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PROCESS FOR MAKING TITANIUM CARBIDE

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My invention relates to a novel process for making titanium carbide.

The process heretofore known and followed, for making what has been called titanium carbide (TiC), consists in carburizing titanium by heating the metal with carbon for a considerable period at a temperature ranging from 1600° to 1900° C., preferably in a reducing atmosphere, or heating a mixture of titanium dioxide (TiO₂) and carbon, in an atmosphere of hydrogen, for several hours at a temperature ranging from 1600° to 1900° C., the TiO₂ being reduced to metallic titanium in the course of such heating. The titanium carbide material resulting from such process is amorphous and has a carbon content considerably lower than the theoretical carbon content of TiC, which is 20.05%. The material usually contains, also, oxides and nitrides of titanium, and considerable free carbon. The material so made is not satisfactory for the manufacture of cemented hard carbide compositions, having the desired hardness and strength.

The principal object of my invention is to provide a novel process for making titanium carbide, which gives a product superior to the titanium carbide material heretofore made, in that cemented hard carbide compositions made from the product of this new process have a combined strength and hardness superior to the combined strength and hardness of like cemented hard carbide compositions made from the material produced by the old process.

Another object of my invention is to provide a process for making titanium carbide which produces a superior product, at a cost not greatly in excess of the cost of the old process, and which is, therefore, competitive with it.

A further object of my invention is to provide a novel process for making titanium carbide, in which the recovery is sufficiently large to make the process economically useful, that is to say, in which a large proportion of the titanium contained in the charge is recovered as titanium carbide.

Further objects, and objects relating to economies and details of operation, will definitely appear from the detailed description to follow. In one instance, I have attained the objects of my invention by the devices and means described in the following specification. My invention is clearly defined and pointed out in the appended claims.

In general, my invention consists in dissolving titanium and carbon in molten iron, cooling the molten mass to solidify it, reducing it to par-

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ticle size suitable for acid treatment and, then, treating the particles with acid and washing with water, followed by decantation, until everything has been dissolved or otherwise removed from the mass, with the exception of the crystals of titanium carbide (TiC). This residue is then dried and is ready for use. I find it desirable and economical to carry out the process by heating a charge comprising titanium dioxide (TiO₂), iron, and carbon, to a temperature of 2800° C. or above, and maintaining the mass at this high temperature for a considerable period. In this way, the TiO₂ is reduced to titanium in the molten mass, with the release of gas which escapes therefrom, and the titanium metal is formed under such conditions that it does not react with the oxygen and nitrogen in the air to form oxides and nitrides of titanium. The carbon may be added as a part of the charge, or may be absorbed from the carbon or graphite crucible, in which the charge is heated. I have found that it is not necessary to use pure iron in the charge, but that steel scrap may be used provided the steel does not contain ingredients which react with the titanium, the iron, or the carbon, to form insoluble compounds.

One example of the successful use of my process is as follows: A charge was made up consisting of titanium dioxide, steel scrap and carbon, in the following percentages by weight:

	Per cent
TiO ₂	64.5
Steel scrap (Fe, 99.25%; C, 0.45%; Mn, 0.30%) ..	24.5
C	11.0

This charge was packed in a graphite crucible, the TiO₂ being placed in the bottom of the crucible, the steel scrap above it, and the carbon being placed in a layer on top of the steel scrap. The charge so packed in the graphite crucible was heated for five hours, the maximum temperature exceeding 2800° C. and being less than 3000° C. The application of the heat to the charge and crucible was gradual, four hours being consumed in raising the temperature of the charge to 2800° C., and the heating being continued thereafter at a temperature of 2800° C. and higher. This gradual application of heat is desirable to control the ebullition resulting from the escape of gases formed by the reduction of TiO₂ to Ti. When the heating had been finished, the mass was allowed to cool gradually and naturally to a temperature at which it could be handled.

