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Publication number: **0 332 463 B1**

**EUROPEAN PATENT SPECIFICATION**

- (45) Date of publication of patent specification: **27.07.94** (51) Int. Cl.<sup>5</sup>: **C04B 35/56, C22C 29/08**  
(21) Application number: **89302400.0**  
(22) Date of filing: **10.03.89**

(54) **Boron-treated hard metal.**

(30) Priority: **11.03.88 US 167000**  
**29.06.88 US 211197**  
**06.03.89 US 317612**

(43) Date of publication of application:  
**13.09.89 Bulletin 89/37**

(45) Publication of the grant of the patent:  
**27.07.94 Bulletin 94/30**

(84) Designated Contracting States:  
**AT BE CH DE ES FR GB GR IT LI LU NL SE**

(56) References cited:  
**EP-A- 0 062 311**  
**EP-A- 0 182 759**

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**EP 0 332 463 B1**

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**Description**

This invention relates to cemented carbide bodies and particularly to cemented carbide bodies that have been treated with boron, and to associated methods of forming such bodies.

5 The cutting and drilling industries continue to place increased demands on cutting implements to hold a sharper edge and to last longer. Ordinary cemented carbide-tipped cutting elements consist of a mixture of tungsten carbide (WC) as a hard metal phase and cobalt (Co) as a binder phase. WC and Co powders are sintered to create a WC/Co cemented carbide body. As is known in the art, many modifications have been made to the simple WC/Co body to enhance its properties for various applications. In general, there is a  
10 trade-off between brittleness and hardness. If a harder metal is chosen to cut better and hold a sharper edge, it tends to be more brittle and therefore to suffer brittle failure sooner than a material that is not as hard.

To avoid the problem of increased brittleness while still improving hardness, some people have provided a boron addition as a thin surface coating or layer onto the carbide body. The surface coating or  
15 layer may be applied by thermal spraying, physical vapour deposition, chemical vapour deposition, and other known methods. It is also known to diffuse boron into the surface of the cemented carbide body to form a thin, hard layer.

A major problem inherent in all of the attempts to provide a boride coating or layer on WC/Co or other carbide bodies is that, once the thin surface has been worn away, the hardness and other improved features  
20 are lost and the tool can no longer be used satisfactorily. If coated saw tips are first brazed onto a saw blade and then sharpened in place, the coating or surface layer may be lost due to the initial sharpening. It would almost certainly be lost on subsequent sharpening. Other problems include the fact that the layer has different thermal expansion and other properties than the substrate and therefore may tend to separate from the substrate during use. Brazing of pieces with layers or coatings is also difficult.

25 EP-A-0062311 discloses a cemented tungsten carbide cut-hard body, which contains a tungsten carbide phase and a cobalt binder phase and can additionally contain from 0.01 to 0.2% by weight of boron, but admits that desirable oxidation resistance and avoidance of brittleness can only be obtained within narrow composition limits.

EP-A-0182759 discloses a cemented carbide body having a core stiffened by the presence of an eta  
30 phase (which is a ternary phase of W, Co and C), with a casing made wear resistant by a gradient of a cobalt binder, in which the good qualities claimed rely on microscale features.

According to one aspect of the present invention, there is provided a cemented carbide body comprising:

35 a tungsten carbide phase;  
a cobalt binder phase; and  
a quaternary third phase comprising cobalt, tungsten, boron and carbon, the third phase being dispersed throughout the body.

The present invention provides a cemented carbide body which provides a better cutting edge with longer wear characteristics than the prior art without encountering the problems involved with coatings and  
40 layers or the problems of increased brittleness encountered in previous attempts.

Surprisingly, the present invention permits the addition of boron to a great depth in the WC/Co or other cemented carbide body without increasing brittleness.

In fact, most of the standard measures, such as hardness, coercive force, and so forth exhibit little change when boron is added in accordance with the present invention, leading one to believe that they  
45 must not cause much improvement over the standard WC/Co body. However, the actual field performance of WC/Co or other carbide bodies made according to the present invention has been substantially improved over the performance of conventional WC/Co implements. It is suspected that the improvement is due to several factors.

Recent analysis of the present invention indicates that the boron causes a third phase to be formed.  
50 This third phase appears to act as another binder phase, which includes cobalt, small amounts of boron and carbon, and substantially more tungsten than appears in the standard binder phase. It is suspected that this third phase causes an improvement primarily by increasing the fracture toughness of the material, thereby making it more difficult for a crack to propagate through the material to cause failure. Corrosion resistance also appears to be improved. It is also thought that the improved microstructure may be able to be sharpened to a finer edger than in the prior art.  
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Preferably the ratio by weight of tungsten to cobalt in the third phase is greater than 1.0:1.0; and preferably the ratio by weight of boron to carbon in the third phase is greater than 1.0:1.0, more preferably the ratio by weight of boron to carbon in the third phase is between 1.0:1.0 and 12.0:1.0.

It has been observed that the tungsten carbide particles are generally angular and blocky in shape but, in the region of the third phase, the tungsten carbide particles are rounded and smaller; and that the average dimensions of the third phase are larger than the average dimensions of the cobalt binder phase.

Another aspect of the present invention provides a method for producing a cemented carbide body having a tungsten carbide phase, a cobalt binder phase, and a quaternary third phase having cobalt, tungsten, boron and carbon, the method comprising the steps of:

a) preparing one or more tungsten carbide bodies in a shape including a tungsten carbide material and a cobalt binder material; and

b) sintering said shape in the presence of a boron-containing material, by surrounding at least some of the tungsten carbide bodies with boron-containing material, such that appreciable quantities of boron from said boron-containing material migrate into said shape and become dispersed throughout the microstructure of the shape to a depth of at least 0.0049 mm (0.125 inch) or completely throughout the shape if the shape is less than 0.0049 mm (0.125 inch) thick, forming the quaternary third phase, wherein the microstructure of said shape, after sintering, exhibits a feathery etch phase throughout the body when etched with a standard acid etchant or Murakami's reagent.

Conveniently the sintering is done in a disassociated ammonia atmosphere, or in a hydrogen atmosphere.

The boron-containing material present during the sintering may be selected from boron powder, boron nitride, boron oxide, boron carbide,  $AlB_2$ ,  $AlB_{12}$ ,  $CrB$ ,  $CrB_2$ ,  $Cr_3B_5$ ,  $MoB$ ,  $NbB_6$ ,  $NbB_2$ ,  $B_3Si$ ,  $B_4Si$ ,  $B_6Si$ ,  $TaB$ ,  $TaB_2$ ,  $TiB_2$ ,  $WB$ ,  $W_2B_5$ ,  $W_2B$ ,  $VB_2$ , and  $ZrB_2$ .

Alternatively the shape is immersed during sintering in a sintering sand which is in an admixture with the boron-containing material which is selected from boron nitride, boron, boron oxide, and boron carbide; in another alternative the shape is immersed in a sintering sand which is in an admixture with the boron-containing material, in which boron constitutes from 0.003 to 50 percent by weight of the sand mixture; or the shape is immersed in a sintering medium which includes from 0.003 to 50 percent by weight boron in the form of a boron-containing material selected from BN, boron, boron oxide, and boron carbide; or during sintering, said shape is immersed in a mixture of a sintering sand and boron-nitride in an amount of 0.05 to 2 percent by weight of the mixture.

If desired the shape may have been previously sintered, and the present operation is a re-sintering of the previously sintered body.

The shape may be painted with a boron-containing paint prior to sintering; alternatively the shape may be placed in contact with a surface which has been coated with a boron-containing material prior to sintering.

A further aspect of the present invention provides a method for producing a cemented carbide body having a tungsten carbide phase, a cobalt binder phase, and a quaternary third phase having cobalt, tungsten, boron and carbon, the method comprising the steps of:

providing one or more tungsten carbide bodies in a shape including a tungsten carbide material and a cobalt binder material;

immersing said shape in a sintering sand which is in an admixture with a controlled amount of a boron-containing material;

and sintering said shape in the sand mixture under controlled conditions by surrounding at least some of the tungsten carbide bodies with boron-containing material providing a gradient of some form of boron throughout said shape, with the amount of boron being greater at the outside and gradually reducing in concentration toward the centre, thereby forming the quaternary third phase, wherein the microstructure of said shape, after sintering, exhibits a feathery etch phase throughout the body when etched with a standard acid etchant or Murakami's reagent.

A yet further aspect of the present invention provides a cemented carbide body, comprising:

a) carbide phase, including a carbide former and carbon;

b) a binder phase made mostly of a binder element; and

c) a quaternary third phase comprising a dispersion of boron-containing material throughout the body, wherein the microstructure of said carbide body, when etched with Murakami's Reagent or and solution, exhibits an etch phase having a feathery structure throughout the body.

In this cemented carbide body, the carbide former may be selected from titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten;

the binder phase may be selected from manganese, iron, cobalt, nickel, copper, aluminium, silicon, ruthenium and osmium; and

the amount of boron in the body may be from 25 to 3000 parts per million.

Preferably the carbide phase is WC and the binder phase is cobalt.

Preferably the distribution of the amount of boron in the body is a controlled gradient, with greater concentrations of boron and the etch phase at the surface and lesser concentrations towards the centre of said body.

5 The etch phase may also include a greater percent by weight of the carbide former than is found in the binder phase.

An additional aspect of the present invention provides a cemented carbide body, comprising:

- a) a carbide phase, including a carbide former and carbon;
- b) a binder phase having less than 30 percent by weight of carbide former; and
- 10 c) a quaternary third phase including a binder material and boron, wherein the third phase comprises a dispersion of boron-containing material throughout the body, wherein the microstructure of the carbide body, when etched with Murakami's Reagent or acid solution, exhibits an etch phase having a feathery structure throughout the body.

15 The third phase may also include at least 40% by weight of carbide former, and the carbide former may be tungsten and the third phase may include approximately 60% by weight of tungsten. Preferably the etch phase, before being etched, includes some of the carbide former, some of the binder element, some carbon, and some boron, and wherein the ratio by weight of carbide former to binder element in the etch phase is greater than 1.0:1.0.

20 With the present invention it is possible to provide an improved boron-enhanced carbide implement suitable for cutting, drilling, grinding, and so forth, which may be sharpened, resharpened, and reused without losing its original properties.

In the present invention, it is the third quaternary phase which improves toughness without adversely affecting hardness.

The present invention will be better understood upon reading the description which follows, with reference to the accompanying drawings, in which:-

25 Figure 1 is a photomicrograph at 200X of a polished section of an untreated (control) extra-fine grain (micrograin) 94.5% WC/5.5% cobalt body which was sintered in a disassociated ammonia atmosphere, the polished section of which has been treated with a standard acid etchant;

30 Figure 2 is a photomicrograph at 100X of an extra-fine grain 94.5% WC/5.5% cobalt body made according to the present invention, where the body was sintered in a disassociated ammonia atmosphere surrounded by sintering sand containing 2.5% by weight of boron nitride (BN), the polished section of which has been treated with an acid etchant;

Figure 3 is a photomicrograph at 200X of a medium grain untreated sample with 87% WC/13% Co which was sintered in a disassociated ammonia atmosphere, the polished section of which has been treated with an acid etchant.

