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3,019,084

PRODUCTION OF REFRACTORY CARBIDES, BORIDES AND THE LIKE

Filed March 3, 1955

2 Sheets-Sheet 1

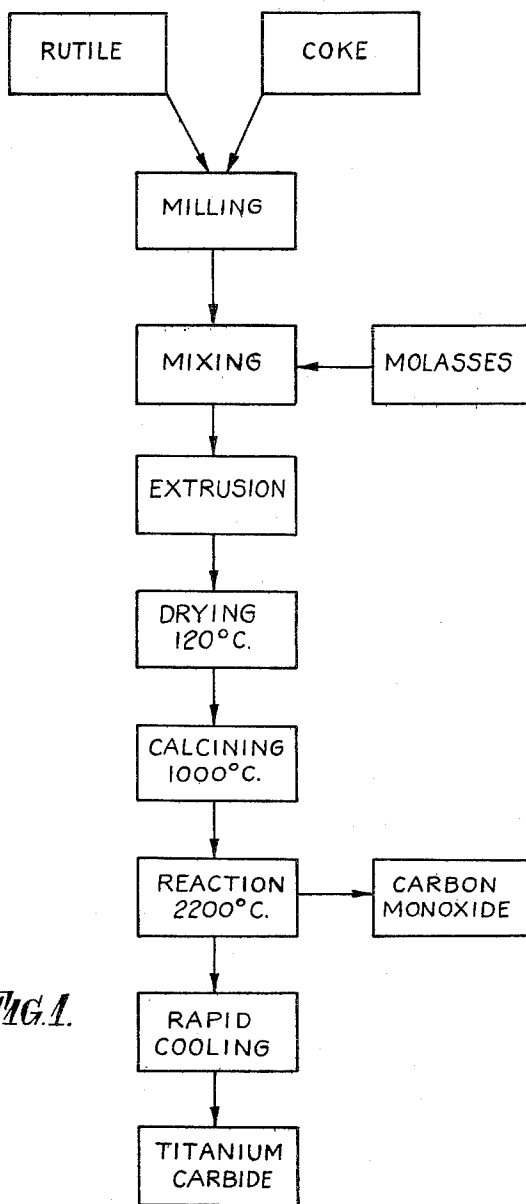


FIG. 1.

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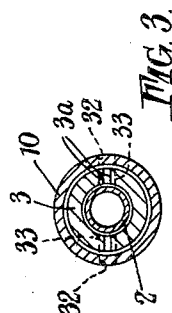
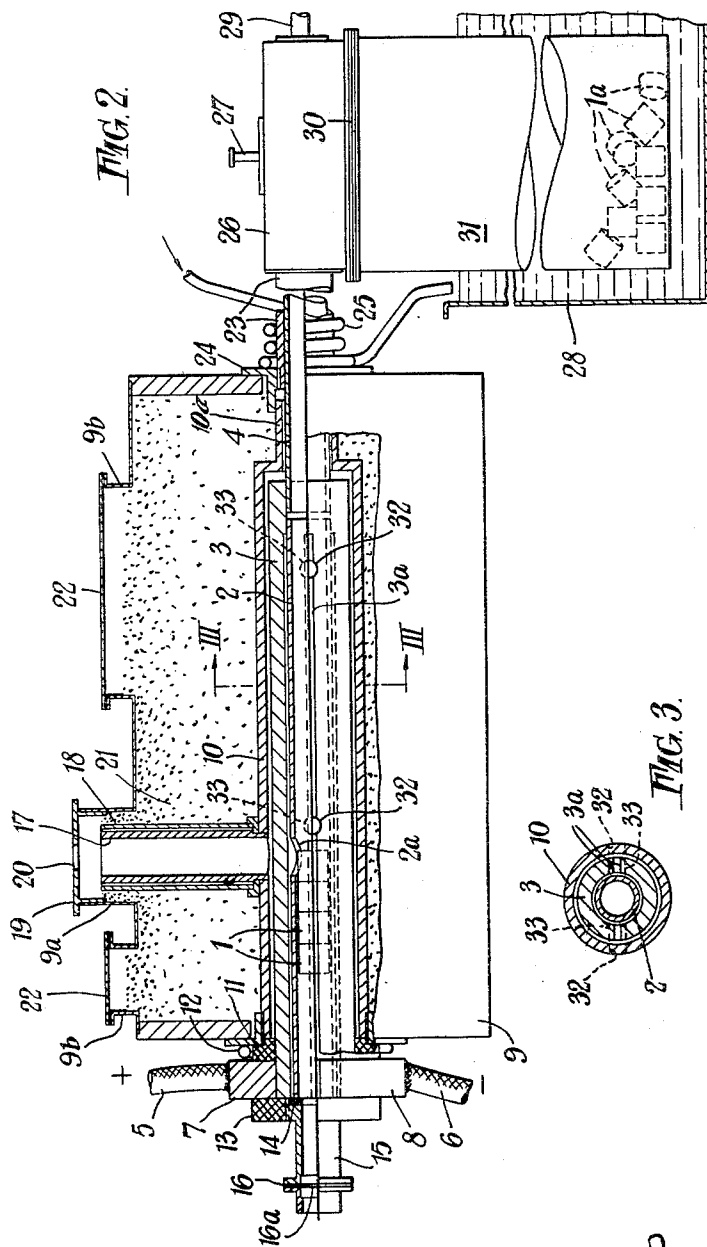
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2 Sheets-Sheet 2



