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HOT STRENGTH CORROSION-RESISTANT CEMENTED REFRACTORY BORIDE MATERIALS AND THEIR PRODUCTION

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This invention relates to refractory composition 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.

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 and 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 in a ball mill until the desired thorough mixture of an average particle size of about 3 microns was obtained. The powder mixture was then filtered, washed and dried. 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 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

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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 temperature below about 950° C. is caused by the development of 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.

The present invention is based on the discovery that the borides of cobalt, nickel, and iron, without or with admixture of boron, substances which lack ductility, and have not been considered as metals, constitute unusually effective addition substances 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 having as the principal ingredient a refractory boride or borides of zirconium, vanadium, niobium, tantalum and also of chromium, molybdenum, and tungsten.

The present invention is based on the discovery that sintered cemented structural materials combining as principal ingredients, particles of refractory metal borides of the group of metals consisting of zirconium, vanadium, niobium, tantalum, which belong to the fourth and fifth group of the periodic system, and also of chromium, molybdenum and tungsten, with the addition of a less refractory boride of cobalt, titanium, nickel and/or iron, without or with a further addition of an excess of boron, has unexpected great hot-strength and corrosion-resistance. Desirable cemented refractory structural material may be produced with the addition of such less refractory boride varying between about 3% to 35% of the composition, and without or with the further addition of boron between about 2% to about 7% of the composition, providing that, if the boron is added, the total of the addition ingredients should not exceed about 25% of the composition.

However, cemented refractory boride bodies of the invention having particularly desirable characteristics are obtained by confining the proportions of the addition substances to a more limited range, namely, the addition of the less refractory boride to from 5% to 20% of the composition, and of boron, if it is added, to from 2% to 7% of the composition, in which case the total of the addition ingredients should be confined to from 10% to 20% of the composition and the excess boron up to 7% of the composition. In general, satisfactory results are obtained with the more refractory boride forming 97 to 65% and the less refractory boride forming 3 to 35% of the composition. Satisfactory results are also obtained with the more refractory boride forming 5 to 25% of the composition. Satisfactory results are also obtained with the more refractory boride forming 90 to 80% and the less refractory boride forming 10 to 20% of the composition.

The borides most suitable for cemented refractory compositions of the invention as principal ingredients, are the borides of zirconium, vanadium, niobium and tantalum. These metals form with boron, interstitial phases of the form MB₂, wherein M represents the metal. There are also available other borides which are very suitable for refractory compositions of the invention—for instance, chromium boride, tungsten boride, and molybdenum boride. Solid solutions of such refractory borides are likewise suitable for cemented refractory boride compositions of the present invention. Such solutions of the different borides may be produced either by heating an intimate mixture of the different borides under a pro-

protective atmosphere at high temperatures, or by simultaneously producing the different borides at high temperatures. This may be accomplished, for instance, by simultaneous reduction of the metals, the borides of which are to be produced. Furthermore, the powder particles of the different metals may be mixed with the addition substance in the manner described above, and the solid solution of the mixture of the different borides may be formed in the process by compacting and sintering the mixture of the powder particles into a cemented refractory structure by hot-pressing, without or with a follow-up sintering operation. To simplify the hot-pressing treatment it may be preceded by cold-pressing the powder mixture in the die in which it is hot-pressed. In the hot-pressing treatment, the length of the sintering operation, and the temperature at which it is carried out, and at which a liquid phase exists, will control the formation of the desired solid solutions of the different borides.

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

The foregoing and other objects of the invention will be best understood from the following more detailed description thereof.

In producing corrosion-resistant hot-strength cemented hard metal borides of the invention, it is desirable that the hard metal boride particles should be comminuted to a great degree of fineness, such as an average particle size of 1 to 2 microns, and that the comminution of the boride particles should be effected under conditions which prevent oxidation of the particles. If the refractory metal boride particles are of a size materially larger than about 3 microns, such as 5 microns or more, the cemented material has somewhat poorer physical characteristics. A very effective way for producing the fine boride particles is ball-milling the particles under an oxidation suppressing cover, such as a bath of purified saturated hydrocarbons, such as mineral oil, within an atmosphere of inert gas such as argon, maintained within the mill space at a small positive pressure.