35 Figure 4 is a photomicrograph at 100X of a medium grain sample with 87% WC/13% Co which was sintered in a disassociated ammonia atmosphere surrounded by sintering sand containing 2.5% by weight of boron nitride, the polished section of which has been treated with an acid etchant.

40 Figure 5 is a photomicrograph at 1250X of a medium grain sample with 87% WC/13% Co which was sintered in a disassociated ammonia atmosphere surrounded by sintering sand containing 0.5% boron nitride, the polished section of which has been treated with an acid etchant.

Figure 6 is a plot of net watts versus lineal feet (30.5 cm) cut for saw blades cutting 0.75 inch (19 mm) thick medium density particle board at 5 feet per minute for untreated blades, blades with Borofuse processed tips, and blades with tips treated in accordance with the present invention.

45 Figure 7 is a plot of apparent fracture toughness (K<sub>a</sub>) versus %BN in the sintering sand for two grades of material.

Figure 8 is a plot of the eddy current signal versus %BN in the sintering sand for Vermont American's 2M12 grade samples.

Figure 9 is a plot of the eddy current signal versus %BN in the sand for Vermont American's OM2 grade samples.

50 Figure 10 is a photograph at a magnification of 2,040 times of a medium grain sample with 91% WC/9% Co which was sintered in sintering sand containing 1% by weight of boron nitride, the polished section of which has been treated with an acid etchant.

Figure 11 is a photograph at a magnification of 2,040 times of a polished section of the sample of Figure 10 without etching.

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Detailed Description of the Preferred Embodiments

The cemented carbide bodies of the present invention are made in accordance with the general teachings of the art in many respects. Generally, cemented carbide bodies are made according to processes in which powders of a carbide material, for example tungsten carbide (WC), and a binder material, for example cobalt (Co), are milled to carefully controlled composition and particle sizes (called "grades") and then dried, for example by spray-drying. The dried grade carbide/binder (for example WC/Co) powder is then pressed in the presence of a lubricant to a selected shape.

If sintering is to be done in a continuous stoking furnace, the shapes are put into graphite boats which have been filled with  $Al_2O_3$  grains or other sintering sand. The shapes are surrounded by the sand and are usually put into the boat in layers. First a layer of sand on the surface of the graphite boat, then a layer of the shapes, then more sand, then another layer of shapes, and so forth, until several layers are positioned in the graphite boat. The sand prevents the pieces from sintering together or chipping and serves as an insulator as the boat moves through the furnace into different temperature zones to facilitate liquid phase sintering. In some embodiments of the present invention, a boron-containing powder is mixed into the sand before the shapes are immersed in the sand.

I have used boron nitride, boron powder, boron carbide, and boron oxide as boron-containing powders and believe that other boron-containing powders would also work. When boron nitride (BN) is used as an additive to the sintering sand, which is my preference, a boron nitride product available from Standard Oil Engineered Materials Company, Semiconductor Products Division, 2050 Cory Road, Special Fibers Building, Sanborn, NY 14132 U.S., and sold under the trademark COMBAT®, Boron Nitride Powder CAS number 10043-11-5 has been found to be satisfactory. This is a BN powder having a screen size specification of minus 325 mesh (44 micrometres). The concentrations of BN used herein are for this size of powder. Basic chemical and physical principles suggest that if powders of different particle size and therefore different surface areas are used, the concentrations should be adjusted to provide the same effective surface area. Alternative boron-containing materials which should work in the present invention are:  $AlB_2$ ,  $AlB_{12}$ ,  $CrB$ ,  $CrB_2$ ,  $Cr_3B_5$ ,  $MoB$ ,  $NbB_6$ ,  $NbB_2$ ,  $B_3Si$ ,  $B_4Si$ ,  $B_6Si$ ,  $TaB$ ,  $TaB_2$ ,  $TiB_2$ ,  $WB$ ,  $W_2B_5$ ,  $W_2B$ ,  $VB_2$ , and  $ZrB_2$ . Since it is probable that the transport of boron into the cemented carbide is by gas, other sources of boron could be boron-containing organo-metallics which have relatively low vaporization temperatures, such as  $B_3N_3H_6$ ,  $B_{10}H_{14}$ ,  $B_2H_7N$ ,  $B_{10}H_{10}C_2H_2$ ,  $B(OCH_3)_3$ ,  $C_6H_5BCl_2$ ,  $C_5H_5NBH_3$ ,  $B(C_2H_5)_3$ , and so forth. Also, other inorganic compounds such as  $CoB$ ,  $FeB$ ,  $MnB$ ,  $NiB$  and combinations of boron with the halogens hold promise of successful use, but we have not tried them.

Then, the graphite boats containing sand and shapes pass into the sintering furnace or furnaces, are heated or pre-sintered to drive off the lubricant, and are then heated to the sintering temperature.

If sintering is to be done in a vacuum furnace, the shapes are put onto trays. In order to prevent the shapes from sticking to the trays and to prevent transfer of carbon between the graphite tray and the shape, some type of paint or coating is usually applied to the tray before putting on the shapes. The coating is then dried, preferably in a vacuum drying oven. In the present invention, some form of boron is added to the paint or coating. Moderately successful to completely successful tests have been conducted with paint made by mixing boron nitride powder with water and/or alcohol to a paint consistency and simply painting it on the tray. In those tests, the boron entered the shape but not as homogeneously as with the sand. It is thought that a more even distribution of boron would be obtained if the whole shape were painted. Other forms of boron-containing powders and other solvents or vehicles likely could be used. Then the tray is inserted into the furnace, is raised to a pre-sintering temperature to drive off the lubricant, and is then raised to a sintering temperature.

Re-sintering of already-sintered bodies may also be conducted in the presence of the boron-containing sand or paint, and the boron will disperse deeply into the body in the same manner. Of course, in this case, pre-sintering is not necessary, because there is no lubricant to drive off.

When the shapes are sintered in the boron-doped sand or paint, some form of boron diffuses or migrates into the shape or body and is dispersed fairly homogeneously for a depth of at least 0.125 inches (3.175 mm) into the microstructure of the sintered body. Preliminary tests of some thicker bodies, 0.5 inches (12.7 mm) in thickness, indicate that some gradient of boron is present, with concentrations being greater toward the surface than toward the center. It is believed that, by controlling the amount of boron-containing material in the environment and by controlling the time and temperature of the sintering process, or even re-sintering, it is possible to create a body with a relatively homogeneous dispersion of boron or a variety of desired gradients. Also, it appears possible to re-sinter a body treated according to the present invention--in a controlled atmosphere with no boron-containing material present during such re-sintering--to achieve the desired gradient or homogeneity. However, in no case when the present invention is followed is

a surface layer or coating formed. The surface layers formed in the various known coating processes are on the order of 0.001 inches (0.025 mm) thick, so there is a difference of at least two orders of magnitude between the thickness of a coating and the depth of substantially homogeneous boron dispersion in the present invention.

5 Surprisingly, the characteristics of the resulting sintered body do not appear to change very much relative to those of identical sintered bodies which are sintered without the presence of boron. Hardness, transverse rupture strength, coercive force, and so forth, are essentially the same. Fracture toughness improves over its value in an otherwise identical body without boron. Resistance to corrosion also appears to improve. And, as test results which will be described below indicate, saw blades with tips made in  
10 accordance with the present invention operate markedly better than their counterparts without boron.

In viewing the microstructure of carbide bodies made in accordance with the present invention, several features are of interest:

15 First, the presence of the boron seems to remove free carbon. When a batch of bodies previously sintered without boron is re-sintered in accordance with the present invention, porosity due to free carbon is greatly reduced or eliminated.

20 Second, when bodies which have been sintered in accordance with the present invention are etched with Murakami's reagent, they exhibit a rapid etch phase, which etches in a manner similar to a defect known as "eta phase", but which is much finer than a similar "eta phase" configuration and is generally found in swirls or feathers homogeneously throughout the body. Also unlike bodies with "eta phase", the bodies of the present invention do not show an increase in brittleness over bodies without the rapid etch phase. An analysis of the carbide bodies, which will be described in some detail later, indicates that boron is present in the feathery structures.

25 Third, the photos of Figures 10 and 11, which are at a higher magnification than the other photos, indicate that the swirls or feathers are actually a third phase, the average dimensions of which are larger than the average dimensions of the standard binder phase. This third phase fills up the spaces between tungsten carbide particles as a binder does. In Figure 11, it can be seen that the tungsten carbide particles generally have straight sides and appear cubic, boxy, or angular. However, in the region of the third phase, the tungsten carbide particles are more rounded, and some have both shrunk in size and become rounded. It appears that the tungsten carbide particles are somehow reacting so that part of the material from the  
30 particles is lost from the particles and becomes part of the third phase. An analysis of these samples indicates that, indeed, a substantial amount of tungsten is present in the third phase. Additionally, analysis shows that boron is present in this phase, as are carbon and cobalt.

Fourth, in some cases, as will be described below, the microstructure after etching shows white spots, the content of which is not known.

35 The present invention has been tested in several variations on several different carbide bodies. Figures 1-5 and 10-11 show the microstructures resulting from some of the tests.

In order to view the microstructure in Figures 1-5, the specimens are prepared in a standard manner. Typically, the specimen is mounted in a thermosetting epoxy resin. The sintered specimen is rough ground on a 220-mesh diamond-embedded wheel using water coolant. The specimen is then fine ground on a 45-  
40 micrometre diamond embedded wheel, using water coolant. Then the specimen is coarse polished on a hard-plane cloth wheel, such as nylon or silk, and then on a paper-based wheel. A charge of 15- or 30-micrometre diamond paste may be applied to the wheel for polishing. The wheel may be lubricated during polishing with oil or water or nothing, depending on the solubility of the diamond carrier. Then the specimen is ultrasonically cleaned in a soapy solution. Next, the specimen is medium polished on a hard-plane cloth  
45 wheel or a paper-based wheel as above except with a charge of 6- or 9-micrometre diamond paste, and then the specimen is ultrasonically cleaned in a soapy solution again. The specimen is then fine polished on a short-nap cloth wheel (such as rayon) or on a paper-based wheel. A charge of 1- or 3-micrometre diamond paste may be applied to the wheel for polishing, again using a lubricant, and then the specimen is ultrasonically cleaned in a soapy solution before processing. An additional polish may be done with a short-  
50 nap cloth charged with 0.25- to 1-micrometre diamond. Polishing is done until a scratch-free mirror-finish is obtained. Then, the sample is ultrasonically cleaned in a soapy solution, rinsed with water, rinsed with alcohol, and dried.

Then, to observe the feathery structure, an etchant is applied. Two chemical etchants have been found which reveal the structure. Murakami's Reagent, which is 10% KOH, 10%  $K_3Fe(CN)_6$ , and 80%  $H_2O$  is  
55 applied, left on for two minutes, rinsed with water, then rinsed with alcohol and dried. Murakami's Reagent rapidly attacks the constituents of the carbides treated in accordance with the present invention, typically in two-to-four seconds. Alternatively, an acid etch prepared by mixing 30 ml  $H_2O$  + 10 ml HCl + 10 ml  $HNO_3$  is applied to the surface until a delayed foaming reaction is completed. Then the sample is rinsed first with

water, then with alcohol, and then is dried. The acid etchant is generally less aggressive than Murakami's Reagent but provides more microstructural detail.

