CHEMISTRY,
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PROCESS OF PREPARING TUNGSTEN TITANIUM CARBIDE

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6 Claims. (Cl. 23—14)

This invention relates to a process of forming a carbide of tungsten and titanium, and more particularly to a process for forming a carbide corresponding substantially to the chemical formula $WTiC_2$.

The principal object of the invention is the production of a carbide containing tungsten and titanium which will be extremely hard and of great value and utility as a material for use, in accordance with the usual principles of powder metallurgy, in the production of hard compositions of matter, in order to effect therein great hardness combined with great strength, together with a low thermal conductivity, and other characteristics, which will enable the hard compositions of matter made from such carbide material to have great utility and durability when used as the cutting points in the cutting of metal at high speeds, when used as dies, and when used to provide corrosion-resisting surfaces, and for other similar uses.

A further object of the invention is the production of such a carbide, containing tungsten, which, when used in the production of hard compositions of matter, in accordance with the usual principles of powder metallurgy, and with a binder material containing powdered tungsten or molybdenum, or carburized tungsten or molybdenum, or other compounds of tungsten or molybdenum, with or without nickel or cobalt, will yield none of its carbon content to any of the metals so used as a binder in such hard compositions of matter.

A still further object of the invention is the production of such a carbide which, when used as an ingredient in such a hard composition of matter, renders it possible to include in such hard composition of matter a higher percentage of metallic tungsten as a binder than has been practicable heretofore, whereby the toughness and breaking strength of such composition of matter can be increased without a material decrease of the hardness and cutting ability of such composition of matter.

Further objects of the invention, together with details of the steps by which the invention is put into practice, will be apparent from the following specification.

The new carbide substance which I have invented, and obtained by the process herein described, is apparently a double carbide of tungsten and titanium corresponding to the chemical formula $WTiC_2$, and containing substantially 71.9% W, 18.7% Ti, and 9.4% C, and it has been invariably obtained by following the process herein described, regardless of wide variations in the amount and proportions of the tungsten and titanium content, the excess of tungsten or titanium remaining uncombined, so as to be readily separable therefrom, along with the other resulting substances.

The new carbide substance is prepared by heating tungsten, or a substance containing tungsten such as tungsten oxide, or alloys of tungsten, with titanium, or a substance containing titanium, such as titanium oxide, in the presence of carbon, in a menstruum metal, for which purpose nickel has been found to be preferable, the substance being then separated by chemical and mechanical means from the resulting mass. I have, likewise, prepared such carbide substance repeatedly by employing as a menstruum metal cobalt, or a mixture of nickel and cobalt, and it is possible that menstruum metals other than nickel and cobalt may be used. However, because of the low cost and the ease of its removal, I consider the use of nickel to be preferable from a commercial standpoint. The amount of menstruum metal or metals, may vary widely, from an effective amount up to an amount considerably in excess of the tungsten content, and I have found that the use of nickel or cobalt in an amount approximately equal to the amount of tungsten gives the best results from a commercial standpoint. If only a small amount of menstruum metal is used, it must function by solution of a little of the tungsten and titanium at a time, such dissolved metals apparently combining in solution to form the carbide, thus freeing the menstruum metal so that it is available to dissolve a further quantity of the tungsten and titanium. As will be apparent, the time necessary to complete the reaction under such circumstances is unduly prolonged.

As stated above, the present application is directed to the process by which this new carbide substance is formed, and the new carbide substance, that is, the product so produced, is described and claimed in my co-pending application, Serial No. 179,551, filed of even date herewith, to which reference is hereby made.

I have likewise invented certain new and useful improvements in hard compositions of matter containing this new carbide substance as an ingredient, described and claimed in my copending application, Serial No. 179,553, filed of even date herewith, and in a process for making such hard compositions of matter, described and claimed in my copending application, Serial No.

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179,554, also filed of even date herewith, to both of which applications reference is hereby made.

In carrying out the process of forming this new carbide substance, the tungsten, titanium and menstruum metal ingredients are heated, preferably in a graphite crucible, for a period of about five hours, at a temperature above 1600° C., and preferably approximately 2100° C. I have used slugs of tungsten metal, with bars of commercial nickel melting stock, with titanium oxide, and graphite chips, all placed together in a graphite crucible. I have also incorporated the tungsten in the form of WO_3 in such melts, with equally good results.