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**PRODUCTION OF REFRACTORY CARBIDES,
BORIDES AND THE LIKE**

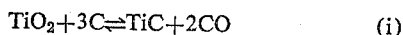
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Claims priority, application Great Britain Mar. 5, 1954
15 Claims. (Cl. 23—204)

This invention relates to the production of refractory carbides, borides, boro-carbides and mixtures of refractory borides and carbides (all being compounds of the transition elements, titanium, zirconium, niobium and tantalum) or of boron carbide itself. The most important of these refractory compounds, at the present day, is titanium carbide and the following description will be directed mainly to the features and details of this invention as they apply to the production of this compound, although it is to be understood that such features and details, with appropriate modification as hereinafter indicated, are also applicable to the production of the other compounds listed above and that the present invention is accordingly not restricted to the specific examples given below.

For economic reasons the reaction almost universally used for the production of titanium carbide on a commercial scale is the reduction of the dioxide TiO_2 with carbon, according to the equation:



The process is normally carried out at temperatures between 2000° and 3000° C. with the adoption of some precautions designed to avoid the occurrence of the back-reaction which would give rise to the presence of oxygen and free carbon in the product. For instance, the reaction has been carried out under reduced pressure or in a vacuum, or the reaction has been carried out in a container which was sealed after reaction was complete, or the reaction has been carried out in a protective atmosphere, such as hydrogen. In spite of these precautions, however, it is extremely difficult to obtain a commercial product containing more than about 92.5% of titanium carbide (i.e. about 18.55% combined carbon) or less than about 1% of free carbon.

The present invention has for its main object to provide an improved and economical process requiring only simple apparatus for its performance which, while utilising Reaction i, will yield a product containing less free carbon than is usual in current commercial products, and if desired, a higher titanium carbide content and lower nitrogen content. A low free carbon content is very desirable in almost every application of titanium carbide, e.g. in hard metals, in cermets, and as cathodes or current leads in electrolytic cells for the production of refining of aluminium.

According to this invention, a process for the production of titanium carbide according to Reaction i which involves heating the reaction mass to a selected temperature in the range 2000° to 3000° C., is characterized by the step of rapidly cooling the mass as soon as possible after it has reached equilibrium at the selected temperature.

It has been found that the reaction rates are such that this rapid cooling will virtually eliminate back-reaction.

Preferably, the process is operated as a continuous one, the reaction mass or charge being passed at an appropriate speed successively through a zone of high temperature (e.g. 2000°–2500° C.) and a zone of low temperature (e.g. a water-cooled zone). Under these conditions a good quality product is obtained without the trouble

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and expense of furnaces operating under vacuum or with a controlled atmosphere and at the same time all the commercial and economic advantages of a continuous process may be secured.

The purity of the product obtained may also be greatly improved by reducing nitride formation, and by making use of a suitably selected binder in preparing the charge of titanium oxide and carbon, the binder containing constituents which have purifying and possibly catalytic properties.

The process according to the invention may be carried out by advancing the charge through a suitable furnace followed by a chilling zone while contained in boats or saggars made of some refractory materials such as graphite. However, not only do the saggars reduce the output of a given size of furnace proportionately to the space occupied by them, but both the heating and the chilling operations are delayed and their loading and unloading entail added process costs and complications. It is preferred, therefore, to produce the charge in the form of self-supporting cylinders (or other convenient shapes) which can be advanced (e.g. either positively or under the action of gravity) as such through a fairly close-fitting graphite tube which is disposed more or less horizontally and is heated by passage of electric current through a graphite resistance element. The exit end of the tube is connected directly to a water-cooled copper quench tube into which the cylinders or the like pass while still at a high temperature. In this way a large output can be obtained from a relatively small, and therefore economical, furnace. It should be noted that the heated zone of the furnace tube is preferably surrounded by heat-insulating material such as carbon black.

