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HOT STRENGTH CORROSION RESISTANT MATERIAL AND PRODUCTION THEREOF

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This invention relates to refractory compositions of matter or structural materials which exhibit great hot-strength and corrosion-resistance at elevated temperatures and to the production of such hot-strength corrosion-resistant refractory structural materials.

This application is a continuation-in-part of my prior applications Serial No. 170,240, filed June 24, 1950; Serial No. 363,041, filed June 22, 1953; and Serial No. 363,043, filed June 22, 1953, all now abandoned.

The hot-strength corrosion-resistant structural materials of the invention are useful for buckets, vanes, nozzles, and other like structural parts of gas turbines, as well as other combustion engines, for tools, and in general for all applications where great strength and corrosion resistance at high temperatures in oxidizing atmospheres is essential.

Although prior scientific and patent literature contains an abundance of data about the physical properties of hard cemented carbides, and also about the properties of chromium boride, such as described in Cole et al. Patent No. 2,088,838, it does not contain any data about the physical properties of cemented metal borides.

In a search for structural material of great hot-strength and corrosion-resistance, many efforts have been made to produce a corrosion-resistant hot-strength cemented metal boride material. Of the various metal borides referred to in prior art literature, chromium boride, trade named Colmonoy, and the only refractory metal boride commercially available, was known to have in addition to great hardness and strength at high temperatures, excellent corrosion-resistance. Accordingly, a great deal of concentrated work was devoted to the production of cemented chromium boride bodies by powder metallurgy technique that would exhibit great strength and corrosion resistance within oxidizing or combustion gas atmospheres at high temperatures such as 700° C. or above. In making such cemented chromium boride material, the best prior addition or binder material, to wit, nickel and/or cobalt, which proved so successful in producing cemented carbide materials, were used, with and without other minor additions, such as molybdenum or tungsten. The best of these cemented chromium boride materials was composed of about 85% chromium boride and 15% nickel (unless otherwise specifically stated, all proportions herein are given by weight throughout the specification and claims). To produce cemented chromium boride material, the chromium boride particles and the nickel were comminuted and mixed in a ball mill to provide an intimate mixture of the pure powder particles of the ingredients. A bar body was then formed of the fine powder mixture by hot-pressing within graphite dies, at a die temperature of about 1300° C., corresponding to an estimated temperature of about 1550° C. inside the die. At room temperature the resulting bar had a modulus of rupture of about 120,000 p. s. i., average Rockwell A hardness 89, and a density of about 6.17 g./cc. Decrease of the particle size of the powder to between 1 to 2 microns increased the hardness of the resulting bar, but

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reduced its strength. Generally similar, though somewhat poorer characteristics were obtained by similar materials using cobalt and/or nickel in proportions 10 to 20 as a binder. However, tests at higher temperatures indicated a liquid phase forming in such refractory boride material at about 1040° C. which limits its use to a maximum temperature of about 950° C. It is believed that the liquid phase which limits the use of this material to temperatures below about 950° C. is caused by the development of less refractory nickel and/or cobalt borides and systems of such less refractory borides.

In making such hard cemented refractory boride bodies, it was heretofore generally believed that in order to give them desired high mechanical strength, it was essential to use, as cementing addition, metals which are ductile, and which have a considerably lower melting temperature than the refractory boride.

In the past, difficulties have also been encountered in providing confining bodies such as molds or nozzles, the walls of which have to withstand contact with molten reactive metals such as molten titanium. Among the objects of the invention are cemented materials or compositions of metal which resist corrosion when used as walls or wall surface layers of bodies holding or guiding liquid reactive metals such as molten aluminum, magnesium, copper, brass, tin and like liquid metals which tend to react with most of the metals or materials heretofore used as containers, guide ducts or molds therefor.

Among the objects of the invention are also cemented materials or compositions of which exhibit the required hot strength and high resistance to corrosion and deterioration when exposed to contact with liquid reactive metals, for use in structures such as guide ducts, nozzles, and molds which guide or confine reactive liquid metals, or as a protective layer of such structures which is in contact with such confined reactive liquid metals.