Another type of sample of the present invention has been prepared by mounting the specimen in a resin, highly polishing the specimen to a point at which it is a bit over-polished so that the harder elements are slightly raised above the softer elements, and placing a conductive material in the resin. This type of sample can then be analyzed using electron optics. A photograph of a sample prepared in this way and magnified approximately 2,000 times is shown in Figure 11. Magnification of the polished, etched and unetched bodies by approximately 2,000 times in a scanning electron microscope as shown in Figures 10 and 11 reveals that the feathery structures are really a third phase, which appears to function as an additional binder phase. An analysis of this third phase will be described later.

As a general rule, the greater the amount of binder relative to carbide particles, the softer and tougher the material. However, in this case, what appears to be happening is that the additional phase serves to improve toughness without adversely affecting hardness.

The following examples describe in detail specific tests that were conducted.

#### Example 1:

One medium grain sample having 91% WC and 9% Co was sintered in a continuous stoking furnace in a disassociated ammonia atmosphere at 1450 °C for one hour while surrounded by an alumina sand heavily saturated in carbon and including 1% Boron Nitride. At high magnification (5,200x) a third, inventive phase was discovered, and the sample was analyzed.

The analysis was as follows:

Phase	W	Co	C	B	O
Third Phase	71	24	0.6	4.0	---
Carbide Phase	94.5	0.4	5 <sup>(1)</sup>	---	---
Binder Phase	14 <sup>(2)</sup>	85	0.8	---	0.3

<sup>(1)</sup> Underestimated.

<sup>(2)</sup> May be overestimated.

It is expected that this third phase will form with tungsten and cobalt reacting within a broad range of compositions, so long as there is sufficient carbon and boron present in acceptable ratios to permit formation of the third inventive phase. The third phase appears capable of existing within a range of compositions, with tungsten varying within a range of 50 to 95 weight percent; cobalt between 5 and 50 weight percent; carbon between 0.1 and 6.5 weight percent; and boron varying between 0.5 and 10.0 weight percent. It is expected that, within the third phase, the ratio of tungsten to cobalt by weight will always be greater than 1.0. It is also expected that the ratio of boron to carbon by weight in the third phase will always be greater than 1.0.

#### Example 2:

A sample of extra fine grain tungsten carbide (WC) powder was mixed in a ratio of 94.5% WC/5.5% Co, mixed with a lubricant, and pressed into a shape. The shape was surrounded with Al<sub>2</sub>O<sub>3</sub> grains mixed with 2.5% BN powder by weight, placed in a graphite boat, and both pre-sintered and sintered in a continuous stoking furnace. A sintering temperature of 1410 °C was maintained for about 70 minutes. During sintering, disassociated ammonia gas (nitrogen and hydrogen) flowed through the furnace.

The resulting microstructure (prepared and etched with the acid etch as described earlier) is shown in Figure 2. When comparing the treated microstructure in Figure 2 with the microstructure in Figure 1, which was prepared in the same way except that no boron nitride was in the sintering sand, it will be noted that the sample which was treated with boron exhibits an unusual feathery or lacy etched constituent. The etched constituent is distributed fairly homogeneously throughout the sample. The tips of the feathers or branches appear darker and thicker than the rest of the etched constituent. Analyses which will be described later indicate that some form of boron is present in the feathery structure.

Example 3:

A sample of a medium grain WC powder was mixed in a ratio of 87% WC/13% Co, mixed with a lubricant, pressed into a shape, and, as in Example 2, sintered in a sand containing 2.5% by weight BN.

5 The sample was polished and etched with an acid etchant as described earlier, and its microstructure is shown in Figure 4. Again, when comparing the microstructure of Figure 4 with the microstructure of the same material sintered without BN, shown in Figure 3, the microstructure of Figure 4 exhibits the branching etched constituent. Again, the tips of the branches are thicker and darker than the rest.

10 Example 4:

A medium grain sample of 87% WC/13% Co was prepared as in Example 1 except that 0.5% by weight of BN was added to the sand. Again, the branching effect is seen, and, upon greater magnification, white spots appear as indicated by the arrows.

15 The emphasis placed on this unusual microstructure is because it was the first way the invention was recognized and because it continues to be the easiest way to tell that the boron has indeed migrated into the body.

Example 5:

20 Vermont American's OM1 grade, which is a medium grain WC powder mixed with a Co binder powder in the ratio of 91% WC/9% Co was prepared and pressed with a lubricant into saw tips of the design of Vermont American's Model C-3110-1 tips. The tips were coated with a paint made of boron nitride (BN) mixed with water. The tips were dried under vacuum so that presumably only BN remained on the tips,  
 25 were then placed on standard graphite trays provided for vacuum sintering, and were both pre-sintered and sintered under vacuum. The vacuum furnace was purged with an inert gas before sintering, and a vacuum was applied during the pre-sintering and sintering. The bodies were held at a sintering temperature of 1410 °C for sixty minutes, then cooled. The Rockwell hardness (A scale) of the samples was 90.7, and the coercive force Hc was 80. The saw tips, when etched, again exhibited the fanning or feathering pattern  
 30 described earlier throughout their microstructure.

Example 6:

35 The saw tip bodies were prepared as in Example 5 (91% WC/9% Co medium grain) except that the painted bodies were pre-sintered and sintered in a continuous stoking furnace. The coated samples were dried under vacuum, then surrounded by alumina (Al<sub>2</sub>O<sub>3</sub>) with no boron mixed in the sand and placed on graphite boats. A sintering temperature of 1410 °C was held for about 70 minutes, during which time disassociated ammonia flowed through the furnace.

40 At the same time that the painted or coated samples were sintered, uncoated samples were also sintered, and the test results were as follows:

	Specific Gravity	Rockwell A	(Hc)
Untreated tips	14.68	90.5	142
Treated tips	14.51	90.9	138

45 Again, the boron on the coated samples migrated throughout the samples, and the resulting samples exhibited the feathery-looking rapid etch phase described earlier throughout their structures, while the uncoated samples did not. The result is a homogeneous sintered body with no surface coating or layer. It will be noted that specific gravity, hardness, and coercive force showed no substantial change.

Example 7:

55 Saw tips which had originally been sintered without boron in Vermont American's Style C-3170-1 from 91% WC powder medium grain mixed with 9% Co powder were resintered in a continuous stoking furnace in a graphite boat surrounded by alumina sand mixed with 0.5% by weight BN powder. The sintering time and temperature and gas flows were as in Example 2. Again, the distinctive feathering microstructure appeared.

The resulting saw tips were brazed onto 10" (25.4 cm), 40 tooth saw blades. The brazed joint strength was tested with a drop weight impact test and compared with brazed joints utilizing standard WC tips. The drop-weight impact test results for the boron-treated tips were 1265 metre-grams (166 inch-ounces) versus 1036 metre-grams (136 inch-ounces) for the regular WC tips, an improvement of 22%.

5 These blades were used to cut 3/4" medium density particle board, and power consumption measurements were recorded after every 50 lineal feet (15.4 m) cut. These blades were tested against blades which were identical except their tips were either (1) untreated or (2) treated by the "Borofuse" process, which is thought to deposit a boride layer on the surface. The test results are shown in a graph in Figure 6, which shows a clear improvement of the blade with tips made according to the present invention over the other  
10 two blades. The blade of the present invention required considerably less consumption of power than the other blades at all stages of the test. The power consumption is directly related to the edge sharpness, so these tests indicate that the blades of the present invention had better initial edge sharpness and better edge retention than the others.

15 Example 8:

WC/Co bodies were sintered in alumina sand in a continuous stoking furnace with a sintering temperature of 1410 °C maintained for about 70 minutes. Samples were made up of various WC/Co grades from micrograin size with 6% Co to medium grain with 13% Co to extra-coarse grade with 6.5% Co. The  
20 amount of BN in the alumina sand varied from 0% to 2.5% at 0.5% increments for each sample. The specific gravity, Rockwell hardness, transverse rupture strength, coercive force, shrink factor and percent weight loss were tested for each sample, and the test results showed that the amount of boron nitride in the sand did not affect those properties to a degree greater than the variation in normal manufacturing. The characteristic feathery constituent appeared in the microstructure of each sample in which BN was present  
25 in the sand.

Example 9:

Carbide test plugs having the dimensions of 5.8 mm X 6.3 mm X 19.0 mm (0.2 inches X 0.25 inches X  
30 0.75 inches) were sintered from a medium grain powder of 91% WC/9% Co in alumina sand without any boron present. Subsequently, these test plugs were re-sintered in alumina sand mixed with different types of boron containing powder in a continuous stoking tube furnace at 1410 °C for about 70 minutes in an atmosphere of disassociated ammonia. In each case, the microstructure showed the same distinct etching pattern indicating the diffusion of boron into the carbide structure. The boron sources, hardness (RWA), and  
35 coercive force (HC) results are shown below:

Type of Boron Source	Amount in sand (Wt. %)	RWA	HC
boron carbide	.1	90.3	156
boron powder	.1	90.5	162
boron oxide	.5	90.8	158
boron oxide	1.0	90.7	157

45 Example 10:

A. A number of multcarbide grades were also tested. Metal cutting saw tips of Vermont American style 170H280, grade MC115 which has a medium grain size and is made up of 77.1% WC, 11.4% Co, 4%  
50 TiC, 5.25% TaC, 2.25% NbC were resintered in alumina sand with 1.0% BN. The characteristic microstructure is again present, indicating that boron has diffused throughout the structure.

B. The same style tips of grade MC85, which is a medium grain made up of 72.0% WC, 8.5% Co, 8% TiC, 11.5% TaC were also resintered in sand containing 1.0% BN, and the characteristic feathery microstructure appeared again.

It is expected that other carbide formers could be used, such as, the IVB, VB and VIB elements, for  
55 example: titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, and tungsten, and combinations thereof. Binder metals might be manganese, iron, cobalt, nickel, copper, aluminum, silicon, ruthenium, osmium used alone, in combination with each other, or in combination with each other and with any of the IVB, VB and VIB elements listed earlier as carbide formers.

Example 11:

Below is a table showing the impact of varying percentages of boron-nitride material added to the alumina sintering sand on the corrosion resistance of the bodies. All of the samples analyzed in this table were prepared from 91% WC/9% Co powders of medium grade and all were sintered in graphite boats surrounded by Al<sub>2</sub>O<sub>3</sub> sintering sand doped with different amounts of boron-containing material (BN) under the same conditions (disassociated ammonia atmosphere with sintering temperature of 1410 °C for about 1 hour); the only difference in their treatment was the percent by weight of boron-containing material (BN) added to the Al<sub>2</sub>O<sub>3</sub> sintering sand.

To test for corrosion resistance, each sample was weighed, placed in HCl for 24 hours at room temperature, then weighed again to determine the percent weight loss due to corrosion. The smallest amount of corrosion occurred with a BN doping of 0.9%.

