COMPOSITE MATERIALS CONTAINING CEMENTED CARBIDES

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FIG. 1.

FIG. 2.

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The present invention relates to hard metal carbides and is particularly concerned with improved composite materials produced by the infiltration of cemented hard metal carbide particles with metallic binders.

Composite materials containing particles of cemented tungsten carbide or a similar hard metal carbide bonded together by a softer binder have been used in the manufacture of oil field drill bits, machine tools and similar articles. Such materials are normally produced by placing chips or similar particles of the cemented carbide in a suitable mold, adding particles of a binder metal capable of wetting the carbide particles in the molten state, and thereafter heating the mold and its contents to an infiltration temperature above the melting point of the binder metal. As it approaches this temperature, the molten binder flows downwardly into the interstices between the carbide particles. An alloying of the binder metal and the particles takes place at the particle surfaces, resulting in the formation of a metallurgical bond as the binder cools and solidifies. The product thus obtained consists of a mass of closely-spaced cemented carbide particles bonded together by a continuous binder phase. Experience has shown that materials produced in this manner are useful in a variety of applications requiring high strength and resistance to abrasion and erosion.

One disadvantage of composite materials produced by the infiltration of cemented carbide particles with metallic binders as described above is that the cemented carbides are degraded to some extent during the infiltration process. This degradation, apparently due to interactions between the cemented carbide and molten binders at high temperatures, is evidenced by the formation of a reaction zone or "halo" near the periphery of each particle. Microhardness studies and other metallographic tests have shown that this reaction zone is significantly softer than the initial cemented carbide and that its formation reduces the effective amount of cemented carbide present in the composite material. Some softening at the center or "core" of each carbide particle also generally occurs. Efforts to avoid such degradation and thus improve the properties of composite materials containing the cemented carbides have in the past been only partially successful.

It is therefore an object of the present invention to at least partially overcome difficulties encountered in the past due to the degradation of cemented carbide particles during the infiltration of such particles with metallic binders. Another object is to provide a method for the production of composite materials containing cemented carbide particles which does not result in substantial softening of the carbides. A further object is to produce an improved composite material containing cemented carbide particles and a metallic binder which is harder and has greater resistance to erosion and abrasion than composite materials available heretofore. Still another object is to overcome the disadvantages of the invention as described in greater detail hereinafter.

In accordance with the invention, it has been found that composite materials significantly harder and more resistant to erosion and abrasion than materials available in the past can be produced by the infiltration of particles of cemented tungsten carbide or a cemented tungsten carbide alloy with a molten binder alloy which contains a metal from Group VIII, Series 4 of the Periodic Table as the major constituent and includes lesser amounts of boron and chromium. Tests have shown that the use of such binders eliminates the softening of cemented carbide particles during infiltration and that the particles contained in the resultant composite materials are instead considerably harder than the cemented carbides employed initially. This hardening of the particles, which may be due in part to the formation of ternary carbides during infiltration, significantly improves the properties of composite materials containing such particles.

The nature and objects of the invention can best be understood by referring to the following detailed description of the constituents employed and the process used for producing the improved composite materials and to the accompanying drawing, in which:

FIGURE 1 is a reproduction of a photomicrograph showing the structure of a composite material produced by infiltrating cemented tungsten carbide particles with a conventional binder having a high nickel content; and

FIGURE 2 is a reproduction of a photomicrograph showing the structure of a composite material produced in accordance with the invention.

The cemented hard metal carbide particles employed in carrying out the invention are particles of cemented tungsten carbide or cemented particles of a mixed carbide containing lesser amounts of titanium, tantalum carbide, niobium carbide or the like in addition to the tungsten carbide. Such materials are normally produced by sintering a mixture of finely divided carbide powder and powdered iron, nickel or cobalt at elevated temperature and high pressure. Commercially available cemented carbides normally contain from about 1 percent to about 25 percent of cobalt or a cobalt alloy including small amounts of iron or nickel as the cementing metal. Carbides having very low cementing metal contents are often quite brittle; while those containing the cementing metals in large quantities are frequently excessively soft. The use of cemented tungsten carbide containing from about 4 percent to about 12 percent cobalt is normally preferred for purposes of the invention because of its high strength and extreme hardness.