The present invention is based on the discovery that boron, a substance which lacks ductility, and which has not been considered a metal, constitutes an unusually effective addition substance for use in lieu of known ductile cementing metals of relatively low melting point, such as cobalt and nickel, in making hard cemented refractory boride bodies.

In particular, the invention is based on the discovery that cemented, compacted and sintered structural material combining refractory metal boride particles with an addition of boron exhibit desired great hot-strength at temperatures as high as 1200° C. and higher, and great corrosion-resistance at temperatures as high as 2500° C. and higher.

In general, desirable cemented refractory boride bodies of the invention, may be made by combining from about 2% up to about 15% of the boron addition substance with about 98% to about 85% of the refractory metal boride particles.

Cemented refractory bodies of the invention having particularly desirable characteristics are obtained by confining the addition substance of carbon-containing boron to a more limited range of proportions, to wit, to from 2% to 7% of the total composition of the cemented refractory body, the balance being formed of the refractory metal boride particles.

A unique characteristic of the refractory metal boride compositions of the invention combining a boron addition with the refractory metal boride particles is the fact that they also exhibit an unexpected high electrical and heat conductivity, notwithstanding the fact that boron is a poor electric and heat conductor. It is believed that the high electrical and thermal conductivity is due to a solidified liquid phase formed by boron with the metal constituent or constituents of the metal borides or boride when producing cemented refractory metal boride

compositions of the invention. As an illustration, cemented zirconium-boride material of the invention made with an addition of about 10% boron, has a modulus of rupture of 130,000 p. s. i. (pounds per square inch), Rockwell A hardness 93, density 5.35 g./cc., and electrical resistivity 14.5 microhms-cm.

A distinct phase of the invention is a discovery that cemented refractory bodies combining particles of a boron addition with particles of refractory borides may be produced by mixing a compound of the metal of the desired boride, such as the metal hydride, with boron in proportions corresponding to the formulae of the mixture of the desired boride with the boron addition. This phase of the invention greatly simplifies the problem of providing the desired refractory metal boride in a degree of purity most suitable for producing cemented bodies combining the boride with the boron addition in accordance with the principles of the invention.

In search for a cemented zirconium boride material of high hot strength and corrosion resistance, I found that zirconium will form with boron three distinct crystalline compounds, to wit, a monoboride ZrB , a diboride ZrB_2 and a dodecaboride ZrB_{12} . The monoboride ZrB , which has a distinct crystal structure and contains about 10% boron, is of limited thermal stability and has no practical value. The diboride ZrB_2 which has a crystal structure of greatest stability and a high melting point of about 3040° C., is most desirable with respect to strength and corrosion-resistance. The dodecaboride ZrB_{12} has high brittleness, poor heat conductivity and poor resistance to corrosion and is stable only over a limited temperature range.

The present invention is based on the discovery that zirconium boride powder particles which are substantially free from impurities may be utilized to form a shaped cemented body of high strength and corrosion-resistance at high temperatures of about 900° C. and higher provided at least about 93% by weight of the cemented body consists of zirconium diboride ZrB_2 , which cemented zirconium diboride consists of ZrB_2 particles bonded by a boron substance containing about 4 to 33 atomic percent carbon in solid solution, provided the boron substance forms 2 to 7% of the cemented zirconium diboride of the body. (Throughout the specification and claims, all proportions are given by weight unless specifically stated otherwise.)

According to the invention, in making shaped hard cemented bodies containing as principal ingredient zirconium diboride ZrB_2 , it is essential to suppress the formation of the dodecaboride ZrB_{12} . In the critical task of preventing the formation of the dodecaboride when forming a cemented refractory body containing as the principal ingredient zirconium diboride ZrB_2 , it is essential to limit the amount of boron present in excess of the amount corresponding to the formula ZrB_2 to about 2 to 7% of the body, and to provide that the excess of 2 to 7% boron shall contain about 4 to 33 atomic percent of carbon in solid solution therewith.

It was found that boron in its crystalline form may be stabilized through carbon in solution with boron. Contrary to previously reported findings, X-ray diffraction and other studies have established that there does not exist a stoichiometric compound of the formula B_4C . The boron addition should contain in solid solution at least 4 atomic percent carbon and up to about 32 to 33 atomic percent carbon. Any further additions of carbon will appear as graphite.

