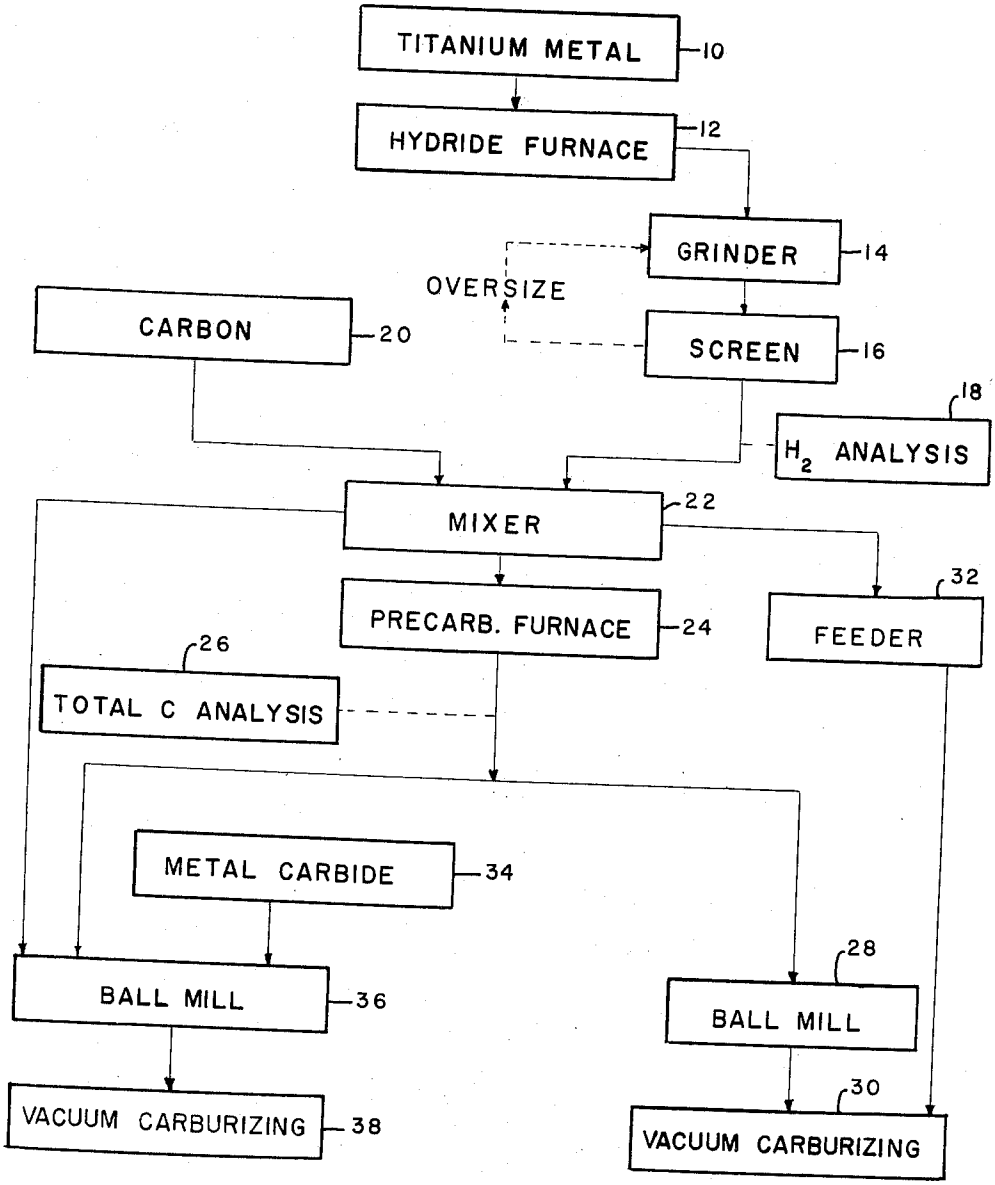
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PRODUCTION OF REFRACTORY METAL CARBIDES

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PRODUCTION OF REFRACTORY METAL CARBIDES

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This invention relates to improvements in the production of metal carbides and in particular to improvements in the production of titanium carbide.

Heretofore, titanium carbide has been produced commercially by reacting the raw material, titanium dioxide, with carbon to produce titanium carbide. This reaction usually took place under hydrogen at atmospheric pressure and resulted in an impure titanium carbide having an oxygent content seldom below one percent. Since the oxygen content of the titanium carbide, produced by the above method, was the source of considerable difficulty, especially in the lowering of the transverse rupture strength to a marked degree, the trend has been to try to produce titanium carbide substantially free from oxygen. In order to achieve this end, the industry has resorted to vacuum carburizing in an effort to reduce the oxygen content of the resulting carbide. While vacuum carburizing showed some improvement, still the resultant titanium carbide usually possessed oxygen in amounts greater than one half percent.