Certain requirements must be fulfilled in regard to the gas outlet from this furnace. The charge in passing through the furnace loses about half its weight in the form of carbon monoxide and at temperatures between about 500° and 1000° C. this gas can decompose according to the equation:



If therefore the carbon monoxide formed in the reaction were to be allowed to escape at the ends of the furnace tube it would deposit carbon both on the charge entering the furnace and on the finished carbide leaving the furnace. Both these deposits would lead to an increase in the amount of free carbon in the product. It has been found that this effect can be eliminated by sealing the ends of the furnace and providing a gas outlet near the high temperature zone of the furnace. For example, the inlet or charging end of the furnace may be fitted with a gas-tight diaphragm which will permit the passage of the charge and the delivery end of the quench tube may open into a gas-tight chamber in which the product is collected. The gas outlet may open into the furnace tube at a zone where the temperature is above approximately 1500° C. and preferably about 2000° C. A further advantage of this arrangement is that any volatile impurities evolved at these high temperatures are carried out of the furnace in the high temperature gas stream and do not give rise to difficulties by condensing in the cooler inlet and outlet sections of the furnace. The carbon monoxide evolved can be disposed of by being burnt at the gas outlet, or it may be removed and stored for use as a fuel gas.

In order that the reactions may be carried out in this way, certain precautions must be taken when preparing the cylinders (or other bodies) which, compose the charge. Thus in spite of the fact that these cylinders are to be quickly heated up to 2000° C. or more and then rapidly cooled, losing half their weight in the process, they must not at any time change their shape, break, or

disintegrate, in such a manner as to make it difficult to maintain the smooth passage of the charge through the furnace. The preparation of a satisfactory charge depends largely on the binder used and on the particle size of the constituents.

In the production of titanium carbide according to this invention the preferred raw materials are a pure grade of mineral rutile, a pure coke, and a carbonaceous binder. Current commercial practice usually requires the use of pure precipitated titanium dioxide and carbon black, with or without a binder. These materials can also be used in the present process but the preferred raw materials are much cheaper and the process makes it possible, nevertheless, to obtain a product which has a lower free carbon content than, and contains as much combined carbon as, the commercial product available at the present time.

The first step in the preparation of the charge is to grind the appropriate quantities of carbon (in the form of coke) and rutile, either together or separately, in, for example, ball mills. When steel balls are used iron contamination of the product may be considerably reduced by lining the mill with rubber. Iron contamination may be still further reduced by using a rubber-lined mill and carbide balls. The finer the particles of the charge, the stronger will be the cylinders or other shaped elements produced therefrom, both during and after the reaction. A strong cylinder is desirable as being unlikely to break in the furnace but, on the other hand, a friable product is desirable when it is to be crushed and ground to produce a carbide powder suitable for any sintering process, including hot pressing, in the manufacture of hard metals, etc. It is possible, by suitably controlling the grinding of the raw materials, to produce carbide cylinders of about optimum strength, i.e. strong enough to feed satisfactorily through the furnace but at the same time sufficiently friable to grind down easily.

The next step is to agglomerate the ground raw material with the aid of a suitable binder, for example, pitch or cane sugar molasses. In the case of pitch, the appropriate quantity (generally 20–25%) is added as a coarse powder to the partly ground rutile-coke mixture in the ball mill, and milling is then continued for about 2 hours. The resultant power can be extruded, to give the desired cylindrical form of charge, provided it is heated to about 200° C. The extruded rod is broken up into appropriate lengths and is now in its final form, except that the volatiles in the pitch must be removed by heating to about 1000° C. in a non-oxidising atmosphere. This can be done in any convenient type of muffle furnace, and the resulting charge fulfills all the requirements of the high temperature furnace for producing the carbide.

The principal difficulty in this step of the process when pitch is used lies in the "calcination" stage (heating to 1000° C.). If the batch size is large, volatiles from the outer hot zones condense in the centre and cooler portion of the batch during heating. This condensate destroys the shape of the cylinders and renders the centre of the batch useless. This difficulty becomes more serious as the scale of the process increases.

It is preferred, therefore, to employ cane sugar molasses as the binder because this is very satisfactory and is found to have quite unexpected effects on the purity of the product. In using this binder, an appropriate quantity (generally 20–25%) is mixed with the ground rutile and coke in a suitable mixer, such as one having sigma blades, and the product is extruded cold. It is dried in an air oven (at say 100–110° C.) and then has an excellent "green" strength. It is then loaded directly, while still hot, into the calcination furnace. No difficulties are experienced due to condensation in the centre of the charge when the temperature in the furnace is raised to about 1000° C. in about 6 hours. It is also possible when using the molasses binder, to calcine the cylinders, with

or without pre-drying, in a continuous operation, the cylinders being passed down a heat-resisting tube which is fitted with gas outlets and is heated by gas or electricity so that in the course of the travel of a cylinder down the tube (during as short a time as 30 minutes) its temperature will be raised from room temperature to 1000° C.

