July 26, 1938. J. A. BOYER 2,124,538

METHOD OF MAKING A BORON CARBIDE COMPOSITION

Filed March 23, 1935

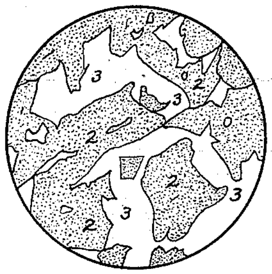

Figure 1

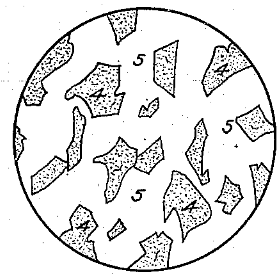

Figure 2

Figure 3

Figure 4

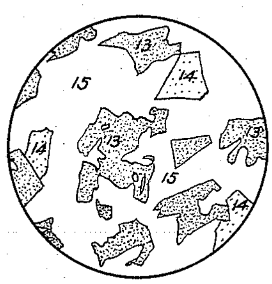

Figure 5

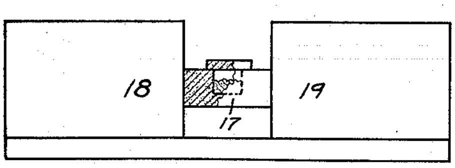

Figure 6

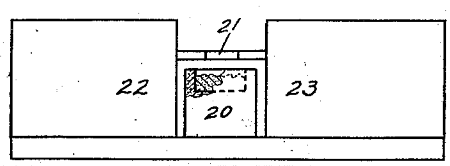

Figure 7

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METHOD OF MAKING A BORON CARBIDE COMPOSITION

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12 Claims. (Cl. 75—137)

This invention relates to metallic alloys containing boron and carbon, and particularly to alloys in which boron carbide separates as a crystalline phase from a melt containing one or more metals. The invention has for one of its objects the provision of a dense tough material having metallic properties, in which one of the constituents present is characterized by extreme hardness.

Boron carbide is one of the hardest materials known, and its hardness even exceeds that of silicon carbide and fused alumina, which are used extensively as abrasives. Although fused boron carbide is relatively tough in comparison with abrasives, it does not possess the mechanical properties ordinarily associated with metals, and in comparison with such materials as copper, nickel, and the common alloys of these metals, it is extremely brittle. Most metallic alloys, on the other hand, do not contain any constituent whose hardness even approaches that of boron carbide.

I have found that boron carbide will alloy readily with most common metals, and that the alloys produced contain an extremely hard constituent either interspersed with metal or embedded in a metallic matrix. In order to produce alloys of this type, mixtures of boron carbide and the metal used as the alloying ingredient are heated to a temperature sufficient to reduce the mass to a state of fluidity or fusion. The temperature required is comparatively high, and is usually in the vicinity of 2000° C. Upon cooling, the boron carbide separates as a crystalline phase, and the metal solidifies in the interstices between the boroncarbide crystals. If the quantity of metal present is sufficient to form a continuous matrix, the boron carbide occurs as small crystals, usually microscopic in size, distributed throughout a matrix of metal. A material of this character thus combines the hardness of the boron carbide crystals with the toughness and ductility of the metal forming the matrix.

The nature of the respective materials and their method of preparation will be more clearly understood from a consideration of the accompanying drawing.

In the drawing:

Figure 1 shows the microstructure of an alloy containing 50 percent boron carbide and 50 percent copper;

Figure 2 shows the microstructure of an alloy containing 20 percent boron carbide and 80 percent copper;

Figure 3 shows the microstructure of an alloy containing 40 percent boron carbide and 60 percent nickel;

Figure 4 shows the microstructure of an alloy containing boron carbide, nickel, and an excess of graphite;

Figure 5 shows the microstructure of an alloy of boron carbide and nickel which contains boron carbide and another crystalline constituent, presumably a boride of nickel, embedded in a metal matrix;

Figure 6 shows diagrammatically a type of furnace which can be used in making the alloys, and

Figure 7 illustrates diagrammatically a method of heating adapted to produce carbon free melts.

