Oct. 8, 1957 R. H. SINGLETON ET AL 2,809,108

METHOD OF PRODUCING TITANIUM

Filed Aug. 14, 1952 2 Sheets-Sheet 1

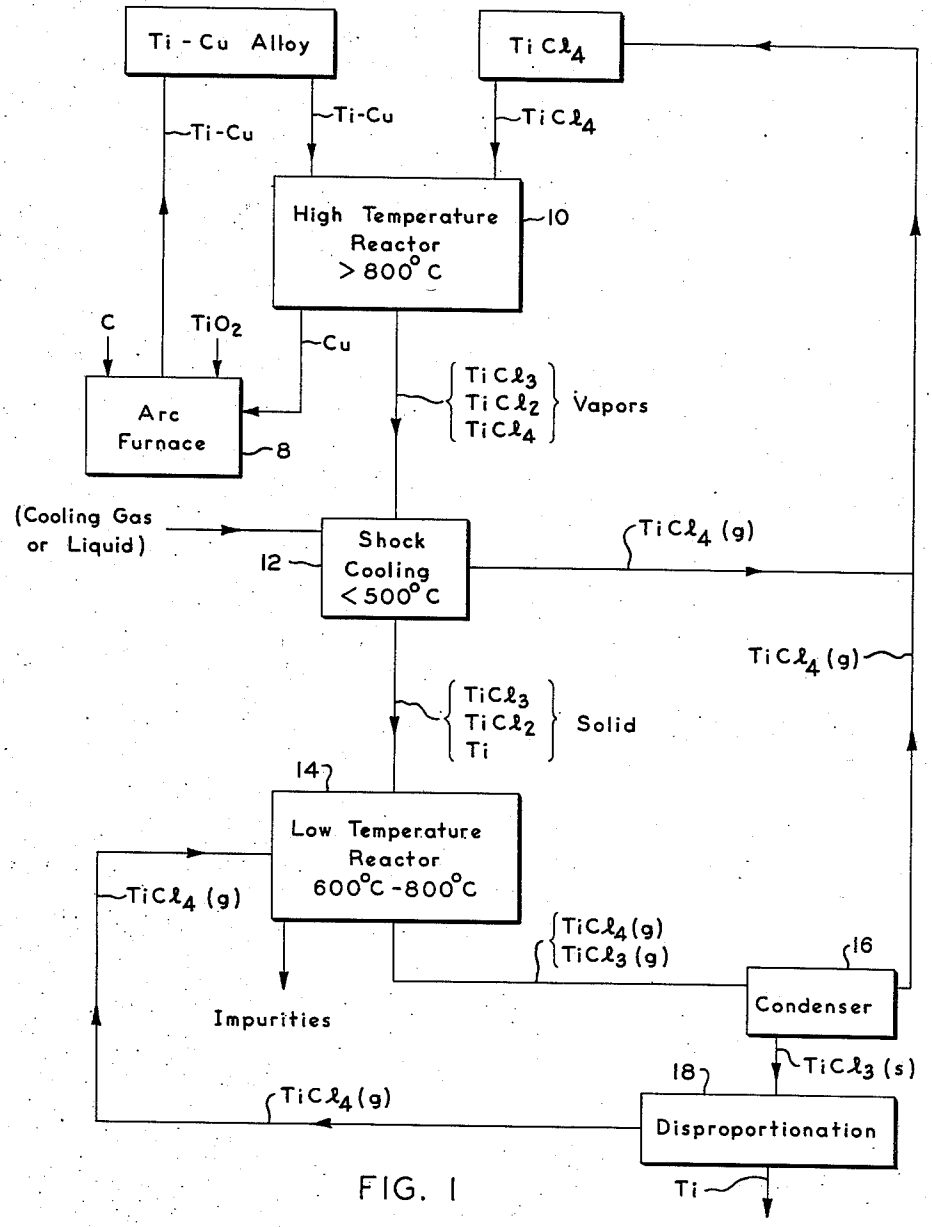


FIG. 1

INVENTORS
Richard H. Singleton
BY William O. DiPietro
Oliver W. Hayes
ATTORNEY

Oct. 8, 1957 R. H. SINGLETON ET AL 2,809,108

METHOD OF PRODUCING TITANIUM

Filed Aug. 14, 1952 2 Sheets-Sheet 2

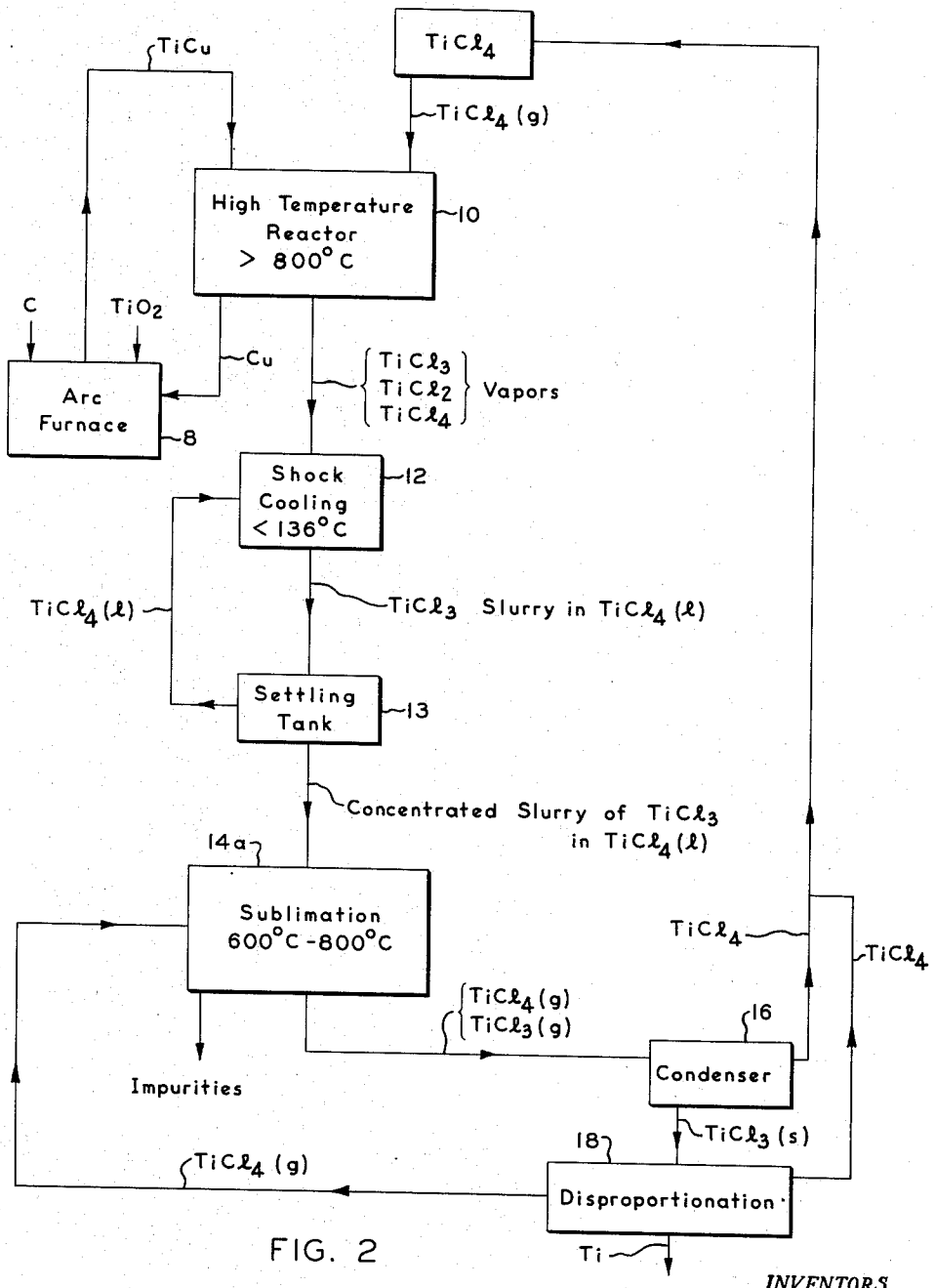


FIG. 2

INVENTORS
Richard H. Singleton
BY William O. DiPietro
Oliver W. Hayes
ATTORNEY

United States Patent Office 2,809,108 Patented Oct. 8, 1957

2,809,108

METHOD OF PRODUCING TITANIUM

Richard H. Singleton, Lexington, and William O. Di Pietro, Watertown, Mass., assignors to National Research Corporation, Cambridge, Mass., a corporation of Massachusetts

Application August 14, 1952, Serial No. 304,389

3 Claims. (Cl. 75—84.5)

This invention relates to the production of titanium metal or lower chlorides of titanium, and more particularly to the production of pure titanium metal or pure titanium trichloride from titanium bearing materials.