The size of the cemented carbide particles employed in producing the composite materials of the invention will generally range between about $\frac{1}{32}$ and about $\frac{1}{8}$ inch along their major dimension. For rotary drill bits and similar tools, particles between about 0.05 inch and about 0.25 inch are preferred. Cemented carbide particles of suitable size are available commercially in various forms. Angular particles or chips produced by fracturing larger pieces of cemented carbide will normally be used but in some cases particles of regular shape, cubes for example, may be employed.

The metallic binders employed with the carbide particles to produce the improved composite materials of the invention are alloys melting between about 1750° F. and about 3000° F. which contain one or more metals from Group VIII, Series 4 of the Periodic Table as the major constituent, from about 0.5 to about 10 percent by weight of boron, and from about 0.1 percent to about 25 percent by weight of chromium. Alloys containing at least 50 percent by weight of iron, nickel, cobalt or a combination of these metals have the ability to wet the hard metal carbide particles in the molten state and hence
can be infiltrated into interstices between the particles. The chromium and boron, as pointed out earlier, result in hardening of the particles during infiltration. In addition to these metals, the binder alloys may contain lesser amounts of copper, tin, manganese, silicon, cadmium, beryllium, bismuth, carbon, silver, aluminum and other constituents in quantities sufficient to reduce the alloy melting point, increase the hardness of the binder metal, or improve the infiltration characteristics of the molten alloy. A variety of commercially available alloys containing iron, nickel or cobalt as the major constituent, "S-Monel" and similar nickel alloys for example, can be modified by the addition of boron and chromium in the required amounts and employed for purposes of the invention.

