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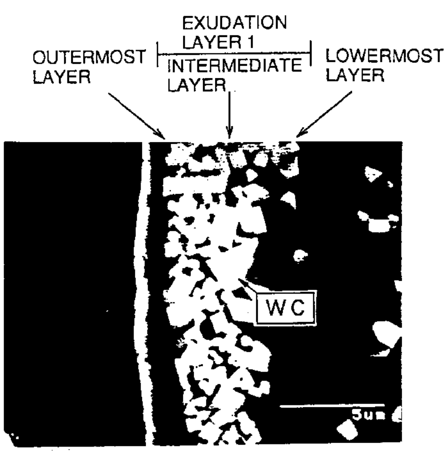
(54) Nitrogen-containing sintered hard alloy

(57) A nitrogen-containing sintered hard alloy includes a hard phase containing WC serving as an essential element and a carbide, nitride or a carbonitride of at least one transition metal being selected from the groups 4,A 5A and 6A of the periodic table or a composite carbo-nitride thereof and a binder phase containing Ni, Co and unavoidable impurities, an exudation layer containing a metal binder phase, mainly composed of Ni and Co, and WC being present on an alloy of this part, wherein the exudation layer is internally divided into a three layers in order of an outermost layer and an intermediate layer and an lowermost layer, wherein the outermost layer containing at least 0 percent by volume and not more than 30 percent by volume of WC with a rest being formed by a metal binder phase, the intermediate layer contains at least 50 percent by volume and not more than 100 percent by volume of WC with a rest being formed by a metal binder phase, the lower layer containing at least 0 percent by volume and not more than 30 percent by volume of WC with a rest being formed by a metal binder phase, wherein the outermost and lowermost layers being at least 0.1 μm and not more than 10 μm in thickness, the intermediate layer being at least 0.5 μm and not more than 10 μm in thickness. According to this composition, it is possible to provide a nitrogen-containing sintered hard alloy which can be employed as a cutting tool having high reliability with no surface coating also in working under conditions bringing a strong thermal shock.

FIG. 1
SEM PHOTOGRAPH



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Description

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a nitrogen-containing sintered hard alloy, and more particularly, it relates to a nitrogen-containing sintered hard alloy which is improved in thermal shock resistance, wear resistance and strength for serving as a material for a cutting tool and enabling application to wet cutting.

Description of the Background Art

A nitrogen-containing sintered hard alloy having a hard phase of a carbo-nitride mainly composed of Ti, which is bonded by a metal containing Ni and Co, has already been put into practice as a cutting tool. This nitrogen-containing sintered hard alloy is widely applied to a cutting tool similarly to the so-called cemented carbide which is mainly composed of WC, since the hard phase is extremely fined as compared with a conventional sintered hard alloy which is free from nitrogen to remarkably improve high-temperature creep resistance as the result.

In this nitrogen-containing sintered hard alloy, however, resistance against a thermal shock is reduced for the following reasons:

(i) The thermal conductivity of this nitrogen-containing sintered hard alloy is about half that of the cemented carbide since the thermal conductivity of Ti which is the main component of the carbo-nitride is extremely smaller than that of WC which is the main component of the cemented carbide, and

(ii) the thermal expansion coefficient of the nitrogen-containing sintered hard alloy is about 1.3 times that of the cemented carbide, since this coefficient also depends on the characteristic value of the main component similarly to the thermal conductivity.

Therefore, the nitrogen-containing sintered hard alloy is disadvantageously inferior in reliability to a coated cemented carbide or the like in cutting under conditions bringing a particularly strong thermal shock such as milling, cutting of a square timber with a lathe or wet copying with remarkable variation in depth of cut, for example.

In order to solve such problems of the conventional nitrogen-containing sintered hard alloy, various improvements have been attempted as follows: For example, Japanese Patent Laying-Open No. 2-15139 (1990) proposes means of improving surface roughness of a material containing at least 50 percent by weight of Ti in terms of a carbide or the like and less than 40 percent by weight of an element belonging to the group 6A (the group VIB in the CAS version) in terms of a carbide and having an atomic ratio N/(C + N) of 0.4 to 0.6 with a high nitrogen content by controlling the sintering atmosphere, for forming a modified part having high toughness and hardness in a surface layer part. On the other hand, Japanese Patent Laying-Open No. 5-9646 (1993) discloses a cermet which is prepared by sintering a material, which is mainly composed of Ti, containing less than 40 percent by weight of W, Mo and Cr in total in terms of a carbide, and thereafter controlling a cooling step for providing a surface part with a region having a smaller amount of binder phase as compared with the interior, to leave compressive stress on the surface.

However, each of the cermets disclosed in the aforementioned gazettes is insufficient in chipping resistance as compared with the coated cemented carbide, although wear resistance and toughness are improved. Further, the cermet is so inferior in thermal shock resistance that sudden chipping is easily caused by occurrence of thermal cracking or crack extension resulting from both thermal and mechanical shocks in particular, and sufficient reliability cannot be attained. Although the manufacturing cost for such prior art is reduced due to omission of a coating step, the performance cannot be sufficiently improved. This suggests that improvement in strength against chipping is naturally limited in the category of the so-called cermet which is prepared on the premise that the same contains Ti in excess of a certain degree of amount.

The inventors have made deep study on analysis of cutting phenomenons such as temperature distributions in various cutting operations and arrangements of material components in tools, to obtain the following recognition:

During cutting, a cutting portion is partially exposed to high-temperature environment in a surface part of an insert which is in contact with a workpiece, a part of a rake face which is fretted by chips, and the like. Comparing the cermet with the cemented carbide, the thermal conductivity of the former is about half that of the latter as hereinabove described, and hence heat which is generated on the surface of the cermet is so hardly diffused into the interior that the temperature is abruptly reduced in the interior although the surface is at a high temperature. Once cracking is caused in such a state, the cermet is extremely easily chipped. When the cermet is rapidly quenched with water-soluble cutting oil from a high temperature state or cooled with cutting in lost motion, further, only an extremely small part of its surface is quenched.

Comparing the cermet with the cemented carbide, further, the thermal expansion coefficient of the former is about 1.3 times that of the latter as hereinabove described, and hence tensile stress is caused on a surface layer part to extremely easily cause thermal cracking. In relation to either characteristic, the cermet is inferior in thermal shock resistance to the cemented carbide.

Comparing the cermet and the cemented carbide having the same grain sizes and the same amounts of binder phases, further, the fracture toughness of the former is reduced by about 30 to 50 % as compared with the latter, and hence crack extension resistance is also reduced in the interior of the alloy.

In the conventional nitrogen-containing sintered hard alloy, as hereinabove described, there are limits to improvement of thermal conductivity, reduction of the thermal expansion coefficient and improvement of crack extension resistance with a large content of Ti which can bring an excellent machined surface and is advantageous in view of the resource.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a nitrogen-containing sintered hard alloy which can be employed as a cutting tool in high reliability with no surface coating also in a working region under conditions bringing a strong thermal shock with no requirement for the high-priced coated cemented carbide which has been employed in general.

The problem is solved by the features of claim 1.

First and second aspects of the present invention are now described.

The nitrogen-containing sintered hard alloy according to the present invention is provided in its interior with a larger amount of WC as compared with the conventional nitrogen-containing sintered hard alloy in structure, to be improved in resistance against crack extension. When a large amount of WC is blended, WC particles toward the alloy surface appear in the conventional nitrogen-containing sintered hard alloy to provide a tool material called a P-type material, while this tool material is inferior in smoothness of the machined surface.
Therefore, this material is also remarkably inferior in abrasive wear resistance to the so-called cermet or coated cemented carbide.

However, it has been proved possible to eliminate WC particles from a soft layer which is present in the outermost surface of the tool, i.e., a surface part up to a specific depth from a portion immediately under the so-called exudation layer, deciding smoothness of the machined surface. Thus, abrasive wear resistance and crater wear resistance can be remarkably improved, while the amount of a binder phase is reduced in the vicinity of the surface layer and a group 6A metal such as W is solidly solved in hard phase particles at the same time when cooling is carried out in a decarburizing atmosphere such as a vacuum. Further, the alloy surface is hardened and toughness can be improved by such an effect that compressive stress against the surface part is caused by difference in thermal expansion coefficient due to a gradient in the amount of the binder phase, whereby wear resistance and thermal shock resistance can be remarkably improved.