It is a principal object of the present invention to provide an improved process for manufacturing titanium from titanium bearing materials so as to obtain the titanium in a form essentially uncontaminated by the original materials associated therewith.

Still another object of the invention is to provide a process which is particularly adapted to the production of relatively pure titanium trichloride from titanium alloys.

Another object of the invention is to provide a process for the manufacture of titanium metal which obviates the necessity of manufacturing large quantities of titanium tetrachloride by chlorination of titanium ores.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the process involving the several steps and the relation and the order of one or more of such steps with respect to each of the others which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description taken in connection with the accompanying drawings wherein:

Fig. 1 is a diagrammatic, schematic flow sheet illustrating one embodiment of the invention; and

Fig. 2 is a diagrammatic, schematic flow sheet illustrating another embodiment of the invention.

The present invention is primarily directed to the production of titanium or lower chlorides of titanium from titanium bearing materials. In particular, the present invention is concerned with the use, as starting materials, of titanium alloys. Of the alloys, copper-titanium alloys are preferred, although alloys such as the alloys of titanium with nickel can be employed. From the standpoint of cheapness and ease of operability of the process, the copper-titanium alloys are much preferred. Copper-titanium alloys can be relatively cheaply manufactured by electric furnace reduction of titanium dioxide in the presence of carbon. When the alloy is to be made, the alloying metal or an oxide of the alloying metal is also present in the electric furnace charge. The use of titanium-copper alloys as a starting material in the present process will be discussed first. This alloy may be made by the arc furnace reduction of ilmenite or the like with carbon in the presence of copper or copper oxide. Equally, it may be made by dissolving impure titanium in molten copper.

The titanium-copper alloy from an electric furnace **8** (Fig. 1) is fed to a first high temperature reactor **10** which is arranged to hold the molten titanium-copper alloy at a temperature above about 800° C. so as to provide a large surface area for contact with titanium tetrachloride vapors. At high temperatures, on the order of 800° C. and above, the copper in the titanium alloy is relatively inert to titanium tetrachloride, while the titanium in the alloy will react with the titanium tetrachloride to form gaseous titanium lower chlorides. Since the melting point of the titanium-copper alloy is a function of the changing titanium content, it is desired to operate above about 1000° C. so that the alloy will be molten at all times. The principal (and idealized) reaction between titanium and titanium tetrachloride is expressed by the following equation:

$$Ti + 3TiCl_4 \xrightarrow{>800^\circ C.} 4TiCl_{3(g)} \qquad (A)$$

The gaseous reaction products from equation (A) are preferably removed from the high temperature reactor as gases and are preferably shock cooled (at **12**) with a cold gas such as argon to a temperature below about 500° C. Excess titanium tetrachloride and the shock-cooling gas (e. g., argon) are removed from the shock-cooling zone, separated and recycled, the titanium tetrachloride being recycled to the high temperature reactor **10** and the argon being chilled and recycled to the shock-cooling zone **12**. This separation and recycling of the argon is not shown in Fig. 1. It should be pointed out, however, that the argon must be very pure due to the possibility of contaminating the titanium compounds in zone **12** if any oxygen or nitrogen is introduced into zone **12**.

The shock-cooled products from zone **12** are next reacted in a low temperature reactor **14** with additional titanium tetrachloride to assure substantially complete conversion of the shock-cooled products to titanium trichloride. As a result of the shock-cooling and the reaction with titanium tetrachloride, essentially all of the titanium is in the form of titanium trichloride. The titanium trichloride leaving the high temperature reactor **10** may disproportionate somewhat to titanium dichloride and to titanium metal during the shock cooling. Thus, the initially shock-cooled products may comprise titanium trichloride, and small amounts of titanium dichloride and titanium metal. However, when an atmosphere of titanium tetrachloride is present in the shock cooling zone, disproportionation does not occur to any great extent.