One phase of the present invention is the discovery that if 2% to 7% carbon-containing boron—containing about 4 to 33 atomic percent carbon in solid solution with the boron—is combined with the principal ingredients consisting of zirconium diboride ZrB_2 , it is possible—by compacting and heating at temperatures considerably below the melting temperature of the zirconium di-

boride—to form a strong corrosion-resistant cemented hard body consisting of zirconium diboride ZrB_2 as the principal constituent. If the excess of carbon-containing boron is less than about 2% of the cemented zirconium diboride ingredients, the resulting cemented body lacks strength. An excess of more than about 7% of carbon-containing boron produces an excess of the liquid phase at the elevated sintering or cementing temperature, and makes it difficult to produce cemented zirconium diboride bodies of the desired physical properties.

For the carbon-containing boron, the required carbon may be provided by adding graphite to the mixture of the zirconium and boron ingredients of the desired cemented body. Alternatively, the required carbon may be introduced into the powder mixture of the zirconium and boron ingredients from the graphite dies in which the mixture of the powder ingredients is compacted and heated to the cementing temperature.

To produce the desired cemented body containing ZrB_2 as the principal ingredient, the mixture of the ingredients should be heated to a temperature between about 2200° to 2700° C.

The production of cemented bodies containing principally zirconium diboride ZrB_2 with 2 to 7% of carbon-containing boron may be readily carried on with molds, dies and crucibles of graphite because the only possible reaction that may occur when the graphite containers are heated to about 2200 to 2700° C. is that the boron ingredient of the heated powder mixture will absorb from the die carbon corresponding to at most 33 atomic percent of the excess boron in the powder mixture. The process of saturating the excess of 2 to 7% boron with up to 33 atomic percent of carbon from the die, involves a very slow reaction and requires high temperatures.

In producing shaped cemented bodies out of the powder ingredients by compacting and heating within dies, the powder ingredient should be comminuted to an average particle size between about 2 and 8 microns. Good results are obtained by comminution within a gaseous vortex mill. Good results are obtained with a 15 inch vortex mill operating with 60 pounds' air pressure in the grinding chamber, and 50 pounds' air pressure in the venturi duct and feeding to the mill the powder of a particle size, such as —100 mesh, at a rate of 100 to 150 grams powder per minute. If the finely comminuted powder so produced is to be stored before using it for the production of cemented bodies, the storing vessels should be purged with an inert gas and then sealed. However, good results are obtained with fine powder produced in the manner described above even if it remains unprotected for about 3 to 4 weeks.

There will now be described examples of procedures for producing cemented articles of the invention, consisting of zirconium diboride ZrB_2 with an excess of 2 to 7% carbon containing boron, which carbon is in solid solution with the excess of boron and forms about 4 to 33 atomic percent thereof.

Preparation of zirconium diboride powder

Amorphous boron in a form in which it is commercially available, zirconium hydride and carbon are used as the starting materials.

In order to give zirconium diboride bodies of the invention having the desired resistance to oxidation, corrosion and heat shock, it is essential that they shall be of a minimum purity of between 96.5 to 99% plus, i. e., that 96.5 to 99% plus of the cemented body shall consist of zirconium, boron and carbon only as ZrB_2 with 2 to 7% carbon-containing boron. The iron impurities should be less than about 0.2% and preferably less than about 0.1%. Impurities of silicon carbide and other silicon impurities should be avoided.

The zirconium and the zirconium hydride contains sometimes a hafnium impurity, which may remain in the

cemented zirconium diboride ZrB_2 , which may also contain in solid solution minor impurities of titanium. These impurities may be present in amounts up to about 5% by weight without materially impairing the oxidation and corrosion-resistance and shock resistance of the cemented material.