I have found it advisable to mix with the other materials chips or turnings of graphite, in an amount constituting about 5% of the tungsten and titanium materials combined. The mass resulting from the heating process, after cooling, is crushed, treated with water solutions of hydrochloric acid and a small amount of nitric acid, at boiling temperatures, or with similar oxidizing acid solutions such as hydrochloric acid to which potassium perchlorate has been added, treated with ammonia or other hydroxide solutions to remove WO_3, again treated with aqua regia, or other oxidizing acid solutions, to dissolve the Ni, and again treated with hydroxide solutions to dissolve any remaining WO_3. At various stages, during such treatments, the powdered material is subjected to mechanical concentration, as by "panning" or gravity concentration, as on a Wilfley table, to remove loose graphite and particles of light impurities. The particles remaining after such chemical separation of other compounds, are grey particles having a metallic lustre. These particles are further treated, preferably in platinum dishes, with strong solutions of hydrofluoric acid, at a temperature up to its boiling point, to dissolve suboxides or blue oxides of tungsten, such as WO_2, and any other impurities. The hydrofluoric acid solution is removed by repeated washing and decantation, and the remaining particles are carefully "panned" or otherwise concentrated, as by gravity methods, and dried, the remaining particles being grey in color, with high metallic lustre, having surfaces which are predominantly conchoidal, and of a size averaging greater than .01mm. in largest cross-section dimensions.

As a specific example of the process followed in the formation of such new carbide substance, and the characteristics, as shown by test, of the product obtained thereby, the following procedure was followed in one instance:

There was placed in a crucible, 6'' in diameter of substantially pure graphite:—

	Grams
Tungsten rods	1840
Powdered TiO_2	800
Ni melting stock	2800

The graphite crucible, with such contents therein, was placed in an electric induction furnace and heated, during a period of approximately an hour, to a temperature of 2100° C., and maintained at such temperature for a period of eight hours. After cooling, the product of such heating process was removed by breaking away the graphite crucible, and the mass was crushed by hammer and by a jaw crusher, together with coarse ball milling, until the particles thereof would pass a 40-mesh screen. The particles were repeatedly treated with water mixtures of hydrochloric acid to which a small amount of nitric acid had been added, the acid mixture being repeatedly boiled. After such acid treatments, the particles were treated with ammonia solutions, to remove any WO_3, and were again treated with aqua regia to dissolve nickel and nickel alloys and other impurities, and finally were again treated with ammonia solutions. At various stages during such acid and hydroxide treatments, the particles were subjected to mechanical concentration by "panning" and were also concentrated by gravity methods on a Wilfley table to remove loose graphite and other light impurities, leaving only grey particles, obviously having a metallic lustre. The particles were further treated, in platinum dishes, with strong solutions of hydrofluoric acid, at a temperature up to the boiling point, to dissolve suboxides of tungsten such as WO_2. The hydrofluoric acid solution was removed by washing with water, and repeated decantation with fresh water and the particles were again carefully "panned" and concentrated by gravity methods. From the above-mentioned mixture of materials, 1030 grams of such particles were obtained.

A carbon analysis was made of samples from such particles, and showed a carbon content of 9.40% C, which is quite close to the carbon content of 9.39% C which theoretically should be present according to the formula $WTiC_2$. This discrepancy of the carbon content found is within the error of analysis of the carbon content of materials of this type. A test of the tungsten and titanium content of such particles showed that they contained 71.86% W and 18.75% Ti, corresponding exactly with the content that theoretically would be present in $WTiC_2$. Such particles were found to have a specific gravity of 9.72, which is much lower than would be indicated theoretically for a mixture of WC and TiC in the proportions of the metallic contents found by tests. Inasmuch as the specific gravity of WC is 15.64 and that of TiC is 5.0055, the calculated specific gravity, on the assumption that this product is a mixture of WC and TiC, would be 10.29. The melting point of the product was found to be higher than that of WC ($2867\pm50°$ C.) and may be higher than that of TiC ($3146\pm50°$ C.). If the substance were a solid solution of TiC in WC, that is, a eutectic, one would expect the melting point to be lower than that of WC. Particles of the new carbide substance were treated with a standardized solution of hydrofluoric acid containing one drop of nitric acid and were found to dissolve in two hours, whereas an equivalent amount of a mixture of WC and TiC was dissolved in the same solution in less than two minutes.