The small amount of titanium dichloride (resulting from disproportionation) is converted to titanium trichloride in low temperature reactor **14** by reaction with titanium tetrachloride in accordance with the following equation:

$$TiCl_{2(g)} + TiCl_{4(g)} \xrightarrow{<1000^\circ C.} 2TiCl_{3(g)} \qquad (B)$$

Any titanium metal in the shock-cooled products reacts with titanium tetrachloride in accordance with the following equation:

$$Ti_{(s)} + 3TiCl_{4(g)} \xrightarrow{<1000^\circ C.} 4TiCl_{3(s)} \qquad (C)$$

The reactions in Equations B and C can be carried out at relatively low temperatures on the order of 300° C. and above. Since some contaminating materials, such as oxides or carbides of titanium, may also be present in the shock-cooled products in the low temperature reaction zone, it is preferred to resublime the titanium trichloride so as to obtain this titanium trichloride in a state of high purity. This resublimation may be readily accomplished by heating the reaction products in the second reactor under an atmosphere of titanium tetrachloride to a temperature on the order of about 600° C. to 800° C. Although this temperature is well above the disproportionation temperature for titanium trichloride, the titanium trichloride will not disproportionate due to the atmosphere of titanium tetrachloride and may be transported to a

suitable condenser **16** for condensing the titanium tri chloride as a solid.

In the Fig. 2 embodiment of the invention the vapors leaving the high temperature reactor comprise essentially titanium trichloride and probably some titanium dichloride and some titanium tetrachloride. These vapors are shock cooled, preferably to a temperature below about 136° C. by being quenched with liquid titanium tetrachloride. This has the advantage of permitting removal of the shock-cooled products as a slurry in liquid titanium tetrachloride. It also provides for the substantially complete prevention of any disproportionation of titanium trichloride to titanium dichloride during the shock-cooling. The gross amounts of titanium tetrachloride are then separated from this slurry by use of a settling tank **13** or other suitable equipment and the concentrated slurry is fed to a sublimation chamber **14***a* where the remaining liquid titanium tetrachloride is evaporated and the titanium trichloride is heated to a temperature on the order of about 600° C. to 800° C. to sublime the titanium trichloride.

The above two processes result in high yields of essentially pure titanium trichloride. This titanium trichloride may be converted to titanium metal by a number of techniques, such as in a disproportionation apparatus **18** of the type described and claimed more fully in the copending application of Singleton and Van Arkel, Serial No. 285,975, filed May 3, 1952. This disproportionation apparatus is particularly useful since it provides large quantities of titanium tetrachloride which can be recycled to the high temperature reactor for reaction with the titanium bearing material.

Equally, the titanium trichloride may be thermally reduced to titanium metal by the use of reducing agents, or may be fed to an electrolysis cell, as described more fully in the copending application of Benner and Chadsey, Serial No. 233,204, filed June 23, 1951.

Additionally, the titanium trichloride may be chlorinated to produce pure titanium tetrachloride for use in thermal reduction processes, such as those shown in the Kroll Patent No. 2,205,854, the Maddex Patent No. 2,556,763, or in the "torch" process described and claimed more fully in the copending application of Findlay, Serial No. 200,606, filed December 13, 1950.

In the preferred form of apparatus employed with the above discussed invention, the various high-temperature portions of the reactor are preferably formed of graphite, carbon or carbides such as silicon carbide. When carbon or graphite is used, the necessary heat input can be readily achieved by using the carbon or graphite as an electrical heating element in either an induction or resistance heating circuit. Where mechanical movement is required in the high-temperature portions, it is preferred to employ refractory metals, such as molybdenum, for those parts requiring high-temperature mechanical strength or wear resistance. Those portions of the apparatus which operate at temperatures of about 600° C. or lower can be formed of stainless steel, nickel or refractory metals, such as molybdenum and the like. Carbon and graphite can equally be used in the relatively low-temperature portions of the apparatus, but, for mechanical reasons, may be less preferred than the metals in many cases.

In general, the high temperature reactor may be a countercurrent still, similar to a zinc still, or a rotary kiln, these arrangements furnishing a large surface area for the titanium bearing material to be reacted with the titanium tetrachloride. The shock cooling may take place in a portion of the high temperature reactor, in which case the shock-cooled products may be removed therefrom as solids. Equally, the shock cooling may take place outside of the high temperature reactor.