According to the first aspect of the present invention, the nitrogen-containing sintered hard alloy includes:

at least 75 percent by weight and not more than 95 percent by weight of a hard phase containing $(Ti \cdot W_xM_y)(C_uN_{1-u})$ (M represents at least one of metals belonging to the group 6A of the periodic table excluding W, $0 < x < 1$, $0 \leq y \leq 0.9$, and $0 \leq u < 0.9$) and WC, and at least 5 percent by weight and not more than 25 percent by weight of a binder phase containing Ni, Co and unavoidable impurities, and contains:
at least 5 percent by weight and not more than 60 percent by weight of Ti in terms of a carbide, a nitride or a carbonitride, and at least 30 percent by weight and not more than 70 percent by weight of a metal belonging to the group 6A of the periodic table in terms of a carbide,
the atomic ratio of nitrogen/(carbon + nitrogen) in the hard phase is at least 0.2 and less than 0.5, and the nitrogen-containing sintered hard alloy is provided with a soft layer containing a binder phase metal and WC in its outermost surface, and has a layer which is hardly provided with the hard phase containing WC in a portion immediately under the soft layer in a thickness of at least 3 μm and not more than 30 μm.

According to this nitrogen-containing sintered hard alloy, the content of the hard phase is set in the range of at least 75 percent by weight and not more than 95 percent by weight. This is because wear resistance and plastic deformation resistance are remarkably reduced if the content of the hard phase is less than 75 percent by weight while strength and toughness are insufficient if the content exceeds 95 percent by weight. The Ti content is set in the range of at least 5 percent by weight and not more than 60 percent by weight in terms of a carbide or the like since wear resistance cannot reach a desired level if the Ti content is less than 5 percent by weight while toughness is deteriorated if the Ti content exceeds 60 percent by weight. The Ti content is preferably at least 5 percent by weight and not more than 50 percent by weight, and particularly preferably at least 20 percent by weight and not more than 50 percent by weight.

The content of the metal belonging to the group 6A of the periodic table is set in the range of at least 30 percent by weight and not more than 70 percent by weight in terms of a carbide since desired toughness cannot be attained if the content is less than 30 percent by weight while a large amount of WC particles remain in the surface to disadvantageously result in insufficient wear resistance if the content exceeds 70 percent by weight. The content of the metal belonging to the group 6A of the periodic table is preferably at least 40 percent by weight and not more than 70 percent by weight, and particularly preferably at least 40 percent by weight and not more than 60 percent by weight in terms of the carbide.

The atomic ratio of nitrogen/(carbon + nitrogen) in the hard phase is set in the range of at least 0.2 and less than 0.5, since both toughness and wear resistance cannot reach desired levels if the atomic ratio is less than 0.2 while the degree of sintering is reduced and toughness is deteriorated if the atomic ratio exceeds 0.5. This atomic ratio is preferably at least 0.2 and less than 0.4.

Further, the thickness of the layer hardly provided with the hard phase containing WC, in an amount of not more than 1 percent by volume in more concrete terms, is set in the range of at least 3 μm and not more than 30 μm in the portion immediately under the soft layer consisting of the binder phase metal and WC located on the outermost surface since desired abrasive wear resistance and crater wear resistance cannot be attained if the thickness is less than 3 μm while no effect of facilitating crack extension resistance is attained and toughness is reduced as the result if the thickness exceeds 30 μm.

In a preferred embodiment of the nitrogen-containing sintered hard alloy according to the present invention, it is preferable that the abundance of the hard phase containing WC is gradually increased toward the interior from the layer hardly provided with the hard phase containing WC up to a maximum depth of 1 mm from the outermost surface in the aforementioned composition.

According to this structure, the abundance of the hard phase containing WC is gradually increased toward the interior from the layer provided with not more than 1 percent by volume of the hard phase containing WC up to the maximum depth of 1 mm from the outermost surface, whereby abrupt change of the WC content distribution is prevented in the boundary between the regions provided and not provided with WC, so that occurrence of residual stress is relieved in this boundary.

In the inventive nitrogen-containing sintered hard alloy, further, the abundance of the hard phase containing WC is preferably at least 5 percent by volume and less than 50 percent by volume in the interior of the depth of at least 1 mm from the outermost surface in the aforementioned composition.

This is because no desired effect of improving toughness is attained if the abundance is less than 5 percent by volume while toughness of the surface layer part against a thermal shock and plastic deformation resistance of the alloy are reduced if the abundance exceeds 50 percent by volume.

According to the second aspect of the present invention, on the other hand, the nitrogen-containing sintered hard alloy includes:

at least 75 percent by weight and not more than 95 percent by weight of a hard phase containing $(Ti \cdot W_xM_y)(C_uN_{1-u})$ (M represents at least one of metals belonging to the groups 4A, 5A and 6A of the periodic table, corresponding to the groups IVB, VB and VIB in the CAS version respectively, excluding Ti and W, $0 < x < 1$, $0 \leq y \leq 0.9$, and $0 \leq u < 0.9$) and WC, and at least 5 percent by weight and not more than 25 percent by weight of a binder phase containing Ni, Co and unavoidable impurities, and contains:
at least 5 percent by weight and not more than 60 percent by weight of Ti in terms of a carbide, a nitride or a carbo-nitride, at least 30 percent by weight and not more than 70 percent by weight of a metal belonging to the group 6A of the periodic table in terms of a carbide, at least 2 percent by weight and not more than 15 percent by weight of Ta and Nb in total in terms of a carbide, a nitride or a carbo-nitride, and not more than 5 percent by weight of V, Zr and Hf in total in terms of a carbide, a nitride or a carbo-nitride,
the atomic ratio of nitrogen/(carbon + nitrogen) in the hard phase is at least 0.2 and less than 0.5, and the nitrogen-containing sintered hard alloy is provided with a soft layer containing a binder phase metal and WC in its outermost surface, and has a layer which is hardly provided with the hard phase containing WC in a portion immediately under the soft layer in a thickness of at least 3 μm and not more than 30 μm.

Also when the nitrogen-containing sintered hard alloy contains a metal belonging to the group 4A of the periodic table excluding Ti and/or the group 5A in addition to the metal belonging to the group 6A of the periodic table excluding W, at least 2 percent by weight and not more than 15 percent by weight of Ta and Nb in total in terms of a carbide, a nitride or a carbo-nitride, and not more than 5 percent by weight of V, Zr and Hf in total in terms of a carbide, a nitride or a carbo-nitride, a functional effect which is similar to that of the composition according to the first aspect can be attained. Crater wear resistance is not improved if the total content of Ta and Nb is less than 2 percent by weight in terms of a carbide or the like, while chipping resistance is reduced if the content exceeds 15 percent by weight. The alloy preferably contains V, Zr and Hf to be improved in strength and hardness under a high temperature, while the degree of sintering is reduced and chipping resistance is also reduced as the result if the total content of V, Zr and Hf exceeds 5 percent by weight in terms of the carbide etc.

In the inventive nitrogen-containing sintered hard alloy, it is preferable that the abundance of the hard phase containing WC is gradually increased toward the interior from the layer hardly provided with the hard phase containing WC up to a maximum depth of 1 mm from the outermost surface in the aforementioned composition.

In the inventive nitrogen-containing sintered hard alloy, further, the abundance of the hard phase containing WC is preferably at least 5 percent by volume and less than 50 percent by volume in the interior of at least 1 mm in depth from the outermost surface in the aforementioned composition.

A third aspect of the present invention is now described.

Thermal cracking is caused by temperature difference between the surface part and the interior of the alloy. In order to prevent such thermal cracking, the thermal conductivity of the nitrogen-containing sintered hard alloy itself may be improved, while the improvement of the thermal conductivity of the nitrogen-containing sintered hard alloy is naturally limited. As a result of study, however, it has been clarified that heat which is generated during cutting is conducted to the overall alloy to attain a heat divergence (fin) effect when a layer having high thermal conductivity which is rich in WC with a rest of a metal binder phase mainly composed of Co and Ni is arranged on a surface part of a nitrogen-containing sintered hard alloy.

