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TITANIUM METAL PRODUCTION PROCESS

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This invention relates to a new and improved process for the production of titanium metal. More particularly, the invention pertains to a continuous method for preparing titanium metal.

In recent years numerous processes have been proposed for the preparation of titanium metal utilizing titanium halides as the starting material. These processes have involved, in general, the reaction of titanium tetrahalides, especially titanium tetrachloride, with alkali metal or alkaline earth metal reductants. Though many variations of this reduction step have been suggested in the prior art, the processes invariably treat the products obtained from reduction in a separate sintering or fusion step. This treatment involves heating the product mixture of the reduction step to temperatures above the melting point of the by-product salts under an inert gas atomsphere or under vacuum. Specific temperatures employed have ranged from 800° to 1500° C., though temperatures above 1000° C. have been discouraged since special equipment must be employed to avoid alloying of the titanium with the walls of the reaction vessels.

The sintering or fusion step appears to serve two purposes: (1) the agglomeration of the titanium particles in the mixture being treated to form relatively large chunks of titanium sponge; and (2) the melting or vaporization of the by-product salts, which facilitates their separation from the desired titanium metal. In actual operations, however, the heat treatment of the reaction product mixture obtained from the reduction step has led to several serious problems. For one thing, the large chunks of titanium metal sponge which are formed are quite difficult to remove from the reaction vessels. In fact, it has been necessary to employ air hammers or other similar devices in order to accomplish this. With respect to separation of the by-product salts, it has been found that, though a major portion of the salt is removed from the titanium sponge, some of the salt becomes trapped or encased in the titanium sponge. Since the removal of this residual salt is essential in order to prepare high quality titanium metal, elaborate procedures have been devised for this purpose. It is obvious that the special equipment and process steps required to recover and treat the titanium sponge obtained from the sintering or fusion step are costly and time consuming in commercial operations. Moreover, additional processing steps are undesirable from the standpoint of possibly introducing contaminants into the titanium sponge at an advanced stage of the process.

It is one object of this invention to provide a titanium manufacturing process which avoids the difficulties encountered in the prior art processes. Another object of the invention is to provide a continuous method which readily permits control over the size of the titanium sponge produced. A further object is to provide a process that has commercial application and produces high quality titanium metal.

In accordance with the present invention, these and other objects are accomplished by reacting a material comprising a titanium subhalide-alkali metal halide complex with an alkali metal reductant under carefully controlled operating conditions. One essential operating condition is the use of reaction temperatures above the melting point of the feed material but below the melting

point of the reaction product mixture, i.e. a mixture of the titanium metal product and the alkali metal halide by-product. More specifically, the reaction temperature will be within the range of about 400° to 700° C., preferably about 500° to 600° C. Thus, for example, when titanium metal and sodium chloride are obtained as the reaction products in accordance with the preferred embodiment of this invention, the reaction temperature will be maintained below about 805° C., the melting point of sodium chloride.

Another essential operating condition involves carrying out the reduction reaction in a stirred or agitated bed comprising particulate titanium metal and finely divided alkali metal halide. This reaction medium may be obtained from any one of known processes; though, as hereinafter described in detail, once the process of the invention is started up the reaction medium constitutes the reaction product mixture. As set forth below, various methods and equipment may be employed in carrying out this particular step of the process for maintaining the desired amount of reaction media in the reaction zone and for recovering the titanium metal product.

In general, the reduction step comprises metering controlled amounts of the titanium subhalide-alkali metal complex mixture and the alkali metal reductant into the reaction zone containing the particulate titanium and the finely divided, solid alkali metal halide, which is maintained under constant agitation. The amount of reactants added to the reaction bed is preferably sufficient to ensure substantially stoichiometric reduction of the titanium subhalide-alkali metal complex mixture, although a slight excess or deficiency of the alkali metal may be utilized without deleterious results. The reactants may either be fed continuously or intermittently into the reaction zone. It is important, however, to control the amount of reactants added so that a large excess of the reaction medium is always present. In actual operations it is advisable to maintain the weight percentage of total reactants below about 10%, preferably within the range of about 3 to 7% by weight, based on the weight of the reaction medium, though higher percentages up to about 25% may be employed.