It is desirable that the ball-milling should be carried on in a mill having an interior surface or lining and balls of material having the same composition as ingredients of the particles which are milled. If a steel mill and steel balls are used, the ferrous impurities should be removed after the milling by a treatment such as leaching with sulphuric acid diluted with water in concentration between 1:20 to 1:40.

Before leaching, the ball-milled powder should be cleaned of oil by diluting it with an agent such as ether, acetone, or alcohol, followed by filtering.

The milled powder from which the ferrous particles have been removed is then washed with a volatile agent, such as alcohol or ether, and dried.

The fine dried refractory boride powder constituting the principal ingredient, is then mixed with the addition ingredient or ingredients, to wit, the fine dried cobalt boride powder without or with the fine dried boron powder, each powdered ingredient having been previously purified and comminuted to the desired fine minute size of about 2 microns or less. However, since cobalt boride has lesser hardness than the more refractory borides, such as zirconium boride, it is sufficient to comminute the cobalt boride ingredient to an average particle size of only minus 50 mesh before adding it to the other ingre-

dients for mixing and reducing all particles of the mixture to about 2 microns or less.

The desired intimate mixture of the different powdered ingredients may be secured by subjecting the powdered mixture mass to ball-milling for a sufficient length of time, such as two or more hours to secure an intimate mixture of the different powdered ingredients and their comminution to about 2 microns or less. The ball-milling to mix is carried on in a ball mill under an oxidation suppressing cover with purified mineral oil within an atmosphere of argon. The oil is then removed from the ball-milled powder mixture and the mass of the fine powder mixture is then leached to remove iron impurities, washed and dried. The ball-milling operations for reducing the size of the particles of the different ingredients and for effecting the intimate mixture of the different powdered ingredients may be carried on within a bath of water, instead of mineral oil, in which case, however, the resulting powder mixture will exhibit poorer characteristics.

A very effective way for producing shaped bodies out of compositions of the invention is by hot-pressing the hard powder mixture at a temperature within the die from about 1200° to 2500° C., with a pressure from about .5 to 3.5 t. s. i. for about one-half to five minutes. By hot-pressing such powder mixtures with graphite dies, the sintered material is maintained in an atmosphere consisting predominantly of carbon dioxide, thus preserving it against oxidation. The sintering should be carried on at a temperature at which a liquid phase is formed, so that the combined pressing and sintering operation takes place in the presence of a liquid phase. To simplify the hot-pressing treatment, it may be preceded by cold-pressing the powder mixture in the die in which it is then hot-pressed.

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.

Any of the known procedures for producing refractory borides may be used in providing the refractory borides for cemented refractory compositions of the invention. Thus, the desired refractory metal boride may be produced by heating, as by induction within a graphite crucible, the oxide of the desired metal, together with boron oxide B_2O_3 and carbon, to produce the desired refractory metal boride by carbon reduction.

The desired refractory metal boride may also be produced by heating the metal constituent and boron within a crucible under a protective cover which prevents oxidizing, carburizing, or nitriding of the contents. The desired refractory metal boride may also be produced by aluminum thermite reduction of the metal oxide and of boron oxide B_2O_3 .

The metal boride powder of 98% to 99% purity is ball milled to size under a cover of purified mineral oil in an atmosphere of purified argon to reduce the powder particles to an average size of about 2 microns, or in general, of the order of 1 to 2 microns. If the ball-milling to size is carried on in a steel ball mill, the ball milled powder particles are subjected to a leaching treatment with very dilute sulphuric acid in a concentration of 1 to

30 for dissolving the iron contents, whereupon the powder is washed with water, followed by washing with alcohol, and drying. Good results are obtained by ball-milling to size with a steel mill.

In general, the same procedure is followed in producing the different refractory metal boride powders, in a form suitable for use in the refractory cemented compositions of the invention by substituting the oxide of the desired other metal for zirconium oxide.

