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METHOD OF PRODUCING TITANIUM

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This invention relates to a process for producing ductile titanium metal of high purity.

Titanium metal is rapidly achieving a position of importance among structural materials. Its properties enable the metal and alloys in which it forms the base to withstand the severe environmental conditions to which such materials are being subjected in many technological fields. The metal retains its strength at elevated temperatures and withstands many types of corrosive environments so that it possesses great utility wherever high temperatures or corrosion present problems. In addition, its high strength per given unit of weight offers advantages in many structural applications.

More widespread use of titanium metal would occur if processes were available by which the cost of production of ductile titanium metal of high purity would be reduced. A process is needed in which the inclusion of embrittling impurities in the metal product is avoided and the number of process steps reduced to a minimum. The process of my invention accomplishes these purposes.

My invention is a process for the production of ductile titanium metal of high purity which process comprises placing two electrodes in a body of a liquid titanium tetrahalide and maintaining an arc between the electrodes to produce a precipitate comprising lower halides of titanium. The lower halides of titanium are then removed from the liquid tetrahalide and treated to produce titanium metal. My invention also encompasses the process by which a titanium dihalide is produced.

There exist several methods by which titanium dihalides may be treated to produce titanium metal. For example, the disproportionation of lower halides of titanium at elevated temperatures to form titanium metal and titanium tetrahalide is well known. The disproportionation of titanium dichloride to form titanium metal and vaporous titanium tetrachloride at elevated temperatures and the disproportionation of titanium dibromide at elevated temperatures to form titanium metal and titanium tetrabromide have been reported by others. Another method is to reduce titanium dichloride in the presence of hydrogen or some other suitable reducing agent at proper conditions of pressure and temperature in order to produce titanium metal. However, the disproportionation of lower halides of titanium at elevated temperatures is a preferred method since the procedure can be carried out under conditions which minimize the introduction of impurities into the final product.

The particular aspect of this invention is the manner in which the titanium dihalide is produced. A unique feature of the process is that the lower halides of titanium are produced in a liquid through the use of electrical current. Accordingly, the reduction of the titanium tetrahalide to the lower halides of titanium is achieved without the use of reducing metals. Other processes for the production of titanium metal involve the reduction of a titanium tetrahalide with aluminum, hydrogen, alkali metals or alkaline earth metals. In such processes the halides of the reducing metals must subsequently be separated from the titanium product. In this process no subsequent separation step is required and problems of contamination by impurities are minimized. The lower halides of titanium are condensed within the liquid so that there is no need for the additional procedure of condensation of the vapors of the lower titanium halides. In addition, the liquid provides a protective layer in that the dissociation reaction is isolated from any overlying gaseous contaminant such as oxygen or nitrogen that may be in the reaction vessel.

A further advantage of this process is that liquid titanium tetrahalide is used as the medium in which reduction to the lower halides occurs. In some processes where reducing metals are used, the titanium tetrahalide is passed over the reducing metal as a vapor at an elevated temperature. This imposes a severe operating condition since the titanium tetrahalide in the vapor state at elevated temperatures is corrosive toward metals. As a result, unusual steps must be taken to protect the reacting vessels from the attack of the titanium tetrahalide.

The manner in which the liquid titanium tetrahalide is produced does not form a part of this invention. One well known process for the production of titanium tetrachloride is to heat rutile, a commonly occurring titanium ore, in the presence of carbon and chlorine gas and subsequently to condense the gaseous reaction product to produce liquid titanium tetrachloride. Similarly, through the use of other halogens, other tetrahalides of titanium may be formed by the same reaction. The process of this invention only requires that a pure titanium tetrahalide substantially free of any contaminant be used.

Titanium metal may be produced by this process when a tetrahalide of titanium selected from the group consisting of titanium tetrachloride, titanium tetrabromide and titanium tetraiodide is used. The process of producing titanium metal will be more clearly understood from the following example in which titanium tetrachloride was used.