Typical alloys which may be employed as binder metals for infiltration purposes include (a) iron—90.6%; carbon—2.8%; boron—1.9%; chromium—4.7%; (b) iron—52.0%, chromium—24.4%, nickel—18.5%, silicon—1.9%, carbon—0.2%, boron—2.4%; (c) iron—75.5%, nickel—14.3%, chromium—2.4%, silicon—2.9%, carbon—0.6%, boron—4.3%; (d) iron—58.0%, nickel—32.7%, chromium—4.5%, boron—4.6%; (e) iron—12.5%, chromium—5.0%, boron—1.3%, silicon—4.7%, carbon—0.0%, nickel—5.0%, chromium—68.67%; (f) iron—0.6%, chromium—2.5%, boron—0.6%, silicon—0.6%, carbon—0.5%, copper—26.25%, tin—7.5%, nickel—61.9%; (g) nickel—62.75%, iron—2.0%, chromium—8.5%, boron—2.5%, silicon—0.5%, tin—5.0%, copper—17.5%; (h) nickel—50.75%, iron—1.0%, silicon—1.0%, carbon—0.25%, copper—26.25%, tin—7.5%, iron—1.0%, chromium—4.25%; (i) nickel—51.0%, copper—19.0%, chromium—18.0%, tin—5.0%, boron—2.0%, silicon—2.0%, iron—1.25%, molybdenum—1.5%, carbon—0.25%; (j) nickel—58.02%, copper—27.0%, tin—7.5%, chromium—4.0%, boron—1.0%, silicon—1.0%, molybdenum—0.75%, iron—0.6%, carbon—0.13%; (k) nickel—40.99%, cobalt—20.0%, copper—17.5%, chromium—9.5%, tin—5.0%, molybdenum—3.0%, silicon—2.0%, boron—1.5%, carbon—0.01%, iron—0.5%; (l) nickel—48.99%, copper—25.25%, cobalt—10.0%, chromium—4.75%, boron—0.75%, iron—0.25%, silicon—1.0%, tin—7.5%, molybdenum—1.5%, carbon—0.01%; (m) nickel—65.75%, copper—16.5%, chromium—8.0%, silicon—4.0%, boron—0.25%; (n) nickel—64.87%, copper—23.25%, chromium—4.0%, silicon—4.0%, iron—2.0%, boron—1.0%, molybdenum—0.75%, carbon—0.13%; (o) nickel—82.35%, chromium—10.0%, iron—2.5%, boron—2.5%, silicon—2.5%, carbon—0.15%; (p) nickel—70.5%, chromium—17.0%, boron—4.0%, iron—4.0%, boron—3.5%, carbon—1.0%; (q) nickel—68.0%, chromium—16.0%, boron—4.0%, silicon—3.0%, copper—3.0%, molybdenum—3.0%, iron—2.5%, carbon—0.5%; (r) cobalt—40.0%, nickel—27.1%, chromium—18.5%, molybdenum—6.0%, silicon—4.0%, boron—3.0%, iron—1.0%; (s) nickel—80.0%, boron—1%, carbon—0.1%, chromium—1.5%, silicon—0.5%, molybdenum—4.7%, tin—5.7%; (t) copper—25.0%, nickel—40.0%, boron—2.0%, carbon—0.5%, chromium—20.0%, silicon—1.5%, iron—5.0%, molybdenum—6.0%; (u) nickel—60.0%, copper—15.0%, boron—4.0%, carbon—0.1%, chromium—10.0%, silicon—3.0%, iron—0.5%, molybdenum—0.8%, tin—6.6%; (v) cobalt—1.3%, chromium—47.0%, chromium—16.9%, copper—21.6%, carbon—2.4%, silicon—4.8%, tin—5.5%; (w) nickel—71.0%, chromium—19.8%, silicon—3.5%, boron—3.2%, iron—1.5%, carbon—1.0%; (x) nickel—82.5%, chromium—9.85%, tin—5.0%, boron—2.5%, carbon—0.15%; (y) cobalt—37.5%, nickel—29.5%, chromium—17.0%, iron—2.5%, silicon—4.0%, boron—3.5%, molybdenum—6.0%.

It will be understood that the compositions set forth above are typical of the alloys employed for purposes of the invention but that other compositions melting at temperatures in the range between about 1750°F. and about 3000°F. which contain a metal from Group VIII, Series 4, of the Periodic Table as their major constituent, include from about 0.5 to about 10 percent by weight of molybdenum and about 75 percent by weight of chromium may also be used.

Before the cemented carbide particles and metallic binders described above are employed for production of the composite materials, the particles are preferably first cleaned with dilute nitric acid and alcohol or similar solvents to remove dust, oils and other foreign matter. The particles are then placed in a clean carbon or ceramic mold of the desired shape. The use of a carbon mold is generally preferred in order to insure a reducing atmosphere during infiltration. The particles are generally placed in the mold in random fashion but in some cases, particularly where cubes or other regularly-shaped particles are used, they may be oriented with respect to the outer surface of the tool or article to be produced. Diamonds may be included by gluing or otherwise affixing them to the inner surface of the mold before the carbide particles are added.

The cemented carbide chips or similar particles are often utilized in conjunction with tungsten carbide powder or a powdered mixed carbide alloy in order to strengthen the matrix between the particles in the finished composite material. The powder employed will preferably range between about 100 mesh and about 400 mesh on the Tyler screen scale. Commercially available powder produced by crushing and milling larger pieces of cast or sintered tungsten carbide or a suitable mixed carbide may be used. Spherical powder obtained by melting the carbide in an electric arc or similar apparatus and then rapidly cooling the resulting spherical granules is also suitable. The mold may be vibrated as the powder is added in order to obtain a dense mass or may instead be pressed at a pressure from about 100 to about 200 p.s.i. in order to assure close packing of the powdered granules within the interstices between the cemented carbide chips or particles. This is seldom necessary where spherical powder is used because the spherical granules readily flow into very small cavities. If desired, the carbide powder employed may be mixed with up to about 35 percent by weight of powdered nickel in order to improve wetting of the powder by the infiltrant metal and to compensate for differences in the coefficients of thermal expansion of the carbide and steel or other materials. The use of powdered carbide and nickel is not essential, however, and in many cases it will be preferred to employ only chips or similar particles of cemented hard metal carbide.