To reduce the powder volume, the mixture of the starting powder ingredients is compacted with pressures of about $\frac{1}{2}$ to 4 t. s. i., which pressure range has no critical significance. The powder mixture compact is then placed into a graphite crucible which has a cover equipped with three stacks. One cover stack serves for the introduction of hydrogen into the crucible and another stack for burning the hydrogen leaving the crucible. The third stack serves for optical control of the temperature in the crucible. The crucible with the powder mixture contents is placed in a high frequency induction furnace, the crucible being provided with an insulating layer of lamp-black powder to reduce heat losses while being heated.

Before starting the heating, the interior of the crucible is purged with hydrogen and after purging, the hydrogen is ignited and the high frequency heating is started while maintaining in the interior of the crucible, an atmosphere of hydrogen. Good results are obtained by induction heating with an alternating current of about 1000 to 3000 cycles per second. By way of example, with a powder mixture load of about 50 to 80 pounds held in a graphite crucible of 18 inches inside diameter, 4 feet height and 2 inches wall thickness, good results are obtained with an induction heater equipment of 60 kilowatt heating energy. Good results are obtained by heating with 40 to 50 kilowatts during the first 60 to 90 minutes of the heating cycle until the load is brought to a temperature of about 700 to 900° C.

Thereafter, the heat input is lowered since a relatively violent exothermic reaction takes place in the powder mixture as the zirconium diboride ZrB_2 is being formed out of the powder ingredients at a temperature between about 1000 and 1200° C. Because of the heat developed by the exothermic reaction, the heat input should be reduced to prevent a too violent reaction that might damage the equipment and result in a loss of the production. By way of example, for a powder mixture load of about 50 pounds, the exothermic reaction lasts approximately 3 to 6 minutes, and the local heat temperature generated by the reaction is estimated to be between about 2500 and 3500° C.

During the initial heating cycle, at which the powder-mixture temperature is increased to about 900° C. the zirconium hydride will gradually decompose and yield continuously atomic hydrogen which provides protection for the powder charge. If zirconium powder other than a hydride is used in the starting mixture, the ultimate zirconium diboride obtained will be of somewhat lower purity.

Upon completion of the exothermic reaction, the full heating power is applied to the crucible and a relatively slow further rise of the temperature from about 1200° C. will occur. It is desirable to have an additional heating cycle of about one hour in which the load is heated from 1200 to 1800° C., in order to eliminate impurities from the zirconium diboride ZrB_2 that have been introduced by impure boron in the original mixture. The principal boron impurity consists of magnesium oxide which is reduced at temperatures about 1400° C. By heating the mixture to about 1800° C. with carbon introduced in the original powder mixture or by an atmosphere of carbon monoxide in the heated carbon crucible, the magnesium oxide will be reduced to magnesium metal which will volatilize between 1600 to 1800° C. and will leave or be expelled from the crucible, yielding a body of high purity zirconium diboride ZrB_2 with the desired excess of 2 to 7% of carbon-containing boron.

The treated powder body should be maintained in the crucible at about 1800° C. for a period sufficient to elim-

inate all magnesium oxide and other volatile impurities present in the original powder mixture of ingredients. For loads of 10 to 75 pounds powder a treatment period of between 1 and 3 to 5 hours is satisfactory. It is desirable to use as the initial boron ingredient of the mixture a grade of amorphous boron which contains the smallest amount of non-volatile impurities. The iron impurities should be less than 0.2% of the original boron of the mixture which should be substantially free from silicon carbide and other silicon impurities, it being desirable that the produced final powder shall contain 96.5 to plus 99% of the primary desired ingredients, to wit, zirconium, boron and carbon in amounts corresponding to zirconium diboride ZrB_2 with 2 to 7% boron, wherein the boron contains 4 to 33 atomic percent carbon in solid solution therewith.