Accordingly, a nitrogen-containing sintered hard alloy according to the third aspect of the present invention, which has been proposed on the basis of the aforementioned result of the study, includes a hard phase containing WC serving as an essential element and a carbide, a nitride or a carbo-nitride of at least one transition metal selected from the groups 4A, 5A and 6A of the periodic table or a composite carbo-nitride thereof, and a binder phase containing Ni, Co and unavoidable impurities, and has the following structure and composition:

An exudation layer 1 containing a metal binder phase, mainly composed of Ni and Co, and WC is present on an alloy surface part (see Figs. 1 to 3), and this layer 1 is internally divided into three layers including an outermost layer containing at least 0 percent by volume and not more than 30 percent by volume (preferably 0 to 5 percent by volume) of WC with a rest formed by a metal binder phase which is mainly composed of Co and Ni, an intermediate layer containing at least 50 percent by volume and not more than 100 percent by volume (preferably 80 to 100 percent by volume) of WC with a rest formed by a metal binder phase which is mainly composed of Co and Ni, and a lowermost layer containing at least 0 percent by volume and not more than 30 percent by volume (preferably 0 to 5 percent by volume) of WC with a rest formed by a metal binder phase which is mainly composed of Co and Ni.

The outermost and lowermost layers are at least 0.1 μm and not more than 10 μm (preferably 0.1 to 0.5 μm) in thickness, while the intermediate layer is at least 0.5 μm and not more than 10 μm (preferably 0.5 to 5 μm) in thickness.

In the nitrogen-containing sintered hard alloy having the aforementioned structure, thermal shock resistance is remarkably improved. While the outermost and lowermost layers are substantially rich in the metal binder phase mainly composed of Ni and Co, these layers are inevitably formed in the manufacturing steps, and no problem is caused in performance when the thicknesses thereof are in the aforementioned range.

In the numeric limitation of the aforementioned structure, the intermediate layer contains at least 50 percent by volume and not more than 100 percent by volume of WC since desired thermal conductivity cannot be attained and the layer cannot serve as a thermal divergence layer if the WC content is not more than 50 percent by volume with a rest of the metal binder phase mainly composed of Co and Ni. The thickness of this intermediate layer is set in the range of at least 0.5 μm and not more than 10 μm since desired thermal conductivity cannot be attained if the thickness is less than 0.5 μm while wear resistance is remarkably deteriorated if the thickness exceeds 10 μm.

Each of the outermost and lowermost layers, which are necessarily formed for obtaining the most important intermediate layer, must have a thickness of 0.1 μm, while the same may cause welding with a main component of a workpiece and iron in cutting leading to chipping if the thickness exceeds 10 μm. It has been proved by a result of study that no influence is exerted on cutting performance if the outermost and lowermost layers are not more than 10 μm in thickness.

In a preferred embodiment, the inventive nitrogen-containing sintered hard alloy of the aforementioned structure has a region containing absolutely no or not more than 2 percent by volume of a metal binder phase in its surface part immediately under the exudation layer 1 containing the metal binder phase, which is mainly composed of Ni and Co, and WC, and this region has a thickness of at least 2 μm and not more than 100 μm (preferably 2 to 50 μm) from the portion immediately under the exudation layer 1 toward the interior. According to this structure, the region immediately under the exudation layer 1 has extremely high hardness, whereby both of wear resistance and thermal shock resistance can be compatibly attained.

In the aforementioned structure, the surface part of the alloy contains not more than 2 percent by volume of the metal binder phase which is mainly composed of Co and Ni since no remarkable improvement of wear resistance is recognized if the metal binder phase is present in a higher ratio. The thickness of the region located immediately under the exudation layer 1 is set in the range of at least 2 μm and not more than 100 μm since no improvement of wear resistance is recognized if the thickness of the region is less than 2 μm while the region is rendered too hard and fragile to deteriorate chipping resistance if the thickness exceeds 100 μm.

In a more preferred embodiment of the inventive nitrogen-containing sintered hard alloy having the aforementioned structure, the region containing absolutely no or not more than 2 percent by volume of WC located immediately under the exudation layer 1 has a thickness of at least 1 μm and not more than 500 μm (preferably 20 to 100 μm) toward the interior of the alloy. Under such conditions, further, the abundance of WC is preferably gradually increased from the aforementioned region located immediately under the exudation layer 1 toward the interior so that the volume percentage of WC reaches the average WC volume percentage of the overall alloy at a depth within 1 mm (preferably 0.3 to 0.7 mm) from the portion immediately under the exudation layer 1. According to this structure, the Young's modulus of the overall alloy is increased due to the presence of WC, whereby mechanical strength is remarkably improved. Further, both of thermal shock resistance and chipping resistance can be compatibly attained by providing WC only in the interior with no presence on the surface part of the alloy.

In the aforementioned structure, the thickness of the region, located immediately under the exudation layer 1, containing absolutely no or not more than 2 percent by volume of WC toward the internal direction is set in the range of at least 1 μm and not more than 500 μm since wear resistance is deteriorated due to influence by reduction in hardness caused by WC if the thickness is less than 1 μm while the effect of improving toughness of the alloy itself by WC cannot be attained if the thickness exceeds 500 μm.

The aforementioned structure of the inventive alloy can be obtained by setting a sintering temperature in the range of 1350 to 1700°C in a specified composition and controlling a sintering atmosphere and a cooling rate. The thicknesses of the three layers forming the exudation layer 1 can be adjusted by controlling the sintering temperature and the cooling rate.

The volume percentage of WC is measured by the following method: A section of a WC-Co cemented carbide member having a known WC content is lapped to take a SEM photograph of 4800 magnifications. An area occupied by WC in this photograph is calculated by an image analyzer, to draw a calibration curve on the area occupied by WC. As to the inventive alloy, a section of a portion to be observed is lapped and an area occupied by WC is calculated from an SEM photograph of 4800 magnifications by an image analyzer, for obtaining the volume percentage of WC from a calibration curve.

The foregoing and other objects, features, aspects and advantages of the present invention will become more apparent from the following detailed description of the present invention when taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a microphotograph (SEM photograph) of an alloy structure indicating an exudation layer which is divided into three layers with presence of Co and Ni binder layers in outermost and lowermost layers and a WC layer in an intermediate layer; and

Figs. 2 and 3 are microphotographs (EDX analysis) indicating distributions of Co and Ni elements in the structure respectively.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Concrete Examples of the present invention are now described.

Example 1

45 percent by weight of $(Ti_{0.85}Ta_{0.04}Nb_{0.04}W_{0.07})(C_{0.56}N_{0.44})$ powder of 2 μm in mean particle size having a cored structure including an outer portion appearing pure white and a core portion appearing jet-black in a reflecting electron microscopic image, 40 percent by weight of WC powder of 0.7 μm in mean particle size, 7 percent by weight of Ni powder of 1.5 μm in mean particle size and 8 percent by weight of Co powder of 1.5 μm in mean particle size were wet-blended with each other, and thereafter the mixture was stamped and degassed in a vacuum of 10^{-2} Torr at 1200°C. Thereafter the mixture was sintered under a nitrogen gas partial pressure of 30 Torr at 1450°C for 1 hour, and then cooled in a vacuum at 5°C/min., to form a sample 1. The sample 1 had a Ti content of 34 percent by weight in terms of TiCN, a W content of 45 percent by weight in terms of WC, and a Ta and Nb content of 6 percent by weight in terms of TaC + Nb. The atomic ratio $N/(C + N)$ was 0.3. Absolutely no WC particles were present in a region of 10 μm in thickness located immediately under a soft layer, and the abundance of a hard phase containing WC was 15 percent by volume in the interior of 1 mm in depth from the outermost surface.

For the purpose of comparison, samples 2 to 4 were prepared by conventional methods respectively. The sample 2 was prepared by sintering a stamped compact which was identical to that of the sample 1 under a nitrogen partial pressure of 5 Torr at 1400°C. The sample 3 was prepared by cooling a sintered body which was identical to that of the sample 2 under a CO partial pressure of 200 Torr after sintering. The sample 4 was prepared by cooling a sintered body which was identical to that of the sample 2 under a nitrogen partial pressure of 180 Torr after sintering.

In the samples 2 to 4, the abundances of hard phases containing WC located immediately under soft layers were 10 percent by volume, 15 percent by volume and 5 percent by volume respectively. In addition to raw materials which were identical to those for the sample 1, further, TaC, NbC, ZrC and VC of 1 to 3 μm in mean particle size were blended in weight ratios shown in Table 1 to form sintered alloys through steps similar to those for the sample 1, thereby preparing samples 5 to 10 having reduced contents shown in Table 1. Ni, Co, ZrC and VC were omitted from Table 1 since the reduced contents thereof were substantially identical to the blending compositions. Table 2 shows atomic ratios N/(C + N) , thicknesses of layers provided with not more than 1 percent by volume of hard phrases containing WC located immediately under soft layers in alloy surface parts, and the abundances of the hard phases containing WC in portions of 1 mm in depth from outermost surfaces.