The final step in the production of titanium carbide is to feed the charge continuously, prepared as above, by way of the airtight diaphragm into the high temperature reaction furnace where it passes successively through the high temperature zone and the zone of low temperature into a hermetically sealed receiver from which it can be removed as required. It is preferred to feed the charge to the furnace at a temperature of 50–100° C. since it has been found that by so doing the corrosion due to water vapour on the furnace tube is minimised. This is particularly necessary if the charge has been standing for a period at room temperature after the calcination step at 1000° C. since a small amount of water vapour is adsorbed by the charge and subsequent heating to 100° C. has been found to remove this water vapour.

As already mentioned, the use of molasses as the binder also confers quite unexpected benefits in yielding a much purer product than do other binders. This increase in purity is thought to be due to some form of catalytic action exercised by the inorganic content of the molasses. An average molasses sample contains about 8% of inorganic material; the principal metallic constituents being potassium, sodium, calcium, iron, silicon, and magnesium, with chloride, phosphate, and sulphate as the acid radicals. These constituents are largely or entirely volatilised during passage through the high temperature furnace and it is quite possible that their catalytic activity is exerted in part in the vapour phase. The effect of these inorganic salts is all the more surprising in that Hüttig (*Z. anorg. u. allgem. Chem.*, 1952, 270, 33) has reported that the chlorides of some of the alkali metals and alkaline earths do not have any beneficial effect on the reaction between TiO_2 and carbon. It is possible, however, that this difference is due to the continuous nature of the process according to this invention, which enables these compounds, whether in the state of solid or vapour, to remain in contact with the charge at all stages of the reaction.

The enhanced purity of the titanium carbide product prepared from a charge bound with molasses is illustrated by the following figures:

	TiC, percent	C, percent	TiN, percent	Fe, percent
Commercial TiC (prepared by the known processes).....	92.5	1.5	3.5	0.2
TiC prepared by the present process (pitch binder).....	93	0.5	1	0.9
TiC prepared by the present process (molasses binder).....	95.5	0.3	1	0.2

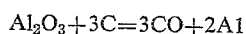
It will be seen that the titanium carbide content is notably high and the free carbon content notably low. In addition, the iron content of the material is reduced as compared with the product from a pitch-bound charge using the same rutile, coke, and preparative procedure. The lowering of the iron content may be explained by assuming that some of it is lost as a volatile compound formed from the inorganic components of the molasses.

Analyses of commercial samples of titanium carbide show the presence of combined nitrogen equivalent to as much as 4% TiN. This contamination is not always desirable and if its formation is not allowed for in making up the furnace charge, then free carbon equivalent to it will be found in the product. This nitrogen contamination can arise either from residual air in the furnace or from the charge itself. Nitrogen from the furnace can be minimised by having a reasonably gas-tight furnace container, and by sweeping it out with an inert gas, e.g. carbon dioxide, before heating the furnace. Nitrogen

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in the charge can be present as gas adsorbed on the fine powders used. In the process of this invention this gas is largely if not entirely removed during the preliminary calcination step. Some forms of carbon, e.g. coke, also contain small amounts of nitrogen which cannot be removed by heating to 1000° C. and which appear as nitride in the titanium carbide produced from them. The remedy here is to choose a coke with a low nitrogen content. By taking all appropriate precautions it has been found possible to reduce the nitride content of the titanium carbide to as little as 0.5%, and a content as low as 1% is easily achieved.

When desired, a further control over the free carbon content of the product, whether produced with the aid of pitch or molasses as the binder, can be achieved by incorporating a small quantity, e.g. about 1%, of alumina into the charge prior to the heating thereof. The alumina can be conveniently incorporated during the milling of the constituents of the charge. Under the conditions obtaining in the process according to this invention, alumina reacts selectively with free carbon contained in the titanium carbide formed, but not with the titanium carbide, according to the equation:



It should be noted moreover, that the alumina does not appear to react with carbon in the charge during the process of carbide formation. It is thus possible to reduce materially the free carbon content of the product by adding to the charge an amount of alumina which is equivalent to the free carbon content that would otherwise be expected to appear in the product, i.e. in the absence of this alumina.

It should perhaps be emphasised that the relatively pure products described were obtained from the comparatively impure raw material—unrefined mineral rutile. It has been found, however, that the vanadium and zirconium which are present as impurities in the mineral rutile are not removed even when using molasses as a binder. The product from mineral rutile therefore contains about 0.5% of both vanadium and zirconium. If in any particular application the presence of these elements is harmful, they can be eliminated by the use of pure precipitated titanium dioxide in place of mineral rutile. In this case the titanium dioxide is mixed with ground coke in the mixer at the point in the process where the molasses is added. Thereafter the process is carried out as when using mineral rutile. The combined carbon content of the product remains unaffected at about 19.2% carbon.

There is given below one practical example of the way in which this invention may be practised in producing titanium carbide, reference being made to the accompanying drawings, wherein:

FIG. 1 is a flowsheet diagram showing the steps in the process,

FIG. 2 is a side view, partly in longitudinal section and with parts broken away, showing a high temperature furnace suitable for use in carrying out the process, and

FIG. 3 is a section taken on the line III—III of FIG. 2.