In the preparation of the alloys, I have found that copper, nickel, cobalt and iron will produce alloys of the type herein described. These metals have consecutive atomic numbers from 26 to 29 inclusive, and owing to their electronic structures have closely related physical properties. Silver and gold can also be employed for certain special applications, but in the case of silver it is advisable to apply pressure to prevent the volatilization of the metal. The metal forming the matrix can of course be toughened or hardened by any of the common alloying ingredients ordinarily used for such purposes. For example, if copper forms the base metal of the matrix, the copper can be alloyed with a small proportion of tin, aluminum or nickel. If a nickel matrix is employed, the nickel can be alloyed with copper or aluminum. In the drawing, typical structures are shown in which the metallic alloying ingredients are pure copper and pure nickel respectively, but it will be realized that alloy matrices or matrices of other metals can be used if desired.

Referring to Figure 1, the structure shown is that obtained by fusing a charge containing equal parts by weight of boron carbide and copper. When such a charge is heated until the mixture becomes fluid, the boron carbide apparently dissolves in the copper, and upon cooling, crystallizes as small crystals 2 dispersed throughout a copper matrix 3. This material has a structure similar to many bearing metals, in which microscopic crystals sufficiently hard to resist wear are embedded in a ductile matrix which imparts toughness, resilience and "workability" to the alloy. The boron carbide is, however, much harder and more resistant to wear than any metallographic constituent found in the usual bearing metals.

Figure 2 shows the structure of an alloy similar to that shown in Figure 1, but in which the copper content is increased to 80 percent by weight. This material can be cut and worked more readily than an alloy having a higher boron carbide content. In considering the metal content of these alloys, it will be understood that the percentage of metal by volume is very much less than the percentage by weight, owing to the great difference in specific gravities of the boron carbide and the metals used as alloying agents. In an alloy containing 50 percent copper, the metal is the continuous constituent, but it forms only a fairly thin network between the boron carbide crystals. In an alloy containing 80 percent copper, the boron carbide and the copper are in approximately equal proportions by volume, and the boron carbide crystals are uniformly scattered throughout the copper matrix, as will be observed in Figure 2. In this figure the boron carbide crystals 4 are embedded in a matrix 5 of copper.

Figure 3, which illustrates the structure of an alloy obtained by fusing together a charge containing 40 percent boron carbide and 60 percent nickel, shows a general similarity in structure to that obtained in the case of copper. The boron carbide crystals 6 are embedded in a metal matrix 7.

Figure 4 shows the structure of a nickel-boron carbide alloy prepared by heating the two materials to a high temperature in a graphite crucible. If a molten alloy of this composition is allowed to remain in contact with the graphite crucible for any appreciable time, the melt absorbs carbon, and on cooling, the mass is permeated by a considerable number of graphite flakes, so that the material has a graphitic structure very similar to grey cast iron. Such a material can be readily cut and worked, although it contains a high proportion by volume of boron carbide. In Figure 4 it will be observed that the graphite flakes 9 break up the structure of the alloy, in which crystals 10 of boron carbide are embedded in a metal matrix 11.

For purposes where toughness is a primary consideration, the graphite flakes can be eliminated by taking special precautions to prevent the absorption of carbon by the melt, and it is even possible to oxidize some of the carbon present so as to produce an alloy containing excess boron or a boride of the metal forming the matrix. The structure of such an alloy is shown in Figure 5, the ingredients of the alloy before fusion being boron carbide and nickel. There are two separate crystalline constituents embedded in the metal matrix; under the microscope both of these constituents are bluish grey, but differ slightly from each other in color. It will be realized that the exact identification of metallographic constituents in ternary alloys presents considerable difficulty, but as the alloy whose structure is shown in Figure 5 was made under conditions which partially oxidized the carbon of the boron carbide, the constituents embedded in the matrix are presumably boron carbide and a second constituent due to the presence of free boron in the melt, the constituent presumably being a boride of nickel. The boron carbide constituent is extremely hard, and can be polished with 400 grit silicon carbide paper on a rotating lap without scratching the boron carbide. In Figure 5 the boron carbide and the second constituent embedded in the matrix are designated by the numerals 13 and 14 respectively, whereas the metal matrix is designated by 15.

In making the alloys, magnesia crucibles or carbon containers lined with magnesia can be used. The absorption of carbon by the alloys can also be minimized or prevented by very rapid heating or by employing a resistor placed above the melt. This latter procedure can be used in conjunction with a magnesia lined crucible or container, or if the alloy is to be made in bulk without regard to the shape of the final product, the unmelted portion of the charge can form the container for the molten alloy. The heating of the charge from above eliminates the necessity of passing the heat through the container, and the crucible holding the melt can be maintained at a very much lower temperature than when all of the heat used for melting the alloy is passed through the container itself.

