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(54) Title: METHOD OF MAKING CEMENTED CARBIDE ARTICLES (57) Abstract The present invention relates to a method of producing a sintered body comprising one or more hard constituents and a binder phase based on cobalt, nickel and/or iron by powder metallurgical methods milling, pressing and sintering of powders. At least part of the binder phase powder consists of non agglomerated particles of spheroidal morphology having dimensions of 0.1 to 20 µm.		

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METHOD OF MAKING CEMENTED CARBIDE ARTICLES

The present invention relates to a method of making cemented carbide articles using binder phase powders with spherical, non-agglomerated particles.

Cemented carbide mainly contains tungsten carbide and cobalt, often along with certain other carbides, e.g. carbides of titanium, tantalum, niobium, chromium etc.

It contains at least one hard but brittle (carbide) phase and a relatively less hard but ductile and tough metal, particularly cobalt. This results in materials combining hardness and toughness which have found many applications, for instance in rock drilling and metal cutting tools, in wear parts etc.

Cemented carbide is made by techniques usual in powder metallurgy, that is :

- mixing the constituent powders (carbides, cobalt, and possibly other hard materials) by milling, using mills (rotating ball mills, vibrating mills, attritor mills etc) equipped with non-polluting milling media which themselves are made of cemented carbide. The milling is made in the presence of an organic liquid (for instance ethyl alcohol, acetone, etc) and an organic binder (for instance paraffin, polyethylene glycol, etc) in order to facilitate the subsequent granulation operation.
- granulation of the milled mixture according to known techniques, in particular spray-drying. The suspension containing the powdered materials mixed with the organic liquid and the organic binder is atomised through an appropriate nozzle in the drying tower where the small drops are instantaneously dried by a stream of hot gas, for instance in a stream of nitrogen. The granules col-

lected at the lower end of the tower have an average diameter adjustable by the choice of appropriate nozzles, between 100 and 200 μm . Such granules flow easily, in contrast to fine or ultrafine powders. The formation of granules is necessary in particular for the automatic feeding of compacting tools used in the subsequent stage.

- compaction of the granulated powder in a matrix with punches (uniaxial compaction) or in a bag (isostatic compaction), in order to give the material the shape and dimensions as close as possible (considering the phenomenon of shrinkage) to the dimension wished for the final body. If necessary, the compacted body can be subjected to a machining operation before sintering.

- sintering of the compacted bodies at a temperature and during a time sufficient for obtaining dense bodies with a suitable structural homogeneity.

The sintering can equally be carried out at high gas pressure (hot isostatic pressing), or the sintering can be complemented by a sintering treatment under moderate gas pressure (process generally known as SINTER-HIP).

The sintered cemented carbides can be characterised in particular by their porosity and their microstructure (observed by optical or electron microscopy).

The cobalt powders conventionally used in the cemented carbide industry are obtained by calcining cobalt hydroxide or oxalate followed by a reduction of the oxide so obtained by hydrogen; see for instance "Cobalt, its Chemistry, Metallurgy and uses", R.S. Young Ed. Reinhold Publishing Corp. (1960) pages 58-59. These conventional cobalt powders are characterised by a broad particle

size distribution, with strongly aggregated particles, in the form of agglomerates with a sponge-like aspect, which are difficult to mill since there are strong binding forces between the elementary particles in these aggregates.

In EP-B-0113281, the making of metallic powders with a process for reducing oxides, hydroxides or metal salts with the aid of polyols, is described. Particularly when starting with cobalt hydroxide, it is possible to obtain powders of metallic cobalt with essentially spherical and non-agglomerated particles. Further studies have shown in particular that it is possible to obtain non-agglomerated metallic powders having controlled average diameters of the particles, for instance by varying the concentration of the starting hydroxide or metal salt, in relation to the polyol(s). It is in this way that, in the case of cobalt, it is possible to obtain particles with an average diameter of, for instance 1, 2 or 3 μm , by using the ratios cobalt hydroxide/polyol of 0.033, 0.1 or 0.340 g cobalt/ cm^3 polyol, respectively. Similarly, it is possible to obtain particles with adjustable average dimensions, smaller than 1 μm by seeding the reaction mixture with the aid of very fine metallic particles (for instance palladium) either by adding a metal salt or hydroxide reacting more quickly than the cobalt salt or hydroxide with the polyol. This is particularly the case with silver salts, in particular silver nitrate, which are quickly reduced to metallic silver in the form of very fine particles of which the number is roughly proportional to the quantity of silver introduced into the reaction chamber. The silver or palladium particles so formed serve as seed for the growth of cobalt particles which are subsequently formed by reduction of the cobalt hydroxide or salt by the polyol. The higher the number of seed particles, the smaller the di-

mensions of the final cobalt particles. For instance, when using a molar ratio silver/cobalt in the range of 10^{-4} - 10^{-2} , one can obtain cobalt particles having average dimensions that vary from 0.1 to 0.3 μm and the
5 range can be extended by varying this ratio between 10^{-5} and 10^{-1} for all the appropriate metals. These various methods for controlling the the size of the metallic particles are particularly known and described by M. FIGLARZ et al. M.R.S.Int'l Mtg on Adv. Mats. Vol 3, Materials Research Society, pp. 125-140 (1989), F.FIEVET
10 et al. Solid State Ionics 32/33, 198-205 (1989) and F. FIEVET et al. MRS Bulletin, December 1989, pp.29-34.

