The latter is withdrawn as a vaporous product and can be condensed and stored, disposed of as such, or treated to recover aluminum metal for re-use in the process. After the reaction has been initiated by heating to at least the minimum temperature of this range, it is exothermic and cooling is required to maintain the temperatures within the desired range. Advantageously, the mass in the reaction zone is stirred while reaction goes on, to expose fresh aluminum surfaces to the $TiCl_4$ vapor. This can be accomplished in any conventional apparatus or device, as known in industry, e. g. a baffled rotary kiln, or a rotating tube device. The solid product of reaction contains the Ti lower chloride or chlorides, any excess aluminum metal and any titanium metal which may have been formed. It is then cooled and is thoroughly mixed. The operations of cooling, mixing and agglomerating are all conducted in a system which is free of air or other reactive gas, which is gas-tight or sealed against entry of air and which can, in a preferred procedure, contain a small amount of inert gas, or be maintained at a pressure slightly above atmospheric to ensure an atmosphere free of air or other reactive gas.

From the mixer the material is conducted to reactor II, which is the second reaction zone. It is there heated to a temperature which increases gradually from about 500° C. to about 1000° C. or 1100° C. This rise in temperature is effected slowly in order that the reaction, with evolution of aluminum chloride vapor, proceeds uniformly through this temperature range, as can be observed by the flow of vaporous products of reaction out of this zone. An atmosphere and a sweep or flow of inert gas is maintained herein by introducing a gas, preferably a noble gas, for example, argon, into this zone. The vaporous products of reaction comprise principally aluminum chloride with a small amount of titanium tetrachloride derived from partial disproportionation of $TiCl_3$ or $TiCl_2$ or both in this zone, and an amount of inert gas.

In an alternative, and preferable, procedure, the mixed material is briquetted or pelleted, that is, agglomerated

under pressure, prior to introduction into the second reaction zone. In this manner a compact metal pellet or agglomerate is obtained which is especially suitable for further processing.

In the first reaction zone the reaction proceeds between solid particles of aluminum and gaseous or vaporous titanium tetrachloride and a solid product of reaction deposits on the aluminum particle. This tends to separate the aluminum particles from each other and to prevent any tendency to agglomerate under the conditions of reaction of the first zone. On the other hand, the deposited crystals of Ti lower chloride or chlorides tend to form a caked mass, and it is preferred, therefore, to break up this cake and thoroughly disperse the unreacted aluminum, in order to enable uniform and complete reduction and utilization of the aluminum metal in the second reaction zone. It has been considered by previous workers in this field that it is impossible to reduce titanium tetrachloride to the metal with the aid of aluminum efficiently and without the formation of prohibitive amounts of large particles of an intermetallic compound, such as $TiAl_3$. It is an advantage of the present invention that, by practicing the steps and the working conditions set forth, reduction by aluminum is enabled to go to substantial completion.

Figure 2 represents another embodiment of the present invention, in flowsheet form. In this embodiment, aluminum powder of the particle sizes described herein, is introduced into a first reaction zone which is maintained at 400° C. to 550° C. $TiCl_4$ is vaporized and is then also introduced into this zone (stage 1) and is there brought into contact with the aluminum metal powder, with stirring. After the exothermic reaction is initiated by suitable heating, it develops sufficient heat that cooling of this zone is effected in order to maintain the temperature within the desired range. The vaporous reaction products, aluminum chloride with possible admixture of a small amount of $TiCl_4$ and of some argon, when argon is added in this zone, are separately withdrawn as shown. The solid products of reaction are moved forward through this zone and are removed at the exit end and then introduced into stage 2 where they are heated at a temperature of from 600° C. to 850° C., to form a small amount of titanium metal. This heating may be carried out for from two to four hours. Some disproportionation occurs in this stage, according to one or both of the following equations:

$$2TiCl_3 \rightarrow TiCl_2 + TiCl_4$$
$$2TiCl_2 \rightarrow Ti + TiCl_4$$

Titanium tetrachloride is withdrawn as a vapor and a small amount of finely divided titanium metal remains in admixture with the principal mass of titanium lower chloride, which at this point is predominantly titanium dichloride. The solid reaction product is removed and cooled in a cooling zone as shown, which can be a container or conduit bathed with a cooling water spray. The cooled mass is conveyed to a surge tank, where it is preferably mixed, and thence to briquetting rolls as needed for the stage 3 reaction.