The alkali metal reductant and the titanium subhalide-alkali metal halide complex may be added to the reaction zone either in solid or in molten form. For the purposes of easier handling, the alkali metal will be molten while the titanium subhalide-alkali metal halide will be finely divided solids.

Conventional equipment may be employed for carrying out the reduction reaction. In order to avoid contaminating the titanium metal product, it is preferred to operate in a closed system or under an inert gas atmosphere such as argon, helium, neon and the like. Since it is an important feature of this invention to maintain the reaction mixture, including the reaction medium, in a constant state of agitation, the reaction vessel must be provided with a mixing device or be capable of being rotated in such a manner that its contents will be subjected to the desired degree of agitation. The mixing equipment can be either paddles, tumbling barrels, ball mills and the like. It will be further understood that the stirring will be sufficiently slow enough to avoid the disintegration of the titanium metal particles that are formed during the course of the reaction.

In accordance with one method of carrying out the process of this invention, the titanium subhalide-alkali metal halide complex mixture and the alkali metal reductant are fed via separate gravimetric feeders and lines into the upper portion of a closed reaction vessel equipped with a blade type of stirrer and containing a reaction medium comprising particulate titanium metal and finely

divided, solid alkali metal halide having an average particle size of less than about 10 mesh. The stirrer is rotated at a speed sufficient to effect constant agitation of the reaction mixture. The reaction mixture is maintained at a temperature within the range of about 400° to 700° C. The reaction between the titanium subhalide-alkali metal halide complex mixture and the alkali metal results in the formation of titanium metal and alkali metal halide by-product. Though the exact nature of reaction mechanism is not understood, it is believed that the titanium subhalide-alkali metal halide complex mixture, molten under the aforementioned operating conditions, deposits in layers on the particulate titanium metal and the finely divided, solid alkali metal halide in the reaction medium. Upon reaction with the alkali metal, granular particles of the titanium metal mixed with by-product alkali metal halide are formed. The process comprises coating a layer of the molten titanium subhalide-alkali metal halide on the particulated or granular solids in the reaction mixture followed by reaction with the alkali metal to form larger granules or porous particles comprising the titanium metal mixed with the alkali metal halide by-product continuously until the granules are recovered from the reaction zone or become so heavy that they fall to the bottom of the reaction zone. Preferably, a portion of the reaction product mixture is removed either continuously or at intervals from the reaction zone. The portion of the reaction product mixture so recovered is then screened or otherwise classified to separate the desired titanium sponge particles from the more finely divided particles, including the particulated titanium metal and finely divided alkali metal halide upon which no titanium metal has been deposited. These finely divided particles may be recycled to the reaction zone to act as the reaction medium. If additional reaction medium is required to maintain bed volume, some of the larger particles recovered from the reaction zone may be crushed or ground to obtain the desired particle size and then recycled to the reaction zone.

The granulated titanium-alkali metal halide particles recovered from the reaction zone and having the desired particle size are washed or leached with water, mineral acids or mixtures thereof to remove the alkali metal halide salt therefrom. Mineral acids such as hydrochloric, sulfuric, etc. may be employed for this purpose. Following the leaching step of the present process, the titanium metal product is dried by conventional means. The dried titanium metal product is characterized as being sponge-like, and it has numerous commercial applications known to the art.

Another method of carrying out the method of this invention is to feed, continuously or intermittently, the titanium subhalide-alkali metal halide complex and the alkali metal separately to the front end of a ribbon mixer containing a bed of particulate titanium metal and finely divided, solid alkali metal halide. Other than the difference in equipment, all of the operating conditions will be the same as previously described. A portion of the reaction products in admixture with the reaction medium is continuously withdrawn from the reaction vessel. In accordance with the preferred method of the invention, some of the withdrawn mixture is recycled back to the front end of the ribbon mixer. As discussed above, the material to be recycled may be crushed or ground prior to being passed to the vessel in order to obtain the particle size required for proper functioning as the reaction medium. The titanium metal granules having the desired particle size are sequentially leached and dried to recover the titanium metal product.

The alkali metal reductant useful in the present process includes sodium, potassium and lithium. Sodium is the preferred reducing agent. As previously set forth, the amount of alkali metal employed in the reduction will be sufficient to ensure stoichiometric reduction of the titanium subhalides in the feed material to the titanium metal.

