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PRODUCTION OF METALLIC TITANIUM

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This invention relates to the production of metallic titanium and has for an object the provision of an improved method or process for producing high-purity metallic titanium. More particularly, the invention contemplates the provision of an improved method or process for producing high-purity metallic titanium by dissociation of titanium tetraiodide.

The term "ore" as employed in the specification and claims is intended to include concentrates and other titanium mineral-bearing materials as well as natural ore.

In accordance with the invention, titanium-bearing ore is subjected to a suitable treatment to recover all or a large proportion of the titanium in the form of pure titanium dioxide.

The conversion of the ore to pure titanium dioxide may be carried out in any suitable manner as, for example, by the sulphuric acid-hydrolysis process commonly employed for producing titanium dioxide from ilmenite in the pigment industry. If titanium dioxide of suitable purity is available at commercially economical prices or if natural titanium dioxide can be obtained at a price sufficiently low to offset the increased cost of operation due to the presence of impurities, this step may be omitted from the complete process of the invention.

The titanium dioxide available or produced is subjected to a suitable treatment which will convert the titanium to a form in which it is capable of reacting with iodine to produce titanium tetraiodide. The titanium of the titanium dioxide may be converted into such a suitable form by reduction to the metallic state. Reduction of the titanium of the titanium dioxide may be carried out by means of either non-carbonaceous reducing agents such as sodium, calcium, magnesium, silicon and aluminum or carbonaceous reducing agents such as charcoal and petroleum coke.

The metallic titanium produced by reduction of the titanium dioxide with a non-carbonaceous reducing agent can be used for producing titanium tetraiodide. I have found, however, that reduction with an excess of carbon produces a product which provides a better reaction material and which is less expensive than the product resulting from reduction by means of non-carbonaceous reducing agents.

I prefer to reduce the titanium of the titanium dioxide with carbon in amount sufficient to produce titanium carbide, as I have found iodine will react with titanium carbide rapidly and efficiently at a temperature near 1100° C.

Titanium carbide can be produced by heating a mixture of titanium dioxide and carbon to a temperature of about 1050° C. at atmospheric pressures, but the reaction is slow and can be made to go to completion only with difficulty. Incompletely reduced material does not react readily with iodine. Therefore, I prefer to carry out the reduction with carbon at a higher temperature. I have found that a highly reactive titanium carbide product may be obtained by carrying out the reduction at temperatures in the range 1300° C. to 1800° C. At temperatures in the lower portion of the range, I prefer to effect the heating and reduction under a vacuum. Products formed at the lower temperatures under reduced pressures are more highly reactive than products formed at higher temperatures under atmospheric pressure. Thus, for example, titanium carbide formed at 1300° C. under vacuum may be as much as ten percent more reactive than titanium carbide formed at 1800° C. under atmospheric pressure. The advantage of greater reactivity may be offset to some

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extent by the cost and inconvenience of operating under a vacuum. Normally, I prefer to operate under atmospheric pressure at a high temperature in the neighborhood of 1800° C. in view of the large quantities of gas produced in the reaction. An electric resistance furnace of the type employed in producing silicon carbide may be employed advantageously in carrying out the reduction of titanium with carbon to produce titanium carbide.

In order to limit contamination of the titanium carbide, I prefer to employ petroleum coke or charcoal as the reducing agent.

The titanium carbide produced is subjected to the action of iodine vapor at an elevated temperature. I have found that the rate of reaction reaches a maximum at 1100° C. and falls off at lower and higher temperatures.

In carrying out the reaction between iodine and titanium carbide at the higher temperatures, I prefer to employ a furnace lined with graphite, as the results of my investigations indicate that graphite is not attacked at any temperature by iodine vapor. I prefer, also, to employ electrical resistance heating because of ease of control, efficiency and the absence of any gaseous products of combustion which, if present, might contaminate the titanium tetraiodide produced.

The titanium tetraiodide produced is subjected to a fractionation treatment to separate pure titanium tetraiodide from such contaminants as iodine and iodides of elements other than titanium which may be present in the gaseous product of the reaction between the iodine and the titanium carbide product. No difficulty is encountered in fractionating the product and producing pure titanium tetraiodide, as, in general, the boiling points of the iodides of the metals which are likely to be present in the titanium carbide as impurities are very much higher than that of titanium tetraiodide. Silicon and tin tetraiodides are exceptions to this rule. The boiling point of silicon tetraiodide is 287° C., almost 100° below that of titanium tetraiodide, and, therefore, its presence should not complicate the fractionating operation. Tin tetraiodide has almost the same boiling point as titanium tetraiodide, but this element is not likely to be present in any appreciable quantity in titanium ore, so no difficulty should be encountered.

One of the more important functions of the fractionating step is to effect the removal of iodides of elements other than titanium which may be present in the gaseous product resulting from treatment of the titanium carbide with iodine.

Another important function of the fractionating step will be to effect the separation of unreacted or unconsumed elemental iodine. Separation of iodine from titanium tetraiodide presents no particularly difficult problem as the two materials have substantially different boiling points, that of iodine being 183° C. and that of titanium tetraiodide being 379° C.

Fractionation may be carried out by means of controlled cooling of the gaseous product of the iodine-titanium carbide reaction, or the gaseous product may be cooled and condensed, and the components of the condensate may be separated by fractional distillation.

Fractional distillation preferably is carried out at temperatures between the melting point and the boiling point of titanium tetraiodide, in the range 150° C. to 379° C., under reduced pressures, that is, under pressures lower than atmospheric pressures. Any suitable pressure which will permit attainment of the results sought may be employed.

When the gaseous product resulting from treatment of titanium-bearing material with iodine contains only titanium tetraiodide and one or more substances like iodine having boiling points lower than that of titanium tetraiodide, the product may be cooled and condensed, and a pure titanium tetraiodide product may be obtained as a residue resulting from distillation of the condensate.

For the fractionating operation and other operations in which liquid or gaseous iodine or titanium tetraiodide are handled, I prefer to employ apparatus comprising nickel and nickel alloys such as Hastelloy B, although any suitable materials may be employed.

According to a method or process of the invention, a gaseous product consisting essentially of titanium tetra-

iodide is passed in contact with a surface heated to and maintained at a temperature in the range 1100° C. to 1700° C. Contact of the titanium tetraiodide with the heated surface results in dissociation of the titanium tetraiodide into titanium and gaseous elemental iodine and deposition of metallic titanium of high purity. The deposition surface may be formed of tungsten or titanium or other suitable material, and it may be heated in any suitable manner.

The gaseous elemental iodine produced is utilized in the process for treating additional titanium-bearing materials for the production of titanium tetraiodide. The elemental iodine produced by the dissociation reaction may be used directly in the vapor state or after condensation to the liquid or solid state for treating additional titanium-bearing material.

I claim:

1. The method of recovering high-purity metallic titanium from titanium-bearing ore which comprises subjecting the ore to a suitable treatment and producing substantially pure titanium dioxide, subjecting the titanium dioxide to a reducing treatment to produce a relatively crude metallic titanium-bearing product capable of reacting with iodine to produce a titanium tetraiodide product, subjecting the crude metallic titanium-bearing product to the action of iodine to produce a titanium tetraiodide-containing product, subjecting the titanium tetraiodide-containing product to a fractionating treatment to separate pure titanium tetraiodide, subjecting the titanium tetraiodide to a dissociation treatment to produce substantially pure metallic titanium and elemental iodine by passing the titanium tetraiodide in vapor form in contact with a body of metallic titanium heated to a temperature in the range, 1100° C. to 1700° C., and utilizing the iodine in the treatment of additional crude metallic titanium-bearing material.

2. The method of recovering high-purity metallic titanium from titanium-bearing ore which comprises subjecting the ore to a suitable treatment and producing substantially pure titanium dioxide, subjecting the titanium dioxide to a reducing treatment with carbon to produce titanium carbide, subjecting the titanium carbide to the action of iodine to form a titanium tetraiodide-containing product, subjecting the titanium tetraiodide-containing product to a fractionating treatment to separate pure titanium tetraiodide, subjecting the titanium tetraiodide to a dissociation treatment to produce substantially pure metallic titanium and elemental iodine by passing the titanium tetraiodide in vapor form in contact with a body of metallic titanium heated to a temperature in the range, 1100° C. to 1700° C., and utilizing the iodine in the treatment of additional titanium carbide.