It has now been discovered that the cobalt powders ha-
15 ving the properties of those obtained by the reduction of cobalt hydroxide or a cobalt salt with the aid of polyol, according to the EP-B-0 113 281 and the references just mentioned, that is powders of individual, essentially spherical non-agglomerated particles, can be used
20 as binder phase powder in the manufacture of cemented carbide and that this preparation gives several advantages which are exposed below.

It has been particularly discovered that when using such
25 non-agglomerated cobalt powders, it is possible to obtain in a reproducible way, cemented carbide exhibiting interesting characteristics, in particular, a reduced porosity. It is also possible to decrease the milling time for starting mixtures (carbide and binder) without
30 impairing the quality of the final cemented carbide. Acceptable results can be obtained even after a simple blending operation. Alternatively, the degree of milling may be further reduced and the cemented carbide subjected to a hot isostatic pressing process, either
35 incorporated into the sintering process or as a separate operation, giving an increase in the grain size of the

hard phase and correspondingly an increase in resistance to thermal cracking.

In addition, it has been discovered that, due to the use of such cobalt powders, it is possible to carry out the sintering at temperatures below those which are generally used. This decrease of sintering temperature is interesting not only from an energy point of view, but also because it permits the possibility of adding to the powder mixture other hard or superhard materials (in the form of powders) which cannot normally be used at the temperature required for conventional sintering. Among these other superhard materials, one can note particularly diamond, of which it is known that it starts transforming into graphite in air at a temperature around 800 °C and cubic boron nitride. Alternatively, the sintering temperature may be lowered even further and the cemented carbide subjected to a hot isostatic pressing process, either incorporated into the sintering process or as a separate operation, giving an increased hardness level and a more uniform grain size and binder phase distribution leading to an increase in mechanical strength.

Generally, the cobalt particles used as binder phase according to the invention have dimensions that can vary from 0.1 to 20 μm , in particular from 0.1 to 10 μm . Particles having dimensions from 0.1 to 5 μm are particularly used. Especially interesting results have been obtained with submicron particles (that is with a size less than 1 μm).

The present invention has thus as object the use - as binder phase, in the preparation of cemented carbide by milling, then sintering a mixture of powders with at least one hard material based on tungsten carbide and a

binder phase - of at least one powder of cobalt, that is homogeneous as regards the size of the particles, and particularly one powder having an average particle size x (in for instance the range 0.1 to 20 μm , in particular
5 between 0.1 and 10 μm), of which at least 80% of the particles have sizes in the interval $x \pm 0.2x$, provided the interval of variation (that is 0.4x) is not smaller than 0.1 μm . The cobalt powder used in accordance with the invention consists of individual, essentially spherical
10 rical and nonagglomerated particles.

Such powders can be especially obtained with the polyol reduction which is recalled below. It is preferable to start with cobalt hydroxide or cobalt acetate.

15

The cobalt powders obtained by the reduction of cobalt hydroxide with the aid of polyol generally contain a small proportion of carbon (most often less than 1.5% by weight) and oxygen (most often less than 2.5% by
20 weight). These powders can be directly used in the manufacture of cemented carbides.

Generally, according to the invention the cobalt powder used as binder in the preparation of cemented carbide
25 will exclusively be a powder such as defined above. But it is possible to use such powders in combination with a second cobalt powder exhibiting other characteristics, provided the proportion of the first powder is sufficient for giving the advantages indicated in the preparation of cemented carbide, for instance a decrease of the
30 sintering temperature. Generally the first powder represents at least 10%, and preferably at least 50% of the total weight of the cobalt used as binder phase.

35 In addition it is possible to use as binder phase a mixture of two or more powders as defined above, these two

powders having different average particle dimensions.

It has also been found that the use of cobalt according to the invention is very suitable to adjust the binder content of an already dried cemented carbide mixture. Such an adjustment is not possible with a conventional binder phase powder since the resulting mixture lacks necessary flowability. Adding polyol cobalt does not adversely affect flowability and can even improve it. Thus, a unique 'mother-mix' may be used for producing a variety of cemented carbide grades having different binder phase contents. After the addition of the polyol-cobalt, preferably with a particle size of $<3\text{ }\mu\text{m}$, up to the desired content the mixture is homogeneized before pressing and sintering.

The starting powder mixture contains cobalt in sufficient proportions for the final cemented carbide to contain 0.1 to 40% by weight of cobalt, and preferably 3 to 25 %. It is particularly advantageous in grades with very low contents of cobalt (typically $<0.5\%$) often referred to as binderless grades.

Sintered cemented carbide bodies based on WC, particularly with a grain size $<1.5\text{ }\mu\text{m}$, manufactured according to the method of the invention has a porosity better than A02 and B00, less than 0.5, preferably less than 0.2, binder phase laves per cm^2 with a maximum dimension of $>25\text{ }\mu\text{m}$ and less than five carbide grains per cm^2 with a grain size of more than 5 times the average grain size of the matrix.

In the manufacture of cemented carbides where the sintered grain size of the hard phases is fine, i.e. $1\text{ }\mu\text{m}$ or less, it is commonplace to substitute a small amount of other refractory metal carbides for tungsten carbide.