When a titanium-copper alloy is used, the percentage of titanium in the alloy is preferably in the range of 40% titanium to 60% titanium, the percent titanium being reduced to about 5% before the copper is recycled to the electric furnace for addition of more titanium.

While resublimation of the product titanium trichloride in the low temperature reactor **14** has been set forth as a highly desirable step in the process, it is not essential in all cases. This is particularly true where this titanium trichloride is essentially pure or sufficiently pure for its subsequent use. This purity will naturally depend upon the purity of the starting materials and the degree of carry-over of contaminants from the high temperature reactor to the shock-cooling zone. The purity requirements of the titanium trichloride will vary considerably with the details of the further processing steps. For example, if disproportionation is to be employed, the titanium trichloride must have a very high purity. If the subsequent step is chlorination to titanium tetrachloride, the titanium trichloride need not be particularly pure, provided the contaminants can be separated from titanium tetrachloride. With regard to electrolysis, the purity requirements will be largely dependent upon the solubility of the impurities in the molten electrolyte.

Since certain changes may be made in the above process without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description, or shown in the accompanying drawings, shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. The process of manufacturing titanium which comprises forming a crude alloy of titanium and copper, heating said alloy in a reaction zone to a temperature above about 800° C., contacting said hot alloy with titanium tetrachloride vapors to convert said titanium to a gaseous lower chloride of titanium and to convert said tetrachloride to a gaseous lower chloride, passing the gaseous products from the reaction zone, shock-cooling the gaseous products leaving said reaction zone to a temperature below about 500° C., heating the shock-cooled products to a temperature of about 600° C. to 800° C. in the presence of titanium tetrachloride to sublime titanium trichloride, condensing said sublimed titanium trichloride, and converting said titanium trichloride to titanium metal.

2. The process of manufacturing titanium trichloride which comprises heating a titanium alloy in a reaction zone to a temperature above about 800° C., said titanium alloy being selected from the class consisting of the alloys of titanium with copper and titanium with nickel, contacting said hot titanium alloy with a vapor of titanium tetrachloride to convert said titanium alloy to a gaseous lower chloride of titanium and to convert said titanium tetrachloride to a gaseous lower chloride, passing the gaseous products from the first reaction zone, condensing the lower titanium chlorides leaving the first reaction zone, heating the condensed products in an atmosphere free of gaseous oxygen compounds and in the presence of titanium tetrachloride vapors to sublime titanium trichloride from said condensed products and to convert to titanium trichloride substantially all titanium and titanium dichloride in the condensed products, and condensing said sublimed titanium trichloride.

3. The process of manufacturing titanium trichloride which comprises heating a titanium alloy in a reaction zone to a temperature above about 800° C. in the presence of titanium tetrachloride to form gaseous lower chlorides of titanium, said titanium alloy being selected from the class consisting of the alloys of titanium with copper and titanium with nickel, passing the gaseous products from the first reaction zone, condensing the lower titanium chlorides leaving the first reaction zone, heating the condensed products in an atmosphere free of gaseous oxygen compounds and in the presence of titanium tetrachloride vapors to sublime titanium trichloride from said condensed products and to convert to titanium trichloride substantially all titanium and titanium dichloride in the condensed products, and condensing said sublimed titanium trichloride.

(References on following page)

References Cited in the file of this patent

UNITED STATES PATENTS

1,173,012	Meyer	Feb. 22, 1916
2,306,184	Pechukas	Dec. 22, 1942
2,452,665	Kroll et al.	Nov. 2, 1948
2,607,675	Gross	Aug. 19, 1952
2,618,549	Glasser et al.	Nov. 18, 1952
2,647,826	Jordan	Aug. 4, 1953
2,670,270	Jordan	Feb. 23, 1954
2,694,652	Loonam	Nov. 16, 1954

OTHER REFERENCES

Comprehensive Treatise in Inorganic and Theoretical Chemistry by Mellor, vol. 7. Published 1927 by Longmans, Green & Co., N. Y. Pages 74–77.

Titanium by Barksdate. Published by The Ronald Press Co., N. Y., in 1949. Page 81.

Report of Investigations 4519, published in August 1949 by Bureau of Mines, Washington, D. C., 37 pages and two figures. Pages 9–13 relied upon.

J. of Research of the Nat'l Bur. of Stds., vol. 46, No. 4, pages 299–300. Research paper 2199, by Sherfey, April 1951.