3620 g. of rutile and 1430 g. of coke (low in ash and nitrogen) are ball-milled together for 10 hours in a 10" rubber-lined mill with a charge of ½" steel balls. The resultant powder is mixed with 1470 g. of cane molasses in a sigma-bladed mixer for 20 minutes and then extruded to give cylinders ⅝" in diameter and about 1½" long. These cylinders are dried for 12–14 hours at a temperature of 100–110° C. and then fired during 6–7 hours up to about 1000° C. in a non-oxidising atmosphere. After they have cooled, the cylinders are fed through a high temperature furnace of the character referred to above. The centre tube of this furnace is ¾" in diameter and is heated electrically for about 12" of its length by means of a graphite resistance element. Over this portion of the length of the furnace there is a

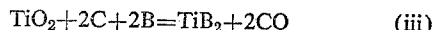
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temperature gradient rising from 1000° C. at the inlet end to 2200° C. at the end nearer the water-cooled quench section. The cylinders are fed through this furnace at a rate such that 1000 g. (2.2 lbs.) of titanium carbide will be produced per hour. The furnace tube is lagged with carbon black and its power input is 8 kw. The yield is quantitative (based on titanium) and the product contains 96.5% TiC, 0.3% free carbon, 2% TiN and 0.2% Fe.

It is also a feature of the present invention to employ the methods and apparatus described above in the preparation of the refractory carbides of the transitional elements such as Zr, Nb and Ta, from the oxides of these elements and carbon.

In these cases, the grinding of the oxide and carbon, and the percentage of binder used in making the furnace charge, are modified as required to yield a material that can be satisfactorily extruded or otherwise compacted, calcined, and fed through the high temperature furnace, and both the higher temperature and the temperature gradient within this furnace, and the time of passage of the charge through the hot zone of the furnace, are suitably chosen to yield a product of optimum purity. The time of passage of the charge through the hot zone of the furnace may be modified, within limits, by changing the linear rate of passage of the charge through the furnace and by changing the length of the hot zone of the furnace.

The methods and apparatus described above may also, as another feature of this invention, be employed in the preparation of the refractory borides and boro-carbides, and in the preparation of mixtures of the refractory borides and carbides, of titanium and the transitional elements listed above, using reactions of the type exemplified in the following equation:



and reactions of the type exemplified by Equation i, the composition of the product being predetermined by controlling the composition of the charge.

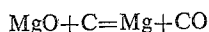
Again, as yet another feature of the invention, the methods and apparatus described above may also be employed in the preparation of refractory borides and boro-carbides, and in the preparation of mixtures of the refractory borides and carbides, of titanium and the transitional elements listed above, using reactions of the type exemplified in the following equation:



and reactions of the type exemplified by Equation i, the composition of the product being predetermined by controlling the composition of the charge. When utilising reactions of type illustrated by Equation iv, the use of these methods and apparatus ensures that the relatively volatile boric oxide is economically used whilst still maintaining the conditions of a continuous process and the rapid cooling of the product which inhibits back-reaction with carbon monoxide.

It will be noted that in reactions of the type exemplified by Equation iv a considerable proportion of the weight of the reactants is lost as carbon monoxide. In consequence if precalcined cylinders are fed to the reaction furnace in the normal way they do not retain their shape during passage through the furnace, and at the same time suffer considerable disintegration. It is therefore preferred to use saggars or boats to contain the charge when using reactions of this type. A further difficulty of this type of reaction (iv) lies in the volatility of the boric oxide, which has already been mentioned, which necessitates the use of quantities of the oxide in excess of the stoichiometric requirement, but still more economical use of boric oxide can be achieved by incorporating in the charge of a quantity of an oxide which combines with or dissolves in the boric oxide. Thus the incorporation of an amount of magnesia equal in weight

to the boric oxide results in a smooth reaction and a substantially complete conversion of the boric oxide to boride. When the final reaction temperature is in excess of 2000° C. the magnesia can be removed from the charge by incorporating an amount of carbon sufficient to react with the magnesia, according to the equation:



the magnesium being volatile at these temperatures.

When utilising Reaction iii, Reaction iii combined with Reaction i, Reaction iv, or Reaction iv combined with Reaction i, it is not possible invariably to prepare a boride entirely free from carbide even when this is desirable. Although the composition of the product can be to a large extent controlled by the composition of the charge, limitations are sometimes imposed by the relative stabilities of the boride and carbide, and of the borocarbide when it exists, of each particular transitional element. Preliminary experiments will, however, serve to establish both the limitations and the optimum conditions in each particular case where prior knowledge is inadequate. For example, 964 g. of rutile and 204 g. of coke are milled together for 10 hours and then 381 g. of commercial boron of about 75% purity are added. The powders are then mixed with 560 g. of molasses and the mixture extruded, dried and calcined as described in the previous example. After cooling the cylinders are fed through the high temperature furnace at a rate such that 500 g. of titanium boride will be produced per hour. The power input of the reaction furnace is adjusted to give a maximum temperature of about 2200° C. The product has the following composition: 95% TiB₂, 2.0% TiC, 0.5% free carbon, 0.5% Fe.