Upon completion of the above-described heating cycle at 1800° C., the crucible with its heated load is removed from the high frequency field and subjected to cooling for a time depending on the magnitude of the heated load which should remain under a hydrogen atmosphere for at least 20 hours subsequent to completion of the heating cycle. In the example here considered, good results are obtained by passing the hydrogen at a rate of 5 cubic feet to 15 cubic feet per hour through the crucible during the first 24 hours from the completion of the heating cycle, followed by cooling with a hydrogen flow at about 5 cubic feet per hour. Excess hydrogen flow through the crucible during the cooling period will result in formation of water vapor at the burn-out region and will tend to contaminate the cooled powder charge. If the powder body is prepared without the addition of carbon to the original powder mixture charge, the hydrogen may be shut off at the completion of the 1800° C. heating cycle described above, and a graphite block is placed over the exhaust. The powder charge in the crucible will then cool within a carbonaceous atmosphere generated by the graphite crucible and the excess boron of the charge will combine with the carbon of the carbonaceous atmosphere within the crucible into boron containing 4 to 33 atomic percent carbon in solid solution.

At the end of the cooling cycle, the powder charge in the crucible will form a lumpy semi-powdery body which is readily removed from the graphite crucible and pulverized by a simple crushing procedure. Iron or steel jaws or like crushers should not be used for this pulverization since the powder body should be protected against contamination with iron. The crushed powder then is subjected to further comminution into a fine powder of a particle size such as between 2 and 8 microns average particle size. A gaseous-type vortex pulverizing equipment of the type described hereinbefore, has been found satisfactory for this purpose. By way of example, a powder body produced in the manner described above contained on chemical analysis about 74% zirconium, 23% boron and 1 to 1.2% carbon, and consisted principally of zirconium diboride ZrB_2 with 4% of excess boron which contained carbon in excess of 4 atomic percent in solid solution with the excess boron. In producing zirconium diboride ZrB_2 powder with the desired excess of 2 to 7% carbon-containing boron, approximately 2% boron is usually lost through oxidation and this factor should be taken into account and compensated for in proportioning the original mixture of the ingredients which are subjected to the treatment. Thus, to produce a powder body with 5% of carbon-containing boron in excess of the zirconium diboride ZrB_2 , the original mixture of the powder ingredients subjected to the treatment described above, should be calculated to contain the required excess boron over the amount required to yield the desired proportion of zirconium diboride ZrB_2 .

In producing the powder mixture of ZrB_2 with 2 to 7% of carbon-containing excess boron, it is important that the mixture shall not contain any uncombined carbon in excess of about 1.5%, and this applies also to the

cemented bodies made of such powder mixtures. If the cemented zirconium diboride ZrB_2 material of the invention contains—in addition to the excess of 2 to 7% boron having in solid solution therein 4 to 33 atomic percent carbon—more than 1.5% uncombined or free carbon, the strength of the material is substantially reduced. For best results, the uncombined carbon should be less than 0.5% of the material.

Production of cemented zirconium diboride bodies

Shaped cemented bodies composed of zirconium diboride ZrB_2 particles bound with 2 to 7% of excess boron containing carbon in solid solution, may be produced by the use of powder metallurgy or ceramic techniques. These techniques include hot pressing, cold pressing and sintering, extrusion and sintering, slip casting and sintering, and any combination of these techniques with intermediate presintering and machining operation.

Because of the unusually high stability of zirconium diboride ZrB_2 mixed with 2 to 7% of carbon-containing excess boron, this powder body will not be detrimentally affected by contact with carbon when forming it into the desired shape by hot pressing in a graphite die. In the hot pressing procedure, the die may be heated either by direct current conduction, by resistance heating or by induction heating. Hot pressing in graphite die may be carried on with a pressure of about 3 to 4 t. s. i. When hot pressing zirconium diboride ZrB_2 powder bonded with 2 to 7% of carbon-containing boron, pressures of 10 to 12 t. s. i. and higher may be applied to the die. In general, pressing with pressures of at least about 2 t. s. i. at temperatures of at least about 2000° C. are required for producing cemented bodies of the desirable high strength, heat shock resistance and corrosion-resistance at elevated temperatures.

Hot pressing process with induction heating is desirable because the pressed powder body may be brought to the desired temperature of about 2200 to 2700° C. in a very short time so that the die will have a slightly lower temperature than the heated powder mixture.