The purified minute refractory boride powder particles which constitute the principal ingredient, and the purified comminuted minute cobalt boride particles of the addition substance, without or with the addition of minute fine boron particles, are then mixed to provide an intimate mixture of the fine particles of the different ingredients having an average particle size of about 2 microns or less. The mixing of the different ingredients may be effectively carried out by ball-milling under an oxidation suppressing cover such as purified mineral oil within an inert atmosphere of purified argon. The ball milled mass of the mixed powdered ingredients is then cleaned of the oil by filtering, and then leached, washed with alcohol and dried. The resulting mass of mixed loose minute particles of the principal boride ingredient, the cobalt boride ingredient, and of boron, if it is used as an ingredient, is then ready for compacting and sintering treatments by which a mass of the powder mixture is formed into a hard refractory structural material or body of the invention, having the desired shape.

Cemented hard, dense refractory metal boride structures of the invention having great hot-strength and corrosion-resistance may be produced from a mass of such fine loose powder mixtures by hot-pressing within graphite dies. To this end, the loose powder mixture of the fine powder particles is filled into a graphite die and hot-pressed at pressures ranging from .5 to 5.5 t. s. i. at temperatures from 1200° to 2500° C. for several minutes. It is also good practice to produce such cemented bodies by subjecting a mass of the powder mixture to successive compacting and sintering operations at successively higher temperatures as the compacted body is given its final desired shape of the required dimension. It is thus possible to obtain refractory cemented boride structures of unusually high strength, density, and hardness, which also exhibit high corrosion-resistance.

Cemented refractory boride bodies produced by the hot-pressing procedure described above may be subjected to a further sintering treatment at temperatures in the range from about 1800° to 2400° C. within a protective atmosphere, such as vacuum, super-dry purified hydrogen, or purified cracked ammonia, for improving the properties of the cemented body.

Cemented hard, dense boride structures of the invention may also be produced from a mixture of such fine loose powder particles prepared in the manner described above, by cold-pressing, followed by a sintering treatment. The cold-pressing of the powder mixture into the desired shape may be effected in a steel die at room temperatures with pressures from 2 to 35 t. s. i. The compact is then sintered at a temperature ranging from 1800° to about 2400° 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 of the powder compacted mass, or by direct conduction heating. The sintering of the compacted mixture of minute powder particles of the several ingredients is carried on at such temperatures as to cause a formation of a liquid phase in the compact.

Without in any way limiting the scope of the invention, but in order to enable those skilled in the art to readily practice the same, there will now be described more specific examples of practical applications thereof.

Thus, in producing cemented refractory boride materials of the invention with zirconium boride as the principal ingredient, the mass of the powder mixture of

zirconium boride powder with the powdered addition of cobalt boride was hot-pressed within a graphite die which was heated by direct electric current applied to the graphite die and the compacted powder mixture by copper electrodes directly connected to and engaging the graphite die.

Example I

A powder mixture of 85% zirconium boride and 15% cobalt boride, hot-pressed with 3.5 t. s. i. pressure at a temperature of 2050° C. for about one minute gave a cemented body of the following characteristics: Modulus of rupture 125,000 p. s. i.; Rockwell A hardness 89; density, 5.0 g./cc.; and electrical resistivity, 60 microhms-cm.

Cemented refractory boride bodies of the invention made with powder mixtures containing only 5% cobalt boride, and with powder mixtures containing 20% and 25% cobalt boride, balance zirconium boride, have generally similar, but slightly inferior physical characteristics. Cemented bodies made of powder mixtures containing cobalt boride in amounts of more than 25% and less than 5% of the total composition of the body, balance zirconium boride, have generally similar, but somewhat more inferior physical characteristics.

Similar cemented bodies of the invention containing 85% zirconium boride as the principal ingredient, and 10% cobalt boride with 5% boron as additional ingredients, have physical characteristics generally similar to a body containing only 15% cobalt boride as an addition ingredient, being however, slightly inferior to the latter body. In general, cemented bodies of the invention containing a supplemental addition of boron in addition to cobalt boride are somewhat inferior in physical characteristics to bodies in which the entire amount of the addition substance is formed by cobalt boride.