Following placement of the cemented carbide chips or other particles and the powder in the mold, pellets of the matrix alloy to be employed may be placed in the mold above the carbide. A mold having a lower section in which the carbide is placed and an upper section or cover in which the binder metal is held is often used. Such molds normally contain openings through which the binder metal may flow downwardly into the interstices between the carbide particles as it melts. An alternate procedure is to heat the binder metal in a crucible or other vessel apart from the mold and then pour it into the mold after the already desired infiltration temperature has been reached. This latter procedure generally permits better control of the infiltration conditions and is preferred. The assembled mold is normally preheated at a temperature between about 300°F. and about 600°F. for an hour or longer in order to eliminate gases. Following this preheating step, the assembled mold and crucible, if used, are placed in a furnace and heated to an infiltration temperature above the melting point of the binder alloy. The temperature employed should not greatly exceed that required for rapid infiltration of the molten binder metal into the inter-
teristics between the particles. The required temperature will depend largely upon the particular binder metal used. Infiltration temperatures from about 100 to about 200° F. above the melting point of the binder are generally satisfactory. The necessary temperature for a particular binder alloy can readily be determined by preparing small specimens containing the binder alloy and the carbide particles to be used, and pouring the molten alloy into the molds at various temperatures. Examinations of the resultant specimens after they have cooled will clearly show whether infiltration took place at the temperatures selected.

After the carbide particles and binder metal in the mold have reached the desired temperature the molten binder metal has been poured from the crucible or other vessel into the mold at this temperature, the mold is held in the furnace for a period of from about 1 minute to about 30 minutes. Furnace periods between about 3 minutes and about 20 minutes are preferable. During this period, the molten binder alloy flows into the interstices between the carbide particles and alloys with the particles. Thereafter, the mold is removed from the furnace and allowed to cool. It is generally preferred that the mold and its contents be cooled quickly to a temperature and other tools which make an extremely hard outer surface resistant to abrasion and erosion. Care should be taken in fabricating such tools to avoid damage to the steel during the cooling step following infiltration. It is generally preferred to cool the mold and its contents rapidly and to use high temperature and high pressure to solidify the binder metal, about 1600° F. for example, and then slowly cool to room temperature. Slow cooling below the binder melting point avoids setting up undue stresses in the steel.

The improved properties of the composite materials of the invention are shown by the results of comparative tests carried out with metallurgical specimens prepared with a conventional binder alloy having a high nickel content and an alloy which contained nickel as the major constituent but also included small amounts of boron and chromium. The specimens tested were prepared by first placing chips of a commercially available cemented tungsten carbide containing 10% cobalt in carbon molds 3/4 inch in diameter and 1 inch long. The chips ranged in size between about 1/4 inch and about 3/4 inch along the longest dimension. Tungsten carbide powder between about 270 mesh and about 325 mesh on the Tyler screen scale was added to fill the spaces between the chips. One of the molds was then infiltrated with a nickel alloy containing about 55% nickel, about 35% copper and about 10% tin at a temperature of 2250° F. The second specimen was prepared with a binder alloy containing 58.85% nickel, 26.25% copper, 4.25% chromium, 0.87% boron, 1.0% iron, 0.25% carbon, 1.0% silicon, and 7.5% tin. The infiltration conditions and procedures used in preparing the two specimens were similar. After the specimens had cooled following infiltration, they were removed from the molds, cut, etched and polished to bring out the metallurgical structure. Microhardness tests were then carried out using a Knoop indenter and a weight of 1,000 grams in a conventional microhardness tester. Measurements were made across each specimen in order to determine the hardness of exposed chips at their centers and near their edges.