Good results are obtained by hot-pressing such bodies with pressures ranging from very low pressures up to about 3 to 4 t. s. i. (tons per square inch). Instead of graphite dies, desired shaped bodies of the invention may be formed with dies made out of the cemented material of the present invention, to wit, consisting principally of zirconium diboride particles which are bonded with 2% to 7% of carbon-containing boron. When using such zirconium diboride dies, shaped bodies of the invention may be hot-pressed with pressures up to 10 to 12 t. s. i. or even higher.

In the hot-pressing procedure, the die with its powder mixture filling the die cavity is heated to a temperature at which a liquid phase is formed out of the carbon containing excess 2% to 7% boron of the powder mixture at about 2200° C. to 2700° C. The die and contents may be heated to the required high temperature by direct-current conduction or by induction. Heating by induction has been found to be of advantage because a very short time is sufficient to bring the die with its contents to the high temperature at which its contents are at about 2200° C. to 2700° C.

Desired shaped articles of zirconium diboride and an excess of 2% to 7% carbon-containing boron may also be produced by first compacting under pressures such as 10 to 25 t. s. i. (tons per square inch), then presintering at temperatures from 1200° C. to 1500° C. followed by shaping or machining with conventional shop equipment to dimensions that are linearly oversized to compensate for the shrinkage in the final sintering. The so presintered shaped compacts are thereafter sintered to the ultimate strength at about 2200° C. to 2700° C. at which the carbon containing excess boron forms a liquid phase.

If the shaped cemented article is to have thin walls,

it may be produced by slip-casting procedure which permits the production of cemented bodies of this material with wall thicknesses of $\frac{1}{16}$ of an inch and less. The slip-casting is carried on by preparing a water slurry containing zirconium diboride powder with an excess of 2% to 7% carbon-containing boron powder of fine particle size. The slurry is then placed in porous molds having cavities of a shape of the desired articles. Such porous molds may be produced by plaster of Paris or a similar material. The porous molds with the powder slurry held therein are then slowly dried. In drying, the powder material of the slurry will shrink away from the walls of the mold and the powder particles will adhere to each other and form self-sustaining shaped green powder bodies which may be readily lifted from the mold cavity. The green powder body is then subjected to presintering at from 1200° C. to 1500° C., followed by further shaping and subsequent final sintering at 2200° C. to 2700° C. If no further machining or shaping is required, the green powder bodies are subjected to a sintering temperature of about 2200° C. to 2700° C. at which the carbon containing excess boron forms a liquid phase and bonds the ZrB_2 particles into the desired cemented body.

When using a presintering process, good results are obtained if the compacting die is so designed, and the additional shaping before final sintering is carried on in such manner, as to provide an oversized shape which, after linear shrinkage of about 16% in the final sintering operation will yield an article of the desired shape and size.

By way of further example, parts weighing 15 pounds have been hot pressed—out of a powder body containing zirconium diboride with an excess of 5% carbon-containing boron—within a graphite die which was heated by induction and subjected to a pressure of 3 t. s. i. in a very short period.

A similar zirconium diboride powder mixture was used for making parts by pressing the powder body hydrostatically in a rubber die with a pressure of 10 to 25 t. s. i. The green compact was then presintered at an elevated temperature between 1200° and 1500° C. The presintered shaped compact was thereafter further shaped and machined to size with ordinary machine shop equipment, the compact having been linearly oversized by about 16% to compensate for shrinkage in the final sintering operation. After shaping, the presintered compact was subjected to the final sintering at a temperature between 2200 and 2700° C. thereby giving it ultimate density and strength.

Cemented bodies produced by hot pressing in the manner described above and consisting of zirconium diboride ZrB_2 bonded with 5% of excess boron containing 4 to 33 atomic percent carbon in solid solution had the following physical properties:

Melting point	2500° C.—2600° C.
Density	5.2 to 5.3 grams per cc. (cubic centimeter).
Hardness	Rockwell A—87 to 89.
Weight gain in air at 1100° C. for 200 hours	About 8 to 15 milligrams per square cm.

It had a stress-to-rupture life given in the table below:

At Temperature	Under Stress, p. s. i.	Hrs. Until Ruptured
980° C.	13,000	310 to 320
980° C.	14,000	300+
980° C.	16,000	300+
980° C.	18,000	80+

Shaped parts made of the material of the invention having the foregoing properties exhibited outstanding per-

formance without deterioration in contact with fluids of a temperature exceeding 2700° C. The cemented material of the invention exhibited good resistance to erosion and good resistance to heat shock.