In producing cemented refractory boride material of the invention with zirconium boride as the principal ingredient, the mass of the powder mixture of zirconium boride powder with the powdered addition of titanium boride was hot-pressed within a graphite die which was heated by direct electric current conduction supplied to the graphite die and the compacted powder mixture by copper electrodes directly connected to and engaging the graphite die.

Example II

A powder mixture of 85% zirconium boride and 15% titanium boride, hot-pressed with 3.5 t. s. i. pressure at a temperature of 2050° C. for about one minute, resulted in a cemented body of the following characteristics: Modulus of rupture 90,000 p. s. i.; Rockwell A hardness 88; density 4.2 g./cc.; electrical resistivity 60 microhms-cm.

Similar bodies made in the same way of a powder mixture containing 90% zirconium boride and 10% titanium boride, and of a powder mixture containing 80% zirconium boride and 20% titanium boride, had somewhat inferior physical characteristics than the body made of 85% zirconium boride and 15% titanium boride.

Cemented refractory boride bodies of the invention made in the same manner with powder mixtures containing 20% and 25% titanium boride, balance zirconium boride, had generally similar, but somewhat more inferior physical characteristics.

Similar cemented bodies of the invention containing 85% zirconium boride as the principal ingredient, and 10% titanium boride, with 5% boron as additional ingredient, had physical characteristics generally similar to a body containing 15% titanium boride, as an addition ingredient.

In order to improve the hot-pressed cemented refractory boride bodies of the examples of the invention described above, they may be subjected to an additional sintering treatment at temperatures in the range from 800° to 2400° C. in a vacuum furnace within a protective

atmosphere such as purified hydrogen. The sintering is carried on at a temperature at which a liquid phase exists.

Similar cemented bodies of a mixture of zirconium boride powder and titanium boride powder in the proportions given above, without or with an addition of boron, may also be produced by cold-pressing, followed by sintering at an elevated temperature of about 1800° to 2400° C. within a protective atmosphere, such as purified dry hydrogen, or purified cracked ammonia. By way of example, a powder mixture containing 85% zirconium boride and 15% titanium boride, compacted at room temperature in a steel die with 15 t. s. i., and then sintered at 2400° C. in a protective atmosphere for six hours, resulted in a body having physical characteristics of the same order, but somewhat inferior to those exhibited by the corresponding hot-pressed body.

Each of the cemented refractory boride compositions of the invention of the type described above has a relatively high electrical conductivity compared with known prior art cemented hard refractory bodies. The higher electrical conductivity of such bodies of the invention, and their correspondingly high heat conductivity contributes to their great practical value in applications such as gas turbines, where they are exposed in operation to high temperatures.

When the mixture of the mass of the refractory metal boride particles constituting the principal ingredient together with powder of a boride of cobalt, titanium, nickel and iron without boron powder as an addition substance, is subjected to compacting and sintering treatments to produce cemented refractory bodies of the invention such as represented by the examples given above, liquid phases are formed during sintering at high temperature. As a result, the cemented body so produced may not actually constitute a composition containing the mixture of the original ingredients out of which it was formed, but rather a system combining the constituents of the principal refractory boride ingredient with the constituents of the addition substances bound in a unique way which is effective in giving the resulting cemented body its unusual physical characteristics. Thus, by way of example, in case of a cemented refractory body produced in accordance with the invention out of a mixture of zirconium boride and titanium boride powder particles, hot-pressed with 3.5 t. s. i. pressure, at a temperature of 2050° C., such cemented body constitutes a system of zirconium, titanium and boron, in which these constituents are present in proportions corresponding to the mixture of the zirconium boride and titanium boride powder particles out of which the cemented body was formed.

Refractory bodies made out of one or more of the other principal refractory boride ingredients, to wit, a boride or borides of vanadium, columbium, tantalum, chromium, molybdenum and tungsten, with an addition of a less refractory boride of cobalt, titanium, nickel and/or iron, without or with a further addition of boron, may be produced in the same way as the examples described above, and they have physical characteristics of the same order.

The same applies to cemented bodies made with solid solutions of the different boride ingredients without or with the boron addition.