While investigators have agreed that the prior art overall reduction of titanium dioxide with carbon takes place in two steps, the intermediate product being titanium monoxide, the reaction never goes to completion. Since the intermediate product of the reaction is titanium monoxide, and titanium carbide and titanium monoxide are isomorphous in crystallographic structure, a large range of solid solubility exists between them so that carburization under vacuum precludes the probability of obtaining titanium carbide having less than one half percent oxygen.

An object of this invention is to provide a method of producing titanium carbide containing less than 0.35% of retained oxygen.

Another object of this invention is to provide a method of producing titanium carbide using titanium metal as the starting material.

A more specific object of this invention is to provide a method of producing titanium carbide whereby titanium metal is rendered friable, reduced to a fine particle size without pyrophoric hazard and reacted with carbon, said titanium carbide having less than 0.35% residual oxygen.

A further object of this invention is to provide a process for producing a binary carbide of titanium carbide and a refractory carbide wherein titanium metal is reacted with carbon and a refractory carbide to produce a binary carbide having very little residual oxygen.

These and other objects will become apparent when read in conjunction with the accompanying drawing, the single figure of which is a schematic flow chart illustrating steps embodying features of the invention.

This invention, in broad terms, comprises reacting titanium metal with hydrogen to form a stable, friable, titanium hydride, crushing the titanium hydride to obtain a predetermined particle size, screening the crushed titanium hydride to remove the oversized particles, mixing a predetermined mass of carbon with the titanium hydride and vacuum carburizing whereby the titanium hydride is converted to titanium carbide having very little residual oxygen.

Referring to the flow chart illustrated in the drawing, reference may be had to the different steps of the process. In practice, titanium metal **10** in the form of solid metal or in the form of sponge is employed as the starting material. The titanium metal available in such forms is substantially free from oxygen. The titanium metal **10** is hydrided in a suitable furnace represented at **12** by heating to a temperature preferably between 325° C. to 350° C. for about four hours. During the heating and holding at temperature, dry hydrogen gas is passed into the furnace. The hydrogen gas, flowing over the heated titanium metal, unites with the titanium metal to form titanium hydride having the general formula TiH_x, where x is about 0.5. The titanium hydride thus produced contains about 2% hydrogen by weight which renders the titanium very friable.

When cooled, the titanium hydride is comminuted as at **14** by means of grinding, ball milling or any other suitable means to reduce it to a desired particle size of about 100 mesh or finer. Since finely divided titanium is quite pyrophoric, it is desirous to conduct the comminution under a protective atmosphere, as for example, argon, helium, or other non-inflammable, non-contaminating gaseous atmospheres to reduce fire hazard. While titanium hydride is more stable than titanium metal itself, it is preferred to use the protective atmosphere to insure the prevention of fire.

The comminuting of the titanium hydride produces a variety of particle sizes of the titanium hydride. Since it has been found that optimum results can be obtained by using material of a select particle size, the comminuted titanium hydride is screened as at **16** through a 100 mesh screen. The oversized titanium hydride may be recirculated through the comminutor **14** while the material of predetermined size, i. e. less than 100 mesh, is employed in practicing the process of this invention.

In order to determine the mass of carbon to be added from a suitable supply **20** to the titanium hydride to produce titanium carbide, a sample of the undersized titanium hydride is analyzed as at **18** to determine the hydrogen content of the titanium hydride. This may be accomplished by heating the sample in vacuum at a temperature in excess of 900° C where the hydrogen is evolved. The weight loss of the sample is computed, and upon this basis, the amount carbon to be added to the titanium hydride can be determined, it being found that carbon should be added in an amout of about 19.5% of the weight of titanium metal content of the titanium hydride. While the theoretical percentage of carbon, which can combine with titanium metal to produce titanium carbide, is slightly greater than 20%, it has now been found that a carbon content of about 19.5% yields the optimum results since it minimizes the amount of un-reacted free carbon remaining in the end product, titanium carbide. Thus, a predetermined amount of carbon, depending upon the titanium content of the hydride, is added to the titanium hydride of the predetermined particle size and the two ingredients are thoroughly mixed in a suitable mixer **22**. The carbon may be in different forms, but a preferred form is as finely divided lampblack. The mixer **22** may be of any suitable type and functions to blend the predetermined quantities of titanium hydride and carbon so that there is intimate contact between all of the titanium hydride and the carbon, thus fostering a more uniform final product of reaction, that is, titanium carbide which is to be produced therefrom. After the ingredients are thoroughly mixed, they are further processed in a number of alternative manners to be more fully described hereinafter.