According to another feature of this invention, the methods and apparatus described above may also be employed with advantage in the preparation of boron carbide using the reaction of the following equation:

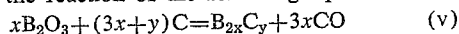


FIG. 1 is a flowsheet diagram showing the steps in a typical production of titanium carbide by the process of this invention, starting from the raw materials rutile and coke and employing molasses as the binder. The steps of milling, mixing, extrusion, drying and calcining are all carried out with the aid of known apparatuses for these purposes. A suitable high temperature furnace equipped with means for rapidly cooling the solid product of the reaction effected therein is illustrated in FIGS. 2 and 3.

In these figures, the calcined cylinders composed of a mixture of ground rutile and coke are indicated by the reference numeral 1 and the cylinders of titanium carbide produced are indicated by the reference numeral 1a.

The furnace comprises a substantially horizontal centre tube 2 of graphite having a relatively thin wall and an internal diameter slightly greater than that of the cylinders 1. This tube is disposed axially of a graphite resistance element 3 in the form of a tube slit longitudinally (at 3a) from its outer end almost up to its inner end where it grips the adjacent end of the centre tube 2 and also the inner end of a co-axially disposed graphite quench tube 4 spaced axially slightly from the centre tube. Electric current is supplied to the element 3 by way of cables 5 and 6 respectively connecting terminal blocks 7 and 8 which are water-cooled and are each secured on one of the halves of the split end of the element, to the poles of a low voltage source of supply of electric current. These blocks are located outside a casing 9 within which the major part of the heating element 3 is received, it being disposed axially of a graphite tube 10 supported from the end walls of the casing. The front or outer end of the element 3 is supported from the tube 10 by means of an insulating bushing 11 the temperature of which is kept within safe limits by a water-cooling system 12. On the front of the terminal blocks 7 and 8 is mounted, by means of an insulating ring 13 and an insulating washer 14, a feed tube 15 which has an apertured rubber dia-

phragm 16 secured therein near its mouth, the circular aperture 16a of this diaphragm being of a diameter somewhat smaller than that of a cylinder 1. Normally, one of these cylinders is left wedged in the aperture 16a, to constitute a gas seal, while another is being placed in position in the mouth of the feed tube, the pushing of the second cylinder into the aperture 16a displacing the first cylinder towards the tube 2. It will be understood that there would be, in practice, a continuous series of cylinders 1 (end-to-end) extending from the diaphragm 16 to the discharge end of the quench tube 4.

In the upper part of the tube 2 is formed a gas outlet aperture 2a and at a corresponding location in the upper part of the tube 10 is formed a further gas outlet aperture in which is secured a vertical gas outlet tube 17 of graphite surrounded by a graphite tube 18, the open end of this tube extending within a cylindrical neck 9a formed on the casing 9 and fitted with a cover 19 having an aperture 20 at which the gas evolved in the reaction may be burnt. Additional necks 9b are formed on the casing 9 to permit of the filling of the latter with a heat insulating material 21, such as carbon black, covers 22 being fitted over the mouths of these necks.

The quench tube 4 extends as a close fit through an outer copper tube 23 secured in a bush 24 serving to support the adjacent reduced diameter end 10a of the tube 10 from the end wall of the housing 9 and the outer tube 23 and bush 24 are intensively cooled by a circulation of water through a coiled copper tube 25. The outer flanged end of the outer tube 23 is secured to the adjacent end wall of a hood 26 which is furnished with a pressure-relief valve 27 and is firmly supported above a water-filled tank 28 by arms (not shown) secured to the furnace. A closure device (not shown) is mounted on the inner end of a rod 29 slidable in a gas-tight manner through the hood wall so that it may be displaced to a position in which it seals the inlet into the hood, when desired. The open underside of the hood 26 has detachably secured thereto, by a gas-tight joint 30, a relatively large gas-tight canister 31 which depends into the body of water contained in the tank 28. The quench tube 4 projects a short distance within the hood 26 so that the cylinders 1a of titanium carbide discharged from the tube may fall into the canister. The latter is removed and emptied from time to time, the inlet to the hood 26 being sealed by the closure device operated by the rod 29 before the canister is removed and being unsealed again when the canister is back in position on the hood.

Aligned apertures 32 and 33 (see FIG. 3) are formed through the tube 10 and element 3 at the locations indicated in FIG. 1, sight tubes (not shown) being provided in register with these apertures and leading to the exterior of the housing 9 so that the temperature of the respective zones of the tube 2 may be determined when required. These tubes are sealed at their inner ends and open to atmosphere at their outer ends.