As explained above, such cemented refractory boride bodies of the invention may be made by combining 3% to 35% of either cobalt boride or titanium boride, or nickel boride, or iron boride, or mixtures thereof, with the refractory borides constituting the principal ingredients. Where boron is included as an addition substance, desirable bodies may be made by including boron in an amount of 2% to 20% of the total composition provided the total amount of the addition substance does not exceed about 25% of the total composition. However, cemented refractory bodies of superior physical characteristics are obtained by confining the amount of

the addition substance to a more limited range, namely, the addition boride substance to from 10% to 20% of the composition, and where a boron addition is used, the added boron should be confined to from 5% to 15% of the composition, in which case the combined amount of the addition substance, to wit, the total amount of the boride addition and of the boron addition should be confined to from 10% to 20% of the total composition.

The novel principles of the invention will suggest various modifications thereof, and it is accordingly desired that the invention shall not be limited in any way to any of the specific exemplifications described herein.

This application is a continuation-in-part of applications Serial Numbers 170,241 and 170,242 both filed June 24, 1950 and both now abandoned.

I claim:

1. A hard, substantially homogeneous solid material consisting essentially of cemented particles of a major ingredient and of an addition ingredient mixed therewith and compacted under pressure and heated at an elevated temperature between about 1200° C. and 2500° C. at which a liquid phase is formed of the substance of at least said addition ingredient, said major ingredient constituting 97% to 65% of said material and consisting essentially of at least one boride of at least one metal of the class consisting of zirconium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten, said addition ingredient constituting 3 to 35% of said material and consisting essentially of a less refractory boride of the class consisting of cobalt boride, titanium boride, nickel boride and iron boride, said material constituting a system combining the chemical elements out of which said ingredients are constituted in proportions in which they are present in said ingredients.

2. A hard substantially homogeneous solid material consisting of cemented refractory boride particles forming 97% to 65% of said material and selected from the class consisting of borides of zirconium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten and mixtures of at least two of said borides, said refractory boride particles being bonded by a solidified bonding phase forming 3 to 35% of said material and formed of a boride of at least one metal selected from the class consisting of cobalt, titanium, nickel and iron and having a lower melting temperature than said refractory borides.

3. The method of manufacturing hard corrosion-resistant material, which comprises providing an intimate mixture of more refractory boride particles selected from the borides of at least one metal of the group consisting of zirconium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten, together with less refractory boride particles selected from the group consisting of the borides of cobalt, titanium, nickel and iron, the more refractory particles forming 97% to 65% and the less refractory particles forming 3% to 35% of said mixture, compacting said mixture under pressure and heating the compacted mixture of said particles at an elevated temperature between 1200° C. and 2500° C., at which a liquid phase is formed of at least some of the substance of said less refractory boride particles, and thereafter cooling the heated particle mixture to a lower temperature at which said liquid phase is solidified and bonds the refractory particles into a hard material.

4. A material as claimed in claim 1, the major ingredient consisting essentially of zirconium boride.

5. A material as claimed in claim 4, the addition ingredient consisting essentially of cobalt boride and forming at most 25% of said material.

6. A material as claimed in claim 1, the major ingredient consisting essentially of zirconium boride, and the additional ingredient consisting essentially of titanium boride and forming at most 25% of said materials.

7. The method as claimed in claim 3, the more re-

fractory boride consisting essentially of zirconium boride, and the less refractory boride consisting essentially of cobalt boride and forming at most 25% of said material.

8. The method as claimed in claim 3, the more refractory boride consisting essentially of zirconium boride, and the less refractory boride consisting essentially of titanium boride and forming at most 25% of said material.

9. A hard, substantially homogeneous solid material consisting essentially of cemented particles of a major ingredient and of an addition ingredient mixed therewith and compacted under pressure and heated at an elevated temperature between about 1200° C. and 2500° C. at which a liquid phase is formed of the substance of at least said addition ingredient, said major ingredient

constituting 97% to 65% of said material and consisting essentially of at least one boride of at least one metal of the class consisting of zirconium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten, said addition ingredient constituting 3% to 35% of said material and consisting essentially of at least one less refractory boride of the class consisting of cobalt boride, titanium boride, nickel boride and iron boride.

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