A method in which the alloy charge can be melted very rapidly so as to minimize contamination from carbon is shown diagrammatically in Figure 6. In the method illustrated a conductive crucible is used and the charge is melted by an electric current passed directly through the crucible. The crucible 17 containing the charge is placed between two large carbon electrodes 18 and 19 and is held in place by pressure applied horizontally against the end of one of the electrodes, the other electrode being rigidly fastened to a base or fixed support. An extremely heavy current of, for example, 5,000 to 20,000 amperes is passed through the crucible, and the charge is melted in a period of from a few seconds to approximately one minute. With extremely rapid heating and solidification, contamination from the carbon of the crucible is reduced to a minimum. A magnesia lining can be employed for the crucible if desired.

In Figure 7 the container 20 for the alloy charge is placed beneath a resistor 21, which is held in position between two large electrodes 22 and 23 in the same manner as the crucible described in Figure 6. The resistor is preferably constricted in its central portion so as to form an extremely hot zone immediately above the center of the charge. A heating current, preferably of several thousand amperes, is passed through the resistor so as to raise the highly heated zone of the resistor to a temperature of approximately 2500 to 3000° C. The charge is heated by radiation from the resistor, and as the container is shielded by the charge, it does not reach as high a temperature as the resistor. The heating process is preferably carried out in a non-oxidizing atmosphere, which can be attained either by enclosing the furnace within a carbon chamber or by surrounding the charge and the resistor with an inert gas. The crucible can be magnesia lined, or can be composed entirely of magnesia.

Heating can also be carried out by high frequency induction. If a conductive carbon crucible is used, the crucible should be lined with a refractory oxide (as for example magnesium oxide) or the heating carried out very rapidly to prevent contamination from carbon. An overhead resistor can also be heated inductively if desired.

Boron carbide substantially free from excess carbon or graphite can be used as a raw material in making the alloys. This material can be purchased on the open market, and is made by surrounding a carbon resistor with a mixture of anhydrous boric oxide and carbon in approximately the proportions of two molecular equivalents of boric oxide to seven atomic equivalents of carbon. The resistor is heated to a temperature somewhat in excess of 2500° C.; the mix shrinks away from the resistor during the formation of the boron carbide, and forms a fused "ingot" which does not come in contact with the resistor during fusion and solidification. The addition of kerosene to the raw mix facilitates the furnace operation. It is possible to produce the alloys by direct reduction of the metallic oxide and boric oxide in the proper proportions, using the process outlined above for the production of pure boron carbide. The alloys in crude or lump form can also be made by heating a mixture of boric oxide, the oxide of the metal desired in the alloy, and carbon in the proper proportions in a furnace of the overhead resistor type shown in Figure 7, using the unreduced portion of the charge, or preferably an unconverted mixture of bore oxide and carbon as a container for the melt. The raw oxide mix can also be reduced by this method while contained in a crucible or mold.

When alloys of the type herein described are reduced to granular form or to a powder, they can be molded to shape and sintered or the metal fused to form a metal bonded abrasive or wear resistant body. Such articles can be made with or without additional metal in powdered form to facilitate bonding. For this purpose it may be desirable to use a metal content in the fused alloy which is less than that required to give a continuous matrix. When the metal is once alloyed with the boron carbide by fusion at a high temperature, the crushed product can be self-bonded, sintered or partially fused at a relative low temperature, as for example, from 800° to 1400° C., depending upon the metal used for a bond, the pressure applied during bonding or sintering, and the time during which the sintering or bonding temperature is maintained.

The materials herein described when cast or formed into shaped articles have a number of abrasive and wear resistant uses, such as for laps, hones, articles subject to abrasion or wear, and similar applications. In using the materials as a lap or hone, it is possible to dress the surface and present fresh abrasive grains by immersing the article in an acid which will attack the metal matrix. In using the materials for bearing surfaces, the face of the alloy must of course be lapped and polished to prevent any abrading action on the part of the crystals of boron carbide embedded within the metal.

Having thus described my invention, I claim:

1. The method of making a metallic composition containing boron carbide crystals which comprises forming a mixture of solid boron carbide and a metal of the group of metals having atomic numbers from 26 to 29 inclusive, the quantity of metal in the said mixture being in the proportions to form a substantially continuous matrix upon fusion and solidification of the mixture, heating the said mixture until it becomes fluid, and thereafter cooling the resultant mass so as to cause crystallization of the dissolved boron carbide.