The titanium subhalide-alkali metal halide complex mixture employed as the feed material may be obtained in accordance with the processes described in United States Patent No. 2,765,270 issued to Brenner et al. on October 2, 1956. As is noted in this patent, the exact nature of the material has not been determined. For the sake of uniformity of nomenclature, therefore, the material will be referred to as a chemical composition or a complex, which conforms to the following empirical formula:

$$M_aTi_bX_c$$

in which M is an alkali metal such as sodium, potassium, lithium, etc. and X is a halide such as chlorine, bromine and iodine. The ratio of a to b to c will be 1–3:1:4. In the preferred feed material, M is sodium and X is chlorine. It will be understood that the titanium subhalide-alkali metal halide complex may be prepared by methods other than those described in Brenner et al., and that, furthermore, the exact method of producing this material does not constitute an essential feature of this invention. One important advantage of the inventive process is that the heat transfer problems encountered in stoichiometrically reducing the titanium tetrahalides to the metal in a one-step operation are avoided. If, for example, the titanium subhalide-sodium halide complex is formed by the reaction of titanium tetrahalide with a controlled deficiency of sodium, such as about 50% of the stoichiometric amount, more than half of the total exothermic heat of reaction involved in stoichiometric reduction is released at this stage. By operating in this manner run-away temperatures and the formation of hot spots are prevented, and the heat released during the subsequent reaction of the titanium subhalide-sodium halide complex with sodium, as carried out in accordance with the invention method, is advantageously utilized to prepare the desired titanium metal product.

The invention will be more fully understood by reference to the following illustrative examples.

Example I

A titanium subchloride-sodium chloride complex, conforming to the empirical formula Na_2TiCl_4, is fed into a sealed reaction vessel equipped with a blade stirrer. The reaction vessel is about three quarters full of a solid, particulated reaction medium comprising titanium particles and sodium chloride. Molten sodium is also fed into the reaction vessel at a rate sufficient to ensure the complete reduction of the complex to form titanium metal and by-product sodium chloride. The resulting reaction mixture is maintained under an argon atmosphere and is subjected to constant agitation by rotating the stirrer at a rate of about 50 r.p.m. The reaction is carried out at a temperature of about 590° C., which is above the melting point of the feed mixture but below the melting point of sodium chloride and titanium. The titanium subchloride-sodium chloride complex, molten under the reaction conditions becomes coated on the discrete particles of the reaction medium and reacts with the molten sodium to form sponge-like porous titanium metal in admixture with sodium chloride. The quantity of the reaction mixture is maintained substantially constant by continuously withdrawing a portion of the reaction mixture. The material withdrawn is filtered through a 40 mesh screen. The particulated material, which passes through the screen, is recycled to the reaction vessel. The granulated particles retained on the screen are passed to a conveyor where they are countercurrently washed with water and HCl to remove the by-product sodium chloride. The granulated titanium metal sponge recovered is substantially free of sodium chloride.

Example II

A feed material comprising titanium subchloride-sodi-

um chloride complex, having the empirical formula Na_2TiCl_4, is intermixed in a ribbon mixer with particulated titanium metal and finely divided solid sodium chloride. The feed line for the complex material is positioned at the top of the ribbon mixer and at a point near the front end. Sodium is also fed continuously into the mixer via a line positioned at a point removed from the feed line for the complex feed material but in the direction in which the reaction mixture is moving with agitation. The feed lines of the reactants are so positioned that the titanium subchloride-sodium chloride which becomes molten under the operating conditions (i.e. a temperature of about 550° C.) is coated on the particulate reaction medium, and then reacts with the sodium added to the mixture to form granules of porous titanium metal in admixture with by-product sodium chloride. The resulting reaction product mixture and that portion of the reaction medium which is left unchanged is recovered from the discharge end of the ribbon mixer. The recovered material is screened to separate the titanium granules formed during the reaction from the particulate titanium metal and sodium chloride. The latter material is recycled to the feed end of the ribbon mixer at a point located in front of the titanium subchloride-sodium chloride complex feed line. The separated titanium metal granules are then leached and dried in the same manner described in Example I. The titanium metal recovered is sponge-like and is substantially free of by-product sodium chloride.