Table 1

Sample No.	Blending Composition (weight %)								Reduced Content (weight %)		
	(TiTaNbW)CN	WC	TaC	NbC	ZrC	VC	Ni	Co	TiCN	WC	TaC + NbC
1 2* 3* 4*	45	40	-	-	-	-	7	8	34	45	6
5	30	40	4	4	2	-	5	15	22	45	11
6	60	20	3	-	-	2	10	5	44	30	9
7*	80	2	2	-	2	-	7	7	58	15	11
8*	89	-	-	-	-	-	5	6	65	14	10
9*	50	40	-	2	-	-	4	4	37	48	7
10*	45	25	2	-	2	-	13	13	3	32	7

Note) Asterisked numerals indicate comparative samples, and underlined numeric values are out of the inventive ranges.

Table 2

Sample No.	N/C+N (Atomic Ratio)	Thickness of Region Provided with Not More Than 1 vol.% of Hard Phase Containing WC	Volume Percentage of Hard Phase Containing WC Particles in Portion of 1 mm in Depth from Surface
1	0.30	10	15
2*	0.30	0	15
3*	0.30	0	15
4*	0.30	0	15
5	0.27	5	20
6	0.41	15	7
7*	0.44	200	3
8*	0.44	Overall Alloy Region	0
9*	0.34	10	35
10*	0.36	60	5

Note) Asterisked numerals indicate comparative samples, and underlined numeric values are out of the inventive ranges.

The nitrogen-containing sintered hard alloys of the aforementioned samples 1 to 10 were employed for cutting work under cutting conditions 1 to 3 shown in Table 3, to consequently obtain results shown in Table 4.

Table 3

	Cutting Condition 1 (Wear Resistance Test)	Cutting Condition 2 (Toughness Test)	Cutting Condition 3 (Thermal Shock Resistance Test)
Tool Shape	TNMG332	SNMG432	SNMG432
Workpiece	SCM435 (H_s=350) Round Bar	SCM435 (H_s=250) Round Bar with Four Longitudinal Flutes	SCM435 (H_s=220) Round Bar
Cutting Speed	150 m/min.	100 m/min.	250 m/min.
Feed Rate	0.36 mm/rev.	0.24 mm/rev.	0.20 mm/rev.
Depth of Cut	1.5 mm	2.0 mm	Changed from 2.5 to 0.2 mm
Cutting Oil	Water Soluble	Not Used	Water Soluble
Cutting Time	30 min.	30 sec.	15 min.
Determination	Flank Wear Width (mm)	Number of Chipped Ones among 20 Inserts	Number of Chipped Ones among 20 Inserts

Table 4

Sample No.		Cutting Condition 1 Flank Wear Width (mm)	Cutting Condition 2 Number of Chipped Ones among 20 Inserts	Cutting Condition 3 Number of Chipped Ones among 20 Inserts
Inventive Sample	1	0.14	4	2
Comparative Sample	2	0.25	10	20
	3	0.34	10	18
	4	0.35	12	6
Inventive Sample	5	0.16	3	5
	6	0.11	6	3
Comparative Sample	7	0.15	16	20
	8	0.28	15	16
	9	0.11	18	9
	10	0.58	6	10

As understood from the results shown in Table 4, the samples 1, 5 and 6 having compositions etc. satisfying the conditions according to the first or second aspect of the present invention are superior in wear resistance, toughness and thermal shock resistance to the samples 2 to 4 and 7 to 10 having compositions etc. which are out of the inventive conditions.

Example 2

Raw powder materials shown in Table 5 were blended and mixed/crushed to attain respective reduced contents, thereby forming samples 11 to 23. Each TiCN powder material had a mean particle size of 2 μm and an atomic ratio C/N of 5/5, while the remaining powder materials were 1 to 3 μm in mean particle size. The sample 12 was prepared with a Ta and Nb source of (TaNb)C powder (TaC:NbC = 2:1 (weight ratio)) of 1.5 μm in mean particle size, while the sample 17 was prepared with a Ti and W source of $(Ti_{0.8}W_{0.2})(C_{0.7}N_{0.3})$ of 2 μm in mean particle size. Table 5 shows the amounts of blending of these solid solution raw powder materials in terms of single compounds. Blending compositions of the respective samples were omitted from Table 5 since the same were substantially identical to the reduced contents.

Table 5

Sample No.	Reduced Content (wt.%)										
	TiCN	TiC	TiN	WC	Mo_2C	TaC	NbC	ZrC	HfC	Ni	Co
11	45	-	-	35	5	-	-	-	-	5	10
12	40	-	-	30	5	4	2	2	2	5	10
13	-	15	21	44	-	-	-	-	-	10	10
14	-	10	16	44	-	-	7	3	-	10	10
15	-	23	12	50	-	-	-	-	-	8	7
16	-	10	25	50	-	-	-	-	-	8	7
17	-	26	17	37	3	3	-	-	-	6	8
18*	55	-	-	<u>25</u>	-	4	-	-	-	8	8
19*	18	-	-	<u>72</u>	-	-	-	-	-	5	5
20*	-	25	10	50	-	-	-	-	-	8	7
21*	-	7	28	50	-	-	-	-	-	8	7
22*	40	-	5	35	-	-	-	<u>3</u>	<u>3</u>	6	8
23*	30	-	5	35	-	<u>10</u>	<u>6</u>	-	-	6	8
Note) Asterisked numerals indicate comparative samples, and underlined numeric values are out of the inventive ranges.											

The samples 11 to 23 were heated in a vacuum of 10^{-2} Torr at 3°C/min., degassed at 1200°C for 15 minutes, thereafter sintered under a nitrogen gas partial pressure of 15 to 40 Torr at 1450°C for 1 hour, thereafter control-cooled in a vacuum to 1200°C at 3°C/min., and thereafter nitrogen-quenched. As to the samples 11 and 12, samples 11A to 11C and 12A to 12C were formed after sintering under the same conditions, under various cooling conditions. The samples 11A and 12A were cooled under a CO partial pressure of 150 Torr after sintering under the same conditions as the samples 11 and 12 respectively, the samples 11B and 12B were cooled under a nitrogen partial pressure of 200 Torr, and the samples 11C and 12C were heated to 1530°C, thereafter sintered for 1.5 hours, and thereafter control-cooled.

Table 6 shows atomic ratios N/(C + N) , thicknesses of regions provided with not more than 1 percent by volume of hard phases containing WC located immediately under soft layers in alloy surface parts, and the abundances of the hard phases containing WC in portions of 1 mm in depth from outermost surfaces as to the samples 11 to 23, 11A to 11C and 12A to 12C.

Table 6

Sample No.	N/C+N (Atomic Ratio)	Thickness of Region Provided with Not More Than 1 vol.% of Hard Phase Containing WC (μm)	Abundance of Hard Phase Containing WC in Portion of 1mm in Depth from Surface (vol.%)
11	0.39	8	12
11A*	"	<u>2</u>	20
11B*	"	<u>35</u>	15
11C*	"	8	<u>3</u>
12	0.37	15	8
12A*	"	<u>0</u>	15
12B*	"	<u>50</u>	10
12C*	"	15	<u>3</u>
13	0.42	10	26
14	0.35	5	15
15	0.23	17	22
16	0.48	8	35
17	0.29	15	24
18*	0.43	<u>Overall Alloy Region</u>	<u>0</u>
19*	0.22	<u>0</u>	<u>60</u>
20*	<u>0.19</u>	23	18
21*	<u>0.54</u>	3	40
22*	0.43	8	12
23*	0.38	9	14
Note) Asterisked numerals indicate comparative samples, and underlined numeric values are out of the inventive ranges.			

The samples shown in Table 6 were employed for cutting work under cutting conditions 4 to 6 shown in Table 7, to obtain results shown in Table 8. For the purpose of comparison, a commercially available coated cemented carbide (grade P10) was also subjected to a cutting test.