2. The method of making a composition containing boron carbide crystals separated by an interstitial metallic matrix, the said method comprising mixing solid boron carbide with approximately 50 per cent or more by weight of copper heating the resulting mixture until it becomes fluid, and thereafter cooling the fluid mass so as to cause crystallization of the dissolved boron carbide.

3. The method of making a composition containing boron carbide crystals separated by an interstitial metallic matrix, the said method comprising mixing solid boron carbide with approximately 50 per cent or more by weight of a metal of the group of metals having atomic numbers from 26 to 29 inclusive, heating the resulting mixture to a temperature above the melting point of the metal but below the melting point of the boron carbide until the mixture becomes fluid, and thereafter solidifying the fluid mass so as to cause crystallization of the dissolved boron carbide.

4. The method of making a composition containing boron carbide crystals separated by an interstitial metallic matrix, the said method comprising forming a mixture of solid boron carbide and a metal of the group of metals having atomic numbers from 26 to 29 inclusive, the said metal being in the proportions to form a substantially continuous matrix upon fusion and solidification of the mixture, heating the said mixture to a temperature of approximately 2000° C. or greater until the mixture becomes fluid, and thereafter solidifying the fused mixture so as to cause crystallization of the dissolved boron carbide.

5. The method of alloying boron carbide with a metal of the group of metals having atomic numbers from 26 to 29 inclusive, the said method comprising mixing solid boron carbide with a quantity of the metal sufficient to form a substantially continuous matrix upon fusion and solidification of the resulting mixture, heating the resulting mixture to a temperature several hundred degrees above the melting point of the metal until the mixture becomes fluid, and thereafter cooling the fluid mass so as to cause crystallization of the dissolved boron carbide.

6. The method of making a composition containing boron carbide crystals separated by an interstitial metallic matrix, the said method comprising mixing solid boron carbide with approximately 50 per cent or more by weight of a metal of the iron group, heating the resulting mixture until it becomes fluid, and thereafter cooling the fluid mass so as to cause crystallization of the dissolved boron carbide.

7. The method of making a composition containing boron carbide crystals separated by an interstitial metallic matrix, the said method comprising mixing solid boron carbide with approximately 50 per cent or more by weight of nickel, heating the resulting mixture until it becomes fluid, and thereafter cooling the fluid mass so as to cause crystallization of the dissolved boron carbide.

8. The method of making a composition containing boron carbide crystals separated by an interstitial metallic matrix, the said method comprising mixing solid boron carbide with approximately 50 per cent or more by weight of cobalt, heating the resulting mixture until it becomes fluid, and thereafter cooling the fluid mass so as to cause crystallization of the dissolved boron carbide.

9. The method of making a composition containing boron carbide crystals separated by an interstitial metallic matrix, the said method comprising mixing solid boron carbide with approximately 50 per cent or more by weight of copper, heating the resulting mixture to a temperature above the melting point of the metal but below the melting point of the boron carbide until the mixture becomes fluid, and thereafter solidifying the fluid mass so as to cause crystallization of the dissolved boron carbide.

10. The method of making a composition containing boron carbide crystals separated by an interstitial metallic matrix, the said method comprising mixing solid boron carbide with approximately 50 per cent or more by weight of a metal of the iron group, heating the resulting mixture to a temperature above the melting point of the metal but below the melting point of the boron carbide until the mixture becomes fluid, and thereafter solidifying the fluid mass so as to cause crystallization of the dissolved boron carbide.

11. The method of making a composition containing boron carbide crystals separated by an interstitial metallic matrix, the said method comprising mixing solid boron carbide with approximately 50 per cent or more by weight of cobalt, heating the resulting mixture to a temperature above the melting point of the metal but below the melting point of the boron carbide until the mixture becomes fluid, and thereafter solidifying the fluid mass so as to cause crystallization of the dissolved boron carbide.

12. The method of making a composition containing boron carbide crystals separated by an interstitial metallic matrix, the said method comprising mixing solid boron carbide with approximately 50 per cent or more by weight of nickel, heating the resulting mixture to a temperature above the melting point of the metal but below the melting point of the boron carbide until the mixture becomes fluid, and thereafter solidifying the fluid mass so as to cause crystallization of the dissolved boron carbide.

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