Titanium tetrachloride was placed as a liquid in a glass vessel. The volume of titanium tetrachloride placed in the vessel was sufficient to submerge electrodes placed in the liquid as described below. While it is not essential to the process, it is preferred that the titanium tetrachloride be placed under a partial vacuum to remove traces of gases present in the liquid. This is because some solubility of oxygen and nitrogen exists in the titanium tetrachloride liquid and these traces of oxygen and nitrogen may contaminate the final product. It is therefore desirable to evacuate the overlying air from the glass vessel and to degas the tetrachloride. Thereupon, an inert gas such as argon, neon or krypton can be admitted to provide an atmosphere of inert gas until such time that the reaction products fill the overlying space.

Two electrodes were then placed in the liquid. The electrodes were made of tungsten. However, other electrode materials such as, for example, molybdenum, titanium carbide, zirconium carbide, carbon, or graphite may be used so long as the electrode material does not contaminate the final product. While some flaking of the electrodes may occur during the arcing process, such material may be readily separated from the lower titanium chlorides prior to the disproportionation procedure. A voltage of 1250 volts was applied across the electrodes at a current of 640 milliamperes provided by a direct current source. The arc struck as a result of the imposition of this voltage was maintained for 60 minutes, and an insoluble black solid which accumulated into flocculated clusters was produced. Evolution of chlorine gas and titanium tetrachloride vapor occurred during the reaction. The chlorine gas was permitted to escape and the titanium tetrachloride was condensed and returned to the reaction vessel as a liquid.

It is probable that the reaction which occurred as a result of the striking of the art was twofold. In the immediate dissociation zone between the electrodes, the tetrachloride was reduced to chlorine gas and titanium metal according to the following reaction:

$$TiCl_4 \rightarrow Ti + 2Cl_2$$

The presence of the liquid titanium tetrachloride provided a quick-cooling means which prevented the reversal of the above reaction. Thereupon, the hot titanium metal reacted with the vaporized tetrachloride in the vicinity of the electrodes to produce the lower chlorides, titanium trichloride and titanium dichloride, according to the following reactions:

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

However most of the reaction product was titanium dichloride.

The arc was discontinued after 60 minutes and the solid reaction products were removed from the bottom of the reaction vessel. This product was then heated and, by the disproportionation of the lower totanium chlorides, titanium metal was produced as a powder. The heating was done in a graphite crucible at a temperature in excess of 500° C. under an atmosphere of flowing argon gas. The disproportionation procedure was performed under an atmosphere of inert gas in order to avoid contamination of the titanium metal by oxygen or nitrogen. As an alternative procedure, the disproportionation procedure may be carried out under vacuum. Substantially pure titanium metal was obtained.

The powdered titanium metal formed as a result of disproportionation may then be melted under conditions adapted to avoid inclusion of contaminants to produce ingots of the metal.

The process of this invention offers distinct advantages of simplicity and economy in the production of titanium metal.

I claim:

1. A process for producing titanium metal of high purity, which process comprises submerging in a body of a liquid titanium tetrahalide two electrodes of a chemically nonreducing substance with respect to said tetrahalide, maintaining a continuous arc between the electrodes in the absence of a reducing substance and of sufficient current intensity to produce, by dissociation of said tetrahalide beneath a layer of liquid titanium tetrahalide, a halogen gas and a precipitate comprising lower halides of titanium, removing the precipitate from the liquid and treating the precipitate to produce titanium metal.

2. A process for producing titanium metal of high purity, which process comprises submerging in a body of a liquid titanium tetrahalide two electrodes of a chemically nonreducing substance with respect to said tetrahalide, maintaining a continuous arc between the electrodes in the absence of a reducing substance and of sufficient current intensity to produce, by dissociation of said tetrahalide beneath a layer of liquid titanium tetrahalide, a halogen gas and a precipitate comprising lower halides of titanium and simultaneously refluxing any vaporized titanium tetrahalide, removing the precipitate from the liquid, and subjecting the precipitate to an elevated temperature to produce titanium metal.