In stage 3, the briquetted mass is fed to a second surge tank and from there is fed through valve V into a tower where it is heated slowly to a final temperature of about 1000° C. to 1100° C. Argon is fed in to the tower at the base thereof to maintain an inert atmosphere in the tower. Vaporous products of the reaction are withdrawn from the top of the tower, and comprise principally aluminum trichloride and a minor portion of titanium tetrachloride, with a small amount of argon admixed therewith also. Titanium pellets are withdrawn as product from the base of the tower, either continuously or intermittently, flow thereof being controlled by the valve V as shown.

Figure 3 represents a third embodiment of the present invention. Aluminum powder is introduced into a first reaction zone maintained at 400° C. to 850° C. The main source of $TiCl_4$ is introduced at a point where the reacting mass has reached a temperature of about 600° C. and flows countercurrently to the flow of solids. Inert gas, which may contain $TiCl_4$ at a partial pressure of up to about 10 to 15 mm. of Hg, is introduced at the end of the apparatus from which the solids are discharged, flows countercurrent to the solids, and mixes with the $TiCl_4$ introduced as described above. The vaporous products of reaction from this heating stage, reaction zone I, are withdrawn at the portion of the zone where the Al powder is added. The portion of the zone beyond where $TiCl_4$ is added, that is, which is at a temperature of above 600° C. and rising to about 850° C. at the exit, is substantially free of $TiCl_4$ and is under a slight sweep of inert gas, preferably argon. The solid product removed at the exit as shown comprises a mixture of titanium lower chlorides, titanium metal and aluminum powder. It is cooled, mixed and is then heated at 500° C. to 1100° C., as previously described. It can be forwarded directly to the reaction zone II and heated to form Ti metal powder, which is at least partially sintered at 1100° C. and which is then preferably maintained under an inert atmosphere until compacted or otherwise stabilized. Preferably, the cooled and mixed product from reaction zone I is agglomerated under pressure and then introduced to reaction zone II for further reaction, to form a compact Ti metal agglomerate.

As a further illustration of the mode of carrying out this process, describing more particularly the amounts and kinds of reactants and the procedural steps, there is given the example below.

*Example*

Titanium tetrachloride is passed concurrently over solid finely divided aluminum, passing a No. 200 mesh and a substantial proportion passing No. 325 mesh screen, in a suitable device, such as a rotary kiln, maintained at 400° C. to 550° C., to form solid titanium di- and trichlorides, which deposit on the surface of the aluminum, and vaporous aluminum chloride, which is separately recovered. The reaction is allowed to proceed to such an extent that the proportion of salt to unreacted aluminum is about 20% in excess of that required to react with all of the aluminum in a subsequent step, based on the reactions:

$$2Al + 3TiCl_2 \rightarrow 2AlCl_3 + 3Ti$$
$$Al + TiCl_3 \rightarrow AlCl_3 + Ti$$

The solid product is then ground, thoroughly mixed, and agglomerated, for example by pelleting under pressure, after which it is heated in a countercurrent stream of inert gas at a temperature gradually increasing from 600° C. to 1100° C. In this step, the remainder of the aluminum reacts according to the equations shown above, producing solid titanium metal in compact form and vaporous aluminum chloride, which, together with a small amount of titanium tetrachloride, is removed in the inert gas stream. The aluminum chloride is separated from titanium tetrachloride by any desired known method, such as fractional condensation or crystallization of $AlCl_3$ from a solution in $TiCl_4$. The excess salt in the material entering this stage disproportionates to titanium metal by one or both of the following reactions:

$$4TiCl_3 \rightarrow 3TiCl_4 + Ti$$
$$2TiCl_2 \rightarrow TiCl_4 + Ti$$

It is particularly advantageous to heat to at least 1000° C. as a final temperature in the last heating stage because this not only ensures vaporizing off all chlorides, but it also provides a sintering effect or a substantial crystal growth which stabilizes the titanium metal formed, and reduces its pyrophoric or reactive characteristics. Although the melting point of titanium is much higher than these temperatures, the metal crystals which are formed by this reaction are very small and of very great

surface, so that they coalesce into larger particles at the "sintering" temperatures above noted. This is advantageous in the case of pellets because the pellets become more compact and dense. It is especially advantageous in production of titanium metal powder because the metal is so fine as to be pyrophoric, i. e. to ignite spontaneously in air, and it is necessary either to compact it in some manner or to maintain it under an inert atmosphere. As stated, this necessity is obviated by heating to at least 1000° C. to effect sufficient crystal growth to stabilize the metal. The sintering step can be effected by increasing the temperature as described in the final heating stage, but if desired, finely divided Ti metal can be removed from this heating stage under a protective atmosphere, e. g. under an inert gas, and sintered or compacted in a separate operation.