The carbides commonly used are those of titanium, tantalum, niobium, vanadium, chromium and hafnium. The effect of these substitutions is to control grain growth of the hard phase during sintering. A side effect is that they inhibit melt formation during sintering with the result that often higher sintering temperatures are needed than would be the case without the substitution to ensure freedom from microporosity and a uniform binder phase (cobalt-rich phase) distribution. The result is to partly negate the advantage of the substitution, leading to a degree of grain growth, recrystallization, of the WC-phase which results in a nonuniform grain size distribution, a less than optimum hardness level and a reduction in mechanical strength. Using the cobalt-powder according to the invention the above-mentioned grain growth inhibitors may be excluded. This applies in particular to high pressure anvils for diamond production in which the cobalt-content of the cemented carbide is 5-7 weight-% and WC grains size $<1.5\text{ }\mu\text{m}$. Another example is tools such as drills, microdrills and routers for machining of printed circuit boards and similar composite materials. Such tools have a cobalt-content of 3-20 weight-%, preferably 4-12 weight-% and a WC grain size of $<1\text{ }\mu\text{m}$, preferably $<0.7\text{ }\mu\text{m}$.

For certain applications where a degree of thermal shock is experienced, for example hot rolling of steel bar, some mining and highway engineering applications and machining of stainless steel, it is desired that the hard phases should be of relatively coarse grain size, typically greater than $4\text{ }\mu\text{m}$ preferably greater than $6\text{ }\mu\text{m}$ and the cobalt content <10 , preferably <8 weight-%. A cemented carbide powder to produce such a sintered hard phase grain size must of necessity be relatively lightly milled in order to control the degree of comminution. The result is that the degree of intimate mixing is re-

- duced, and, owing to the coarse particle size, the area available for reaction during sintering to produce a melt is relatively small. Consequently, such cemented carbide powders prove to be difficult to sinter and require high temperatures to approach a fully dense condition. Using the non-agglomerated, spherical cobalt powder dense bodies can be obtained at a lower sintering temperature.
- 10 In EP-A-0182759 it has been shown that an increased strength was obtained in sintered bodies of cemented carbide being used in tools for rock drilling. The buttons according to this patent has a core consisting of a fine-grained eta-phase M_6C (e.g. Co_3W_3C) and/or $M_{12}C$
- 15 (e.g. Co_6W_6C), embedded in normal alpha (WC) and beta (Co binder phase) structure at the same time as the sintered body has a surrounding surface zone which consists of alpha and beta-phase in two areas whereas the outer shell is cobalt depleted and the inner part has a high
- 20 content of binder phase. Surprisingly it has now been found that cemented carbide bodies manufactured in such a way as described above give a more optimized toughness behaviour when cobalt according to the invention is used in the production of the buttons. The effect is most utilized for cemented carbide with a cobalt content of
- 25 more than 10% and less than 25% by weight and preferably 13% to 20% by weight of cobalt. The mean grain size of the hard constituents is larger than $1,5\ \mu m$. The same appearance has also been obtained for cemented carbide
- 30 bodies with mean grain size of alpha-phase (WC) of less than $1,2\ \mu m$ and a binder content of equal or less than 6% by weight of cobalt. When cobalt according to the invention is used in the sintering/heat treatment procedure the sintering temperature can be reduced which results in a lower carbon content in the binder-phase and
- 35 a low porosity level. The benefit of this sintering/heat

treatment gives a product with a high carbon activity and a fine grain size eta-phase which results in a cemented carbide body with a more pronounced difference in cobalt content in the surface zone between the outer cobalt depleted shell and the inner part rich with cobalt. The cemented carbide produced with the cobalt according to the invention has a cobalt content with greater difference and reduced width of the shells in the surface zone which leads to higher compressive stresses in the surface zone and has also positive effects on strength and toughness.

The invention has been described above with reference to the manufacture of conventional cemented carbide i.e. based upon WC and with a binder phase of cobalt. It is evident that the invention also can be applied to the manufacture of articles of other composite materials with hard constituents (borides, carbides, nitrides, carbo-nitrides etc) and a binder phase, based on cobalt, nickel and/or iron, such as titanium based carbonitride alloys usually named cermets. Said alloys are manufactured by milling powders of carbides, nitrides and/or carbonitrides of mainly Ti but also of other metals from groups VIa, Va and VIA of the periodical table of the elements (V, Zr, Nb, Mo, Ta, W etc) together with powders of nickel and cobalt. The mixture is then dried, pressed and sintered as described above for conventional cemented carbide.

30 Example 1

A suspension of cobalt hydroxide was put in a mixture of monoethylenglycol and diethylenglycol, while agitating. The suspension, containing about 200 g of cobalt hydroxide per liter, was progressively heated to a temperature of at least 200 °C, while strongly agitating. A solution

of silver nitrate was then added in the monoethylenglycol, so that between 0.07 and 0.3 g silver per liter was introduced. The mixture was kept at the same temperature during 2 hours, and was then left to cool to room
5 temperature.

In this way a cobalt powder (reference P1) was obtained with the following properties:

- SEM diameter of the particles: 0.4 μm
- 10 - C : 1.36% by weight
- O : 2.23% by weight

The SEM diameter is the average diameter of the particles measured in the scanning electron microscope.

15

In addition the following raw materials were used:

Tungsten carbide :

- Origin : Eurotungstène Poudres (France)
- 20 - Total carbon : 6.15% by weight
- Free carbon : 0.05% by weight
- Average diameter (Fisher) : 0.9 μm

Tantalum carbide :

- 25 - Origin : H.C.STARCK
- Total carbon : 6.81% by weight
- Free carbon : 0.10% by weight
- Niobium : 9.09% by weight

30 Cobalt (reference F) obtained by reduction of the oxide with hydrogen according to the conventional process:

- Origin : Eurotungstène Poudres
- Diameter according to Fisher : 1.30 μm
- C : 0.012% by weight

35

With the aid of these materials the following mixtures

were prepared:

- Cobalt: 3% or 6.5% by weight
- Tantalum carbide: 0.5% by weight
- Tungsten carbide balance

5

The powder mixture (500 g) was obtained by milling in a mill of the type "Attritor" with a capacity of 9 liter, containing 3.5 kg of milling media (balls of cemented carbide with a diameter of 3 mm) turning at 250

- 10 turns/minutes, in the presence of 200 ml of ethyl alcohol (or acetone) and with the addition of polyethylene glycol (2 g per 100 g of mixture). The powder was milled during 7 or 14 hours and thereafter granulated using a sieve with 120 μ m mesh size. The compaction was carried
- 15 out under uniaxial compaction from two directions, with matrix and punches of cemented carbide under a pressure of 125 MPa. Sintering was performed at 1375, 1410 and 1450 °C respectively. After sintering microsections were prepared and the porosity and recrystallisation were de-
- 20 termined.

The porosity was determined according to the standard ISO 4505 and is expressed with the aid of a scale of increasing porosity from A00 to A08.

25

The recrystallisation of tungsten carbide (or general grain growth) was determined by microscopic examination and visual comparison with an internal standard scale (analogous to that of the ISO scale for the porosity)

30 since no standard exists up to this day. The results are expressed with a scale going from R1 (quasi-absence of recrystallisation) to R5 (very strong recrystallisation).

- a) -Cobalt : 6.5% by weight
 -Milling : 14 hours
 -Sintering : 1450 °C

5

Results:

Type of cobalt	P1	F
Porosity	A02	A03/04
Recrystallisation	R2/R3	R4/R5

10

- b) -Cobalt : 6.5% by weight
 -Milling : 7 hours
 -Sintering : 1450 °C

15 Results :

Type of cobalt	P1	F
Porosity	A02	A04
Recrystallisation	R2	R2/R3

- 20 c) -Cobalt : 3% by weight
 -Milling : 14 hours
 -Sintering : 1375, 1410, or 1450 °C
 -Results before HIP :

25 Results :

Sintering temperature, °C	1375	1410	1450
Type of cobalt	P1 F	P1 F	P1 F
Porosity	A02 A08	A02 A04	A02 A03
Cobalt lakes*	s N	s N	s N

- 30 * The average number of cobalt lakes was determined by counting (in an optical microscope) the lakes on ten optical fields at a magnification of 1500 times and taking the average.

s : a few

- 35 N : Numerous

- d) -Cobalt : 3% by weight
 -Milling : 14 hours
 -Results after HIP

5 The HIP treatment consists in putting the samples sintered during the previous experiment in a HIP furnace at 1350 °C, during 2 hours, under 100 MPa (atmosphere : argon).

10 Result :

Sintering temperature, °C	1375		1410		1450	
Type of cobalt	P1	F	P1	F	P1	F
Porosity	A01	A01	A01	A01	A01	A01
Cobalt lakes	s	N	0	N	0	N

- 15 s : a few
 N : numerous
 0 : no

These tests show clearly, that all other factors equal,
 20 the use of cobalt according to the present invention shows itself as beneficial in comparison with a conventional cobalt since it entails a decrease of porosity and of the number of cobalt lakes.

25 Example 2

Two laboratory scale batches of cemented carbide powder were made using the same batch of tungsten carbide, this batch having an average particle size of about 1 µm as
 30 measured by the Fisher sub-sieve sizer method. In grade A 6% by weight of conventional hydrogen-reduced cobalt powder was added and in grade B 6% by weight of ultra-fine spherical cobalt powder was added. The same small addition of chromium carbide powder was added to each
 35 grade. A fairly intense degree of milling was given to each grade by milling 1 kg of powder with 15 kg of mil-

ling bodies in a liquid for 13.5 hours in a rotary mill. Compacts were made from the dried cemented carbide powders and sintered, in close proximity with each other, under vacuum at a range of temperatures. Following sintering, microsections were prepared and the porosity levels were assessed by comparison with standard micrographs according to method ISO 4505. The binder phase distribution was assessed by an arbitrary method. The specimens were first etched for 4 minutes at room temperature in Murakami's reagent and examined under an optical microscope at a magnification of 1500X. The average number of "cobalt lakes" present in a field of view was assessed by counting the number observed in 10 fields and dividing the total count by 10. Cobalt lakes are regions of binder phase, typically from 2-10 μm in diameter, which occur when the sintering temperature was inadequate. The results obtained were as follows:

	Sintering temperature, °C	Microporosity	Co lakes per field
20			
	A 1450	A02	0
	B 1450	A00	0
	A 1410	A02	4.9
	B 1410	A00	0
25	A 1360	A08	>200
	B 1360	A02	5.6

From the above results it can be seen that the use of ultrafine spherical cobalt powder in grade B had a marked effect on the level of microporosity and binder phase distribution, especially apparent at the lowest sintering temperature employed. As well as permitting a lower sintering temperature to be employed, the use of ultra-fine spherical cobalt powder confers an improved degree of tolerance to temperature variations within the sintering furnace.

Example 3

Two laboratory scale batches of cemented carbide powder
5 were made using the same batch of tungsten carbide. This
batch having a particle size of about 40 μm according to
the Fisher subsieve sizer method. The true particle size
was however approximately 15 μm , the higher Fisher value
being due to agglomeration. In grade C 6% by weight of
10 conventional cobalt powder was added and in grade D 6%
of ultra-fine spherical cobalt powder was added. No
other carbides were added. A 1 kg charge of cemented
carbide powder was milled with 5 kg of milling bodies
and a liquid for 13.5 hours in a rotary mill. Compacts
15 were made from the dried cemented carbide powders and
sintered, in close proximity to each other, under vacuum
at a range of temperatures. Following sintering micro-
sections were prepared and the porosity levels assessed
according to the method detailed in ISO 4505. The re-
20 sults obtained were as follows:

Grade	Sintering temperature, $^{\circ}\text{C}$	Microporosity
C	1520	A02
25 D	1520	A00
C	1450	A06
D	1450	A02
C	1410	A08
D	1410	A02
30 C	1360	>A08
D	1360	A06

The above results illustrate that using ultra-fine spher-
ical cobalt powder a marked reduction in porosity le-
35 vels was achieved. Thus, lower sintering temperatures
may be employed and again an improved degree of tole-

rance to temperature variation within a furnace change is conferred.

Example 4

5

Anvils for the 60 mm diamond production system have been tested according to the performance represented as life length in a diamond production. The anvils were manufactured in three different grades of cemented carbide and marked with random numbers prior to the testing. The performance test was applied in a diamond production plant during "normal" working conditions whereas the results were reported with life lengths in comparison to presently used anvils. All anvils have a core consisting of a small amount (2%) of eta-phase in the structure.

The anvils of grade A were manufactured according to the conventional production route of cemented carbide and were used as a reference in the test. The anvils were produced as described in example 1 with 6% by weight of conventional hydrogen-reduced cobalt and a small addition of chromium carbide. The sintering temperature was 1450 °C and the cemented carbide had a microporosity of A02. The microstructure did not show any cobalt lakes.

25

The anvils of grade B had a similar composition as described for anvils of grade A without the chromium carbide content. The anvils were subjected to a hot isostatic pressing process at 4 MPa and 1410 °C instead of standard sintering. No microporosity was obtained in the microstructure and 5,2 cobalt lakes per field were presented from microscopic examination of the cemented carbide. The microstructure was even and no influence of discontinuous or local grain growth could be seen.

35

The anvils of grade C had a composition according to the

invention as described in Example 2 without the chromium carbide content. The anvils were subjected to a hot isostatic pressing procedure with the same conditions as for the anvils of grade B. The microstructure examination of the cemented carbide did not show any microporosity (A00) or cobalt lakes. The structure was even without any influence of discontinuous grain growth.

The α -phase (WC) in the microstructure of the three grades of anvils had a mean grain size of about 1,2 μm .

The performance results were reported in actual number of pressings per anvil and scaled in a performance ranking. Each cemented carbide grade was represented by six anvils.

Results:	Anvil No	Number of pressings	Performance/Rank
20	Grade A: 1	299	D
	2	99	E
	3	50	F
	4	921	A
	5	384	C
	6	<u>50</u>	<u>F</u>
	Average	300	C
30	Grade B: 1	568	C
	2	289	D
	3	270	D
	4	580	C
	5	602	B
	6	<u>430</u>	<u>C</u>
	Average	456	C

Grade C:	1	702 (still in use)	B
	2	1399	A
	3	608	B
5	4	592	C
	5	820	B
	6	<u>906</u>	<u>A</u>
	Average	837	B

- 10 The results of grade A were uneven and the anvils with the low numbers of pressings had cracks in the top of the anvils. Grade B had a better performance but got the same ranking level as grade A. Three anvils had small cracks in the top surface. Grade C had the best performance ranking in the test and the best pressing behaviour of all anvils. Obviously the anvils according to the invention had the most optimized hardness and toughness behaviour due to a well dispersed cemented carbide matrix and a narrow grain size distribution of α -phase.

20

Example 5

- A coarse grained tungsten carbide with a grain size of 18 μm was in the as supplied state used to produce test batches of very coarse cemented carbide for concrete and asphalt cutting tools. Cemented carbide with low cobalt content and very coarse grain size is needed to achieve optimum combination of toughness to wear resistance properties together with maximum thermal fatigue crack resistance.

30

The same procedure as in Example 3 was used except for that the milling time was reduced to 9,5 hours.

- 35 Grade X was produced with 6% of conventional cobalt and grade Y with 0.3 μm of ultrafine spherical cobalt pow-

der. Sintering was performed at 1520 °C in vacuum. Grade X showed a porosity level of A06, B06 plus 8 pores of 25 µm, and had to be HIP'ed. Grade Y was fully dense with maximum porosity of A02, due to the effective and uni-
5 form reduction of the WC-grains together with excellent mixing of the spherical cobalt with the tungsten carbide grains.

The metallographical analysis showed as follows:

10

	<u>Grade X</u>	<u>Grade Y</u>
Grain size mean value	7 ± 4 µm	7 ± 1,5 µm
maximum size	18 µm	10 µm
minimum size	1.8 µm	5 µm
15 structure:	uneven with 10-15 cobalt lakes of 10-20 µm	even
hardness, (HV3):	1215	1205

Road planing tips were made from the two test batches
20 and were compared with a conventional grade, Z with 8 w/o Co, 5 µm WC grains and a hardness of 1200 HV3. Point attack tools from the three grades were made, and they were geometrically identical with the carbide tips (Ø9 mm, length 18 mm with a conical top) brazed at the same
25 time.

The test was made in hard concrete with an Arrow CP 2000 road planing machine.

30 Drum diameter: 1 m, drum width; 2.2 m
Toolpick speed: 2.0 m/s, cutting depth: 25 mm
180 tools, 60 per grade, were evenly distributed throughout the drum.

Test result (mean value of 50 tools)

Grade	<u>Wear,</u> mm height reduction	<u>Fractured</u> carbide (no of pieces)	<u>Rank</u>
5			
X	5,3	8	2
Y	4,8	1	1
Z	8,1	7	3

10 Example 6

Buttons for roller bits with diameter 12 mm having a multiphase structure were produced from a small production batch. The average particle size of the WC was 3.5 μm and the nominal cobalt content was 13.5% by weight. The added cobalt was ultra-fine spherical cobalt powder with a Fisher grain size of 0.3 μm . Compacts of the cemented carbide powder were sintered at 1340°C. Corresponding buttons were produced with the same production process parameters except of the sintering temperature which was 1380°C. These buttons originating from a cemented carbide powder blending with conventional cobalt powder with a Fisher grain size of 1.4 μm . All buttons were thermally treated in a carburizing atmosphere for 2 hours. In the following examination of the microstructure of buttons from the two batches it could be seen a multiphase structure with a core that contained eta-phase surrounded by a surface zone of cemented carbide free of eta-phase having a low content of cobalt at the surface and a higher content of cobalt next to the eta-phase "core".

Microprobe studies of the microsections gave the following results:

Grade A (with ultra-fine cobalt):

Etaphase core (Ø5.0 mm):

mean grain size of etaphase: 4,1 µm

5 mean cobalt content: 11.5 weight-%

Cobalt "rich" zone (width 1,5 mm)

mean cobalt content: 14.2 weight-%

Cobalt "depleted" zone (width 2.0 mm)

mean cobalt content: 10.0 weight-%

10

Grade B (according to prior art with conventional cobalt)

Eta phase core (Ø7.0 mm):

mean grain size of eta-phase: 4,8 µm

15 mean cobalt content: 11.5 weight-%

Cobalt "rich" zone (width 1 mm)

mean cobalt content: 15.3 weight-%

Cobalt "depleted" zone (width 1,5 mm)

mean cobalt content: 8.7 weight-%

20

No porosity could be seen in the surface zone. It is obvious that buttons prepared according to the invention gave a more distinct multi-phase structure with a higher cobalt-gradient in the surface zone.

25

Example 7

Wear and toughness tests were performed with roller bits in an open-cut copper mine. The roller bits were of type
30 9 7/8" CS consisting of three roller cones with spherical buttons. The diameter of the buttons was 12 mm. For one roller bit the buttons according to the invention were placed in all positions of the buttons in row 1. Three types of roller bits were used in the test.

35

Bit A Buttons according to Example 6 were placed as

above and in the excepted positions comparative buttons with the same composition according to prior art.

- 5 Bit B Comparative buttons of Example 6 according to prior art in all positions.

- Bit C Standard cemented carbide with the same composition as in Example 6 but being free of eta-phase
10 and without the multi-phase structure.

Drill rig: 1 pce. BE 45R
Feed: 0-60000 lbs
Rpm: 60-85
15 Hole depth: 18-20 m
Type of rock: Biotite gneiss, mica schist.

Results:

Grade	drilled meters	index	drilling depth (m/h)	index
20 A	1900	160	18	140
B	1650	140	16	120 prior art
C	1170	100	13	100 prior art

- 25 The grade according to the invention has obtained longer life length as well as greater drilling rate.

The wear of the buttons was measured at 800 drilled meters.

30

Results

Grade A: Row 1: Buttons according to the invention
Average wear 3.0 mm
Row 2: Average wear 2.8 mm
35 Row 3: Average wear 2.5 mm

The wear profile gave a self-sharpening effect due to a wear looking like "egg shells". This effect was most marked at row 1. One button was missing in row 1.

5 Grade B: Row 1: Average wear 3.2 mm
 Row 2: Average wear 2.8 mm
 Row 3: Average wear 2.4 mm

10 The wear of the buttons was of "egg shells"-type. From row 1 three buttons from one roller cone and two respectively one from the other two were missing. Two buttons were missing in row 2.

15 Grade C: Row 1: Average wear 3.6 mm
 Row 2: Average wear 3.0 mm
 Row 3: Average wear 2.6 mm

From row 1 five buttons from one roller cone and four respectively one from the other two were missing. The penetration rate was slow at 800 drilled meters.

20

This test gave surprisingly good results for the roller bit attached with buttons made according to the invention. The penetration of the roller bit was also very good.

25

Example 8

From a 91.5 : 8.5 WC(2 μ m)/Co(1.2 μ m) powder mixture, granules (hereafter referred to as basic granules) were prepared according to the conventional technique. Then a sufficient amount of cobalt (polyol-type 1 μ m) was added to the granules until the respective proportions of WC/Co reached 88:12. After mixing for 30 minutes in a Turbula-type mixer, the resulting mixture ('modified granules') was tested for flowability according to ISO 4490 with the following results:

	Time/100 g, s
Basic granules	53
Modified granules	46

5

After compaction and sintering a cemented carbide was prepared with the basic granules and the modified granules. The Vickers hardness was determined with the following result:

10

	HV50
Basic granules	1455
Modified granules	1300

- 15 As expected the hardness of the cemented carbide with the modified granules was lower than that of the basic cemented carbide in view of the higher cobalt content. The structure of the carbide obtained with the modified granules was satisfactory.

Claims

1. Method of producing a sintered body comprising one or more hard constituents and a binder phase based on cobalt, nickel and/or iron by powder metallurgical methods milling, pressing and sintering of powders characterized in that at least part of the binderphase powder consists of non agglomerated particles of spheroidal morphology having dimensions of 0.1 to 20 μm .
2. Method according to claim 1 characterized in that said particles have dimensions 0.1 to 10 μm .
3. Method according to any of the preceding claims characterized in that said particles have dimensions 0.1 to 5 μm .
4. Method according to any of the preceding claims characterized in that said particles have dimensions smaller than 1 μm .
5. Method according to any of the preceding claims characterized in that at least 80% of said particles have dimensions in the interval $x \pm 0.2x$, provided that the interval of variation (that is $0.4x$) is not smaller than 0.1 μm .
6. Method according to any of the preceding claims characterized in that said binder phase powder represents at least 10% by weight, preferably at least 50% by weight, of the binder phase.
7. Method according to any of the preceding claims characterized in that said binder phase represents 100% of the total weight of the binder phase.

8. Method according to any of the previous claims
c h a r a c t e r i z e d in that said binderphase powder is added to a granulated powder mixture.

5 9. Method according to any of the preceding claims
c h a r a c t e r i z e d in that said binderphase powder is made by chemical reaction of an oxide, hydroxide or salt with a polyol or mixture of polyols and subsequent separation of the precipitated particles.

10 10. Method according to the preceding claim
c h a r a c t e r i z e d in that said binderphase powder is obtained by reduction with the aid of a polyol with seeding of the reaction space with metallic particles according to known methods, in particular seeding
15 with particles of palladium or silver.

11. Method according to any of the preceding claims
c h a r a c t e r i z e d in that the sintered body is
20 subjected to a hot isostatic pressing process either incorporated into the sintering process or as a separate operation.

12. Method according to the preceding claim
25 c h a r a c t e r i z e d in that the degree of milling and/or the sintering temperature has been lower than the conventional.

13. Method according to any of the preceding claims,
30 c h a r a c t e r i z e d in that the final sintered body contains 0.1 to 40 % by weight, preferably 3-25% of binderphase.

14. Method according to any of the preceding claims
35 c h a r a c t e r i z e d in that in addition diamond or cubic boron nitride powder is added.

15. Method according to any of the preceding claims
c h a r a c t e r i z e d in that the hard constituents
comprise carbides, nitrides and carbonitrides of at le-
5 ast one of a metal of group IVa, Va or VIa of the perio-
dical table of elements.

16. Method according to any of the preceding claims
c h a r a c t e r i z e d in that said sintered body
10 comprises WC with a grain size $>4\text{ }\mu\text{m}$ and <10 weight-%
cobalt.

17. Method according to any of the preceding claims 1-13
c h a r a c t e r i z e d in that said sintered body
15 comprises WC with a grain size $<1.5\text{ }\mu\text{m}$ and 5-7 weight-%
cobalt.

18. Method according to any of the preceding claims 1-13
c h a r a c t e r i z e d in that said sintered body
20 comprises WC with a grain size of $<1\text{ }\mu\text{m}$, preferably $<0.7\text{ }\mu\text{m}$ and a cobalt-content of 3-20 weight-%, preferably 4-
12 weight-%.

19. Method according to any of the preceding claims 1-13
25 c h a r a c t e r i z e d in that the mixture of hard
constituents and binder phase powders is substoichiome-
tric with respect to carbon and that said sintered body
comprises WC with a grain size $>1.5\text{ }\mu\text{m}$ and 10-25 weight-
% cobalt and is partially carburized.

30
20. Sintered cemented carbide body based on WC and with
a binder phase based on cobalt and/or nickel
c h a r a c t e r i z e d in a porosity better than A02
and B00, less than 0.5, preferably less than 0.2, binder
35 phase lakes per cm^2 with a maximum dimension of $>25\text{ }\mu\text{m}$
and less than five carbide grains per cm^2 with a grain

size of more than 5 times the average grain size of the matrix.