In order to test further the new carbide substance $WTiC_2$, as compared with a mixture of WC and TiC having the same ultimate metallic content, pairs of test pieces of hard compositions of matter were formed, as described in my copending application, Serial No. 179,554, and using the same amount of the same binding materials, and following exactly the same process, except that one contained $WTiC_2$ and the other contained an equivalent amount of a mixture of WC and TiC. A number of such pairs of test pieces were made, using different binding materials, and with different proportions of carbide material and of binding material. In every case the hard compositions containing the new carbide substance $WTiC_2$ were found to exhibit a characteristically lower thermal conductivity than those made with mixtures of WC and TiC, showed greater strength and hardness, and likewise showed on repeated

tests, in which such new hard compositions of matter were used as a metal-cutting tool point in machining steels and copper-silicon cast iron, much greater resistance to "cratering" and resistance to erosion and wear from chips of both steel and cast iron, the compositions containing $WTiC_2$ lasting from four to five times as long as did the compositions containing mixtures of WC and TiC, when used under identical conditions in the same machine, and cutting the same material at the same rate of speed.

The new carbide substance has been manufactured on a commercial basis in large quantities, and has been unvarying in its physical characteristics and in its chemical analysis, being always produced in the expected quantity, as particles of a rather uniform size, with high metallic lustre, and with the surfaces of the particles predominantly conchoidal as seen under a high-power microscope.

I believe that the hard carbide substance, made by the process described, is a new chemical compound corresponding chemically to the formula $WTiC_2$. My reasons for such belief are (1) the unvarying composition of the substance produced as described and always corresponding to the formula $WTiC_2$ by analysis, even when the quantities of the ingredients of the mixture initially heated are widely varied to include a large excess of W or of Ti; (2) its chemically different behavior when treated with aqua regia, as compared with WC and TiC, as well as its chemically different behavior when treated with hydrofluoric acid containing a small amount of nitric acid; (3) its producing, when formed into a hard composition of matter in a binder of nickel or cobalt or other binder material, a composition which lasts from four to five times as long as a similar hard composition of matter made in identically the same way but with a mixture of WC and TiC, and having the same ultimate chemical analysis; (4) the characteristically lower thermal conductivity of hard compositions of matter containing it; (5) its lower density, as compared with that of a mixture of WC and TiC having the same ultimate analysis; (6) its melting point, which is higher than that of WC or a eutectic.

As stated above, the process herein described invariably produces a carbide material containing the same proportions, in spite of repeated efforts to form other tungsten titanium carbides by incorporating in the mixture an excess of tungsten or titanium. While nickel is preferably used as the menstruum metal, it will be understood that changes may be made in the menstruum metal used, in the amount of menstruum metal used, in the temperature used, especially if the length of the heating period is correspondingly altered, and in the reagents used to separate the impurities, that is, in both the oxidizing acid solutions and the hydroxide solutions, as well as in the means used for effecting mechanical separation of impurities, without departing from the spirit of the invention which is defined in the following claims:

What I claim is:

1. The process of producing a compound containing tungsten and titanium in monatomic ratio combined with one atom of carbon for each atom of metal, which comprises reacting such metals with carbon in a molten metallic menstruum selected from the group consisting of nickel and cobalt.

2. The process of producing a new chemical compound corresponding to the formula $WTiC_2$, which comprises reacting tungsten and titanium with carbon in a molten menstruum of one or more metals selected from the group consisting of nickel and cobalt, and separating the compound from the resultant mass.

3. The process of producing a new chemical compound corresponding to the formula $WTiC_2$, which comprises heating tungsten and titanium in the presence of carbon and in a molten metallic menstruum selected from the group consisting of nickel and cobalt at a temperature above 1600° C., and separating said compound from the resultant mass.

4. The process of producing a carbide containing tungsten and titanium in monatomic ratio, which comprises heating tungsten and titanium in the presence of carbon in a molten metallic menstruum selected from the group consisting of nickel and cobalt at a temperature above 1600° C., and treating the resultant mass with an oxidizing acid solution and with a hydroxide solution, separately, to separate the remainder of the mass from said carbide.

5. The process of producing a carbide containing tungsten and titanium in monatomic ratio, which comprises heating tungsten and titanium in the presence of carbon in a menstruum of molten nickel, and separating said carbide from the resulting mass.

6. The process of producing a carbide containing tungsten and titanium in monatomic ratio, which comprises heating tungsten and titanium in the presence of carbon in a menstruum of molten nickel at a temperature of approximately 2100° C., and separating said carbide from the resulting mass.

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