FIGURE 1 of the drawing shows a reproduction of a photomicrograph which shows the specimen prepared with the conventional binder. The dark area at the left side of the photomicrograph is the core of a cemented tungsten carbide chip, the intermediate zone is the halo in the outer portion of the chip, and the light area at the far right in the picture is the binder metal. Granules of tungsten carbide powder are visible in the binder. The diamond shaped areas shown in the picture are indentations made in determining the microhardness values of the specimen. The size of each indentation indicates the hardness at that particular point. It will be observed that the indentations in the halo are much larger than those in the core, showing that formation of the halo resulted in softening of the outer portion of the chip. The cemented tungsten carbide chips used in preparing this specimen had an initial hardness of 1287. Measurements with the microhardness tester following infiltration with the binder alloy gave a hardness value of 1302 at the center of the chip and values of 785, 781 and 804 in the halo at the edge of the chip. These results are typical of those obtained with conventional binders. A substantial softening normally occurs due to the formation of the halo. In many cases the halo may occupy 50% or more of the total chip volume and the major part of each chip in the composite material may be much softer than the cemented carbide initially employed.

The photomicrograph represented in FIGURE 2 of the drawing shows the structure of the specimen prepared in accordance with the invention with a nickel based binder alloy containing small amounts of boron and chromium. It can be seen from FIGURE 2 that the cemented carbide chips shown in this specimen do not have a halo but that the indentations made in determining the microhardness values were of about the same size at the center of the chip and in the halo. This indicates that the halo formed by the binder containing boron and chromium was considerably harder than that produced by the conventional binder. This was confirmed by the readings made with the testing apparatus. Knoop hardness values of 1358 and 1350 were obtained respectively at the center of the chip and in the halo near the edge of the chip. Since the initial hardness of the cemented tungsten carbide was again 1287 Knoop, it is apparent that the composition of the halo formed by the binder containing boron and chromium was different from that in the earlier specimen and that considerable hardening of the chip occurred. The harder chips thus obtained by using binders containing boron and chromium result in composite materials able to withstand more severe abrasion and erosion than materials produced by infiltrating cemented carbide chips in the past.

Following the test described above, additional specimens were prepared with the copper-nickel-tin binder and with other binders containing boron and chromium in various amounts. These specimens were prepared by infiltrating cemented tungsten carbide chips and carbide powder with the binder alloys in carbon molds in the manner described earlier. Infiltration temperatures between about 2275° F. and about 2600° F. were used. The results obtained in the earlier test and those obtained with the later specimen are shown in the following table.
It can be seen from the microhardness values in the above table that the use of binder alloys containing boron and chromium in addition to the metals from Group VIII, Series 4 of the Periodic Table resulted in a case in appreciable hardening of the cemented carbide chips. The chips after infiltration were significantly harder than the initial cemented carbide employed. The invention thus provides a means for avoiding the softening and degradation of cemented carbide chips during the infiltration of such chips with molten binder alloys and permits the production of composite materials which have greater resistance to wear and abrasion than those available in the past.

What is claimed is:

1. A process for the production of a composite material which comprises infiltrating a mass of discrete, closely-spaced, cemented hard metal carbide particles containing primarily of tungsten carbide with a molten binder alloy which melts at a temperature between about 1750° F. and about 3000° F. and which contains a metal from Group VIII, Series 4 of the Periodic Table as the major constituent, from about 0.5 to about 10% by weight of boron, and from about 1.0 to about 25% by weight of chromium.

2. A process for the production of a composite material which comprises infiltrating a mass of discrete, closely-spaced, cemented hard metal carbide particles containing primarily of tungsten carbide at the major constituent with a molten nickel alloy which melts at a temperature between about 1750° F. and about 3000° F. and contains from about 0.5 to about 10% by weight of boron and from about 1.0 to about 25% by weight of chromium.