Table 7

	Cutting Condition 4 (Wear Resistance Test)	Cutting Condition 5 (Toughness Test)	Cutting Condition 5 (Milling Cutter Thermal Shock Resistance Test)
Tool Shape	TNMG332	SNMG432	SDKN42
Workpiece	SCM435 (H_s=250) Round Bar	SCM435 (H_s=250) Round Bar with Four Longitudinal Flutes	SCM435 (H_s=240) Plate with Three Longitudinal Flutes (Flute of 5mm in Width Every 20mm)
Cutting Speed	180 m/min.	150 m/min.	160 m/min.
Feed Rate	0.3 mm/rev.	0.2 mm/rev.	0.28 mm/rev.
Depth of Cut	1.5 mm	2.0 mm	0.2 mm
Cutting Oil	Water Soluble	Not Used	Water Soluble
Cutting Time	20 min.	30 sec.	5 Passes
Determination	Flank Wear Width (mm)	Number of Chipped Ones among 20 Inserts	Number of Inserts Chipped by Thermal Cracking etc. among 20 Ones

Table 8

Sample No.		Cutting Condition 4 Flank Wear Width (mm)	Cutting Condition 5 Number of Chipped Ones among 20 Inserts	Cutting Condition 6 Number of Chipped Ones among 20 Insets
Inventive Sample	11	0.15	5	4
Comparative Sample	11A	exceeded 0.8mm in 12min.	9	10
	11B	0.28	11	13
	11C	0.22	14	17
Inventive Sample	12	0.12	7	3
Comparative Sample	12A	0.41	5	10
	12B	0.18	15	12
	12C	0.16	17	14
Inventive Sample	13	0.20	8	8
	14	0.15	7	6
	15	0.13	8	5
	16	0.18	9	8
	17	0.12	7	5
Comparative Sample	18	0.13	20	20
	19	exceeded 0.8mm in 5 min.	8	12
	20	0.12	13	14
	21	0.25	16	18
	22	0.14	18	12
	23	chipped in 10 min.	20	11
	Coated Cemented Carbide (Grade P10)	0.15	7	4

As understood from the results shown in Table 8, the samples 11, 12 and 13 to 17 having compositions etc. satisfying the conditions according to the first or second aspect of the present invention are superior in wear resistance, toughness and thermal shock resistance to the samples 11A to 11C, 12A to 12C and 18 to 23 having compositions etc. which are out of the inventive conditions.

Example 3

TiCN powder, WC powder, TaC powder, NbC powder, Mo_2C powder, VC powder, $(Ti_{0.5}W_{0.3}Ta_{0.1}Nb_{0.1})C_{0.5}N_{0.5}$ powder, Co powder and Ni powder of 1.5 μm in mean particle size were blended into a composition shown at A in Table 9, mixed with each other in a wet attriter for 12 hours, thereafter worked into green compacts of a CNMG432 shape under a pressure of 1.5 ton/cm^2, and the green compacts were honed to thereafter prepare sintered hard alloys having structures shown in Tables 11 to 13 under sintering conditions shown in Table 10. Referring to Tables 11 to 13, the columns "structure from portion immediately under exudation layer toward interior" show composition rates of hard phases and binder phases varied with depths toward interiors of alloys with reference to portions immediately under exudation layers which are set at 0. In a sample a-7, for example, the WC content is identical to the alloy-average WC volume percentage from the portion immediately under the exudation layer toward the interior, while the binder phase content is 1.8 percent by volume up to 2.5 μm, gradually increased from 2.5 μm up to 60 μm, and identical to the alloy-average binder phase volume percentage in an internal portion beyond 60 μm. The content of the hard phase forming the rest is expressed in 100 - (alloy-average binder phase volume percentage) - (alloy-average WC volume percentage) in each depth.

Table 9

Blending Composition (wt.)		
	Hard Phase Component	Binder Phase Component
A	TiCN 46 % WC 40 %	Co 7 % Ni 7 %
B	TiCn 41 % WC 30 % TaC 5 % NbC 5 % Mo_2 C3 % VC 2 %	Co 7 % Ni 7 %
C	$(Ti_{0.5}, W_{0.3}, Ta_{0.1}, Nb_{0.1})$ $(C_{0.5}, N_{0.5})$ 86 %	Co 7 % Ni 7 %
D	TiCN 66 % WC 16 %	Co 9 % Ni 9 %

Table 10

Sintering No.	Sintering Condition			
	Sintering Temperature (°C)	Sintering Atmosphere (Torr)	Cooling Rate Cooling (°C/min) Atmosphere (Torr)	
1	1530	Nitrogen : 5	8	Nitrogen : 3
2	1520	Nitrogen : 50	2	Nitrogen : 4
3	1400	Nitrogen : 3	4	Nitrogen : 4
4	1460	Nitrogen : 6	2	Nitrogen : 5
5	1460	Nitrogen : 10	2	Nitrogen : 10
6	1420	Nitrogen : 5	1	Nitrogen : 12
7	1435	Nitrogen : 6	4	Vacuum
8	1530	Nitrogen : 5	8	Vacuum
9	1520	Nitrogen : 2	2	Methane : 2
10	1400	Nitrogen : 50	4	Methane : 1
11	1460	Nitrogen : 6	2	Methane : 2
12	1420	Nitrogen : 5	1	Argon : 2
13	1435	Nitrogen : 6	4	Argon : 5
14	1530	Nitrogen : 5	8	Vacuum
15	1420	Nitrogen : 10	1	Vacuum

Table 11

Sample No.	Raw Material Grade Powder	Sintering No.	Exudation Layer Structure			Structure from Portion immediately under Exudation Layer toward Interior
			Outermost Layer	Intermediate Layer	Lowermost Layer	
a-1	A	1	No	No	No	Binder Phase: Alloy-Average Volume Percentage from Surface part to Interior WC: Alloy-Average Volume Percentage from Surface Part to Interior Hard Phase: Rest
a-2	A	2	Binder Phase (Co + Ni) 2μm 90vol.%	WC 5μm 59vol.%	Binder Phase (Co + Ni) 2μm 90Vol.%	ditto
a-3	A	3	Binder Phase (Co + Ni) 12μm 90vol.%	WC 5μm 59vol.%	Binder Phase (Co + Ni) 12μm 90vol.%	ditto
a-4	A	4	Binder Phase (Co + Ni) 5μm 90vol.%	WC 12μm 80vol.%	Binder Phase (Co + Ni) 5μm 90vol.%	ditto
a-5	A	5	Binder Phase (Co + Ni) 3μm 90vol.%	WC 6μm 48vol.%	Binder Phase (Co + Ni) 3μm 90vol.%	ditto
a-6	A	6	Binder Phase (Co + Ni) 3μm 90vol.%	WC 6μm 98vol%	Binder Phase (Co + Ni) 3μm 90vol.%	ditto

Table 12

Sample No.	Raw Material Grade Powder	Sintering No.	Exudation Layer Structure			Structure from Portion Immediately under Exudation Layer toward Interior
			Outermost Layer	Intermediate Layer	Lowermost layer	
a-7	A	7	Binder Phase (Co + Ni) 3μm 90vol.%	WC 6μm 90vol.%	Binder Phase (Co + Ni) 3μm 90vol.%	Binder Phase: 1.8vol.% up to 2.5μm, thereafter gradually increased, Alloy-Average Volume Percentage at 60μm WC: Alloy-Average Volume Percentage from Surface Part to Interior Hard Phase: Rest
a-8	A	8	ditto	ditto	ditto	Binder Phase: 1.8vol.% up to 98μm, thereafter gradually increased, Alloy-Average Volume Percentage at 200μm WC: Alloy-Average Volume Percentage from Surface Part to Interior Hard Phase: Rest
a-9	A	9	ditto	ditto	ditto	Binder Phase: 1.5vol.% up to 1μm, thereafter gradually increased, Alloy-Average Volume Percentage at 20μm WC: Alloy-Average Volume Percentage from Surface Part to Interior Hard Phase: Rest
a-10	A	10	ditto	ditto	ditto	Binder Phase: 1.2vol.% up to 105μm, thereafter gradually increased, Alloy-Average Volume Percentage at 320μm WC: Alloy-Average Volume Percentage from Surface Part to Interior Hard Phase: Rest
a-11	A	11	ditto	ditto	ditto	Binder Phase: Alloy-Average Volume Percentage from Surface Part to Interior WC: 1.8vol.% up to 1.8μm, thereafter gradually increased, Alloy-Average Volume Percentage at 250μm Hard Phase: Rest
a-12	A	12	ditto	ditto	ditto	Binder Phase: Alloy-Average Volume Percentage from Surface Part to Interior WC: 1.8vol.% up to 498μm, thereafter gradually increased, Alloy-Average Volume Percentage at 700μm Hard Phase: Rest

