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METHOD OF PRODUCING TITANIUM

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This invention relates to the production of titanium metal and more particularly to the manufacture of ductile titanium through the reduction of oxygen-free compounds of titanium by metallic reducing agents.

Titanium compounds such as the oxides and halides can be reduced by strong reducing agents such as magnesium, calcium, lithium, and the like, as well as by carbon. The latter has been proposed to remove oxygen from titanium oxygen compounds, but the reduction product has always contained carbon or oxygen or both. Such a product has not found use as a structural material because of inherent deficiencies, the most important of which is lack of ductility. Ductile titanium has resulted from the reduction of titanium tetrachloride by strongly reducing metals and specifically by magnesium by various processes, including those disclosed in U. S. Patents 2,148,345 and 2,205,854. The reaction between pure titanium tetrachloride and pure magnesium gives elementary titanium which may be purified by volatilizing or otherwise removing residual magnesium chloride and magnesium to give titanium metal of high purity and excellent ductility. Fluid reagents are used and the desired titanium metal reaction product, in sponge form, adheres to the chamber or vessel in which it is prepared and must be forcibly removed therefrom. This has necessitated batch operation and involves considerable transfer difficulties and expense in effecting the removal and recovery of the sponge product.

Prior methods for producing titanium metal are characterized by the reaction between a gaseous titanium halide, such as titanium tetrachloride, and a liquid or molten reducing metal, such as magnesium, to obtain solid titanium and the liquid halide of the reducing metal as the reaction products. The titanium sponge and metal halide reaction products are intimately associated in the final product, and, to obtain the sponge in uncontaminated condition, resort is had to grinding, leaching, vacuum purification or like procedures. Removal of the sponge from the reaction vessel chamber must be effected by chipping or an equivalent operation which is a time-consuming, costly operation.

It is among the objects of this invention to overcome the disadvantages of prior methods for producing titanium metal and to provide a novel, improved method for obtaining titanium from its halide salts in a more straightforward and economical manner. A further object is to obtain the metal without effecting its separation in sponge form during the course of the reduction operation as heretofore contemplated and practiced. An additional object is to effect the reduction operation in the presence of an alloying reagent for the titanium as it is produced and which will enable one to remove the same from the chamber as desired and in liquid condition. Further objects and advantages will appear from the ensuing description of the invention.

In its broader aspects, the invention comprises producing titanium metal by reacting a titanium halide with a reducing metal dissolved in another metal having a low

melting point which is also a solvent for the titanium metal resulting from the process, and thereafter recovering the titanium metal product from the metal alloy product so produced.

In a more specific and preferred embodiment, the invention comprises obtaining titanium in metallic condition by reacting vaporized titanium tetrachloride with magnesium and while the reducing metal is dissolved in molten zinc, and thereafter recovering the titanium metal by distillation from the resulting titanium and zinc alloy.

In practically adapting the invention in accordance with a preferred embodiment thereof, a solution of magnesium in zinc, containing from, say, 5–10% of magnesium, is reacted with vaporous titanium tetrachloride in accordance with conventional procedures and within a closed, jacketed reaction vessel, the walls of which can be suitably cooled by means of a cooling fluid and within which the reactants are maintaitned under molten magnesium chloride which forms as a result of the reaction and floats on top of the molten metal, while the titanium reduction product is dissolved therein. As a consequence, a gradual depletion of the reducing metal, magnesium, takes place and a gradual increase or build-up of titanium in the liquid metal phase in the zinc melt occurs. This is accompanied by a gradual increase in the melting point of the molten metal. The reaction between the titanium tetrachloride and magnesium is continued until a substantial part of the magnesium becomes converted to magnesium chloride and the fluidity of the molten metal is materially decreased. At this point, the zinc-titanium-magnesium solution is transferred to a suitable conventional type distilling furnace wherein the zinc-magnesium and residual magnesium chloride present are removed as vapor from the titanium and the latter is recovered for direct use or further purification treatment, as desired.