3. A process for producing titanium metal of high purity, which process comprises a process of placing a liquid titanium tetrahalide in a vessel, removing by vacuum any overlying gas and any gases soluble in the liquid titanium tetrahalide, admitting an inert gas to

provide a layer of inert gas overlying the tetrahalide, submerging in the tetrahalide two electrodes of a chemically nonreducing substance with respect to said tetrahalide, maintaining a continuous arc between the electrodes in the absence of a reducing substance and of sufficient current intensity to produce, by dissociation of said tetrahalide beneath a layer of liquid titanium tetrahalide, a halogen gas and a precipitate comprising lower halides of titanium and simultaneously refluxing any vaporized titanium tetrahalide, removing the precipitate from the liquid, and subjecting the precipitate to an elevated temperature to produce titanium metal.

4. A process for producing titanium metal of high purity, which process comprises submerging in a body of liquid titanium tetrachloride two electrodes of a chemically nonreducing substance with respect to said tetrachloride, maintaining a continuous arc between the electrodes in the absence of a reducing substance and of sufficient current intensity to produce, by dissociation of said tetrachloride beneath a layer of liquid titanium tetrachloride, chlorine gas and a precipitate comprising lower chlorides of titanium and simultaneously refluxing any vaporized titanium tetrachloride, removing the precipitate from the liquid, and treating the precipitate to produce titanium metal.

5. A process for producing titanium metal of high purity, which process comprises submerging in a body of liquid titanium tetrachloride two electrodes of a chemically nonreducing substance with respect to said tetrachloride, maintaining a continuous arc between the electrodes in the absence of a reducing substance and of sufficient current intensity to produce, by dissociation of said tetrachloride beneath a layer of liquid titanium tetrachloride, chlorine gas and a precipitate comprising lower chlorides of titanium and simultaneously refluxing any vaporized titanium tetrachloride, removing the precipitate from the liquid, and subjecting the precipitate to an elevated temperature to produce titanium metal.

6. A process for producing titanium metal of high purity, which process comprises placing liquid titanium tetrachloride in a vessel, removing by vacuum any overlying gas and any gases soluble in the liquid titanium tetrachloride, admitting an inert gas to provide a layer of inert gas overlying the tetrachloride, submerging two electrodes of a chemically nonreducing substance with respect to said tetrachloride in the tetrachloride, maintaining a continuous arc between the electrodes in the absence of a reducing substance and of sufficient current intensity to produce, by dissociation of said tetrachloride beneath a layer of liquid titanium tetrachloride, chlorine gas and a precipitate comprising lower chlorides of titanium and simultaneously refluxing any vaporized titanium tetrachloride, removing the precipitate from the liquid, and subjecting the precipitate to an elevated temperature to produce titanium metal.

7. A process for producing titanium dihalide, which process comprises submerging in a body of a liquid titanium tetrahalide two electrodes of a chemically nonreducing substance with respect to said tetrahalide, maintaining a continuous arc between the electrodes in the absence of a reducing substance and of sufficient current intensity to produce, by dissociation of said tetrahalide beneath a layer of liquid titanium tetrahalide, a halogen gas and a precipitate comprising substantially titanium dihalide, and simultaneously refluxing any vaporized titanium tetrahalide.

8. A process for producing titanium dichloride, which process comprises submerging in a body of liquid titanium tetrachloride two electrodes of a chemically nonreducing substance with respect to said tetrachloride, maintaining a continuous arc between the electrodes in the absence of a reducing substance to produce, by dissociation of said tetrachloride beneath a layer of liquid titanium tetrachloride, chlorine gas and a precipitate

comprising substantially titanium dichloride, and simultaneously refluxing any vaporized titanium tetrachloride.

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