Table 13

Sample No.	Raw Material Grade Powder	Sintering No.	Exudation Layer Structure			Structure from Portion Immediately under Exudation Layer toward Interior
			Outermost Layer	Intermediate Layer	Lowermost Layer	
a-13	A	13	Binder Phase (Co + Ni) 3μm 90vol.%	WC 6μm 90vol.%	Binder Phase (Co + Ni) 3μm 90vol.%	Binder Phase: Alloy-Average Volume Percentage from Surface Part to Interior WC: 3vol.% at Surface Part, thereafter gradually increased, Alloy-Average Volume Percentage at 60μm Hard Phase: Rest
a-14	A	14	ditto	ditto	ditto	Binder Phase: Alloy-Average Volume Percentage from Surface Part to Interior WC: 1.8vol.% up to 600μm,thereafter gradually increased, Alloy-Average, Volume Percentage at 900μm Hard Phase: Rest
a-15	A	15	ditto	ditto	ditto	Binder Phase: 1.8vol.% up to 2.5μm,thereafter gradually increased, Alloy-Average Volume Percentage at 60μm WC: 1.8vol.% up to 1.8μm,thereafter gradually increased, Alloy-Average Volume Percentage at 250μm Hard Phase: Rest

The samples a-1 to a-15 were subjected to a thermal shock resistance test and a wear resistance test under conditions (A) and (B) respectively. Table 14 shows the results.

(A)

Workpiece: SCM435 (HB: 250) with four flutes
Cutting Speed: 100 (m/min.)
Depth of Cut: 1.5 (mm)
Feed Rate: 0.20 (mm/rev.)
Cutting Time: 30 sec.
Wet Type

(B)

Workpiece: SCM435 (HB: 250) with four flutes
Cutting Speed: 180 (m/min.)
Depth of Cut: 1.5 (mm)
Feed Rate: 0.30 (mm/rev.)
Cutting Time: 20 min.
Wet Type

Table 14

	Sample	(A)	(B)
	a-1	38 Inserts	0.29 mm
*	a-2	16 Inserts	0.19 mm
	a-3	36 Inserts	0.30 mm
	a-4	37 Inserts	0.31 mm
	a-5	38 Inserts	0.29 mm
*	a-6	16 Inserts	0.25 mm
*	a-7	10 Inserts	0.10 mm
*	a-8	10 Inserts	0.08 mm
*	a-9	11 Inserts	0.18 mm
*	a-10	19 Inserts	0.08 mm
*	a-11	10 Inserts	0.19 mm
*	a-12	10 Inserts	0.18 mm
*	a-13	12 Inserts	0.23 mm
*	a-14	17 Inserts	0.18 mm
*	a-15	5 Inserts	0.07 mm

*: inventive samples
(A): number of chipped ones among 40 inserts
(B): flank wear width

It is understood that thermal shock resistance which is superior to that of the prior art can be attained when a sintered hard alloy having a hard phase consisting of TiCN and WC is provided with an exudation layer as specified. It is also understood that wear resistance and thermal shock resistance are improved respectively when binder phase and WC distributions as specified are provided.

Example 4

Raw powder materials which were identical to those of Example 3 were blended into a composition shown at B in Table 9, worked into green compacts by a method identical to that in Example 3, and the green compacts were honed to prepare sintered hard alloys having structures shown in Tables 15 to 17 under the sintering conditions shown in Table 10. Samples b-1 to b-15 were subjected to a thermal shock resistance test and a wear resistance test under conditions (C) and (D) respectively. Table 18 shows the results.

(C)

Workpiece: SCM435 (HB: 300) with four flutes
Cutting Speed: 120 (m/min.)
Depth of Cut: 1.5 (mm)
Feed Rate: 0.20 (mm/rev.)
Cutting Time: 30 sec.
Wet Type

(D)

Workpiece: SCM435 (HB: 300) with four flutes
Cutting Speed: 200 (m/min.)
Depth of Cut: 1.5 (mm)
Feed Rate: 0.30 (mm/rev.)
Cutting Time: 20 min.
Wet Type

Table 15

Sample No.	Raw Material Grade Powder	Sintering No.	Exudation Layer Structure			Structure from Portion Immediately under Exudation Layer toward Interior
			Outermost Layer	Intermediate Layer	Lowermost Layer	
b-1	B	1	No	No	No	Binder Phase: Alloy-Average Volume Percentage from Surface Part to Interior WC: Alloy-Average Volume Percentage from Surface Part to Interior Hard Phase: Rest
b-2	B	2	Binder Phase (Co + Ni) 3µm 90vol.%	WC 7µm 70vol.%	Binder Phase (Co + Ni) 3µm 90vol.%	ditto
b-3	B	3	Binder Phase (Co + Ni) 12µm 90vol.%	WC 3µm 61vol.%	Binder Phase (Co + Ni) 12µm 90vol.%	ditto
b-4	B	4	Binder Phase (Co + Ni) 5µm 90vol.%	WC 12µm 80vol.%	Binder Phase (Co + Ni) 5µm 90vol.%	ditto
b-5	B	5	Binder Phase (Co + Ni) 3µm 90vol.%	WC 7µm 48vol.%	Binder Phase (Co + Ni) 3µm 90vol.%	ditto
b-6	B	6	Binder Phase (Co + Ni) 3µm 90vol.%	WC 5µm 98vol.%	Binder Phase (Co + Ni) 3µm 90vol.%	ditto

Table 16

Sample No.	Raw Material Grade Powder	Sintering No.	Exudation Layer Structure			Structure from Portion immediately under Exudation Layer toward Interior
			Outermost Layer	Intermediate Layer	Lowermost Layer	
b-7	B	7	Binder Phase (Co + Ni) 3μm 90vol.%	WC 7μm 90vol.%	Binder Phase (Co + Ni) 3μm 90vol.%	Binder Phase: 1.8vol.% up to 2.5μm, thereafter gradually increased, Alloy-Average Volume Percentage at 60μm WC: Alloy-Average Volume Percentage from Surface Part to Interior Hard Phase: Rest
b-8	B	8	ditto	ditto	ditto	Binder Phase: 1.8vol.% up to 98μm, thereafter gradually increased, Alloy-Average Volume Percentage at 200μm WC: Alloy-Average Volume Percentage from Surface Part to Interior Hard Phase: Rest
b-9	B	9	ditto	ditto	ditto	Binder Phase: 1.5vol.% up to 1μm, thereafter gradually increased, Alloy-Average Volume Percentage at 20μm WC: Alloy-Average Volume Percentage from Surface Part to Interior Hard Phase: Rest
b-10	B	10	ditto	ditto	ditto	Binder Phase: 1.2vol.% up to 105μm, thereafter gradually increased, Alloy-Average Volume Percentage at 320μm WC: Alloy-Average Volume Percentage from Surface Part to Interior Hard Phase: Rest
b-11	B	11	ditto	ditto	ditto	Binder Phase: Alloy-Average Volume Percentage from Surface Part to Interior WC: 1.8vol.% up to 1.8μm, thereafter gradually increased, Alloy-Average Volume Percentage at 250μm Hard Phase: Rest
b-12	B	12	ditto	ditto	ditto	Binder Phase: Alloy-Average Volume Percentage from Surface Part to Interior WC: 1.8vol.% up to 498μm, thereafter gradually increased, Alloy-Average Volume Percentage at 700μm Hard Phase: Rest

Table 17

Sample No.	Raw Material Grade Powder	Sintering No.	Exudation Layer Structure			Structure from Portion immediately under Exudation Layer toward Interior
			Outermost Layer	Intermediate Layer	Lowermost Layer	
b-13	B	13	Binder Phase $(Co + Ni)$ 3μm 90vol.%	WC 7μm 90vol.%	Binder Phase $(Co + Ni)$ 3μm 90vol.%	Binder: Alloy-Average Volume Percentage from Surface Part to Interior WC: 4vol.% at Surface Part, thereafter gradually increased, Alloy-Average Volume Percentage at 60μm Hard Phase: Rest
b-14	B	14	ditto	ditto	ditto	Binder: Alloy-Average Volume Percentage from Surface Part to Interior WC: 1.8vol.% up to 600μm, thereafter gradually increased, Alloy-Average Volume Percentage at 900μm Hard Phase: Rest
b-15	B	15	ditto	ditto	ditto	Binder: 1.7vol.% up to 2.5μm, thereafter gradually increased, Alloy-Average Volume Percentage at 60μm WC: 1.8vol.% up to 1.8μm, thereafter gradually increased, Alloy-Average Volume Percentage at 250μm Hard Phase: Rest