% BN/Sintering Media Ratio	% Weight Loss
0	00.057
.1	00.113
.5	00.056
.9	00.012
2.0	00.0215
25.0	00.0357
50.0	00.0494
75.0	00.0580
100.0	00.0781

Additional tests were conducted to see how much or how little BN was needed on the sand in order to obtain the feathery microstructures, and it was found that the present invention is successful in incorporating boron into the bulk chemistry of a WC/Co carbide body with as little as .006% BN added to the sintering sand and with as much as a total replacement of the sintering sand with BN. The practical working range of the present invention for WC/Co carbide bodies appears to be to utilize between 0.1 and 5.5% of boron-nitride material in the sintering sand. Optimum corrosion resistance was achieved with a BN doping of about 0.9% in the alumina sand. It will be seen from other tests described below that other optimum characteristics seem to occur with about the same amount of doping.

Example 12:

Fracture toughness and Eddy Current tests were conducted on various types of samples made in accordance with the present invention. The first group of samples was made with Vermont American's grade 2M12, a coarse grain 89.5% WC/ 10.5% Co. Varying amounts of boron nitride were mixed in the alumina. The second group of samples was made with Vermont American's grade OM2, a fine grain 94% WC/ 6% Co. Varying amounts of boron nitride were mixed in the alumina sand. The sintering was done in a disassociated ammonia atmosphere in a continuous stoking furnace with the sintering temperature of 1410 °C held for about 70 minutes.

A bulk analysis is shown in the table below.

% by Weight BN in the sand	ppm Boron for OM2 samples	ppm Boron for 2M12 samples
0.5	336.6±2.4	377.5±2.6
1.0	383.4±3.1	408.9±2.9
1.5	376.3±2.3	537.4±3.8
2.0	543.0±3.8	806.9±4.8
2.5	501.4±4.0	730.8±3.6

In order to measure fracture toughness, the samples were made up in short cylindrical rods of 0.5 inch (12.7 mm) diameter and .750 inch (19 mm) height, and a cut was then made into the rod in accordance with the procedure set out in International Journal of Fracture, Vol. 15, No. 6, Dec. 1979, pp. 515-536.

Figure 7 shows a plot of apparent fracture toughness ( $K_{Ic}$ ) versus percentage by weight of boron nitride in the alumina sand. The apparent Fracture Toughness ( $K_{Ic}$ ) shows significant improvement for each alloy upon the addition of BN to the sand. It appears that percent by weight of BN in the sand of between 0.5 and 2 gives optimum fracture toughness. This translates to an amount of boron in the sand of 0.2 to 0.9 percent by weight.

Figures 8 and 9 are plots of Eddy current results for the same samples. The peak for the OM2 grade is at 1.5% BN in the sand for both fracture toughness and Eddy Current, and the 2M12 grade peaks at 1.0%BN in the sand for both tests. These appear to be the optimum BN dopings.

Additional analysis of these samples indicates that the concentration of Boron in these samples is greater toward the outside and gradually reduces to a lower concentration toward the center. It has been demonstrated that a post treatment diffusion process at elevated temperatures of 1410 °C for about 70 minutes will produce a more uniform distribution of the etch pattern in large samples in which a change in boron concentration from surface to core has been observed. When this was done, the morphology of the third phase changed from feathery to rounded clusters, so it is possible for the boron to be distributed throughout the body without the presence of a feathery etch phase.

Another analysis of these samples was done for the distribution of boron in the samples and found that the boron is distributed in a fern-type pattern which is virtually identical to the pattern shown in the treated metal when etched with acid or Murakami's reagent. Because the distribution of boron is in the same pattern displayed by the acid etch of the treated metal sample described earlier, the conclusion is drawn that boron is present in the fern-type pattern that is revealed when the treated metal samples are etched.

#### Example 13:

A test was conducted with commercial sawmill blades in which a standard WC/Co tipped blade was tested against the identical blade in which fine grain tips of 94% WC/6%Co, already-sintered under the standard process, were re-sintered in a continuous stoking furnace in alumina sand mixed with 1% BN by weight. The standard blade lasted 40 hours. The blade with re-sintered tips treated according to the present invention lasted 462 hours and was still cutting well when it was removed for evaluation.

#### Example 14:

A test was conducted with carbide-tipped circular saw blades, comparing the standard 94% WC/6% Co fine grain tips to identical tips re-sintered in 1% BN mixed in the alumina sand. Both blades were cutting copper tubing. The standard blade made 5,408 cuts, and the treated blade made 22,743 cuts. The treated blade was then resharpened and made 16,000 more cuts.

#### Example 15:

This test was done to compare the treated and non-treated carbide tips in cutting fiberglass. The tips were made of fine grain 95.5% WC/4.5% Co, and some tips were treated by re-sintering in alumina sand with 1% BN added. The tips were put on hole saws. The regular untreated carbide tipped hole saws cut 16-18 fiberglass panels. The hole saw with treated tips cut 24 fiberglass panels.

#### Example 16:

A test was run to see what would happen if unsintered carbide bodies were sintered in pure boron powder. Saw tips were placed on trays in a vacuum furnace. Argon gas was present at the full sinter temperature and disassociated ammonia was present at intermediate temperatures. The green (unsintered) body was surrounded by boron powder and sintered. The result was a deformed plug with a surface layer. Thus, sintering in 100% boron powder does not achieve the present invention.

However, other carbide bodies which were in the same furnace during this test, were not surrounded by the boron powder and were remote from it, and some of these remote bodies showed the feathery microstructure, indicating that boron had entered into their microstructure. This indicates that the boron entered the body in a gas phase and raises the possibility that the desired homogeneous boron dispersion in the body could be accomplished by passing some type of boron-containing gas through the furnace during sintering. It is thought that the boron could be supplied by boron-containing inorganic or organometallic compounds having vaporization temperatures convenient for the introduction of their vapors or of gaseous, boron-containing breakdown species into the treatment zone.

Example 17:

Tests were conducted to see whether the atmosphere in the sintering furnace affected the amount of boron in the sample. In these tests, the samples were OM1 grade containing 91% WC and 9% Co. They were sintered in a continuous stoking furnace in a sand containing 1% BN, and were sintered at 1400 °c for one hour. After sintering, a bulk analysis was done to determine the amount of boron in the sample. It was found that an ammonia atmosphere permitted much more boron to enter the microstructure than did a nitrogen atmosphere and that a pure hydrogen atmosphere permitted even more boron to enter the microstructure. In the case of an atmosphere of N<sub>2</sub> or dry N<sub>2</sub>, the sintered sample contained about 30 parts per million (ppm) of boron. In the NH<sub>3</sub> atmosphere, the sample contained about 430 ppm boron, and the dry NH<sub>3</sub> atmosphere produced a sample having 365 ppm boron. The pure dry hydrogen produced a sample having 1376 ppm boron.

**Claims**

1. A cemented carbide body, comprising:
  - a tungsten carbide phase;
  - a cobalt binder phase; and
  - a quaternary third phase comprising cobalt, tungsten, boron and carbon, the third phase being dispersed throughout the body.
2. A cemented carbide body as claimed in claim 1, wherein the ratio by weight of tungsten to cobalt in the third phase is greater than 1.0:1.0.
3. A cemented carbide body as claimed in claim 1 or 2, wherein the ratio by weight of boron to carbon in the third phase is greater than 1.0:1.0.
4. A cemented carbide body as claimed in claim 3, wherein the ratio by weight of boron to carbon in the third phase is between 1.0:1.0 and 12.0:1.0.
5. A cemented carbide body as claimed in any preceding claim, wherein the tungsten carbide particles are generally angular and blocky in shape but, in the region of the third phase, the tungsten carbide particles are rounded and smaller.
6. A cemented carbide body as claimed in any preceding claim, wherein the average dimensions of the third phase are larger than the average dimensions of the cobalt binder phase.
7. A method for producing a cemented carbide body having a tungsten carbide phase, a cobalt binder phase, and a quaternary third phase having cobalt, tungsten, boron and carbon, the method comprising the steps of:
  - a) preparing one or more tungsten carbide bodies in a shape including a tungsten carbide material and a cobalt binder material; and
  - b) sintering said shape in the presence of a boron-containing material, by surrounding at least some of the tungsten carbide bodies with boron-containing material, such that appreciable quantities of boron from said boron-containing material migrate into said shape and become dispersed throughout the microstructure of the shape to a depth of at least 0.0049 mm (0.125 inch) or completely throughout the shape if the shape is less than 0.0049 mm (0.125 inch) thick, forming the quaternary third phase, wherein the microstructure of said shape, after sintering, exhibits a feathery etch phase throughout the body when etched with a standard acid etchant or Murakami's reagent.
8. A method according to claim 7, wherein the sintering is done in a disassociated ammonia atmosphere.
9. A method according to claim 7, wherein the sintering is done in a hydrogen atmosphere.
10. A method according to claim 7, 8 or 9, wherein the boron-containing material present during the sintering is selected from boron powder, boron nitride, boron oxide, boron carbide, AlB<sub>2</sub>, AlB<sub>12</sub>, CrB, CrB<sub>2</sub>, Cr<sub>3</sub>B<sub>5</sub>, MoB, NbB<sub>5</sub>, NbB<sub>2</sub>, B<sub>3</sub>Si, B<sub>4</sub>Si, B<sub>6</sub>Si, TaB, TaB<sub>2</sub>, TiB<sub>2</sub>, WB, W<sub>2</sub>B<sub>5</sub>, W<sub>2</sub>B, VB<sub>2</sub>, and ZrB<sub>2</sub>.

11. A method according to claim 7, 8 or 9, wherein said shape is immersed during sintering in a sintering sand which is in an admixture with the boron-containing material which is selected from boron nitride, boron, boron oxide, and boron carbide.
- 5 12. A method according to claim 7, 8 or 9, wherein, during sintering, said shape is immersed in a sintering sand which is in an admixture with the boron-containing material, in which boron constitutes from 0.003 to 50 percent by weight of the sand mixture.
- 10 13. A method according to claim 7, 8 or 9, wherein said shape is immersed in a sintering media um which includes from 0.003 to 50 percent by weight boron in the form of a boron-containing material selected from BN, boron, boron oxide, and boron carbide.
14. A method according to claim 7, 8 or 9, wherein, during sintering, said shape is immersed in a mixture of a sintering sand and boron-nitride in an amount of 0.05 to 2 percent by weight of the mixture.
- 15 15. A method as claimed in any one of claims 7 to 14, wherein said shape has been previously sintered, and the present operation is a re-sintering of said previously sintered body.
16. A method as claimed in claim 7, 8 or 9, wherein said shape is painted with a boron-containing paint prior to sintering.
- 20 17. A method as claimed in claim 7, 8 or 9, wherein said shape is placed in contact with a surface which has been coated with a boron-containing material prior to sintering.
- 25 18. A method for producing a cemented carbide body having a tungsten carbide phase, a cobalt binder phase, and a quaternary third phase having cobalt, tungsten, boron and carbon, the method comprising the steps of:  
 providing one or more tungsten carbide bodies in a shape including a tungsten carbide material and a cobalt binder material;  
 30 immersing said shape in a sintering sand which is in an admixture with a controlled amount of a boron-containing material;  
 and sintering said shape in the sand mixture under controlled conditions by surrounding at least some of the tungsten carbide bodies with boron-containing material providing a gradient of some form of boron throughout said shape, with the amount of boron being greater at the outside and gradually  
 35 reducing in concentration toward the centre, thereby forming the quaternary third phase, wherein the microstructure of said shape, after sintering, exhibits a feathery etch phase throughout the body when etched with a standard acid etchant or Murakami's reagent.
- 40 19. A cemented carbide body, comprising:  
 a) carbide phase, including a carbide former and carbon;  
 b) a binder phase made mostly of a binder element; and  
 c) a quaternary third phase comprising a dispersion of boron-containing material throughout the body, wherein the microstructure of said carbide body, when etched with Murakami's Reagent or and  
 45 solution, exhibits an etch phase having a feathery structure throughout the body.
- 50 20. A cemented carbide body as claimed in claim 19, wherein:  
 a) the carbide former is selected from titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten;  
 b) the binder phase is selected from manganese, iron, cobalt, nickel, copper, aluminium, silicon, ruthenium and osmium; and  
 c) the amount of boron in the body is from 25 to 3000 parts per million.
- 55 21. A cemented carbide body as claimed in claim 19, wherein the carbide phase is WC and the binder phase is cobalt.
22. A cemented carbide body as claimed in any one of claims 1 to 16, 19, and 21, wherein the amount of boron in the body is from 25 to 3000 parts per million.

23. A cemented carbide body as claimed in any one of claims 19 to 22, wherein the distribution of the amount of boron in the body is a controlled gradient, with greater concentrations of boron and the etch phase at the surface and lesser concentrations towards the centre of said body.
- 5 24. A cemented carbide body as claimed in any one of claim 19 to 23, wherein said etch phase also includes a greater percent by weight of the carbide former than is found in the binder phase.
- 10 25. A cemented carbide body, comprising:  
a) a carbide phase, including a carbide former and carbon;  
b) a binder phase having less than 30 percent by weight of carbide former; and  
c) a quaternary third phase including a binder material and boron, wherein the third phase comprises a dispersion of boron-containing material throughout the body, wherein the microstructure of the carbide body, when etched with Murakami's Reagent or acid solution, exhibits an etch phase having a feathery structure throughout the body.
- 15 26. A cemented carbide body as claimed in claim 25, wherein said third phase also includes at least 40% by weight of carbide former.
- 20 27. A cemented carbide body as claimed in claim 25 or 26, wherein the carbide former is tungsten and the third phase includes approximately 60% by weight of tungsten.
- 25 28. A cemented carbide body as claimed in claim 19, wherein said etch phase, before being etched, includes some of the carbide former, some of the binder element, some carbon, and some boron, and wherein the ratio by weight of carbide former to binder element in the etch phase is greater than 1.0:1.0.
- 30 29. A cemented carbide body as claimed in any one of claims 1 to 6, wherein the boron in the third phase is derived from baron powder, baron nitride, boron oxide, baron carbide,  $AlB_2$ ,  $AlB_{1,2}$ ,  $CrB$ ,  $CrB_2$ ,  $Cr_3B_5$ ,  $MoB$ ,  $NbB_6$ ,  $NbB_2$ ,  $B_3Si$ ,  $B_4Si$ ,  $B_6Si$ ,  $TaB$ ,  $TaB_2$ ,  $TiB_2$ ,  $WB$ ,  $W_2B_5$ ,  $W_2B$ ,  $VB_2$ , and  $ZrB_2$ .

### Patentansprüche

- 35 1. Verfestigter Carbidkörper, umfassend  
eine Wolframcarbidphase;  
eine Kobalt-Binderphase; und  
eine quarternäre dritte Phase, enthaltend Kobalt, Wolfram, Bor und Kohlenstoff, wobei die dritte Phase durchgehend im Körper verteilt ist.
- 40 2. Verfestigter Carbidkörper nach Anspruch 1, worin in der dritten Phase das Gewichtsverhältnis von Wolfram zu Kobalt größer ist als 1,0:1,0.
3. Verfestigter Carbidkörper nach Anspruch 1 oder 2, worin in der dritten Phase das Gewichtsverhältnis von Bor zu Kohlenstoff größer ist als 1,0:1,0.
- 45 4. Verfestigter Carbidkörper nach Anspruch 3, worin in der dritten Phase das Gewichtsverhältnis von Bor zu Kohlenstoff zwischen 1,0:1,0 und 12,0:1,0 ist.
- 50 5. Verfestigter Carbidkörper nach irgendeinem vorhergehenden Anspruch, worin die Wolframcarbid-Partikel im allgemeinen winkelig- und blockförmig sind, aber im Bereich der dritten Phase gerundet und kleiner.
6. Verfestigter Carbidkörper nach irgendeinem vorhergehenden Anspruch, worin die Durchschnittsgrößen der dritten Phase größer sind als die Durchschnittsgrößen der Kobalt-Binderphase.
- 55 7. Verfahren zur Herstellung eines verfestigten Carbidkörpers mit einer Wolframcarbidphase, einer Kobalt-Binderphase und einer quarternären dritten Phase mit Kobalt, Wolfram, Bor und Kohlenstoff, das die Verfahrensschritte aufweist:

- a) Bereitstellen von ein oder mehreren Wolframcarbidkörpern, enthaltend ein Wolframcarbidmaterial und ein Kobalt-Bindermaterial, in einer Form; und  
 b) Sintern der Form in Gegenwart von borhaltigem Material unter Umgeben von mindestens einigen der Wolframcarbidkörper mit borhaltigem Material, so daß merkliche Mengen Bor aus dem borhaltigen Material in die Form übergehen und sich in der Mikrostruktur der Form bis in eine Tiefe von  
 5 mindestens 0,0049 mm (0,125 Inch) oder über die ganze Form, falls die Form weniger als 0,0049 mm (0,125 Inch) dick ist, durchgehend verteilen unter Bildung der quarternären dritten Phase, wobei nach dem Sintern die Mikrostruktur der Form, wird sie mit einem sauren Standard-Ätzmittel oder Murakamis Reagens geätzt, im Körper durchgehend eine gefederte Ätzphase zeigt.
- 10
8. Verfahren nach Anspruch 7, wobei das Sintern unter einer disassozierten Ammoniak-Atmosphäre erfolgt.
9. Verfahren nach Anspruch 7, wobei das Sintern unter einer Wasserstoffatmosphäre erfolgt.
- 15
10. Verfahren nach Anspruch 7, 8 oder 9, wobei das beim Sintern vorliegende borhaltige Material ausgewählt ist aus Borpulver, Bornitrid, Boroxid, Borcarbid,  $AlB_2$ ,  $AlB_{12}$ , CrB,  $CrB_2$ ,  $Cr_3B_5$ , MoB,  $NbB_6$ ,  $NbB_2$ ,  $B_3Si$ ,  $B_4Si$ ,  $B_6Si$ , TaB,  $TaB_2$ ,  $TiB_2$ , WB,  $W_2B_5$ ,  $W_2B$ ,  $VB_2$  und  $ZrB_2$ .
- 20
11. Verfahren nach Anspruch 7, 8 oder 9, wobei beim Sintern die Form in einen Sintersand getaucht wird, der eine Mischung ist mit borhaltigem Material, ausgewählt aus Bornitrid, Bor, Boroxid und Borcarbid.
12. Verfahren nach Anspruch 7, 8 oder 9, wobei beim Sintern die Form in Sintersand getaucht wird, der eine Mischung ist mit borhaltigem Material und worin das Bor 0,003 bis 50 Gew.% der Sandmischung stellt.
- 25
13. Verfahren nach Anspruch 7, 8 oder 9, wobei die Form in ein Sintermedium getaucht wird, das 0,003 bis 50 Gew.% Bor in Form von borhaltigem Material, ausgewählt aus BN, Bor, Boroxid und Borcarbid, enthält.
- 30
14. Verfahren nach Anspruch 7, 8 oder 9, wobei beim Sintern die Form in eine Mischung aus Sintersand und Bornitrid, das in einer Menge von 0,05 bis 2 Gew.% der Mischung vorliegt, getaucht wird.
15. Verfahren nach einem der Ansprüche 7 bis 14, wobei die Form zuvor gesintert wurde und der Vorgang nunmehr ein erneutes Sintern des zuvor gesinterten Körpers ist.
- 35
16. Verfahren nach Anspruch 7, 8 oder 9, wobei die Form vor dem Sintern mit einem borhaltigen Anstrich versehen wird.
- 40
17. Verfahren nach Anspruch 7, 8 oder 9, wobei die Form in Kontakt mit einer Oberfläche gebracht wird, die vor dem Sintern mit einem borhaltigen Material beschichtet wurde.
18. Verfahren zur Herstellung eines verfestigten Carbidkörpers mit einer Wolframcarbidphase, einer Kobalt-Binderphase und einer quarternären dritten Phase mit Kobalt, Wolfram, Bor und Kohlenstoff, wobei das Verfahren die Schritte aufweist:  
 Bereitstellen von ein oder mehreren Wolframcarbidkörpern, enthaltend ein Wolframcarbidmaterial und eine Kobalt-Bindermaterial, in einer Form;  
 Tauchen der Form in einen Sintersand, der eine Mischung ist mit einer kontrollierten Menge eines borhaltigen Materials; und  
 50 Sintern der Form in einer Sandmischung unter kontrollierten Bedingungen unter Umgeben von mindestens einigen der Wolframcarbidkörper mit borhaltigem Material, wobei in der Form durchgehend ein Gradient hergestellt wird mit irgendeiner Form von Bor - wobei die Menge an Bor an der Außenseite höher ist und deren Konzentration zur Mitte hin allmählich abnimmt - so daß eine quarternäre dritte Phase geschaffen wird, in der nach dem Sintern die Mikrostruktur der Form, erfolgt ein Ätzen mit einem sauren Standard-Ätzmittel oder Murakamis Reagens, im Körper durchgehend eine  
 55 federartige Ätzform zeigt.
19. Verfestigter Carbidkörper, umfassend

- a) eine Carbidgephase, enthaltend einen Carbidgebildner und Kohlenstoff;  
 b) eine Binderphase, die hauptsächlich aus einem Binderelement hergestellt ist; und  
 c) eine quarternäre dritte Phase, die im Körper durchgehend eine Dispersion von borhaltigem Material enthält, wobei die Mikrostruktur des Carbidgekörpers, erfolgt ein Ätzen mit Murakamis Reagens oder einer Säurelösung, im Körper durchgehend eine Ätzphase mit gefederter Struktur zeigt.
- 5
20. Verfestigter Carbidgekörper nach Anspruch 19, worin  
 a) der Carbidgebildner ausgewählt ist aus Titan, Zircon, Hafnium, Vanadium, Niob, Tantal, Chrom, Molybdän und Wolfram;  
 10 b) die Binderphase ausgewählt ist aus Mangan, Eisen, Kobalt, Nickel, Kupfer, Aluminium, Silicium, Ruthenium und Osmium; und  
 c) die Menge an Bor im Körper 25 bis 3000 ppm ist.
- 15 21. Verfestigter Carbidgekörper nach Anspruch 19, worin die Carbidgephase WC ist und die Binderphase Kobalt.
22. Verfestigter Carbidgekörper nach irgendeinem der Ansprüche 1 bis 16, 19 und 21, worin die Menge an Bor im Körper 25 bis 3000 ppm ist.
- 20 23. Verfestigter Carbidgekörper nach irgendeinem der Ansprüche 19 bis 22, worin die Verteilung der Menge an Bor im Körper ein gesteuerter Gradient ist, wobei die Borkonzentration in der Ätzphase an der Oberfläche höher ist und zur Mitte des Körpers hin abnimmt.
- 25 24. Verfestigter Carbidgekörper nach irgendeinem Anspruch 19 bis 23, worin die Ätzphase auch einen höheren Gewichtsprozentsatz Carbidgebildner enthält als die Binderphase.
25. Verfestigter Carbidgekörper, umfassend  
 a) eine Carbidgephase, enthaltend einen Carbidgebildner und Kohlenstoff;  
 30 b) eine Binderphase mit weniger als 30 Gew.% Carbidgebildner; und  
 c) eine quarternäre dritte Phase, enthaltend ein Bindermaterial und Bor,  
 worin die dritte Phase im Körper durchgehend eine Dispersion von borhaltigem Material enthält, wobei die Mikrostruktur des Carbidgekörpers, wird sie mit Murakamis Reagens oder einer Säurelösung geätzt, im Körper durchgehend eine Ätzphase einer federartiger Struktur zeigt.
- 35 26. Verfestigter Carbidgekörper nach Anspruch 25, worin die dritte Phase auch mindestens 40 Gew.% Carbidgebildner enthält.
27. Verfestigter Carbidgekörper nach Anspruch 25 oder 26, worin der Carbidgebildner Wolfram ist und die dritte Phase ca. 60 Gew.% Wolfram enthält.
- 40 28. Verfestigter Carbidgekörper nach Anspruch 19, worin vor dem Ätzen die Ätzphase etwas von dem Carbidgebildner, etwas von dem Binderelement, etwas Kohlenstoff und etwas Bor enthält und worin in der Ätzphase das Gewichtsverhältnis von Carbidgebildner zu Binderelement größer ist als 1,0:1,0.
- 45 29. Verfestigter Carbidgekörper nach irgendeinem der Ansprüche 1 bis 6, worin das Bor in der dritten Phase herkommt von Borpulver, Bornitrid, Boroxid, Borcarbid,  $\text{AlB}_2$ ,  $\text{AlB}_{12}$ , CrB,  $\text{CrB}_2$ ,  $\text{Cr}_3\text{B}_5$ , MoB,  $\text{NbB}_6$ ,  $\text{NbB}_2$ ,  $\text{B}_3\text{Si}$ ,  $\text{B}_4\text{Si}$ ,  $\text{B}_6\text{Si}$ , TaB,  $\text{TaB}_2$ ,  $\text{TiB}_2$ , WB,  $\text{W}_2\text{B}_5$ ,  $\text{W}_2\text{B}$ ,  $\text{VB}_2$  und  $\text{ZrB}_2$ .

50 **Revendications**

1. Corps fritté en carbure, comprenant  
 une phase en carbure de tungstène,  
 une phase de liant en cobalt, et  
 55 une troisième phase quaternaire contenant du cobalt, du tungstène, du bore et du carbone, la troisième phase étant dispersée dans tout le corps.

## EP 0 332 463 B1

2. Corps fritté en carbure conforme à la revendication 1, caractérisé en ce que le rapport en poids du tungstène au cobalt dans la troisième phase est supérieur à 1,0/1,0.
3. Corps fritté en carbure conforme à la revendication 1 ou 2, caractérisé en ce que le rapport en poids du bore au carbone dans la troisième phase est supérieur à 1,0/1,0.
4. Corps fritté en carbure conforme à la revendication 3, caractérisé en ce que le rapport en poids du bore au carbone dans la troisième phase est compris entre 1,0/1,0 et 12,0/1,0.
5. Corps fritté en carbure conforme à une quelconque des revendications précédentes, caractérisé en ce que les particules de carbure de tungstène ont généralement une forme angulaire et compacte mais sont plus rondes et plus petites dans la région de la troisième phase.
6. Corps fritté en carbure conforme à une quelconque des revendications précédentes, caractérisé en ce que les dimensions moyennes de la troisième phase sont plus importantes que les dimensions moyennes de la phase liante en cobalt.
7. Procédé de préparation d'un corps fritté en carbure ayant une phase de carbure de tungstène, une phase liante en cobalt et une troisième phase quaternaire contenant du cobalt, du tungstène, du bore et du carbone, le procédé comprenant les étapes de :
  - a) préparation d'un ou de plusieurs corps en carbure de tungstène en une forme, contenant un matériau en carbure de tungstène et un matériau liant en cobalt, et
  - b) frittage de ladite forme en présence d'un matériau contenant du bore, en entourant au moins une partie des corps en carbure de tungstène avec du matériau contenant du bore, de manière à ce que des quantités appréciables de bore migrent dudit matériau contenant du bore vers l'intérieur de la forme et soient dispersées dans la microstructure de la forme à une profondeur d'au moins égale à 0,0049 mm (0,125 pouces) ou dans toute la forme si l'épaisseur de la forme est inférieure à 0,0049 mm (0,125 pouces), formant ainsi la troisième phase quaternaire, caractérisé en ce que, après frittage, ladite forme, attaquée par un réactif d'attaque acide standard ou par le réactif de Murakami, montre, sur tout le corps, une phase de gravure ayant une microstructure ramifiée.
8. Procédé conforme à la revendication 7, caractérisé en ce que le frittage est réalisé sous une atmosphère d'ammoniac dissocié.
9. Procédé conforme à la revendication 7, caractérisé en ce que le frittage est réalisé dans une atmosphère d'hydrogène.
10. Procédé conforme à la revendication 7, 8 ou 9, caractérisé en ce que le matériau contenant du bore, présent pendant le frittage, est choisi parmi la poudre de bore, le nitrure de bore, l'oxyde de bore, le carbure de bore,  $\text{AlB}_2$ ,  $\text{AlB}_{12}$ ,  $\text{CrB}$ ,  $\text{CrB}_2$ ,  $\text{Cr}_3\text{B}_5$ ,  $\text{MoB}$ ,  $\text{NbB}_6$ ,  $\text{NbB}_2$ ,  $\text{B}_3\text{Si}$ ,  $\text{B}_4\text{Si}$ ,  $\text{B}_6\text{Si}$ ,  $\text{TaB}$ ,  $\text{TaB}_2$ ,  $\text{TiB}_2$ ,  $\text{WB}$ ,  $\text{W}_2\text{B}_5$ ,  $\text{W}_2\text{B}$ ,  $\text{VB}_2$  et  $\text{ZrB}_2$ .
11. Procédé conforme à la revendication 7, 8 ou 9, caractérisé en ce que ladite forme est immergée pendant le frittage dans du sable de frittage qui est sous forme de mélange avec le matériau contenant du bore, choisi parmi le nitrure de bore, le bore, l'oxyde de bore et le carbure de bore.
12. Procédé conforme à la revendication 7, 8 ou 9, caractérisé en ce que, pendant le frittage, ladite forme est immergée dans du sable de frittage qui est sous forme de mélange avec le matériau contenant du bore, dans lequel le bore représente entre 0,003 et 50 % en poids du mélange de sable.
13. Procédé conforme à la revendication 7, 8 ou 9, caractérisé en ce que ladite forme est immergée dans un milieu de frittage contenant entre 0,003 et 50 % en poids de bore sous forme de matériau contenant du bore, choisi parmi BN, le bore, l'oxyde de bore et le carbure de bore.
14. Procédé conforme à la revendication 7, 8 ou 9, caractérisé en ce que pendant le frittage, ladite forme est immergée dans un mélange de sable de frittage avec du nitrure de bore à raison de 0,05 à 2 % en poids du mélange.

15. Procédé conforme à une des revendications 7 à 14, caractérisé en ce que ladite forme a été frittée préalablement et la présente opération est un re-frittage du corps préalablement fritté.
- 5 16. Procédé conforme à une des revendications 7, 8 ou 9, caractérisé en ce que ladite forme est peinte avec une peinture contenant du bore avant le frittage.
17. Procédé conforme à une des revendications 7, 8 ou 9, caractérisé en ce que ladite forme est mise en contact, avant le frittage, avec une surface qui porte un revêtement d'un matériau contenant du bore.
- 10 18. Procédé de préparation d'un corps fritté en carbure comportant une phase de carbure de tungstène, une phase liante en cobalt et une troisième phase quaternaire contenant du cobalt, du tungstène, du bore et du carbone, le procédé comprenant les étapes de :
- 15       préparation d'un ou de plusieurs corps en carbure de tungstène en une forme, contenant un matériau de carbure de tungstène et un matériau liant en cobalt,
- 15       immersion de ladite forme dans du sable de frittage qui est un mélange avec une quantité contrôlée de matériau contenant du bore, et
- 20       frittage de ladite forme dans le mélange de sable, dans des conditions contrôlées, en entourant au moins une partie des corps en carbure de tungstène avec le matériau contenant du bore, créant ainsi dans ladite forme un certain gradient de bore, la quantité de bore étant plus importante à l'extérieur et la concentration diminuant graduellement vers le centre, formant ainsi la troisième phase quaternaire, caractérisé en ce que, après frittage, ladite forme, attaquée par un réactif d'attaque acide standard ou par le réactif de Murakami, montre une phase de gravure ayant une microstructure ramifiée sur tout le corps.
- 25 19. Corps fritté en carbure, comprenant :
- 25       a) une phase de carbure contenant un métal formant des carbures et du carbone,
- 25       b) une phase liante composée principalement d'un élément liant, et
- 30       c) d'une troisième phase quaternaire comprenant une dispersion de matériau contenant du bore dans tout le corps, caractérisé en ce que ledit corps en carbure, attaqué par le réactif de Murakami ou par une solution acide, montre une phase de gravure ayant une microstructure ramifiée sur tout le corps.
- 30 20. Corps fritté en carbure conforme à la revendication 19, dans lequel,
- 35       a) le métal formant des carbures est choisi parmi le titane, le zirconium, l'hafnium, le vanadium, le niobium, le tantale, le chrome, le molybdène et le tungstène,
- 35       b) la phase liante est choisie parmi le manganèse, le fer, le cobalt, le nickel, le cuivre, l'aluminium, le silicium, le ruthénium et l'osmium, et
- 35       c) la quantité de bore dans le corps est comprise entre 25 et 3000 parties par million.
- 40 21. Corps fritté en carbure, conforme à la revendication 19, caractérisé en ce que la phase de carbure est du WC et la phase de liant est du cobalt.
22. Corps fritté en carbure conforme à une quelconque des revendications 1 à 16, 19 et 21, caractérisé en ce que la quantité de bore dans le corps est comprise entre 25 et 3000 parties par million.
- 45 23. Corps fritté en carbure conforme à une quelconque des revendications 19 à 22, dans lequel la distribution de la quantité de bore dans le corps est un gradient contrôlé, avec des concentrations plus élevées de bore dans la phase de gravure à la surface, et des concentrations plus faibles vers le centre dudit corps.
- 50 24. Corps fritté en carbure conforme à une quelconque des revendications 19 à 23, caractérisé en ce que ladite phase de gravure contient également un pourcentage en poids plus élevé du métal formant des carbures que celui trouvé dans la phase de liant.
- 55 25. Corps fritté en carbure, comprenant :
- 55       a) une phase de carbure, contenant un métal formant des carbures et du carbone,
- 55       b) une phase de liant contenant moins de 30 % en poids de métal formant des carbures, et

c) une troisième phase quaternaire, contenant un matériau liant et du bore, caractérisé en ce que, après frittage, ladite forme, attaquée par un réactif d'attaque acide standard ou par le réactif de Murakami, montre une phase de gravure ayant une microstructure ramifiée sur tout le corps.

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**26.** Corps fritté en carbure conforme à la revendication 25, caractérisé en ce que ladite troisième phase contient également au moins 40 % en poids de métal formant des carbures.

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**27.** Corps fritté en carbure conforme à la revendication 25 ou 26, caractérisé en ce que le métal formant des carbures est le tungstène, et la troisième phase contient approximativement 60 % en poids de tungstène.

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**28.** Corps fritté en carbure conforme à la revendication 19, caractérisée en ce que ladite phase de gravure, contient, avant la gravure, un peu du métal formant des carbures, un peu de l'élément du liant, un peu de carbone et un peu de bore, et caractérisé en ce que le rapport en poids du métal formant des carbures à l'élément du liant dans la phase de gravure, est supérieur à 1,0/1,0.

20

**29.** Corps fritté en carbure conforme à une quelconque des revendications 1 à 6, caractérisé en ce que le bore dans la troisième phase provient de poudre de bore, de nitrure de bore, d'oxyde de bore, de carbure de bore, de  $AlB_2$ ,  $AlB_{12}$ ,  $CrB$ ,  $CrB_2$ ,  $Cr_3B_5$ ,  $MoB$ ,  $NbB_6$ ,  $NbB_2$ ,  $B_3Si$ ,  $B_4Si$ ,  $B_6Si$ ,  $TaB$ ,  $TaB_2$ ,  $TiB_2$ ,  $WB$ ,  $W_2B_5$ ,  $W_2B$ ,  $VB_2$  et  $ZrB_2$ .

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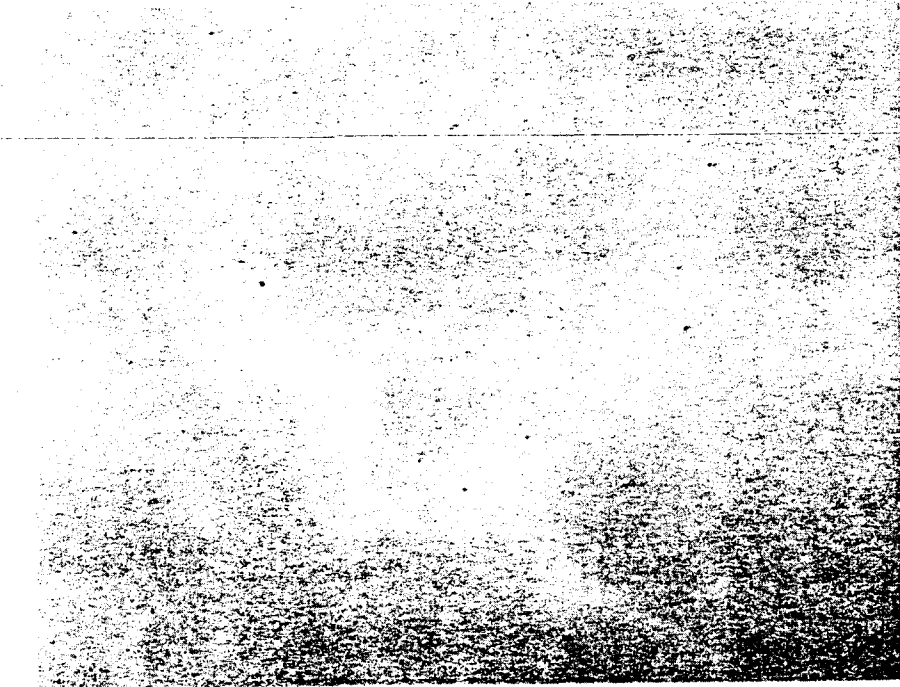
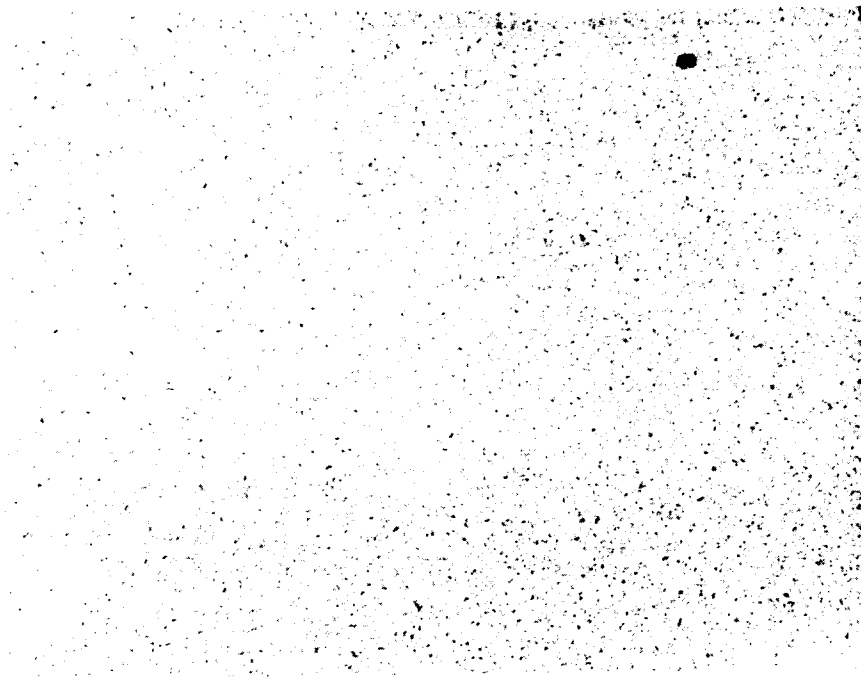


FIG. 1



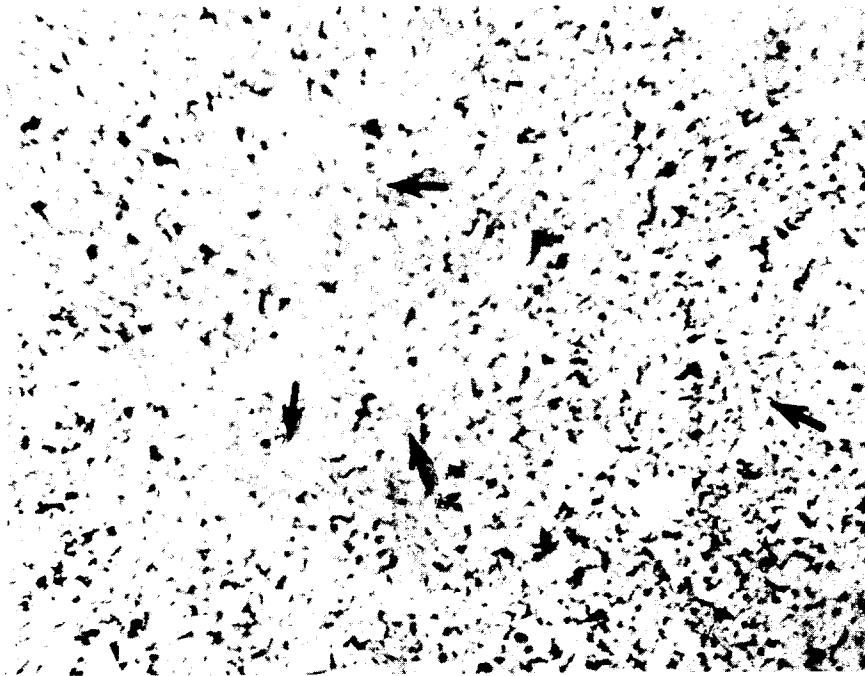
**FIG. 2**



**FIG. 3**

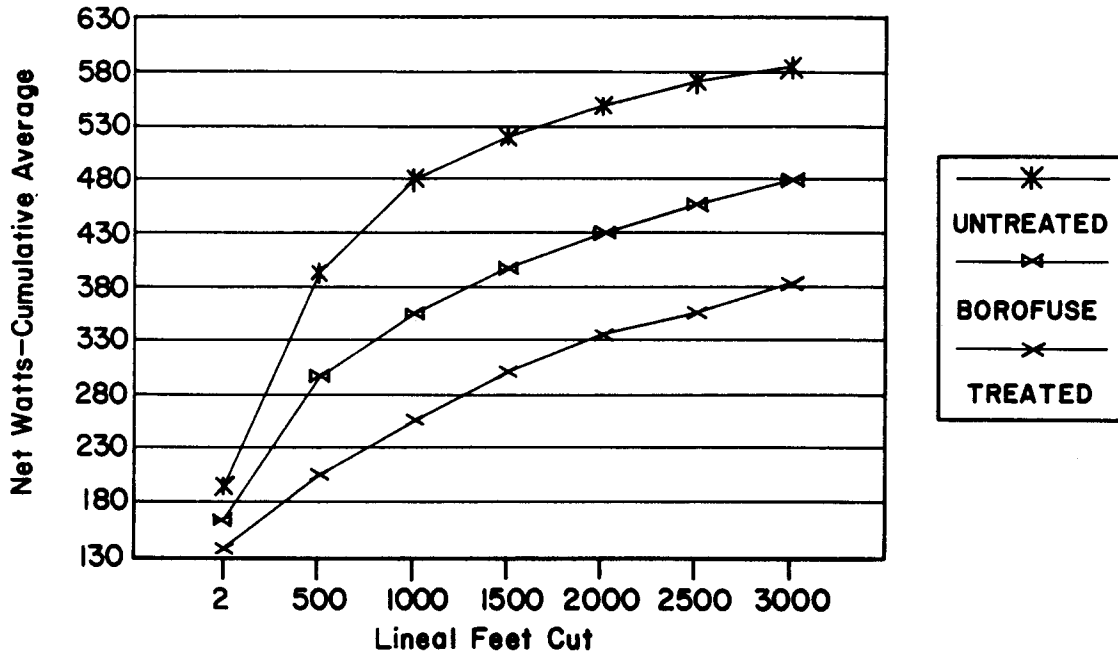


**FIG. 4**



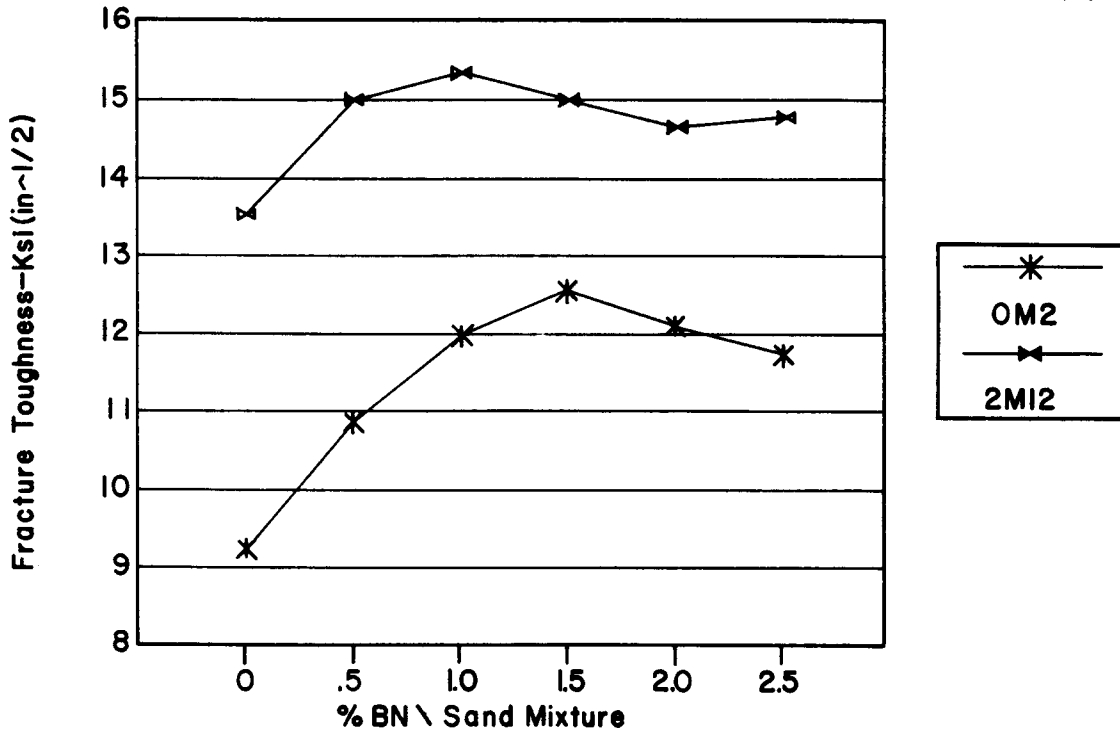
**FIG. 5**

**NET WATTS vs. LINEAL FEET CUT**  
**3/4" Particle Board @ 5 Ft.\Min.**



**FIG. 6**

**% BN SAND vs. FRACTURE TOUGHNESS K(app)**



**FIG. 7**

### % BN\SAND vs. EDDY CURRENT Scale: 10 KHZ

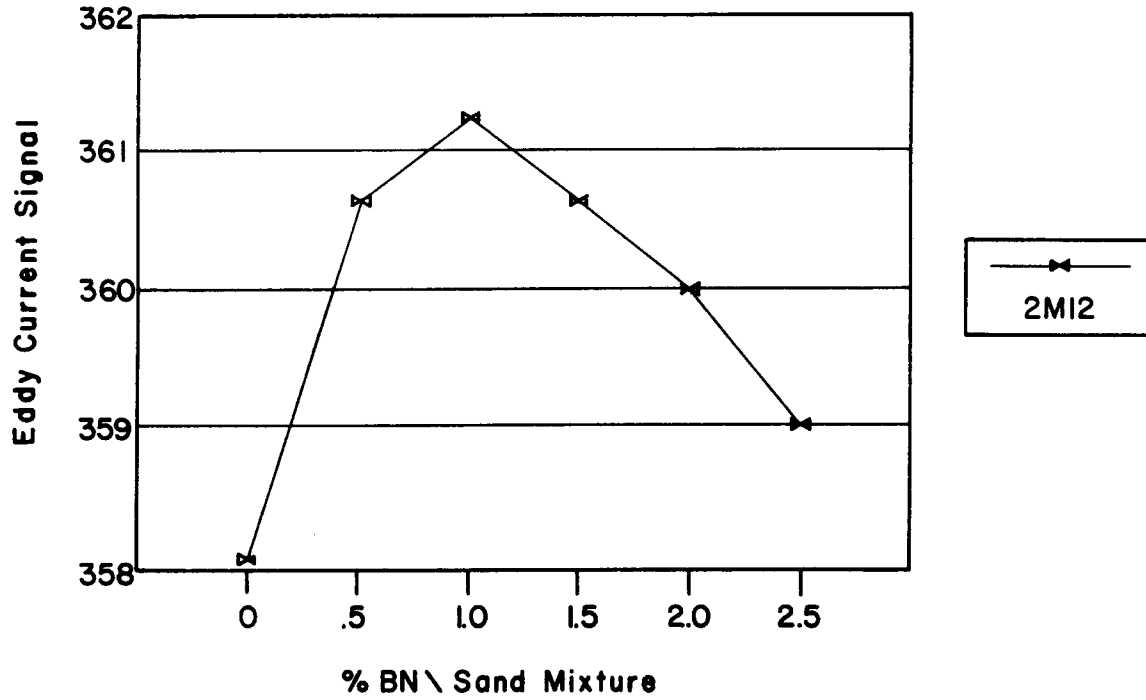


FIG. 8

### % BN\SAND vs. EDDY CURRENT Scale: 1 KHZ

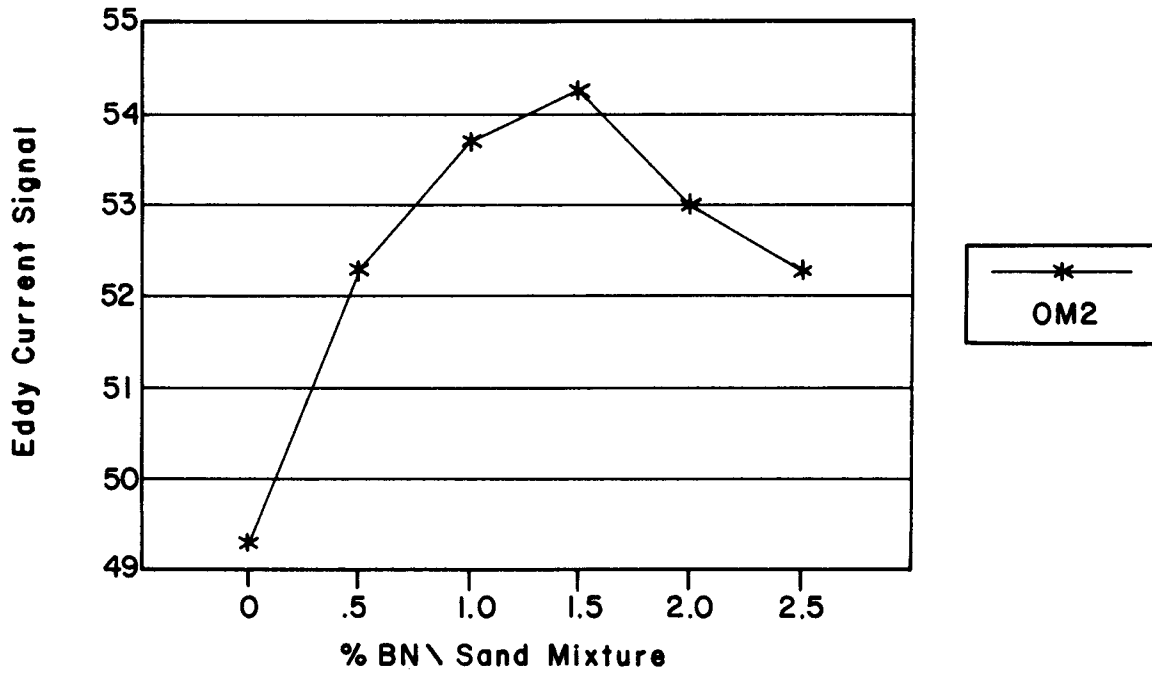


FIG. 9

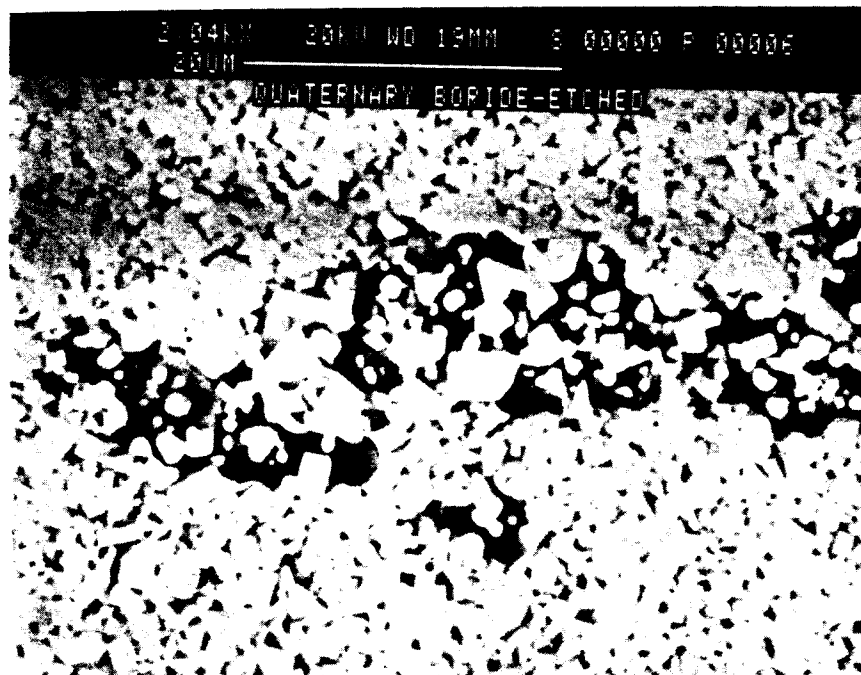


FIG. 10

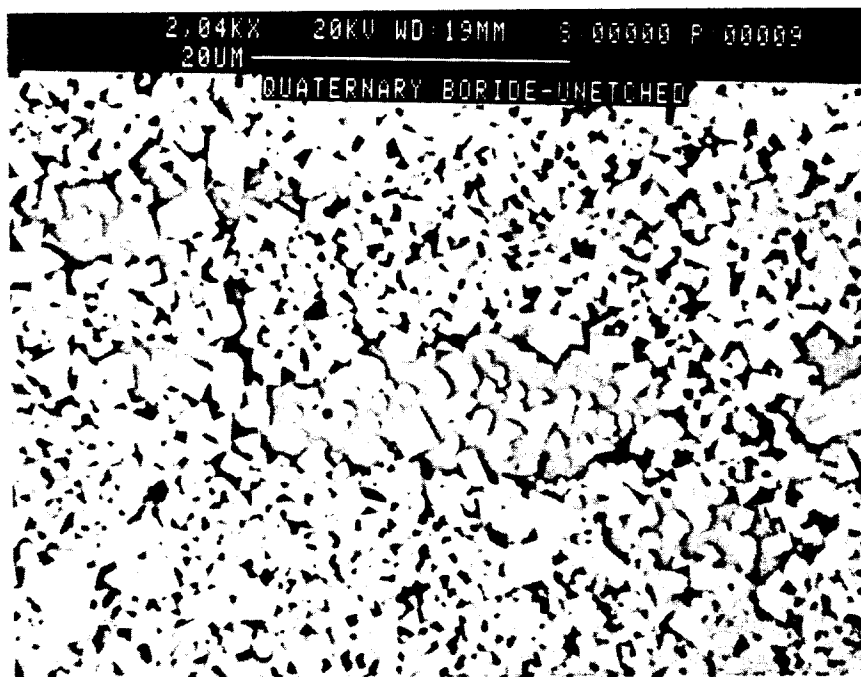


FIG. II