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After cooling, the button or regulus was removed from the crucible, for instance, by breaking the graphite crucible which surrounds it, and this regulus was then crushed, in any suitable apparatus, sufficiently so that all particles passed through a 10-mesh screen. These particles were then leached with hydrochloric acid (commercial muriatic acid was found satisfactory) until the ebullition of gas due to dissolving iron ceased. The leaching with hydrochloric acid was repeated, the particles were washed with water and the acid and water decanted therefrom, after each acid treatment and this acid leaching was repeated and continued until there was no indication that any more iron was being dissolved. The particles were then ground, under water, in a ball mill, with steel balls, and hydrochloric acid treatment and washing was repeated. This ball milling and acid treatment was repeated and continued, until all particles passed a 100-mesh screen and there was no indication that any more iron was being dissolved therefrom.

The residue from this acid treatment should consist entirely of particles of TiC with the possible presence of some free carbon. Much of the free carbon would be floated away and decanted, in the course of the acid treatments and washings incident thereto, but, after the acid treatment had been finished, additional free carbon was removed by panning with water and floating off the free carbon. Such treatment may be carried out also on one of the usual forms of flotation tables. This treatment was repeated until free carbon was substantially eliminated, leaving nothing but particles of titanium carbide. Finally, the residue was washed with hydrofluoric acid, followed by several washings with water, and was then dried and ready for use.

In carrying out this process as described above, I have obtained a recovery of TiC amounting to 32.25% of the weight of the initial charge, that is to say, the weight of the TiC recovered was half the weight of the TiO₂ contained in the charge. Stated in another way, 65% of the titanium contained in the initial charge formed TiC and was recovered as such.

The titanium carbide produced by the process described above is of a grayish color, has a brilliant metallic luster and appears to be composed of many crystals or crystallites, which are highly reflecting. The material is distinctively different in appearance from the amorphous material, which was the product of the process heretofore known for making titanium carbide.

Theoretically, titanium carbide (TiC), consisting as it does of one atom of titanium and one atom of carbon, should have a carbon content of 20.05%. I have found that the carbon content of the material, produced by the process described above, may vary from a minimum of 19.50% to a maximum of 20.05%. The carbon content of this material, determined by analysis, thus approximates rather closely the theoretical carbon content of TiC. This variation in carbon content may be explainable on the theory that TiC is one of those chemical compounds having what is known as a defect lattice, which means, in this instance, that the compound may exist with some of the carbon atoms missing from the lattice. This would explain the production of material having the characteristics of titanium carbide, but having less than the theoretical carbon content.

X-ray diffraction examination of the substance produced by the process described above shows

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the pattern that is characteristic of TiC. This compound has a lattice of the NaCl type and I have determined, from the records of the X-ray diffraction examination of this product, that it has a lattice parameter of 4.32 Angstrom units. The theoretical density may be calculated from the following formula:

$$\frac{A(B+C)D \times 10^{-24}}{(E \times 10^{-8})^3}$$

wherein A is the number of molecules in the unit cell, B is the atomic weight of titanium, C is the atomic weight of carbon, D is the weight of one atom of a hypothetical element having the atomic weight of unity, and E is the observed distance between the titanium atoms in the lattice. Using, in the above formula, the revised atomic weights for Ti and C of 47.9 and 12.01, respectively, and taking the value of A as 4, the value of D as 1.65, the value of E as 4.32, the calculation gives, as the theoretical density of TiC, 4.90. The density of the material produced by the process described above, as determined by pyknometric methods, approximates very closely the theoretical density of 4.90, as determined from the lattice parameter. This establishes that the product of this new process is true TiC, in substantially pure form.

Titanium may be present in the charge as titanium metal or as titanium dioxide (TiO₂). When it is present as an oxide, the heating in the presence of carbon reduces the oxide to titanium metal. The iron does not need to be present in the charge as pure iron. It may be introduced into the charge as cast iron or steel scrap, provided the scrap does not contain any ingredient that would combine with the other ingredients of the charge to form alloys or compounds insoluble under the acid treatment. Thus, I have found that the process operates successfully using steel scrap containing 0.45 C and 0.30 Mn. Certain ingredients in the steel scrap might be objectionable. For instance, a steel scrap which included considerable tungsten would be objectionable because the iron and tungsten might form insoluble alloys or compounds that could not be separated from the titanium carbide. It is not necessary to add all of the carbon as one of the constituents of the charge, when the charge is heated in a graphite crucible because some, at least, of the carbon, necessary to oxidize the TiO₂ and to form TiC, will be absorbed from the crucible. However, best results are obtained when the necessary carbon is added as one of the constituents of the charge.