Table 18

	Sample	(C)	(D)
	b-1	39 Inserts	0.31 mm
*	b-2	15 Inserts	0.17 mm
	b-3	37 Inserts	0.32 mm
	b-4	38 Inserts	0.33 mm
	b-5	39 Inserts	0.31 mm
*	b-6	15 Inserts	0.23 mm
*	b-7	9 Inserts	0.08 mm
*	b-8	9 Inserts	0.06 mm
*	b-9	10 Inserts	0.15 mm
*	b-10	18 Inserts	0.05 mm
*	b-11	9 Inserts	0.16 mm
*	b-12	9 Inserts	0.15 mm
*	b-13	11 Inserts	0.20 mm
*	b-14	16 Inserts	0.15 mm
*	b-15	4 Inserts	0.04 mm

*: inventive samples
(C): number of chipped ones among 40 inserts
(D): flank wear width

It is understood that thermal shock resistance which is superior to that of the prior art can be attained when a sintered hard alloy having a hard phase consisting of an element belonging to the group 4A, 5A or 6A is provided with an exudation layer as specified. It is also understood that wear resistance and thermal shock resistance are improved respectively when binder phase and WC distributions as specified are provided.

Example 5

Raw powder materials which were identical to those of Example 3 were blended into a composition shown at C in Table 9, worked into green compacts by a method identical to that in Example 3, and the green compacts were honed to prepare sintered hard alloys having structures shown in Tables 19 to 21 under the sintering conditions shown in Table 10. Samples c-1 to c-15 were subjected to a thermal shock resistance test and a wear resistance test under conditions (E) and (F) respectively. Table 22 shows the results.

(E)

Workpiece: SCM435 (HB: 280) with four flutes
Cutting Speed: 120 (m/min.)
Depth of Cut: 1.5 (mm)
Feed Rate: 0.20 (mm/rev.)
Cutting Time: 30 sec.

Wet Type

(F)

Workpiece: SCM435 (HB: 280)
Cutting Speed: 200 (m/min.)
Depth of Cut: 1.5 (mm)
Feed Rate: 0.30 (mm/rev.)
Cutting Time: 20 min.
Wet Type

Table 19

Sample No.	Raw Material Grade Powder	Sintering No.	Exudation Layer Structure			Structure from Portion immediately under Exudation Layer toward Interior
			Outermost Layer	Intermediate Layer	Lowermost Layer	
c-1	C	1	No	No	No	Binder Phase: Alloy-Avarage Volume Percentage from Surface Part to Interior WC: Alloy-Avarage Volume Percentage from Surface Part to Interior Hard Phase: Rest
c-2	C	2	Binder Phase (Co + Ni) 3μm 90vol.%	WC 7μm 70vol.%	Binder Phase (Co + Ni) 3μm 90vol.%	ditto
c-3	C	3	Binder Phase (Co + Ni) 12μm 90vol.%	WC 3μm 61vol.%	Binder Phase (Co + Ni) 12μm 90vol.%	ditto
c-4	C	4	Binder Phase (Co + Ni) 5μm 90vol.%	WC 12μm 80vol.%	Binder Phase (Co + Ni) 5μm 90vol.%	ditto
c-5	C	5	Binder Phase (Co + Ni) 3μm 90vol.%	WC 7μm 48vol.%	Binder Phase (Co + Ni) 3μm 90vol.%	ditto
c-6	C	6	Binder Phase (Co + Ni) 3μm 90vol.%	WC 7μm 48vol.%	Binder Phase (Co + Ni) 3μm 90vol.%	ditto

Table 20

Sample No.	Raw Material Grade Powder	Sintering No.	Exudation Layer Structure			Structure from Portion immediately under Exudation Layer toward Interior
			Outermost Layer	Intermediate Layer	Lowermost Layer	
c-7	C	7	Binder Phase ($Co + Ni$) 3μm 90vol.%	WC 7μm 90vol.%	Binder Phase ($Co + Ni$) 3μm 90vol.%	Binder Phase: 1.8vol.% up to 2.5μm, thereafter gradually increased, Alloy-Average Volume Percentage at 60μm WC: Alloy-Average Volume Percentage from Surface Part to Interior Hard Phase: Rest
c-8	C	8	ditto	ditto	ditto	Binder Phase: 1.8vol.% up to 98μm, thereafter gradually increased, Alloy-Average Volume Percentage at 60μm WC: Alloy-Average Volume Percentage from Surface Part to Interior Hard Phase: Rest
c-9	C	9	ditto	ditto	ditto	Binder Phase: 1.5vol.% up to 1μm, thereafter gradually increased, Alloy-Average Volume Percentage at 60μm WC: Alloy-Average Volume Percentage from Surface Part to Interior Hard Phase: Rest
c-10	C	10	ditto	ditto	ditto	Binder Phase: 1.2vol.% up to 105μm, thereafter gradually increased, Alloy-Average Volume Percentage at 320μm WC: Alloy-Average Volume Percentage from Surface Part to Interior Hard Phase: Rest
c-11	C	11	ditto	ditto	ditto	Binder Phase: Alloy-Average Volume Percentage from Surface Part to Interior WC: 1.8vol.% up to 1.8μm, thereafter gradually increased, Alloy-Average Volume Percentage at 250μm Hard Phase: Rest
c-12	C	12	ditto	ditto	ditto	Binder Phase: Alloy-Average Volume Percentage from Surface Part to Interior WC: 1.8vol.% up to 498μm, thereafter gradually increased, Alloy-Average Volume Percentage at 700μm Hard Phase: Rest

Table 21

Sample No.	Raw Material Grade Powder	Sintering No.	Exudation Layer Structure			Structure from Portion immediately under Exudation Layer toward Interior
			Outermost Layer	Intermediate Layer	Lowermost Layer	
c-13	C	13	Binder Phase (Co + Ni) 3μm 90vol.%	WC 7μm 90vol.%	Binder Phase (Co + Ni) 3μm 90vol.%	Binder Phase: Alloy-Average Volume Percentage from Surface Part to Interior WC: 4vol.% at Surface Part, thereafter gradually increased, Alloy-Average Volume Percentage at 60μm Hard Phase: Rest
c-14	C	14	ditto	ditto	ditto	Binder Phase: Alloy-Average Volume Percentage from Surface Part to Interior WC: 1.8vol.% up to 600μm,thereafter gradually increased, Alloy-Average Volume Percentage at 900μm Hard Phase: Rest
c-15	C	15	ditto	ditto	ditto	Binder Phase: 1.7vol.% up to 2.5μm,thereafter gradually increased, Alloy-Average Volume Percentage at 60μm WC: 1.8vol.% up to 1.8μm,thereafter gradually increased, Alloy-Average Volume Percentage at 250μm Hard Phase: Rest
D-1	D	1	No	No	Binder Phase (Co + Ni) 3μm 90vol.%	Binder Phase: Alloy-Average Volume Percentage from Surface Part to Interior WC: not contained Hard Phase: Rest

Table 22

	Sample	(E)	(F)
	c-1	39 Inserts	0.32 mm
*	c-2	16 Inserts	0.16 mm
	c-3	37 Inserts	0.33 mm
	c-4	38 Inserts	0.34 mm
	c-5	39 Inserts	0.32 mm
*	c-6	17 Inserts	0.22 mm
*	c-7	10 Inserts	0.07 mm
*	c-8	10 Inserts	0.05 mm
*	c-9	11 Inserts	0.14 mm
*	c-10	19 Inserts	0.04 mm
*	c-11	10 Inserts	0.15 mm
*	c-12	10 Inserts	0.14 mm
*	c-13	12 Inserts	0.19 mm
*	c-14	17 Inserts	0.14 mm
*	c-15	5 Inserts	0.03 mm

*: inventive samples
(E): number of chipped ones among 40 inserts
(F): flank wear width

It is understood that thermal shock resistance which is superior to that of the prior art can be attained when a sintered hard alloy having a solid solution hard phase consisting of an element belonging to the group 4A, 5A or 6A is provided with an exudation layer as specified. It is also understood that wear resistance and thermal shock resistance are improved respectively when binder phase and WC distributions as specified are provided.