To a clearer understanding of the invention, the following specific examples thereof are given, which are merely illustrative and not in limitation of the invention:

Example I

A solution of magnesium in zinc containing 8% magnesium was placed in a closed graphite vessel provided with exterior cooling means for controlling the temperature of its walls. Titanium chloride vapor was introduced into the vessel for reaction through a nickel tube near the bottom thereof. The nickel tube was cooled by means of a circulating salt bath with temperature controlled at approximately 450° C. Argon gas was led through the $TiCl_4$ inlet to hold it open during periods when the $TiCl_4$ vapor feed was interrupted. The reaction proceeded smoothly with formation of magnesium chloride layer taking place above the titanium-zinc solution. This was tapped off periodically. The excess heat of the reaction was removed by cooling through the graphite walls and also by means of a reflux condenser which returned zinc as it volatilized out. The temperature was maintained at near the boiling point of zinc and the reaction was continued until a substantial part of the magnesium had been converted to magnesium chloride and the fluidity of the molten metal became materially decreased. At this point, transfer of the resulting zinc-titanium-magnesium solution to a graphite distilling furnace was effected, said furnace being heated by radiant heat from graphite resistors. The zinc-magnesium and residual quantities of magnesium chloride present in the alloy were removed as vapor, condensed, and the values recycled for reuse. The titanium comprised a pure metal product suitable for any desired use or fabrication.

Example II

The procedure of Example I was duplicated, except that the molten bath employed at the start of the opera-

tion consisted of a 5% solution of aluminum in zinc, and the by-product chloride formed during the process was removed continuously as a vapor through a reflux condenser which returned zinc vapor as condensate back to the reaction. It was necessary in this case also to provide heat to compensate for heat losses through the walls and with the $AlCl_3$ vapor. This was effected by introducing controlled amounts of chlorine with the titanium tetrachloride. The reaction was allowed to continue until the molten metal thickened and the aluminum content of the bath became materially decreased. Thereafter, the zinc-titanium-aluminum solution was transferred to a distillation furnace to volatilize and remove its zinc values, as in Example I. The titanium product recovered was not as pure as that recovered in Example I since it was found to contain some residual aluminum.

While the invention has been described in its application to certain specific embodiments, it is obvious that variance therefrom can be resorted to without departing from its underlying spirit and scope. Thus, the reducing metal used may comprise, in addition to magnesium, any of several which are more electropositive than titanium, e. g., the alkali metals (sodium, potassium, etc.), the alkaline earth metals (calcium, barium, strontium), and aluminum. All of these elements except aluminum can be converted to liquid halides in the present process and without resorting to pressure equipment. Since the resulting liquid reaction products are lower in specific gravity than the liquid metal, they appear in the process as a molten salt layer on the molten metal. The titanium halide reactant can be introduced below the surface of the latter where reaction occurs with evolution of heat.

While zinc comprises a preferred type of solvent metal for use herein, since it possesses satisfactory melting point, boiling point, and solvent action for titanium and the reducing agents mentioned, cadmium, which is also a member of subgroup B, group II, of the periodic table, also can be employed as a solvent metal. Zinc melts at 419° C., boils at 907° C. at atmospheric pressure, and is a liquid at a convenient operating temperature. It possesses a solvent action for each of the metals mentioned and with some, e. g., aluminum and magnesium, forms solutions of all proportions with the reducing element. It is especially useful when employed as a solution containing from about 2% to 20% of the reducing agents, because such compositions produce zinc solutions of titanium in which the titanium will also be approximately within the range of about 2–20% and can be removed as a liquid to a recovery system to separate the zinc and titanium by distillation of the zinc from the less volatile titanium.

Since the molten zinc-titanium system tends to rapidly corrode various materials of construction, including graphite, copper, iron, etc., care should be taken to carry out the reaction with molten zinc out of contact with equipment containing such materials. This can be conveniently effected by operating the reaction chamber with exterior cooled walls and making use of the high heat of reaction to maintain a satisfactory reaction temperature. Accordingly, the walls of the reaction vessel can be constructed of graphite or of metal, if resort is had to associated cooling means adapted to reduce and maintain such walls in cooled state and at a temperature low enough to form a protective coating of either a reducing metal salt layer or a frozen zinc metal layer over the internal walls of the reactor. Either of these protective coatings will prevent corrosion of the reaction vessel and thereby permit operation of the system in a satisfactory manner. Thus, magnesium chloride has a melting temperature of 708° C. and when cooled to below that temperature will form a frozen layer within and over the chamber walls. Pure zinc melts at 419° C., but this melting point may be altered considerably by adding a metal thereto to obtain lower or high melting points.