Because of the rapidity of the titanium-carbon reaction

in vacuo, which reaction is highly exothermic and explosive in nature, coupled with the difficulties presented by the evolution of large volumes of hydrogen gas from the dissociation of titanium hydride above 450° C., it may be desirable to employ a precarburizing step in the process as indicated at **24**. The precarburizing treatment may be carried out by heating the mixture of carbon and titanium hydride in an inclined rotary furnace (not shown) which is heated by induction. A protective atmosphere of pure hydrogen is generated by the rapid evolution of hydrogen from the titanium hydride at temperatures in excess of 850° C. The precarburizing step is preferably carried out at a temperature in the range between 850° C. and 1300° C. The resultant product will have a very low hydrogen content and in addition, the material will be carburized, thereby eliminating the violence of the titanium-carbon reaction, to be more fully described. This step may also tend to partially agglomerate the particles.

In order to insure a more positive control over the ultimate product, the precarburized material may be analyzed as at **26** to determine the total carbon content of the mass. Since, with most of the hydrogen removed, the total carbon content may vary slightly from the preferred amount of about 19.5%, additions of either carbon or titanium hydride may then be made to adjust the composition for optimum results. After the additions, if any, of carbon or titanium hydride have been made, the material is further processed as will be more fully described hereinafter.

If substantially pure titanium carbide is to be the end product, the precarburized materials, after being adjusted for carbon content, are placed in a closed ball mill represented at **28** for homogenization. In this step, any agglomeration of the particles from the precarburization treatment is broken. In addition, a thorough blending of any additions which have been made for carbon adjustment after the precarburizing treatment is also accomplished.

The homogenized ingredients are removed from the ball mill **28** and placed in a suitable vacuum furnace to complete the carburizing as represented at **30**. Since the temperature of the precarburizing treatment as at **24** is not high enough nor is the pressure low enough to expel substantially all of the gases, oxygen, hydrogen and nitrogen, it is desirable to subject the homogenized ingredients to a vacuum treatment. The vacuum treatment serves a two-fold purpose for in addition for effecting the removal of any of the remaining gaseous elements, it also permits the completion of the reaction of any unreacted ingredients remaining from the precarburization treatment **24**. By thus converting any of the unreacted ingredients, the end product, titanium carbide, is more uniform and contains a minimum amount of free carbon as was referred to hereinbefore. The vacuum treatment is usually a batch operation wherein the ingredients are placed in the furnace and heated to a temperature in the range between 1800° C. and 2000° C. The furnace is supplied with a vacuum supplying means (not shown) so that a vacuum in the range between 1 and 100 microns may be maintained throughout the vacuum treatment. Since some of the hydrogen remains with the titanium after the precarburizing treatment, as well as oxygen and nitrogen which was present in the starting material, the vacuum is desired so that the gaseous products may be removed during this treatment thereby insuring optimum results.

Since titanium metal is the starting material in the process, the oxygen content of the resultant product, titanium carbide, is extremely low in contradistinction to titanium carbide produced by either the conventional titanium dioxide or the vacuum carburized titanium dioxide processes of the prior art. Titanium carbide produced by the process of this invention has consistently assayed less than 0.05% oxygen. While lattice parameter measurements have shown values of about 4.3275 A. and the extrapolated value of pure titanium carbide is placed at 4.330 A., it is apparent that the titanium carbide produced by the process of this invention is of unique purity. This is further substantiated by fluorescent analysis which reveals the absence of cations. The titanium carbide, thus produced, is suitable for use in the production of cemented carbides utilizing titanium carbide and a binder metal, or titanium carbide in addition to other refractory metal carbides with binder metals.

In another embodiment of this invention, the same results, that is, extremely pure titanium carbide, can be achieved by a slight variation in the overall process previously described. Referring again to the flow chart, the titanium metal **10** is hydrided as at **12**, comminuted as as **14**, screened as at **16**, and mixed as at **22** with the predetermined mass of carbon from the supply **20** as was hereinbefore described. After thorough mixing as at **22**, the step of precarburizing the ingredients as at **24** is omitted, and instead, the ingredients are placed in a "feeder" represented at **32** of any suitable type, for example, vibratory, mechanical, etc. which is connected to the vacuum carburizing furnace **30**. The feeder **32** is operated at a predetermined rate, thereby metering the ingredients into the furnace for the vacuum carburizing treatment at **30** at a rate depending upon the size of the furnace; for example, it has been found that a vacuum furnace capable of accommodating a 100 pound charge has been satisfactorily fed at a rate of between 10 to 20 pounds per hour. If the capacity of the furnace is larger, the feed rate may be accordingly increased and vice versa. The metering of the ingredients is an essential feature of this alternative process since, as was stated hereinabove, the titanium-carbon reaction is highly exothermic and takes place with explosive violence at about 900° C. However, if the ingredients are metered into the furnace **30** at a predetermined rate, as described in this alternative process, the reaction will take place continuously on a small mass at any one instant thereby controlling the violence of the exposive reaction. Thus, the ingredients are fed into the furnace which is heated to a temperature in the range between 1100° C. and 1300° C. without danger of violence from the explosive reaction. The furnace is also provided with an atmosphere of argon or hydrogen, usually at atmospheric pressure, before the titanium hydride and carbon are metered therein. The hydrogen from the titanium hydride is thus evolved in proportion to the rate of feed of the ingredients from the feeder **32**. At the same time, the reaction between titanium and carbon occurs so that when all of the ingredients are in the vacuum furnace **30**, the reaction of the titanium hydride and carbon has been completed and the titanium carbide is formed. Upon completion of the reaction, a vacuum in the range between 1 and 100 microns is applied and maintained within the furnace **30** and the temperature is raised to between 1800° C. and 2000° C. during the vacuum treatment.

In another embodiment of this invention, a binary carbide consisting of binary crystals of titanium carbide and a metal carbide selected from the group consisting of tungsten, columbium, tantalum, and vanadium carbides is produced. In this particular embodiment the titanium metal **10** is hydrided as at **12**, comminuted as at **14**, screened as at **16**, mixed as at **22** with carbon from the supply **20** and precarburized as at **24** as was hereinbefore described with reference to the previous embodiments and illustrated in the accompanying flow chart. After the total carbon analysis has been checked as at **26** and adjustments have been made by the addition of either titanium hydride or carbon to the mass, a predetermined mass of metal carbide, for example, tungsten carbide, is added from a supply **34** to the precarburized materials and all of the ingredients are placed in a closed ball mill **36** and milled until uniformly blended.

After the ingredients are substantially homogenized, they are placed in a suitable vacuum furnace **38** and heated to a temperature in the range between 1800° and

2000° C. A vacuum of about 1 to 100 microns is applied to the furnace **38** and maintained throughout the thermal cycle of the vacuum carburizing treatment. The binary carbide thus formed may be further processed in any suitable manner similar to the pure titanium carbide as was referred to hereinbefore.

The above-described process for preparing a binary carbide may be modified as illustrated in the accompanying flow chart. Thus, the titanium metal **10** is hydrided as at **12**, comminuted as at **14**, screened as at **16**, and mixed as at **22** with the proper amount of carbon from the supply **20** as was previously described. After the ingredients are thoroughly mixed, they are then placed directly in the closed ball mill **36** with a predetermined mass of metal carbide from the supply **34**, for example, tungsten carbide, where they are milled until homogenized. The ingredients are then removed to the vacuum carburizing furnace **38** where they are slowly heated to a temperature in the range between 900° C. and 1100° C., the temperature range in which the titanium hydride and carbon is converted to titanium carbide. The furnace is supplied with pure hydrogen which is evolved from the dissociation of the titanium hydride. After carburization has been accomplished, the hydrogen atmosphere is removed and the furnace is supplied with a vacuum of about 1 to 100 microns after which the temperature is raised to a range between 1800° C. and 2000° C. for the vacuum.

It is to be noted that in the latter process described for the production of a binary carbide, the violence of the titanium-carbon reaction may be so minimized by the presence of the metal carbide addition to the mass that the step of vacuum carburizing can be accomplished without the use of a feeder **32** to meter the ingredients into the vacuum carburizing furnace **38**. However, to insure a more positive control over the reaction as well as over the ultimate product, the use of a feeder as was hereinbefore described, may be desirable.

There are several significant factors to be noted concerning this process and the products produced therefrom. Perhaps the foremost feature of this process is the purity of the titanium carbide component thus produced. Reference may be had to Table I comparing the purity of the product of the process of this invention as contrasted to the product produced by currently known conventional processes.