The inert gas employed herein is free of oxygen, nitrogen, moisture or other gases reactive with titanium metal. Such gas can be that obtainable in commerce and it is "gettered," e. g. by passing it over titanium metal, to remove all traces of reactive constituents before introduction into the reaction system. Where inert gas is employed in the first heating step, it tends to promote formation of a predominant or major portion of titanium dichloride. To initiate the reaction in the first heating stage the reactants are heated to at least 400° C., as further described above. The exact amount of Ti metal which is formed by heating the reaction mass in the first stage to 850° C. is not precisely known, but it is a minor amount, i. e. less than 50%, with respect to the total weight of the solid reaction product.

In the specification and claims, percentages are by weight unless otherwise indicated; and screen sizes, where shown, are U. S. Standards screens as described in Handbook of Chemistry and Physics, 32nd edition, 1950–1951, Chemical Rubber Publishing Co., page 2797.

Having now described the invention, what is claimed is:

1. A process for making ductile titanium metal which comprises heating finely divided aluminum metal and titanium tetrachloride at a temperature of from 400° C. to 600° C., in the absence of a reactive gas, to form a lower chloride of titanium, and vaporous aluminum chloride, removing said vaporous aluminum chloride, admixing said titanium lower chloride and less than the stoichiometric amount of finely divided aluminum metal, heating said admixture in an inert atmosphere at a temperature gradually increasing from 500° C. to about 1100° C. to form titanium metal and vaporous aluminum chloride, withdrawing said vaporous aluminum chloride, and separately recovering said titanium metal.

2. Process as in claim 1 wherein said finely divided aluminum is of a particle size substantially entirely passing through a No. 200 screen.

3. Process as in claim 1 wherein said finely divided aluminum is of a particle size substantially entirely passing through a No. 325 screen.

4. Process as in claim 1 wherein said inert gas is a noble gas.

5. Process for making a ductile titanium metal which comprises heating titanium tetrachloride and excess aluminum metal of particle size substantially entirely passing a No. 200 screen, at from 400° C. to 600° C., in the absence of a reactive gas, to form a lower chloride of titanium and vaporous aluminum chloride and less than stoichiometric amount of finely divided aluminum metal, removing said vaporous aluminum chloride, mixing said titanium lower chloride and finely divided aluminum, agglomerating said mixture under pressure, heating said agglomerates at a temperature gradually increasing from 500° C. to at least 1000° C., under a stream of inert gas, to form vaporous aluminum chloride and compact titanium metal, separately withdrawing said vaporous aluminum chloride, and recovering said titanium metal.

6. Process as in claim 5 wherein said aluminum metal and titanium tetrachloride are reacted until slightly more than 50% the aluminum has been reacted.

7. Process as in claim 5 wherein about 20% excess of said lower titanium chloride is heated with said aluminum.

8. Process for making ductile titanium metal which comprises heating in a reaction zone an excess of finely divided aluminum metal and titanium tetrachloride, in the absence of a reactive gas, at a temperature of from 400° to 550° C., to form lower chlorides of titanium with admixed unreacted aluminum metal, in less than stoichiometric amount and vaporous aluminum chloride, then increasing the temperature in said reaction zone, in the absence of $TiCl_4$, to about 850° C. to form a small amount of finely divided titanium metal, separately withdrawing said vaporous aluminum chloride, mixing and briquetting said titanium lower chlorides, titanium and unreacted aluminum metal, heating said briquetted material in a stream of inert gas at a temperature gradually increasing from 500° C. to 1100° C. to form compact titanium metal and vaporous aluminum trichloride, and separately withdrawing said aluminum trichloride.

9. Process as in claim 8 wherein said inert gas is argon.

10. Process as in claim 8 wherein said lower chloride of titanium is predominantly titanium dichloride.

11. Process for making ductile titanium metal which comprises heating in a reaction zone, under an inert gas atmosphere, aluminum metal free of oxygen and of particle size substantially entirely passing through a No. 200 screen, and titanium tetrachloride, at a temperature of from 400° C. to 550° C. to form a solid reaction product containing excess aluminum metal, titanium dichloride and a minor proportion of titanium trichloride, and vaporous aluminum trichloride, separately removing said vaporous aluminum trichloride, mixing said titanium dichloride and titanium trichloride and less than the stoichiometric amount of finely divided aluminum metal and heating at a temperature gradually increasing from 500° C. to about 1100° C., under a stream of argon, to form titanium metal and vaporous aluminum chloride, withdrawing said vaporous aluminum chloride, and separately recovering said titanium metal.

12. Process as in claim 11 wherein said admixture of titanium di- and trichlorides and aluminum is briquetted prior to heating.

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