The gas outlet aperture 2a is located at a zone where the temperature of the tube 2 is in the region of about 1500° to 2000° C., the gases evolved during the reaction passing out of the tube 2 at that temperature to flow through the slits 3a in the element 3, and the annular space between the latter and the tube 10, to the outlet tube 17.

What I claim is:

1. A process for the continuous production of a refractory low free-carbon-content material consisting essentially of at least one of the compounds selected from the group consisting of the carbides of titanium, zirconium, niobium, tantalum and boron and the borides of titanium, zirconium, niobium and tantalum which comprises preparing a reaction mass into a self-supporting solid body from an intimate mixture of at least one oxide from the group consisting of the oxides of titanium, zirconium, niobium, tantalum and boron, with at least the first mentioned of the two non-metals, carbon and

boron, continuously introducing said prepared reaction mass through an inlet portion of a reaction chamber having inlet and outlet portions, passing said reaction mass through a high temperature zone in said chamber wherein said reaction mass is heated to a selected temperature in the range of 2000 to 3000° C., while maintaining the mass as a self-supporting solid body, to cause at least part of the carbon to combine with the oxygen of said reaction mass to form carbon monoxide, removing the carbon monoxide gas out of contact with the reaction mass through a gas outlet at a point removed from said inlet and outlet portions of said reaction chamber and in a zone wherein the temperature is above approximately 1500° C., holding said reaction mass at said selected temperature until reaction equilibrium is reached, continuously passing the solid reaction products through said outlet portion, and then cooling said solid reaction products at a rate sufficient to prevent back reaction thereof.

2. In the process claimed in claim 1, preforming the reaction mass into self-supporting solid bodies, before it is heated, with the aid of a binder composed of cane sugar molasses.

3. In the process claimed in claim 1, the steps of intimately mixing the molasses with the ingredients of the reaction mass, extruding the mixture into a solid rod, and breaking the rod into appropriate lengths.

4. In the process claimed in claim 3, the step of heating the lengths of extruded rod in a non-oxidising atmosphere to remove volatiles in the molasses binder prior to subjecting said lengths to the selected temperature in the range 2000° to 3000° C.

5. In the process claimed in claim 4, the step of drying the lengths of extruded rod at a relatively low temperature before heating them to remove volatiles.

6. In the process claimed in claim 1, the step of incorporating a small quantity of alumina into the reaction mass prior to the heating thereof.

7. In the process claimed in claim 1, the step of incorporating a small quantity of magnesia into the reaction mass prior to the heating thereof.

8. A process according to claim 1 wherein the carbon monoxide gas is removed while it is at a temperature of about 2000° C.

9. A process for the continuous production of the carbide of an element selected from the group consisting of titanium, zirconium, niobium, tantalum and boron, said carbide having a low free-carbon-content, which comprises intimately mixing an oxide of the selected element with carbon, continuously introducing the mixture through an inlet portion of a reaction chamber having inlet and outlet portions, passing said mixture through a high temperature zone in said chamber wherein said mixture is heated to a selected temperature in the range of 2000° to 3000° C., while maintaining the mass as a self-supporting solid body, to cause at least part of the carbon to combine with the oxygen of said mixture to form carbon monoxide, removing the carbon monoxide gas out of contact with the mixture through a gas outlet at a point removed from said inlet and outlet portions of said reaction chamber and in a zone wherein the temperature is above approximately 1500° C., holding said reaction mass at said selected temperature until reaction equilibrium is reached, continuously passing the solid reaction product through said outlet portion and then cooling said solid reaction products at a rate sufficient to prevent back reaction thereof.

10. A process for the continuous production of boride of an element selected from the group consisting of titanium, zirconium, niobium and tantalum, said boride having a low free-carbon-content, which comprises intimately mixing an oxide of the selected element with carbon and boron, continuously introducing said mixture through an inlet portion of a reaction chamber having inlet and outlet portions, passing said mixture through a high tem-

perature zone in said chamber wherein said mixture is heated to a selected temperature in the range of 2000° to 3000° C., while maintaining the mass as a self-supporting solid body, to cause at least part of the carbon to combine with the oxygen of said mixture to form carbon monoxide, removing the carbon monoxide gas out of contact with the mixture through a gas outlet at a point removed from said inlet and outlet portions of said reaction chamber and in a zone wherein the temperature is above approximately 1500° C., holding said mixture at said selected temperature until reaction equilibrium is reached, continuously passing the solid reaction products through said outlet portion, and then cooling said solid reaction products at a rate sufficient to prevent back reaction thereof.