Table I

Process Type	Percent Oxygen	Lattice parameter, A
Conventional TiO_2	+2.0	4.305–4.310
Vacuum carburized TiO_2	+1.0	4.315
Hydride (this invention)	0.197	4.3275

The accepted extrapolated value of the lattice parameter of pure titanium carbide is placed at 4.330 A. When the oxygen content of titanium carbide decreases, the lattice parameter increases and since a fluorescent analysis shows the absence of cations, it is apparent that the titanium carbide thus produced by the process of this invention, as described hereinafter, is of unique purity.

Further, by hydriding the metal, the fine powder which is desirable for the optimum results may be produced in a more stable form (hydride) thus reducing the hazard of handling the material in the pyrophoric metal powder form. Moreover, by employing the metal hydride and later decomposing it, the hydrogen thus released being extremely pure nascent hydrogen, exerts a refining influence on the ingredients as a whole. Also, the charge from the precarburizing furnace has a minimum of gas or gas-evolving reactants so that comparatively large masses may be vacuum processed in one batch. No special technique or special equipment is needed. The overall process, with its various embodiments provides a very flexible operation in addition to a substantial economy in the end product.

I claim:

1. In the production of titanium carbide, the steps comprising, heating titanium metal in an atmosphere of hydrogen at a temperature between 325° C. and 350° C. to form titanium hydride, mechanically comminuting the titanium hydride, screening the comminuted titanium hydride to obtain a predetermined particle size of no greater than 100 mesh, adding a predetermined mass of carbon in the form of fine powder to the titanium hydride, mixing the titanium hydride and carbon to produce a substantially uniformly blended mixture, and vacuum carburizing the mixture at a temperature between 1800° C. and 2000° C.

2. In the production of titanium carbide, the steps comprising, reacting titanium metal with hydrogen at a temperature between 325° C. and 350° C. to form titanium hydride, mechanically comminuting the titanium hydride, screening the titanium hydride to obtain a predetermined particle size of less than 100 mesh, adding a predetermined mass of carbon in the form of fine powder to the titanium hydride of the predetermined particle size, mixing the titanium hydride and carbon to produce a substantially uniformly blended mixture, precarburizing the mixture at a temperature in the range between 850° C. to 1300° C. in an atmosphere of hydrogen, ball milling the precarburized mixture, and vacuum processing the precarburized mixture at a temperature in the range between 1800° C. and 2000° C. to convert the titanium hydride to titanium carbide containing less than 0.35% oxygen.

3. In the production of a binary carbide product, the steps comprising, reacting titanium metal with hydrogen at a temperature between 325° C. and 350° C. to form titanium hydride, mechanically comminuting the titanium hydride, screening the comminuted titanium hydride to obtain a predetermined particle size of no greater than 100 mesh, adding a predetermined mass of carbon to the titanium hydride of the predetermined particle size, mixing the titanium hydride and carbon to produce a substantially uniformly blended mixture, adding a predetermined quantity of metal carbide selected from the group consisting of tungsten carbide, vanadium carbide, columbium carbide and tantalum carbide to the mixture of titanium hydride and carbon, ball milling to substantially uniformly blend the metal carbide and mixture, and vacuum carburizing at a temperature of 1800° C. to 2000° C. to convert the titanium hydride of the mixture to titanium carbide having less than 0.35% oxygen and produce a binary carbide product composed of titanium carbide and the metal carbide selected from the group consisting of tungsten carbide, vanadium carbide, columbium carbide and tantalum carbide.

4. In the production of a binary carbide product, the steps comprising, reacting titanium metal with hydrogen at a temperature between 325° C. and 350° C. to form titanium hydride, mechanically comminuting the titanium hydride, screening the comminuted titanium hydride to obtain a predetermined particle size of no greater than 100 mesh, adding a predetermined mass of carbon to the titanium hydride of the predetermined particle size, mixing the titanium hydride and carbon to produce a substantially uniformly blended mixture, precarburizing the mixture of titanium hydride and carbon in a hydrogen atmosphere, adding a predetermined quantity of metal carbide selected from the group consisting of tungsten carbide, vanadium carbide, columbium carbide and tantalum carbide to the precarburized mixture, ball milling the precarburized mixture and metal carbide to substantially uniformly blend the same, and vacuum processing the ball milled material at a temperature of 1800° C. to 2000° C. to convert the ball milled material to a binary carbide product composed of titanium carbide and the metal carbide selected from the group consisting of tungsten carbide, vanadium carbide, columbium carbide and tantalum

carbide, said titanium carbide of the binary carbide product containing less than 0.35% oxygen.

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