3. The method of recovering high-purity metallic titanium from titanium-bearing ore which comprises subjecting the ore to a suitable treatment and producing substantially pure titanium dioxide, subjecting the titanium dioxide to a reducing treatment with carbon to produce titanium carbide, subjecting the titanium carbide to the action of iodine to form a titanium tetraiodide-containing product, subjecting the titanium tetraiodide-containing product to a fractionating treatment to separate pure titanium tetraiodide, subjecting the titanium tetraiodide to a dissociation treatment by passing the titanium tetraiodide in contact with a refractory surface comprising metallic titanium maintained at a temperature in the range 1100° C. to 1700° C. to produce substantially pure metallic titanium and elemental iodine, and utilizing the iodine in the treatment of additional titanium carbide.

4. The method of recovering high-purity metallic titanium from titanium-bearing ore which comprises subjecting the ore to a suitable treatment and producing substantially pure titanium dioxide, subjecting the titanium dioxide to a reducing treatment with carbon to

produce titanium carbide, subjecting the titanium carbide to the action of iodine in vapor form at an elevated temperature near 1100° C. to form a titanium tetraiodide-containing product, subjecting the titanium tetraiodide-containing product to a fractionating treatment to separate pure titanium tetraiodide, subjecting the titanium tetraiodide to a dissociation treatment to produce substantially pure metallic titanium and elemental iodine by passing the titanium tetraiodide in vapor form in contact with a body of metallic titanium heated to a temperature in the range, 1100° C. to 1700° C., and utilizing the iodine in the treatment of additional titanium carbide.

5. The method of recovering high-purity metallic titanium from titanium-bearing ore which comprises subjecting the ore to a suitable treatment and producing substantially pure titanium dioxide, subjecting the titanium dioxide to a reducing treatment with carbon to produce titanium carbide, subjecting the titanium carbide to the action of iodine in vapor form at an elevated temperature near 1100° C. to form a titanium tetraiodide-containing product subjecting the titanium tetraiodide-containing product to a fractionating treatment to separate pure titanium tetraiodide, subjecting the titanium tetraiodide to a dissociation treatment by passing the titanium tetraiodide in contact with a refractory surface comprising metallic titanium maintained at a temperature in the range 1100° C. to 1700° C. to produce substantially pure metallic titanium and elemental iodine, and utilizing the iodine in the treatment of additional titanium carbide.

6. The method of recovering high-purity metallic titanium from titanium dioxide which comprises subjecting the titanium dioxide to a reducing treatment to produce a relatively crude metallic titanium-bearing product capable of reacting with iodine to produce a titanium tetraiodide product, subjecting the crude metallic titanium-bearing product to the action of iodine to produce a titanium tetraiodide-containing product, subjecting the titanium tetraiodide-containing product to a fractionating treatment to separate pure titanium tetraiodide, subjecting the titanium tetraiodide to a dissociation treatment by passing the titanium tetraiodide in contact with a refractory surface maintained at a temperature in the range 1100° C. to 1700° C. to produce substantially pure metallic titanium and elemental iodine, and utilizing the iodine in the treatment of additional crude metallic titanium-bearing material.

7. The method of recovering high-purity metallic titanium from titanium dioxide which comprises subjecting the titanium dioxide to a reducing treatment with carbon to produce titanium carbide, subjecting the titanium carbide to the action of iodine in vapor form at an elevated temperature near 1100° C. to form a titanium tetraiodide-containing product, subjecting the titanium tetraiodide-containing product to a fractionating treatment to separate pure titanium tetraiodide, subjecting the titanium tetraiodide to a dissociation treatment by passing the titanium tetraiodide in contact with a refractory surface maintained at a temperature in the range 1100° C. to 1700° C. to produce substantially pure metallic titanium and elemental iodine, and utilizing the iodine in the treatment of additional titanium carbide.

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