Thus, with 15.6% magnesium present in the zinc, its melting point is elevated to 590° C., and with 46.5% magnesium it is lowered to 340° C. Titanium also has a marked effect on the melting point of zinc and gives higher melting points for the mixture as the titanium content increases above .15% titanium. It will thus be seen that the system may be varied considerably and is characterized by great flexibility. The reducing metal consumed in the reaction is replaced by the titanium formed and this tends to increase the melting point of the molten zinc metal. A gradual depletion of the reducing metal, magnesium, thus occurs and a gradual increase of titanium in the liquid metal phase results in the zinc melt. This is accompanied by a gradual increase in the melting point of the metal. The reaction need not be carried to the point where magnesium is completely consumed since the zinc is to be separated from the titanium by distillation with the magnesium being separated from the titanium in the same manner. It will thus be seen that one may use a liquid zinc-magnesium reagent as the reducing agent and recover titanium from a zinc system containing titanium with or without appreciable amounts of magnesium.

As already noted, other metal reducing agents, and particularly aluminum, may be employed in the process. Aluminum dissolves readily in zinc and gives a reagent which readily reacts with titanium tetrahalides, particularly $TiCl_4$. Aluminum chloride is formed as a gas under the existing conditions which may be led from the system and separated from titanium tetrachloride by resort to the usual physical means. This system permits contact of a molten metal surface with a reactive titanium tetrachloride atmosphere since there is no molten salt floating on the molten metal thereby isolating the latter from the gases in the reaction chamber. On the other hand, the slight disadvantage exists that the vaporous halide of the reducing metal is contaminated by the vaporous titanium reactant, requiring some purification and recovery expense.

It will be recognized that, although the reduction operation is usually conducted at temperatures ranging from 750–1100° C., at substantially atmospheric pressure and below the boiling point of the zinc alloy, higher temperatures generally will favor higher concentrations of titanium in the system and that, advantageously, the process can be conducted in a closed vessel under pressures in excess of atmospheric to prevent excessive evaporation of zinc during the reaction period. Such higher pressures can be generated from the vapor pressure of the reactants and through use of argon or other inert gas as diluents. Depending on the reducing agent used, it is necessary to make provision for removing excess heat or also to add heat. Excess heat removal can be conveniently effected by resorting to a reflux return of zinc vapor to the reaction vessel, while additional heating can be had through resort to well-known conventional means, as for example, suitably installed radiant heaters or electric arc heaters associated with the reactor. If desired, chlorine may be added with the $TiCl_4$ to induce additional heating, since thereby one gains the heat which arises from the resultant formation of a metal chloride during the involved reaction.

The zinc recovered from the distillation step can be handled in any conventional manner for recycling to the reaction vessel. The by-product chlorides, either aluminum, magnesium or sodium, can be handled also for recovery by conventional means; for example, via an electrolytic cell system. It has been found advantageous to return the zinc via the electrolytic cells where it serves as a molten cathode rather than directly to the reaction vessel. The zinc-magnesium or zinc-aluminum solution has a melting point in the range of 400° C. and substantial advantage is realized by operating the electrolytic cells at these low temperatures. Moreover, saving in electric cur-

rent is realized since the zinc can be returned at a temperature near its boiling point with consequent decrease in electricity necessary to heat the contents of the cell system.

As disclosed above, aluminum, the various alkali metals and alkaline earth metals (lithium, rubidium, potassium, strontium, barium, calcium, sodium, magnesium, aluminum and beryllium) are usefully employable herein as reducing agents. Each of these metals is more electropositive than titanium and will effect reduction of the halides of titanium. Obviously, titanium tetrachloride is the commercially preferred utilizable halide of titanium, but other titanium halides, such as the bromides or iodides, may be substituted for use, if desired and economically available.