The cemented material of the invention has been found to be of unique value when used as molds, containers, guide ducts, pumps and like confining structures for molten magnesium, brass and aluminum, liquid gallium and like active metals, which have a deteriorating effect on the materials heretofore used for retaining them in molten or liquid condition.

Thus by way of example, the material of the invention has been found of great value as a pump component for pumping liquid molten aluminum, as a spray nozzle for liquid magnesium used in producing magnesium powder, and in various other applications representing similar critical problems.

According to the invention, liquid spraying nozzles which have relatively long life and are free from cracking, and of relatively low weight are obtained by forming the throat part of the nozzle out of a short thin-walled throat section of cemented zirconium boride and combining it with adjoining inlet and outlet nozzle wall sections of refractory material having considerably lower density than zirconium boride into a unitary integral and strong nozzle structure.

By making the spray nozzles with a distinct thin-walled throat section, the throat section may be made out of the zirconium diboride material bonded with 2 to 7% of carbon-containing boron by a simple hot pressing procedure.

By making only the thin short throat wall section of the spray nozzle out of the very hard cemented zirconium diboride material, the grinding operation required for giving the throat wall the desired finish is greatly simplified.

According to a phase of the invention, the formation of hair line cracks or like disturbances is suppressed by making the throat wall section of such spray nozzle out of a plurality of angular segments which are assembled and joined in assembled aligned position as a strong unitary structure to form a unitary fluid guide nozzle of the desired shape.

The graphite dies should not be too hard in order to avoid their cracking. By subjecting the powder mass to successive compacting and sintering treatments at successively higher temperatures, refractory cemented boride compositions of extremely high strength, density and hardness may be produced. In order to improve its physical characteristics, the hot-pressed cemented refractory boride material may be subjected to a similar additional sintering treatment within a protective atmosphere.

Strong sintered cemented bodies of the invention may also be produced by first cold-pressing the fine powder mixture into a green compact with a pressure from 1 to about 35 t. s. i., followed by sintering in a non-oxidizing, non-carburizing atmosphere, such as purified hydrogen or purified cracked ammonia, at a temperature in the range from about 1800° to 2400° C., for about one-half to twelve hours.

Because of the unusually high thermal conductivity of the refractory boride compositions of the present invention, they may be operated in media of higher temperatures than any other known prior cemented refractory bodies. When a cemented refractory boride body of the invention is exposed to hot gases, it will be able to withstand temperatures higher than the melting temperature of its least refractory constituent because the high heat conductivity of such body may be utilized to maintain its temperature at a lower level than the temperature of the gases to which it is exposed.

Because of their relatively high electric conductivity, the cemented refractory boride compositions of the invention are also very effective as electrical contact ma-

terial for electric switches, and for similar applications. The cemented refractory boride material of the invention may be brazed or similarly united to contact members of switches, or in general, to the work parts such as tools, on which they are to be used in operation.

Cemented hard, dense boride structures of great strength may also be produced from such fine loose powder mixtures prepared in the manner described above by cold-pressing, followed by sintering. The cold-pressing of the powder mixture into the desired compacted shape may be effected in a steel die at room temperatures with pressures of 2 to 35 t. s. i. The compact is then sintered at a temperature ranging from 1800° to about 2350° C. within a vacuum, or in an atmosphere of purified super-dry hydrogen or purified cracked ammonia. The sintering may be effected either by induction heating, or by direct conduction heating.

The sintering of the compacted fine powder-particle mass is carried on at such temperature as to cause the formation of a liquid phase of a eutectic composition of some of the different ingredients in the compact.

Thus in case of a cemented body formed of particles of zirconium boride having a melting temperature of about 3000° C. and of boron having a melting temperature of about 2300° C., very good results are obtained with a sintering temperature of about 2050° C. at which a eutectic composition of the substance of the different ingredients form a liquid phase.

