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METHOD OF REDUCING TITANIUM OXIDE

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2 Claims. (Cl. 75—84)

This invention relates to processes for the production of titanium. It is a division of application Serial No. 457,796, filed September 22, 1954, now Patent No. 2,783,192, issued February 26, 1957. It has for its object the production of pure titanium by a process which combines a procedure for producing an impure titanium having a specific distribution of the impurities in the mass with the anodic dissolution of the titanium from such a mass, leaving the impurities in a form readily separated from the electrolyte and reducing the dissolved titanium by cathodic action.

I am fully aware of the prior art in reducing titanium oxide to titanium in admixture with the oxide of the reducing agent such as calcium or magnesium. I am likewise familiar with two-step reduction of titanium dioxide to metallic titanium by reduction to an intermediate oxide, for example by carbon, and the further reduction to metal by a more expensive reducing agent such as magnesium. I am also familiar with procedures for separating the reduced titanium from the other products of reduction, including acid solution of the latter and separating the titanium from a reduction mixture containing a large excess of magnesium by impingement in accordance with my copending application Serial No. 421,420, filed April 6, 1954, now Patent No. 2,830,893.

For the practice of my present invention, the impure titanium mass may be most simply and economically produced by agglomerating and separating the titanium from the reduction mass of metal and alkaline earth oxide and then melting the crude titanium. The agglomeration of the titanium in the reduction product with magnesium is preferably accomplished by adding a suitable flux such as barium chloride. Other non-oxidizing halide fluxes may be used. The amount of flux added is only enough to produce a suitable surface relationship between the titanium metal and magnesium oxide so that with mechanical work the titanium will agglomerate excluding the slag. This is from 5–25% by weight of the titanium in the mass. This sort of procedure has its counterpart in the so-called Krupp-Renn process in which iron ore is mixed with carbon and lime and then mechanically treated to agglomerate the reduced iron and separate it from the slag. The mechanical working necessary to agglomerate the titanium may be accomplished in a rotating tube at 1000° C. with or without balls of rods. Such tube must, of course, be kept free from active gases. Alternatively, the agglomeration may be performed in a closed tube or sheath and in this instance the product may be a consolidated titanium mass sufficiently free from slag to be used directly as an anode without the melting step. Such an anode has the impurities in the form of fairly large slag masses which do not form anode slime but provide an anode residue which separates readily from the electrolyte. It will be clear, however, that other steps than those described may be used. It is important only that the titanium metal be separated as far as possible by

simple mechanical means from the alkaline earth oxides and other impurities.

In a preferred form of my invention the agglomerated titanium is then melted and allowed to solidify slowly. Under these circumstances it is well known that titanium free from suspended impurities will crystallize at the cooling surface, and that the inclusions will be segregated in the last metal to solidify. This is not new, and I do not claim it. Ingots of titanium with a core of impurities have heretofore been produced. Such ingots have not, however, been useful because even if the impure core were mechanically removed there would still remain oxygen dissolved in the solid titanium. My invention makes the first practical use of such ingots because by using them as anodes in a fused chloride electrolyte I cause the dissolved oxygen to diffuse into the core which I remove from the electrolytic bath before it mechanically disintegrates. Here again I do not claim the refining procedure in which oxygen diffuses into the discarded part of the anode. This has been done by others. This embodiment of my invention resides in the production of a cored titanium anode and the electrorefining of such an anode only to the extent that the core does not disintegrate.

This combination of steps in producing pure titanium from its oxide is highly important from a practical standpoint. In the known procedures the impurities in the titanium being more or less uniformly distributed appear during the electrolysis as anode slime. The separation of this slime from the electrolyte is very difficult. With my invention no such slime is formed. The absence of anode slime permits the use of an improved electrorefining process in accordance with which unidirectional direct current is passed through a suitable fused salt bath electrolyte from one to the other of two electrodes of crude titanium, and periodically reversing the direction of the current. Under these conditions pure titanium is formed adjacent both electrodes, and falls to the bottom of the bath. It will be clear that anode slime would contaminate the titanium, and my present invention which permits the separation of the anode residue, is therefore particularly applicable to this process.