Aluminum and magnesium have been employed as reducing agents in the above examples and since they are more readily available in commercial quantities and at reasonable cost. Other members of the more electropositive group of elements may be substituted, particularly sodium and calcium, without excessive raw material penalty. Sodium has limited solubility in molten zinc (2.5%) and in this instance it is possible to float the reducing metal on the top of the zinc so that it may react with the titanium chloride which then dissolves in the molten zinc. One may also resort to the addition of sodium as well as other reducing metals of limited solubility to the molten zinc intermittently or continuously as the sodium is being depleted. Other minor innovations of this sort may be made without departing from the present invention.

The reducing metal may be regenerated by known methods such as the electrolytic cells. Magnesium chloride cells are well-known in industry and this by-product salt may be transferred to such cells wherein magnesium is produced for reuse in the system and chlorine is generated, this being useful in the production of more titanium chloride. The solution of the reducing metal in the zinc may be produced at the cell by combining the two metals at this point and while both are in the molten state.

As already indicated, corrosion of the equipment may be avoided by lining the reaction container with a frozen coating by maintaining the wall temperature at a temperature not in excess of the melting point of a liquid present in such container. It is possible to have a metal phase melting at a lower temperature than the molten salt by-product. For instance, a zinc solution containing 15.6% magnesium melts at 590° C. while the reaction product, magnesium chloride, melts at 708° C. It is thus possible to have magnesium chloride as a coating on the inside of the reaction chamber while it contains molten zinc metal having magnesium dissolved therein. As the titanium content of the zinc increases, the melting point also increases and as a result one may also operate the system under conditions wherein a frozen metal layer will protect the reaction vessel from corrosion. The melting point of the metal in this instance will be greater than the melting point of the salt by-product.

One may also modify the melting point of the salt during regeneration of the reducing metal by electrolysis by adding thereto a second salt. For instance, lithium chloride, sodium chloride, etc., may be added to magnesium chloride cells to enable one to use lower cell operating temperatures. When feeding molten zinc to such a cell, the magnesium may become dissolved in the liquid zinc by making the latter the cathode of the cell.

It will thus be seen that the present process is subject to many variations and no undue limitations should be deduced from the foregoing detailed description. Hence, the invention should not be considered as limited to the specific embodiments set forth above but only as defined in the appended claims.

I claim as my invention:

1. A process for the production of titanium metal which comprises reducing a vaporous tetrahalide selected from the group consisting of the chloride, iodide, and bromide of titanium with a molten reducing metal selected from the group consisting of alkali metals, alkaline earth metals, beryllium, and aluminum in the presence of a molten titanium alloying metal selected from the group consisting of zinc and cadmium thereby producing a molten solution of titanium and said alloying metal, the starting amount of said reducing metal ranging from 2–20% by weight of the combined amounts of reducing and alloying metals, removing from the reaction zone the fluid halide of the reducing metal formed by the reduction reaction, and then distilling the alloying metal from said solution of titanium and alloying metal.

2. The process of claim 1 in which the reducing metal is magnesium, and the alloying metal is zinc.

3. The process of claim 2 in which the titanium halide is titanium tetrachloride.

4. The process of claim 1 in which the reducing metal is aluminum, and the alloying metal is zinc.

5. A process for the production of titanium metal which comprises reducing a vaporous tetrahalide selected from the group consisting of the chloride, iodide, and bromide of titanium with a molten reducing metal selected from the group consisting of alkali metals, alkaline earth metals, beryllium, and aluminum in the presence of a molten titanium alloying metal selected from the group consisting of zinc and cadmium thereby producing a molten solution of titanium and said alloying metal, the starting amount of said reducing metal ranging from 2–20% by weight of the combined amounts of reducing and alloying metals, removing from the reaction zone the fluid halide of the reducing metal formed by the reduction reaction, and also removing said molten solution of titanium and alloying metal to a distilling zone, and then distilling the alloying metal from said solution.

6. The process of claim 5 in which the reducing metal is magnesium and the alloying metal is zinc.

7. The process of claim 6 in which the titanium halide is titanium tetrachloride.

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