11. A process for the continuous production of the boride of an element selected from the group consisting of titanium, zirconium, niobium and tantalum, said boride having a low free-carbon-content, which comprises intimately mixing an oxide of the selected element with carbon and boric oxide, continuously introducing said mixture through an inlet portion of a reaction chamber having inlet and outlet portions, passing said mixture through a high temperature zone in said chamber wherein said mixture is heated to a selected temperature in the range of 2000° to 3000° C., while maintaining the mass as a self-supporting solid body, to cause at least part of the carbon to combine with the oxygen of said mixture to form carbon monoxide, removing the carbon monoxide gas out of contact with the mixture through a gas outlet at a point removed from said inlet and outlet portions of said reaction chamber and in a zone wherein the temperature is above approximately 1500° C., holding said mixture at said selected temperature until reaction equilibrium is reached, continuously passing the solid reaction products through said outlet portion, and then cooling said reaction products at a rate sufficient to prevent back reaction thereof.

12. A process for the continuous production of a low free-carbon-content titanium carbide, which comprises intimately mixing titanium dioxide and carbon, continuously introducing said mixture through an inlet portion of a reaction chamber having inlet and outlet portions, passing said mixture through a high temperature zone in said chamber wherein said mixture is heated to a selected temperature in the range of 2000° to 3000° C., while maintaining the mass as a self-supporting solid body, to cause at least part of the carbon to combine with the oxygen of said mixture to form carbon monoxide, removing the carbon monoxide gas out of contact with the mixture through a gas outlet at a point removed from said inlet and outlet portions of said reaction chamber and in a zone wherein the temperature is above approximately 1500° C., holding said mixture at said selected temperature until reaction equilibrium is reached, continuously passing the solid reaction products through said outlet portion, and then cooling said solid reaction products at a rate sufficient to prevent back reaction thereof.

13. A process for the continuous production of a low free-carbon-content titanium boride which comprises intimately mixing titanium dioxide with carbon and boron, continuously introducing said mixture through an inlet portion of a reaction chamber having inlet and outlet portions, passing said mixture through a high temperature zone in said chamber wherein said mixture is heated to a selected temperature in the range of 2000° to 3000° C., while maintaining the mass as a self-supporting solid body, to cause at least part of the carbon to combine with the oxygen of said mixture to form carbon monoxide, removing the carbon monoxide gas out of contact with the mixture through a gas outlet at a point removed from said inlet and outlet portions of said reaction chamber and in a zone wherein the temperature is above approximately 1500° C., holding said mixture at said se-

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lected temperature until reaction equilibrium is reached, continuously passing the solid reaction products through said outlet portion, and then cooling said solid reaction products at a rate sufficient to prevent back reaction thereof.

14. A process for the continuous production of a low free-carbon-content titanium boride which comprises intimately mixing titanium dioxide, carbon and boron trioxide, continuously introducing said mixture through an inlet portion of a reaction chamber having inlet and outlet portions, passing said mixture through a high temperature zone in said chamber wherein said mixture is heated to a selected temperature in the range of 2000° to 3000° C., while maintaining the mixture as a self-supporting solid body, to cause at least part of the carbon to combine with the oxygen of said mixture to form carbon monoxide, removing the carbon monoxide gas out of contact with the mixture through a gas outlet at a point removed from said inlet and outlet portions of said reaction chamber and in a zone wherein the temperature is above approximately 1500° C., holding said mixture at said selected temperature until reaction equilibrium is reached, continuously passing the solid reaction products through said outlet portion, and then cooling said reaction products at a rate sufficient to prevent back reaction thereof.

15. A process for the continuous production of the boride of an element selected from the group consisting of titanium, zirconium, niobium and tantalum, said boride having a free-carbon-content not over about 1%, comprising the steps of mixing an oxide of the selected element with carbon, boron and cane sugar molasses, pressing the mixture into self-supporting shapes, calcining said shapes in a non-oxidizing atmosphere, continuously introducing said calcined shapes through an inlet

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portion of a reaction chamber having inlet and outlet portions, passing the said shape through a high temperature zone in said chamber wherein said shapes are heated to a selected temperature in the range of 2000° to 3000° C., while maintaining the shapes as self-supporting solid bodies, to cause at least part of the carbon to combine with the oxygen of said shapes to form carbon monoxide, removing the carbon monoxide gas out of contact with the shapes through a gas outlet at a point removed from said inlet and outlet portions of said reaction chamber and in a zone wherein the temperature is above approximately 1500° C., holding said shapes at said selected temperature until reaction equilibrium is reached, continuously passing the shapes through said outlet portion, and then cooling the shapes at a rate sufficient to prevent back reaction thereof.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,019,084

January 30, 1962

Edmund Hollis Amstein

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, lines 49 and 58, for "Reaction i", each occurrence, read -- reaction (i) --; column 6, line 73, strike out "of", first occurrence; column 10, line 17, for "anelement" read -- an element --.

Signed and sealed this 10th day of July 1962.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents