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METHOD OF HARDENING SINTERED CEMENTED-CARBIDE COMPOSITIONS BY BORONIZING

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ABSTRACT OF THE DISCLOSURE

Sintered, cemented-carbide compositions, e.g., cobalt-bonded tungsten carbide, are hardened by permeating a boron-containing material into the surface of the sintered composition. This boronizing treatment can be effected, for example, by heating the composition with a solid form of the boron-containing material, or by electrolysis in a molten boron salt bath.

SIMPLE DESCRIPTION OF DRAWINGS

FIG. 1 shows an electro microscopic picture of a conventional hard alloy of K01 in JIS (magnification 3,000). FIG. 2 shows an electro microscopic picture of an ultra hard alloy shown in the Example 1 of the invention (magnif. 3,000). FIG. 3 shows an electro microscopic cross section view of an ultra hard alloy shown in the Example 4 of the invention, the surface of which is boronized during sintering (magnif. 1,000). FIG. 4 shows an electro microscopic cross section view of an ultra hard alloy shown in the Example 6 of the invention, in the surface of which boron carbide (B_4C) is permeated and diffused during sintering (magnif. 3,000). FIG. 5 shows an electro microscopic cross section view of an ultra hard alloy shown in the Example 9 of the invention, the surface of which is boronized. FIG. 6 shows an electro microscopic cross section view of an ultra hard alloy shown in the Example 10 of the invention, in which the surface of the cermet is boronized (magnif. 1,000).

DETAILED DESCRIPTION OF INVENTION

The present invention relates to ultra hard alloys in which hardness is improved by adding boron or borides with high hardness, to hard alloy of carbide type which is called hard alloy or cermet. The object of the present invention is to provide ultra hard alloys suitable for cutting metallic materials. There are three basic manufacturing methods; the first one includes boron or borides from the beginning in the carbide type hard alloy, in the second one boron or borides are permeated and diffused in the surface of the carbide type hard alloy during pre-sintering, sintering or after-sintering, in the third one boron or borides are again permeated and diffused in the surface of ultra hard alloys which include boron or borides from the beginning.

The conventional hard alloys are formed by sintering one or more than two of tungsten carbide (WC), titanium carbide (TiC), niobium carbide (NbC), vanadium carbide (VC), tantalum carbide (TaC), etc. with one or more than two of metallic binders of cobalt (Co), nickel (Ni) and iron (Fe).

In the conventional hard alloys, abrasive resistance and impact resistance can be controlled within certain limits, by changing the ratio of the hard carbides and the soft metallic binders. Namely, if the soft metallic binder is small in its ratio, hardness and abrasive resistance increase, and if its ratio is large, increases impact resistance. However, from a practical point of view, as it is used as cutting tools, the ratio of soft metallic binders is restricted in its upper limit. Accordingly it should be within 5 to 20% by weight. If it is less than 5%, impact resistance of the hard alloys decreases and the alloys tend to brittle. With soft metallic binders over 20%, abrasive resistance of the alloys is too weak for practical use. With this composition, mechanical properties are also stable. Table 1 shows an example of some conventional hard alloys and their mechanical properties.

From this table it can be seen that the maximum hardness is about 1,800 Vickers. There are no other hard alloys at present which have higher hardness than this. When using these conventional hard alloys to cut such materials as tungsten alloy, stainless steel, cobalt alloy, titanium alloy, beryllium-copper alloy etc. which are difficult to cut, for machining watch parts, requiring extremely precise finish, there are found many disadvantages and shortages in the tool life, dimensional accuracy, surface smoothness and productivity.

Though the hard alloys have higher hardness and abrasive resistance than such tool steels as die-steel and high speed steel etc., its impact resistance is small. For this reason, the hard alloys with high impact resistance have long been sought. Little effort has been made to increase the hardnes sof these alloys.

The present invention seeks to eliminate the above defect and to provide tool materials suitable for precise cutting such as watch parts manufacturing.

The invention noticed that boron and borides had ex-

TABLE 1.—MECHANICAL PROPERTY OF HARD ALLOYS

Class and use	Grade	Composition: WC, percent	Composition: TiC TaC, percent	Composition: Co	Density, g./cm.³	Hardness (Hv) kg./mm.²	Transverse rupture strength, kg./mm.²
P—Steel, cast iron and malleable cast iron which forms long chip in cutting.	P01-2	30	64	6	7.2	1,800	75
	P01-3	51	43	6	8.5	1,750	90
	P01-4	62	33	5	10.1	1,750	100
	P05	77	18	5	12.2	1,700	110
	P10	63	28	9	10.7	1,600	130
	P20	76	14	10	11.9	1,500	150
	P25	71	20	9	12.4	1,450	175
	P30	82	8	10	13.1	1,450	175
	P40	75	12	13	12.7	1,400	195
	P50	68	15	17	12.5	1,300	220
M—Steel, cast steel, manganese steel, alloy cast iron and austenite steel.	M10	84	10	6	13.1	1,700	135
	M20	82	10	8	13.4	1,550	160
	M30	81	10	9	14.4	1,450	180
	M40	79	6	15	13.6	1,300	210
K—Cast iron, quenched steel, non-ferrous metal and synthetic resins.	K01	92	4	4	15.0	1,800	120
	K05	91	3	6	14.5	1,750	135
	K10	92	2	6	14.8	1,650	150
	K20	92	2	6	14.8	1,550	170
	K30	89	2	9	14.4	1,400	190
	K40	88	--------	12	14.3	1,300	210

tremely high hardness and abrasive resistance. By adding boron and borides in the hard alloys, alloys having such high hardness as not obtained before can be obtained.

Material		Hardness
Steel		740
Quartz	SiO_2	800
Zirconium nitride	ZrN	510
Zirconium boride	ZrB	1,560
Titanium nitride	TiN	1,770
Tungsten carbide	WC	1,870
d-Alumina	Al_2O_3	2,000
Zirconium carbide	ZrC	2,090
Titanium carbide	TiC	2,470
Boron	B	2,500
Silicon carbide	SiC	2,550
Titanium boride	TiB_2	2,710
Boride compound	TiB_2-B_4C	2,750
Boron carbide	B_4C	2,800
Diamond	C	7,000

The ultra hard alloy according to the first method of this invention includes one or more of boron (B), aluminium boride (AlB_2, AlB_{12}), chromium boride (CrB, CrB_2, Cr_5B_3), molybdenum boride (MoB, MoB_2), niobium boride (NbB_6, NbB, NbB_2), silicon boride (B_3Si, B_4Si, B_6Si), tantalum boride (TaB, Tab_2), titanium boride (TiB_2), tungsten boride (WB, W_2B_5, W_2B), vanadium boride (VB_2) and zirconium boride (ZrB_2), etc. in the hard alloys of carbide type comprising one or more than two of aluminium carbide (Al_4C_3), chromium carbide (Cr_3C_2), molybdenum carbide (Mo_2C), niobium carbide (NbC), silicon carbide (SiC), tantalum carbide (TaC), titanium carbide (TiC), tungsten carbide (WC), vanadium carbide (VC) and zironium carbide (ZrC) etc. and having hardness of 1,000 to 1,800 Vickers.

By this method, it was possible to produce the ultra hard alloy having hardness of 2,000 to 2,500 Vickers.

The ultra hard alloy according to the second method is produced by permeating and diffusing one or more than two of said boron and borides in the surface of said hard alloys of carbide type during pre-sintering, sintering or after sintering. The ultra hard alloy obtained shows extremely high hardness, i.e. maximum hardness of about 3,000 Vickers.

The ultra hard alloy according to the third method is produced by hardening again the surface of the ultra hard alloy which is produced by the first method. The ultra hard alloy obtained shows the highest hardness of all the alloys according to the invention. The maximum hardness was over 3,000 Vickers.

As described in Japanese patent Sho-25 (1950)-21, the conventional boronizing is applied to steel with low hardness which is hardened in melted boracic acid bath by electrolysis at about 1,000° C. This low hardness i.e. 1,000 to 1,300 Vickers can be also easily obtained by usual carbonizing or nitriding.

On the other hand, a boronizing according to this invention is applied to the hard alloys or the ultra hard alloy which have extremely high hardness from the beginning, and moreover, the hardness after the treatment is very high, i.e. 2,500 to 3,000 Vickers. And this boronizing is applied not only after sintering but also during presintering or sintering. According to this method, it is possible to permeate and diffuse all kinds of boron and borides.

The conventional hard alloys of carbide type referred to as "hard alloy" and cermet" is known as the best material for tools, because of its high hardness from the beginning. However, it shows inferior ductility.

The inventor seeking a new hard alloy, noticed that cobalt (Co), iron (Fe), nickel (Ni), tantalum (Ta), titanium (Ti) and tungsten (W) etc. tend to combine with boron and form hard borides and that the hard alloys were porous enough during presintering and sintering to permeate and diffuse boron or borides into the alloys. Thus we succeeded in producing the ultra hard alloy having desirable property.

According to the invention, completely novel alloy can be obtained by using the former equipments.

The following example will illustrate the present invention more clearly.

EXAMPLE 1

Producing method of the ultra hard alloy according to the invention is not much different from the conventional one. Powders of tungsten carbide (WC)—78%, tungsten boride (WB)—14%, tantalum-niobium carbide

(Ta(Nb)C)—3%

and cobalt—5% by weight, were put into a ball mill box and ground and mixed for about 100 hours in wet process. After that, it was dried in vacuum and small quantity of lubricant was added and mixed thoroughly for producing high density product and good pressing effect. And it was pressed by 3 t./cm.^{2} and presintered at about 900° C. in hydrogen gas, and was sintered at 1400 to 1450° C. in vacuum for 60 minutes. The resulting product was the ultra hard alloy having a hardness of 2,000 to 2,300 Vickers and a transverse rupture strength of 80 to 100 kg./mm.^{2} The polished surface of the ultra hard alloy was observed by an electron microscope, and no mold cavities and pinholes were found. The sintering state was very good.

As tungsten carbide (WC), it is difficult to sinter tungsten boride (WB), but tungsten boride well fits to tungsten carbide (WC) and it easily combines with cobalt (Co). So by using tungsten boride, we can obtain an extremely hard and flexible sintered alloy.

FIG. 1 shows an electro microscopic picture (magnif. 3,000) of an ordinary hard alloy, K01 of JIS which is composed of tungsten carbide (WC)—92%, tantalum-niobium carbide (Ta(Nb)C)—3% and cobalt (Co)—5% by weight. FIG. 2 shows an electro microscopic picture of the ultra hard alloy according to this invention.

EXAMPLE 2

Powders of tungsten carbide (WC)—9%, boron (B)—1%, tantalum-niobium carbide (Ta(Nb)C)—3% and cobalt (Co)—5% by weight were put into a ball mill box and treated in the same manner as the Example 1. And after presintering, it was sintered at about 1390° C. to 1440° C. in vacuum for 60 minutes. The resulting product was the ultra hard alloy having a hardness of about 2,100 to 2,350 Vickers and a transverse rupture strength of about 120 to 140 kg./mm.^{2}. Using boron carbide (B_4C) instead of boron (B), we could also obtain the ultra hard alloy having a hardness of about 2,000 to 2,300 Vickers.

EXAMPLE 3

The piece (2 x 2 x 20 mm.) of the ultra hard alloy comprising tungsten carbide (WC)—85%, titanium boride (TiB_2)—7%, tantalum-niobium carbide (Ta(Nb)C)—3% and cobalt (Co)—5% by weight was soldered to the cutting tool (7 x 7 x 40 mm.) for manufacturing watch parts, and formed. Using it, watch parts made of high carbon free-cutting steel of 1.25 mm. in diameter, in which 0.2% of lead (Pb) is added to the high carbon steel SK-4(JIS) was cut by the automatic lathe at cutting speed of 28 m./min., cutting depth of 0.37 mm. and feed of 0.005 mm./rev. while lubricating with cutting oil. As a result, it was found that this ultra hard alloy had the life three times as long as that of the usual hard alloy such as K01 having a hardness of 1,800 Vickers. It also increases the accuracy of the cutting surface and decreases time for changing tools, which result in improvement in the working efficiency.

EXAMPLE 4

Powders of tungsten carbide (WC)—92%, tantalum-niobium carbide (Ta(Nb)C)—3% and cobalt (Co)—5% by weight were ground, mixed, dried, pressed, formed to the piece (5 x 10 x 30 mm.) and presintered at 900° C. in the usual method. And that piece was packed into a graphite boat, the inner diameter of which was 50 mm.

and the depth was 30 mm., with 1 to 3μ of boron (B) powders to cover the piece with 5 to 10 mm. in thickness, and sintered at 1400° C. in vacuum for 60 minutes. After polishing the cross-section and the surface of the resulting piece as smooth as 1μ by the diamond wheel and the diamond paste, its hardness was measured. The hardness of the piece in the center was 1,810 Vickers, and the surface hardness was about 1,990 to 2,200 Vickers. Increase in hardness was about 400 Vickers and the hardened layer observed by the electron microscope was 10 to 15μ in thickness.

In the above described example, the effect was greatly increased by adding a boronizing accelerator to the powder of boron (B). The surface hardness of the piece was 2,350 to 2,550 Vickers and the hardened layer was 20 to 25μ in thickness.

FIG. 3 shows an electro microscopic cross section view (magnif. 1,000) of the sintered piece in the above example which was packed with the powder of boron (B) comprising boronizing accelerator, sintered finally, and after that mirror-polished as smooth as 1μ and etched. Fine white part on the right shows the permeated layer and carbide particles on the left shows the characteristic structure of the hard alloy. Before polishing the piece, copper (Cu) was plated on it to prevent dullness on the edge. As can be seen from the figure, all the pieces were permeated homogeneously with boron. It had a hardness of 2,400 Vickers up to 15μ in depth. Although boronizing layer was formed on the surface of the sintered piece during sintering, such defects as deformation and surface roughness were not found, except ordinary contraction at sintering.

EXAMPLE 5

As to the boronizing of the surface of steel comprising tungsten (W), molybdenum (Mo), chromium (Cr) etc., it is already known that it is possible to boronize the surface of steel at the temperature range of 800 to 1,000° C. See, for example, Japanese Patent Sho-25 (1950)-21. It is also possible to permeate and diffuse boron (B) or borides into the green compact of the hard alloy during the presintering process at about 1,000° C.

Powders of tungsten carbide (WC)—85%, cobalt (Co)—15% by weight were ground, mixed, dried and pressed to form the piece (5 x 10 x 30 mm.) in the usual method. And that piece was packed into graphite boat, the inner diameter of which was 50 mm. and the depth was 30 mm., with 1 to 3μ of boron powder to cover the piece with 5 to 10 mm. in thickness, and was presintered at 1,000° C. for one hour in hydrogen gas. After that, it was sintered at 1390° C. for one hour in vacuum. After polishing the cross-section and the surface of the resulting piece as smooth as 1μ by the diamond wheel and the diamond paste, its hardness was measured. The hardness was 1,700 to 1,830 Vickers. Permeance effect of boron (B) was observed on the finally sintered piece, as the presintered piece was not sintered thoroughly and still porous.

The best hard alloy was obtained under the condition of presintering temperature at 950 to 1,100° C., variable according to the composition of the alloy and the lubricant added.

EXAMPLE 6

Powders of titanium carbide (TiC)—92%, molybdenum carbide (MoC)—3% and nickel (Ni)—5% by weight were ground, mixed, dried, pressed to form the piece (5 x 10 x 30 mm.) and presintered at 900° C. in the usual method for producing cermet. And that piece was packed into the graphite boat, the inner diameter of which was 50 mm. and the depth 30 mm., with 1 to 3μ of boron carbide (B_4C) powder to cover the piece with 5 to 10 mm. in thickness, and was sintered at 1,400° C. for one hour in vacuum. After polishing the cross-section and the surface of the resulting piece as smooth as 1μ by the diamond paste, its hardness was measured. The hardness of the piece was 1,740 Vickers in its center, and the surface hardness was 1,900 to 2,150 Vickers. And it was observed by the electron microscope. The depth of the hardened layer was 6 to 9μ in thickness. In the above mentioned example, the effect was greatly increased by adding a boronizing accelerator to the powder of boron (B). The surface hardness of the piece was 2,200 to 2,500 Vickers and the hardened layer was 10 to 15μ in thickness.

FIG. 4 shows an electro microscopic cross section view (magnif. 3,000) of the sintered piece in the above mentioned example which was packed with the boron (B) powder comprising boronizing accelerator, sintered finally, and after that mirror-polished as smooth as 1μ and etched. Fine white part on the right shows the permeated layer of boron carbide (B_4C), and the carbide particles on the left shows the characteristic structure of the cermet. Before polishing the piece, copper was plated on it for preventing dullness on the edge.

As can be seen from the figure, all the piece was permeated homogeneously with boron carbide and it had a hardness of 2,350 Vickers up to 15μ in depth. As shown in the example, although boronizing layer was formed on the surface of the sintered piece during sintering, such defects as deformation and surface roughness were not found, except the ordinary contraction at sintering. And as the result of presintering the cermet powder which comprises the elements in the Example 6, the ultra hardened layer was also formed by permeating boron carbide (B_4C) in the same manner shown in the Example 5.

EXAMPLE 7

A piece was made from powders of tungsten carbide (WC)—92%, tungsten boride (W_2B)—3%, tantalum-niobium carbide (Ta(Nb)C)—92% and cobalt (Co)—4% by sintering in the same manner as shown in the Example 4. The hardness of the resulting piece was 2,170 Vickers in its center and that of the surface was 2,450 Vickers, and the boronized layer was 13 to 14μ in thickness by electro microscope.

In the above example, it was found that by adding a boronizing accelerator to the powder of boron (B), the effect was greatly increased. And any defect such as deformation and surface roughness was not found, except an ordinary contraction at sintering.

EXAMPLE 8

The ultra hard alloy was produced from the powders comprising tungsten carbide (WC)—89%, vanadium boride (VB_2)—2%, tantalum-niobium carbide (Ta(Nb)C)—5% and cobalt (Co)—4% under the same condition as the Example 5, except sintering temperature at 1430° C. The hardness of the piece was 2,075 Vickers in its center and the surface hardness was 2,300 Vickers.

EXAMPLE 9

After polishing the surface of the piece of the hard alloy (7 x 25 mm.) having a hardness of 1,720 Vickers comprising tungsten carbide—92%, titanium carbide (TiC)—1%, tantalum carbide (TacC)—1% and cobalt (Co)—6% by weight, by the diamond wheel as smooth as 1μ, the piece was put into the melting salt of borax anhydride at 900° C. and was electrolysed in the cathode under the condition of 50 a./dm.^{2} current density for one hour. Copper was plated on the surface of the piece to prevent dullness on the edge and polished to produce the mirror bright surface by the diamond paste. The piece was measured by Vickers Hardness Meter. The boronized layer shows a hardness of 3,012 Vickers, which was never obtained from the group of carbide hard alloy before. The surface of the piece etched by Murakami etching solution was observed through the electro microscope.

FIG. 5 shows an electro microscopic picture (magnifi. 1,000) of the etched piece. Fine smooth part in the center shows the boronizing layer and the carbide particles on the lower right shows the characteristic structure of

the hard alloy. The upper left portion was the copper plated layer. As shown in the figure, all the layer was permeated homogeneously and the depth of the permeated layer was over 30μ in thickness. And no deformation was found.

EXAMPLE 10

After polishing the surface of the cermet (10 x 10 mm.) comprising titanium carbide (TiC)—93%, nickel (Ni)—5%, molybdenum (Mo)—2% having hardness of 1,720 Vickers, as smooth as 1μ by the diamond wheel, the piece was put into the melting salt of boric anhydride ($Na_2B_4O_7$)—60%, barium chloride (BaCl)—35% and caustic soda (NaOH)—4% and boron (B)—1% at 900° C. and was electrolysed in the cathode under the condition of 60 a./dm.^{2} current density for one hour. Copper was plated on the surface of the piece to prevent dullness on the edge when polished for measuring hardened layer. Surface was mirror-polished by the diamond paste. The hardness of the boronized layer measured by Vickers Hardness Meter was 2,970 Vickers.

The surface of the piece etched by Murakami etching solution was observed through the electro microscope.

FIG. 6 shows an electro microscopic picture (magnif. 1,000) of the etched piece. Fine smooth part on the upper right shows the boronizing layer and the carbide particles on the lower left shows the characteristic structure of the hard metal. As can be seen from the figure, all the layer was permeated homogeneously. The depth of the permeated layer was over 40μ. And no deformation was found.

EXAMPLE 11

A single cutter of the hard alloy comprising tungsten carbide (WC)—95%, and cobalt (Co)—5% by weight and having a hardness of 1700 Vickers and an outer diameter of 20 mm. was packed into the graphite boat, the inner diameter of which was 50 mm. and the depth was 30 mm., with fine powder (1–3μ) including boron—50% and borides—50% by capacity including boronizing accelerators to cover the cutter with 10 to 15 mm. in thickness, and heated at 950° C. in vacuum for 60 minutes. The hardness of ultra hard alloys obtained was 2050 to 2150 Vickers. Using it, watch parts made of high carbon free-cutting steel in which lead is added to the high carbonsteel SK–4 (JIS), was cut by the automatic lathe at cutting speed of 3000 r.p.m., cutting depth of 0.1 mm. and feed of 0.005 mm./rev. while lubricating with cutting oil.

As a result it was found that the life of this cutter was three times as long as that of the non-boronized usual cutter. Besides, the working efficiency was improved. No deformation was found. So it is suitable for practical tools.

EXAMPLE 12

After boronizing, in the same manner as described in the Example 9, the ultra hard alloy (7 x 25 mm.) comprising tungsten carbide (WC)—92%, tungsten boride (W_2B_5)—2%, tantalum-niobium carbide (Ta(NB)C)—2% and cobalt (CO)—4% by weight, and having a hardness of 2010 Vickers, the hardness of the boronized layer was measured as in the Example 9. The hardness was 3150 Vickers. Its hardness was extremely higher than that of the usual carbide type hard alloy and the carbide type hard alloy boronized.

In the above description, are shown some examples of the combinations of carbides such as Al_4C_3, Cr_3C_2, MoC, TaC, NbC, TiC, VC, WC, ZrC, SiC, boron and borides such as AlB_2, AlB_{12}, CrB, CrB_2, CrB_3, MoB, MoB_2, NbB_6, NbB, NbB_2, B_3Si, B_4Si, B_6Si, TaB, TaB_2, TiB_2, WB, W_2B, W_2B_5, VB_2, ZrB_2, and metallic binders such as Co, Fe, Ni for producing ultra hard alloys. The ultra hard alloys obtained from all the combinations of one or more than two of said carbides. Boron and borides, and metallic binders also showed higher hardness and abrasive resistance than those of the usual hard alloys. The effect was proved to be the same as the above examples by the practical experiments.

In the above description are shown some examples of the methods for permeating and diffusing boron and borides in the surface of the present invention. The practical experiments showed that the same super hardened layer as in the above examples could be obtained from all the combinations of one or more than two of boron and borides such as B_4C, TiB_2, CrB_2, MoB, WB, B_3Si, B_4Si, B_6Si, ZrB_2, VB_2 etc. with carbide type hard alloys comprising one or more than two of Al_4C_3, Cr_3C_2, Mo_2C, NbC, SiC, TaC, TiC, WC, VC, ZrC etc., or with ultra hard alloys of carbide-boron and borides type comprising one or more than two of said boron and borides such as AlB_2, AlB_{12}, CrB, CrB_2, Cr_5B_3, MoB, MoB_2, NbB_6, NbB, NbB_2, B_3Si, B_4Si, B_6Si, TaB, TaB_2, TiB_2 WB, W_2B_5, W_2B, VB_2, ZrB_2 etc. Besides the effect was proved, by the experiments to be the same as the above examples.

In the above description, are shown a solid method for boronizing a test piece in powder of boron or borides and a liquid method in melted boracic acid bath by electrolysis. In addition to these methods, there are other methods such as heating the alloys in liquid powder during sintering or after sintering, using boron obtained when boron tri-chloride(BCl_3) is reduced in hydrogen gas, and boronizing in gas of boron tri-fluoride(BF_3) or boron hydride(B_2H_6) etc. A solid method, a liquid method, a gaseous method and its combinations may be applied to increase the abrasive resistance more by permeating and diffusing boron and borides in the surface of sintered alloys of carbide type (hard alloys or cermets) and ultra hard alloys of carbide-boron and borides type which have high abrasive resistance from the beginning without departing the spirit of the present invention, The electrolysis method in melting borax is most desirable, for by this method it is possible to obtain high hardness in a short time, besides the simple equipments are sufficient and the work is easy.

The ultra hard alloy according to the invention has extremely high hardness, intrinsic high strength and impact resistance as base metal, so it completely eliminates chipping and peeling of surface hardened layer.

As described above, according to the present invention, the ultra hard alloy having extremely higher hardness and abrasive resistance than the conventional hard alloy or cermet without mold cavities and pin-holes can be obtained. They can be applied not only to the cutting tools but to other tools as gauges, dies, rolls, taps, drills and reamer etc. which are made of hard alloys or cermets.

What is claimed is:

1. Method of increasing the hardness of an alloy selected from the group consisting of hard alloys and ultra-hard alloys, wherein said hard and said ultra-hard alloys contain at least one binder metal selected from the group consisting of Fe, Ni, and Co, and have been sintered, said hard alloys further containing at least one carbide selected from the group consisting of Al_4C_3, Cr_3C_2, Mo_2C, NbC, SiC, TaC, TiC, WC, VC and ZrC and said ultra-hard alloys contain at least one carbide selected from the group consisting of Al_4C_3, Cr_3C_2, Mo_2C, NbC, SiC, TaC, TiC, WC, VC and ZrC and at least one boron-containing material selected from the group consisting of B, AlB_2, AlB_{12}, CrB, CrB_2, Cr_5B_3, MoB, MoB_2, NbB_6, NbB, NbB_2, B_3Si, B_4Si, B_6Si, TaB, TaB_2, TiB_2, WB, W_2B_5, W_2B, VB_2 and ZrB_2, comprising the step of permeating into the surface of said alloy at least one boron-containing material selected from the group consisting of B, AlB_2, AlB_{12}, CrB, CrB_2, Cr_5B_3, MoB, MoB_2, NbB_6, NbB, NbB_2, B_3Si, B_4Si, B_6Si, TaB, TaB_2, TiB_2 WB, W_2B_5, W_2B, VB_2 and ZrB_2.

2. Method as described in claim 1 further comprising the steps of polishing the surface of said sintered alloy, placing said alloy in a molten 900° C. bath containing about 60% $Na_2B_4O_7$, 35% of $BaCl_2$, 4% of NaOH and 1% of B, all values being by weight, passing current

through the surface of said alloy at a current density of about 60 a./dm.^{2} for about 1 hour in a direction such that said alloy is cathodic.

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