Example 6

The samples a-1 and a-2 shown in Table 11 and the sample a-1 shown in Table 21 were subjected to a thermal shock resistance test under conditions (G). Table 23 shows the results.

(G)

Workpiece: SCM435 (HB: 280) with four flutes
Cutting Speed: 100 (m/min.)
Depth of Cut: 1.5 (mm)
Feed Rate: 0.20 (mm/rev.)
Cutting Time: 30 sec.
Wet Type

Table 23

	Sample	(G)
*	a-1	15 Inserts
	a-2	32 Inserts
	a-3	36 Inserts

*: inventive sample
(O): number of chipped ones among 40 inserts

It is understood that no improvement of thermal shock resistance is recognized despite an exudation layer, if no layer which is mainly composed of WC is present.

Although the present invention has been described and illustrated in detail, it is clearly understood that the same is by way of illustration and example only and is not to be taken by way of limitation, the spirit and scope of the present invention being limited only by the terms of the appended claims.

Claims

1. A nitrogen-containing sintered hard alloy including a hard phase containing WC serving as an essential element and a carbide, a nitride or a carbo-nitride of at least one transition metal being selected from the groups 4A, 5A and 6A of the periodic table or a composite carbo-nitride thereof, and a binder phase containing Ni, Co and unavoidable impurities, an exudation layer containing a metal binder phase, mainly composed of Ni and Co, and WC being present on an alloy surface part, said exudation layer being internally divided into three layers in order of an outermost layer, an intermediate layer and a lowermost layer, said outermost layer containing at least 0 percent by volume and not more than 30 percent by volume of WC with a rest being formed by a metal binder phase mainly composed of Co and Ni, said intermediate layer containing at least 50 percent by volume and not more than 100 percent by volume of WC with a rest being formed by a metal binder phase mainly composed of Co and Ni, said lowermost layer containing at least 0 percent by volume and not more than 30 percent by volume of WC with a rest being formed by a metal binder phase mainly composed of Co and Ni, said outermost and lowermost layers being at least 0.1 μm and not more than 10 μm in thickness, said intermediate layer being at least 0.5 μm and not more than 10 μm in thickness.

2. The nitrogen-containing sintered hard alloy in accordance with claim 1, being provided with a region containing absolutely no or not more than 2 percent by volume of said metal binder phase mainly composed of Co and Ni in a portion immediately under said exudation layer, said region having a thickness of at least 2 μm and not more than 100 μm from said portion immediately under said exudation layer toward the interior.

3. The nitrogen-containing sintered hard alloy in accordance with claim 1, being provided with a region containing absolutely no or not more than 2 percent by volume of WC in a portion immediately under said exudation layer, said region having a thickness of at least 1 μm and not more than 500 μm from said portion immediately under said exudation layer toward the interior.

4. The nitrogen-containing sintered hard alloy in accordance with claim 3, wherein the abundance of WC is gradually increased from a portion immediately under said region containing absolutely no or not more than 2 percent by volume of WC toward the interior so that the volume percentage of WC reaches the average WC volume percentage of overall said alloy at a depth within 1 mm from a portion immediately under said exudation layer.

5. The nitrogen-containing sintered hard alloy in accordance with claim 2, wherein an exudation layer containing a

metal binder phase, mainly composed of Ni and Co, and WC is present on an alloy surface part, and a region containing absolutely no or not more than 2 percent by volume of WC is provided in a portion immediately under said exudation layer, said region having a thickness of at least 1 μm and not more than 500 μm from said portion immediately under said exudation layer toward the interior.

6. The nitrogen-containing sintered hard alloy in accordance with claim 5, wherein the abundance of WC is gradually increased from a portion immediately under said region containing absolutely no or not more than 2 percent by volume of WC toward the interior so that the volume percentage of WC reaches the average WC volume percentage of overall said alloy at a depth within 1 mm from a portion immediatly under said exudation layer.

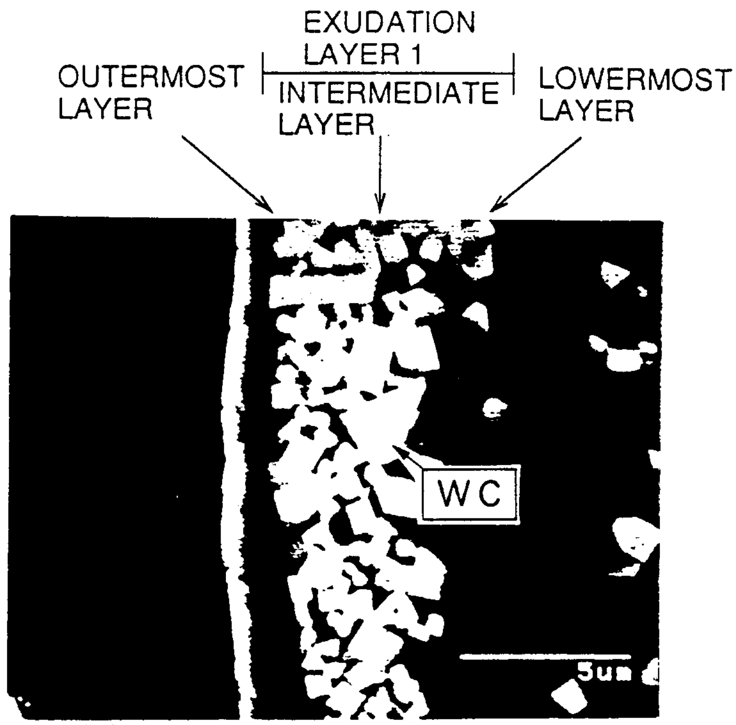

FIG. 1
SEM
PHOTOGRAPH

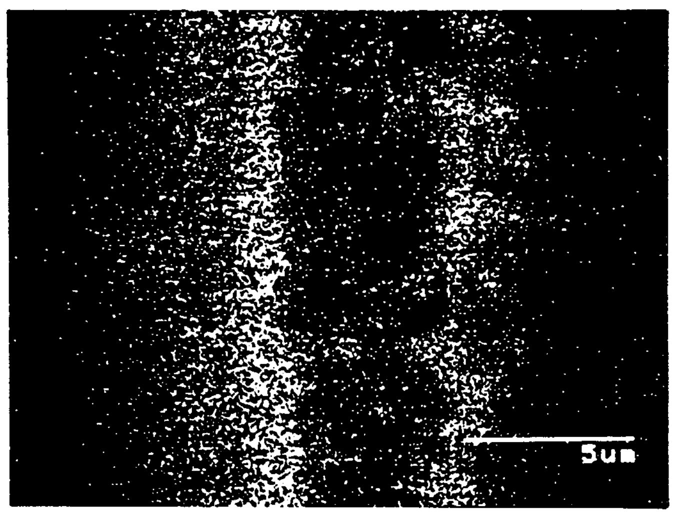

FIG. 2
EDX
ANALYSIS
(Co)

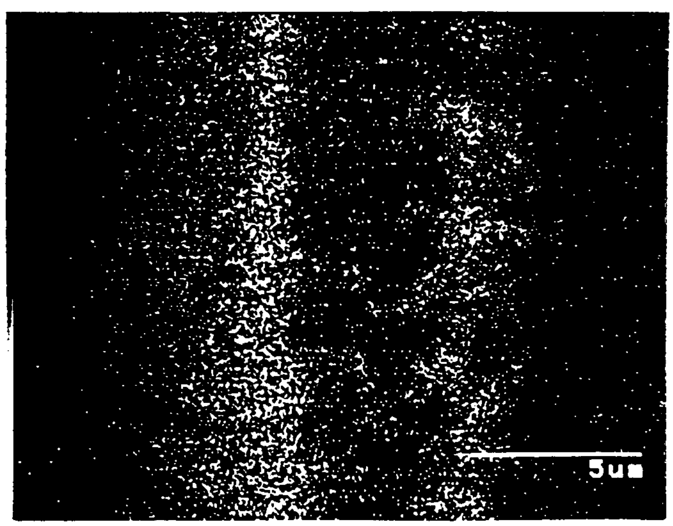

FIG. 3
EDX
ANALYSIS
(Ni)