The foregoing embodiments describe only two possible ways of operating the process of this invention. It will also be understood that these methods may be modified without departing from the broader aspects of the invention. The essential features of the invention include the use of a titanium subhalide-alkali metal halide complex feed material and a reaction medium comprising a mixture of solid, particulated titanium metal and alkali metal halide. Important operating conditions are reaction temperatures above the melting point of the complex feed material but below the melting point of the alkali metal halide, and constant agitation of the reaction mixture. As shown above, the process of this invention readily permits control over the size of the titanium metal particles which can be produced. Thus, for example, large sponge-like titanium particles can be obtained by utilizing one or more of the following procedures: (1) retaining the reaction mixture in the reaction vessel for a longer period of time, (2) recycling a major portion of the reaction product mixture to the reaction zone and (3) separating only the largest titanium particles from the reaction product mixture and recycling the remaining product material, including unchanged reaction medium, back to the reaction zone. Granulated titanium metal particles within the range of about 10 to 100 mesh, preferably about 20 to 80 mesh, can be achieved in the inventive process.

As previously described, once the process is on stream, the reaction medium comprising particulate titanium metal and solid, finely divided sodium chloride may be maintained at the desired volume by recycling the unchanged material withdrawn along the granulated titanium product. Additional reaction medium can be supplied by grinding or crushing portions of the titanium granules or by utilizing the product mixture obtained from the stoichiometric reduction of titanium tetrahalides with alkali metal.

The titanium metal product obtained in accordance with the process of this invention has a number of distinct advantages. Since the elevated sintering temperatures employed in the prior art process have been avoided, the removal of by-product alkali metal halide is simplified. Moreover, the titanium product is of high quality and can be employed in various processes calling for the use of titanium sponge such as, for example, the formation of titanium bars, etc.

What is claimed is:

1. A process for producing titanium metal sponge which comprises adding a material, having the empirical formula

$$M_aTi_bX_c$$

wherein M is an alkali metal, X is a halide and the ratio of *a* to *b* to *c* is 1–3:1:4, to a large excess of an agitated mixture comprising solid, finely divided titanium metal particles and an alkali metal halide at a temperature above the melting point of said material but below the melting point of said alkali metal halide and within the range of about 400° to 700° C. whereby said material coats a portion of said agitated mixture; adding an alkali metal to said partially coated mixture while continuing agitation, said alkali metal being in an amount sufficient to react with said material, the weight percentage of said reactants being maintained below about 25% based on the weight of said agitated mixture, to form titanium metal sponge at said temperature; recovering the resulting reaction product mixture; and separating therefrom the titanium metal sponge.

2. The process of claim 1 wherein the material has an empirical formula of Na_2TiCl_4.

3. The process of claim 1 wherein said alkali metal reactant is sodium.

4. The process of claim 1 wherein the reaction product mixture, following removal of the titanium metal sponge, is recycled to said agitated mixture.

5. The process of claim 1 wherein said reaction is carried out in an inert atmosphere.

6. The process of claim 1 wherein said titanium metal sponge has a particle size greater than said finely divided titanium metal.

7. A continuous process for preparing granulated titanium metal which comprises the following steps: (1) agitating a mixture comprising solid, finely divided titanium particles and sodium chloride in a reaction zone at a temperature of above about 400° C. but below about 805° C., (2) adding titanium subchloride-sodium chloride complex to said agitated mixture whereby said complex coats a portion of said agitated mixture; (3) adding sodium to said agitated coated mixture while continuing agitation to effect reaction at said temperature with said titanium subchloride-sodium chloride complex to form titanium metal in admixture with sodium chloride, the weight percentage of said reactants being maintained below about 25% based on the weight of said agitated mixture; (4) repeating steps (2) and (3) in a continuous manner until large titanium granules are formed; (5) continuously removing a portion of the resulting reaction product mixture from the reaction zone; (6) separating the titanium granules from the reaction product mixture.

8. The process of claim 7 wherein said temperature is about 500° to 600° C.

9. The process of claim 7 wherein said complex has an empirical formula Na_2TiCl_4.

10. The process of claim 7 wherein a portion of the recovered reaction product mixture is recycled to the reaction zone.

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