Having described my invention, which resides in the steps of producing a titanium mass with the insoluble impurities segregated in a suitable manner and then electrorefining the mass, I will now illustrate it by several examples.

Example I

I take 100 lbs. of titanium dioxide and mix it into 65 lbs. of magnesium and 5 lbs. barium chloride at 650° C. At this temperature there is very little reaction. I then heat this mass to 1000° C. for 15 minutes. All of this may conveniently be done in a graphite crucible in an induction furnace provided with an inert atmosphere. I then subject the mass to a tumbling and agglomerating action at 1000° C. The titanium pellets formed are separated from the pulverulent slag by known means such as screening. I then melt the titanium pellets. The molten titanium is poured into a mold. The mold is lined with magnesium oxide and insulated to produce slow cooling. The mold is cylindrical and 3 inches in diameter. A microscopic examination of the ingot shows that all of the insoluble impurities are segregated in a core 1 inch in diameter. The outer section of the ingot contains 3% oxygen. It will be obvious that such an ingot is worthless by the standards of the known art. I now take this ingot and make it an anode in a bath of fused sodium chloride at 850° C. I provide a titanium cathode, and pass a direct current through the cell at a current density of 300 amperes per square foot on both anode and cathode. The cell is

maintained in an inert atmosphere, and 3% titanium dichloride is added to the electrolyte. I continue the electrolysis until the diameter of the anode is slightly more than 1 inch. I then remove the cathode and the anode and cool them in an inert atmosphere. The metal on the cathode is washed with hot water and found to be 99.9% titanium. The anode core is added to another melt for the formation of anodes. The impurities in the anode are not thereby increased since the separation of insoluble impurities in the melting and casting operation is constant.

Example II

In this example I proceed as in Example I, except that I first heat titanium dioxide with carbon at 1400° C., producing an intermediate reduction product analyzing 68% titanium and containing a little carbide. I mix this with 70 lbs. of comminuted calcium. I then proceed as in Example I with the final reduction, melting, and casting steps. The electrolysis is carried out as in Example I except that two similar ingots are used as the electrodes and the current is reversed every minute to obtain a finer powder. This powder, which is titanium of substantially 99.9% purity, falls to the bottom of the bath and is recovered by dissolution of the salt after the electrolyte has solidified.

Example III

In this example I proceed as in Example I, except that the material to be agglomerated is placed in an iron tube and consolidated, the tube is evacuated and sealed by welding. The sealed tube is heated to 1000° C. and rolled into diamond shape with a reduction in area of 50%. The tube is cooled and the tube stripped off. The titanium has been welded into a coherent mass and most of the slag composed of magnesium oxide and

barium chloride squeezed to the end of the tube, the remainder is present in the titanium as macroscopic particles. I use this coherent titanium mass as an anode as set forth in Example I, except that the anode is completely consumed. The titanium is continuously removed from the cathode as it deposits and drained to provide a metal having a minimum of included electrolyte. The particles of slag are removed from the bottom of the cell.

I claim:

1. Process of converting titanium dioxide into a metallic titanium product, which comprises reacting the titanium dioxide, at a temperature of the order of 1000° C. and in an inert atmosphere, with substantially the chemical equivalent of an alkaline earth metal, in the presence of a molten fluxing agent selected from the group consisting of non-oxidizing alkali and alkaline earth metal chlorides, the amount of fluxing agent used being within the range of from about 5% to about 25% by weight of the titanium present in the reaction mixture, thereby forming a reaction product comprising particulate titanium dispersed in a slag at least partially molten, agglomerating the titanium into pellets by mechanically working the reaction product in an inert atmosphere and at an elevated temperature by tumbling the reaction product in a closed rotating vessel, and thereafter separating the titanium pellets from the slag.

2. The process defined in claim 1, in which the reaction product is tumbled in association with solid objects.

References Cited in the file of this patent

UNITED STATES PATENTS

1,602,542	Marden	Oct. 12, 1926
2,618,550	Hampel	Nov. 18, 1952
2,676,882	Hatch	Apr. 27, 1954
2,698,267	Halversen	Dec. 28, 1954