By following procedures similar to those described above in connection with the production of cemented bodies consisting of zirconium diboride particles which are bonded by a solidified liquid phase of an addition of 2% to 7% carbon-containing boron, similar desirable cemented bodies may also be formed out of powder particles of the refractory borides of titanium, vanadium, niobium, tantalum, chromium, tungsten and molybdenum, and also of solid solutions thereof, by combining powder particles of such refractory borides with an excess of 2% to 7% carbon-containing boron (containing 4 to 33 atomic percent carbon) and compacting and heating the compacted powder mixture to a temperature at which a boron-containing liquid phase is formed which upon cooling and solidification binds the refractory higher melting metal boride particles into a strong hard, erosion-resistant body.

The features and principles underlying the invention described above in connection with specific exemplifications will suggest to those skilled in the art many other modifications thereof. It is accordingly desired that the appended claims shall not be limited to any specific feature or details thereof.

I claim:

1. A hard homogeneous solid body of high strength and corrosion resistance at high temperatures, consisting essentially of about 93% to about 98% of refractory diboride particles selected from the group consisting of the diborides of zirconium, titanium, vanadium, niobium, tantalum, chromium, and solid solutions of at least two of said diborides, and about 2% to about 7% of a boron substance bonding together said refractory particles, said boron substance being boron in solid solution with 4 to 33 atomic percent carbon and in the liquid state at a temperature of less than 2700° C., said hard body being free of uncombined carbon in excess of 1.5% of said body, said body having been formed by subjecting its constituents to mechanical pressure and a temperature between 1400° C. and 2700° C.

2. An article having a surface region that is subjected to corrosion action at high temperatures, said surface region being formed to hard homogeneous material of high strength and corrosion resistance at high temperatures, said hard material consisting essentially of about 93% to about 98% of refractory diboride particles selected from the group consisting of the diborides of zirconium, titanium, vanadium, niobium, tantalum, chro-

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mium, and solid solutions of at least two of said diborides, and about 2% to about 7% of a boron substance bonding together said refractory particles, said boron substance being boron in solid solution with 4 to 33 atomic percent carbon and in the liquid state at a temperature of less than 2700° C., said hard material being free of uncombined carbon in excess of 1.5% of said material, said material having been formed by subjecting its constituents to mechanical pressure and a temperature between 1400° C., and 2700° C.

3. The method of manufacturing a hard solid material of high strength and corrosion resistance at high temperatures, which comprises compacting and heating at elevated temperatures between 1400° C. and 2700° C. an intimate mixture of about 93% to about 97% of refractory diboride particles selected from the group consisting of the diborides of zirconium, titanium, vanadium, niobium, tantalum, chromium, and solid solutions of at least two of said diborides, together with about 2% to about 7% of particles of a boron substance consisting of boron containing in solid solution 4 to 33 atomic percent carbon and which boron substance is in a liquid state at a temperature of less than 2700° C., which mixture is free of uncombined carbon in excess of 1.5% of said material, and continuing the heating of said mixture of said diboride particles and said boron substance at said elevated temperatures to cause said boron substance to liquefy, and thereafter cooling said mixture to cause the liquefied boron substance to solidify and bond said refractory diboride particles into a hard, solid material.

4. A hard body as claimed in claim 1, consisting essentially of zirconium diboride bonded by said boron substance.

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5. A hard body as claimed in claim 1, consisting essentially of titanium diboride bonded by said boron substance.

6. A hard body as claimed in claim 1, consisting essentially of tantalum diboride bonded by said boron substance.

7. A hard body as claimed in claim 1, consisting essentially of chromium diboride bonded by said boron substance.

8. In an article as claimed in claim 2, the homogeneous material of said surface region consisting essentially of the diboride of zirconium bonded by said boron substance.

9. In an article as claimed in claim 2, the homogeneous material of said surface region consisting essentially of the diboride of titanium bonded by said boron substance.

10. In an article as claimed in claim 2, the homogeneous material of said surface region consisting essentially of tantalum diboride bonded by said boron substance.

11. In an article as claimed in claim 2, the homogeneous material of said surface region consisting essentially of chromium diboride bonded by said boron substance.

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