The proportions of titanium, iron and carbon contained in the charge may vary within rather wide limits. For instance, the amount of titanium in the charge may vary from 40% of the weight of iron in the charge, to 200% of the weight of iron. I have found that the process works most efficiently, and that the best recoveries are obtained, when the weight of titanium in the charge amounts to 160% of the weight of iron therein. The charge should contain sufficient carbon to convert all of the titanium in the charge into TiC. In other words, the carbon in the charge should weigh at least 25% of the weight of the titanium in the charge, and at least 15% of the weight of TiO₂ in the charge.

As stated above, the charge should be heated to a temperature between 2800° C. and 3050° C. and should be maintained, for a considerable

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period, at a temperature of 2800° C. or above, to give time for the completion of the reaction. When TiO₂ is used as a constituent of the charge, it is desirable to raise the temperature to 2800° C. very gradually, so as to give time for the complete reduction of the TiO₂ and to permit the escape of the gases caused thereby.

It is important to continue the acid treatment and washing of the particles of the broken-up regulus, until all iron has been dissolved out and removed therefrom and, in fact, until the residue consists only of TiC and free carbon. Thereafter, the washing and decantation of the particles to remove free carbon, or the treatment of these particles on a flotation table, if such is used, should be repeated and continued until substantially all free carbon is eliminated, so that the residue is nothing but pure TiC. The separation of the TiC from the other materials contained in the regulus, is a matter of considerable importance because the presence of free carbon and traces of iron in the titanium carbide is a source of weakness in compositions made by sintering the titanium carbide with an auxiliary metal such as cobalt.

It is believed that one source of weakness, in cemented compositions made from the titanium carbide produced by processes heretofore known, has been the presence of titanium oxides and nitrides in such material. Titanium metal, especially when heated, reacts very readily with the oxygen and nitrogen of the air to form such oxides and nitrides and, hence, in the prior processes, it is impossible to avoid formation of titanium oxides and nitrides, which contaminate the titanium carbide material. According to my novel process herein described, the titanium atoms react with the carbon atoms to form TiC, in the menstruum of molten iron, so that the oxygen and nitrogen of the air cannot get at the titanium to form oxides and nitrides, and the acid treatment and washing eliminates all titanium and iron, leaving only the pure TiC.

The fact is that the product of the process herein described is noticeably different in characteristics from the titanium carbide made by prior processes and, when the product of my process is sintered with an auxiliary metal, such as cobalt, to form a cemented hard carbide composition, such composition has a combined strength and hardness that is superior to like compositions made from the product of the prior processes.

I am aware that my process is susceptible of considerable variation without departing from the spirit of my invention and, therefore, I claim my invention broadly, as indicated by the scope of the appended claims.

Having thus described my invention, what I claim as new and useful, and desire to secure by Letters Patent, is:

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1. The process for making titanium carbide including the steps of dissolving titanium and carbon in molten iron, the ratio by weight of titanium to iron being not less than 2 to 5, maintaining the molten mass for at least one hour at a temperature above at least about 2800° C. until the titanium has reacted with the carbon to form titanium carbide, cooling the molten mass to solidify it, treating the cooled material with a solvent and washing to dissolve and remove all ingredients thereof other than titanium carbide and free carbon, separating and removing the free carbon from the titanium carbide, and drying the residue.

2. The process of making titanium carbide comprising the heating to a temperature between 2800° C. and 3050° C. of a charge of titanium dioxide, iron and carbon, until the titanium has reacted with the carbon to form titanium carbide, the weight of titanium dioxide in the charge amounting to at least two-thirds of the weight of the iron therein, cooling the mass to solidify it, treating the cooled material with acid and washing to dissolve and remove therefrom all ingredients other than titanium carbide and free carbon, separating and removing the free carbon from the titanium carbide, and drying the residue.

3. The process of claim 2 in which the weight of titanium dioxide in the charge does not exceed three and one-third times the weight of the iron in the charge.

4. The process of claim 3 in which the temperature of the charge is gradually raised to about 2800° C. and maintained for a substantial period at a temperature between 2800° C. and 3050° C.

5. The process of claim 4 in which the temperature of the charge is raised to 2800° C. during a period of four hours and maintained at from 2800° C. to 3050° C. during one hour.

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