3. A process for the production of a composite material which comprises infiltrating a compact of discrete cemented tungsten carbide particles between about 0.54 inch and about 0.54 inch in size and tungsten carbide powder granules with a molten binder alloy which melts at a temperature between about 1750° F. and about 3000° F. and contains from about 0.5 to about 10% by weight of boron and from about 1.0 to about 25% by weight of chromium.

4. A process for the production of a composite material which comprises preparing a mass of discrete, closely-spaced, cemented tungsten carbide chips between about 0.05 inch and about 0.25 inch in size and tungsten carbide powder; infiltrating said mass with a molten alloy which melts at a temperature between about 1750° F. and about 3000° F. and contains at least 50% by weight of nickel, from about 0.5 to about 10% by weight of boron, and from about 1.0 to about 25% by weight of chromium, and allowing said mass to cool.

5. A process for the production of a composite material which comprises preparing a mass of discrete, closely-spaced, particles of a cemented hard metal carbide containing primarily of tungsten carbide, said particles being between about 0.025 and about 0.25 inch in size; infiltrating said mass with a molten alloy having a melting point in the range between about 1750° F. and about 3000° F., said alloy containing at least 50% by weight of iron, nickel and cobalt, from about 0.5 to about 10% by weight of boron, and from about 1.0 to about 25% by weight of chromium; and cooling said solid mass to solidify said binder alloy.

6. A process for the production of a composite material which comprises packing discrete particles between about 0.05 and about 0.25 inch in size of a cemented hard metal carbide composed primarily of tungsten carbide into a refractory mold; heating said mold to a preselected infiltration temperature; pouring a molten alloy which melts at a temperature between about 175° F. and about 3000° F. and contains at least 50% by weight of a metal from Group VIII, Series 4 of the Periodic Table, from about 0.5 to about 10% by weight of boron, and from about 1.0 to about 25% by weight of chromium into said mold; holding said mold at said temperature for a period of from about 1 minute to about 30 minutes, and thereafter cooling said mold.

7. A process for the production of a composite material which comprises packing discrete cemented tungsten carbide particles between about 0.05 and about 0.25 inch in size of tungsten carbide powder grains into a refractory mold; heating said mold to a preselected infiltration temperature; infiltrating a molten nickel alloy which melts at a temperature between about 175° F. and about 3000° F. and contains at least 50% by weight of nickel, from about 0.5 to about 10% by weight of boron, and from about 1.0 to about 25% by weight of chromium into interstices between said cemented carbide particles and powder grains; holding said mold at said infiltration temperature for a period of from about 3 minutes to about 20 minutes; and thereafter cooling said mold and its contents.

8. A composite material comprising a plurality of closely-spaced cemented hard metal carbide particles between about 0.54 inch and about 0.54 inch in size metallurgically bonded within a metallic matrix containing an alloy which melts between about 1750° F. and about 3000° F. and includes a metal from Group VIII, Series 4 of the Periodic Table as the major constituent, from about 0.5 to about 10% by weight of boron, and from about 1.0 to about 25% by weight of chromium, said particles being composed primarily of tungsten carbide.

9. A composite material comprising a plurality of closely-spaced cemented tungsten carbide particles between about 0.05 inch and about 0.25 inch in size metallurgically bonded within a metallic matrix containing an alloy which melts between about 1750° F. and about 3000° F. and includes nickel as the major constituent, from about 0.5 to about 10% by weight of boron, and from about 1.0 to about 25% by weight of chromium.

References Cited in the file of this patent

UNITED STATES PATENTS
2,791,025 Ballhausuer -------------- May 7, 1957
2,791,026 Ballhausuer -------------- July 1, 1957
FOREIGN PATENTS
753,454 Great Britain ---------- July 25, 1956
OTHER REFERENCES