21. Sintered cemented carbide body according to claims
5 c h a r a c t e r i z e d in that said sintered body
comprises WC with a grain size $>4\text{ }\mu\text{m}$ and $<10\text{ weight-}\%$
cobalt.
22. Sintered cemented carbide body according to claim 17
10 c h a r a c t e r i z e d in that said sintered body
comprises WC with a grain size $<1.5\text{ }\mu\text{m}$ and $5\text{-}7\text{ weight-}\%$
cobalt.
23. Sintered cemented carbide body according to claim 17
15 c h a r a c t e r i z e d in that said sintered body
comprises WC with a grain size of $<1\text{ }\mu\text{m}$, preferably $<0.7\text{ }\mu\text{m}$
and a cobalt-content of $3\text{-}20\text{ weight-}\%$, preferably $4\text{-}12\text{ weight-}\%$.
- 20 24. Use of a sintered cemented carbide body according to
any of claims 1 - 12 or 20 with a grain size $<1.5\text{ }\mu\text{m}$ and
 $5\text{-}7\text{ weight-}\%$ cobalt as anvils for high pressure synthe-
sis of diamond.
- 25 25. Use of a sintered cemented carbide body according to
any of claims 1 - 12 or 20 with a WC grain size of $>4\text{ }\mu\text{m}$
and a binder phase content of $<10\text{ weight-}\%$ for hot
rolling of steel bar, mining and highway engineering ap-
plications or machining of stainless steel.
- 30 26. Use of a sintered cemented carbide body according to
any of the claims 1 - 12 or 20 with a WC a grain size of
 $<1\text{ }\mu\text{m}$, preferably $<0.7\text{ }\mu\text{m}$ and a cobalt-content of $3\text{-}20\text{ weight-}\%$,
preferably $4\text{-}12\text{ weight-}\%$ in tools for machi-
35 ning of printed electronic circuit boards and similar
composite materials.

INTERNATIONAL SEARCH REPORT

International Application No PCT/SE 92/00234

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC5: C 22 C 1/05, 29/00, 29/08, 32/00														
II. FIELDS SEARCHED Minimum Documentation Searched⁷ <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 25%; border-bottom: 1px solid black;">Classification System</td> <td style="border-bottom: 1px solid black;">Classification Symbols</td> </tr> <tr> <td style="height: 40px; vertical-align: bottom;">IPC5</td> <td style="vertical-align: bottom;">B 22 F; C 22 C</td> </tr> </table> Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched⁸ SE,DK,FI,NO classes as above			Classification System	Classification Symbols	IPC5	B 22 F; C 22 C								
Classification System	Classification Symbols													
IPC5	B 22 F; C 22 C													
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹ <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%;">Category *</th> <th style="width: 60%;">Citation of Document,¹¹ with indication, where appropriate, of the relevant passages¹²</th> <th style="width: 30%;">Relevant to Claim No.¹³</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td>EP, A1, 0113281 (UNIVERSITE PARIS VII) 11 July 1984, see page 1, line 7 - line 14; page 1, line 31 - line 33; page 2, line 17 - line 24 --</td> <td style="text-align: center; vertical-align: top;">1,9,10, 20</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td>US, A, 3215510 (F.J. KELLY ET AL) 2 November 1965, see column 4, line 14 - line 44 --</td> <td style="text-align: center; vertical-align: top;">1-8,13-19</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td>US, A, 4145213 (ROLF G. OSKARSSON ET AL) 20 March 1979, see column 2, line 15 - column 3, line 28; column 3, line 62 - column 4, line 12; column 9, line 22 - line 33 --</td> <td style="text-align: center; vertical-align: top;">1-8,11, 13-19, 20-23, 25</td> </tr> </tbody> </table>			Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	X	EP, A1, 0113281 (UNIVERSITE PARIS VII) 11 July 1984, see page 1, line 7 - line 14; page 1, line 31 - line 33; page 2, line 17 - line 24 --	1,9,10, 20	X	US, A, 3215510 (F.J. KELLY ET AL) 2 November 1965, see column 4, line 14 - line 44 --	1-8,13-19	X	US, A, 4145213 (ROLF G. OSKARSSON ET AL) 20 March 1979, see column 2, line 15 - column 3, line 28; column 3, line 62 - column 4, line 12; column 9, line 22 - line 33 --	1-8,11, 13-19, 20-23, 25
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* Special categories of cited documents:¹⁰ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family														
IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border-bottom: 1px solid black;">Date of the Actual Completion of the International Search</td> <td style="width: 50%; border-bottom: 1px solid black;">Date of Mailing of this International Search Report</td> </tr> <tr> <td style="border-bottom: 1px solid black;">13th July 1992</td> <td style="border-bottom: 1px solid black; text-align: center;">1992 -07- 17</td> </tr> <tr> <td style="border-bottom: 1px solid black;">International Searching Authority</td> <td style="border-bottom: 1px solid black;">Signature of Authorized Officer</td> </tr> <tr> <td style="text-align: center; border-bottom: 1px solid black;">SWEDISH PATENT OFFICE</td> <td style="text-align: center; border-bottom: 1px solid black;">Nils Engnell / </td> </tr> </table>			Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	13th July 1992	1992 -07- 17	International Searching Authority	Signature of Authorized Officer	SWEDISH PATENT OFFICE	Nils Engnell /				
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13th July 1992	1992 -07- 17													
International Searching Authority	Signature of Authorized Officer													
SWEDISH PATENT OFFICE	Nils Engnell /													

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
X	US, A, 4150984 (HIROSHI TANAKA ET AL) 24 April 1979, see column 2, line 10 - line 60; column 5, line 1 - line 38 --	1-8,13- 19
X	DE, A1, 3514299 (MAZDA MOTOR CORP) 31 October 1985, see page 5, line 11 - line 23 --	12
A	--	1-11,13- 23
X	DE, A, 2029501 (E.I. DU PONT DE NEMOURS AND COMPANY) 18 February 1971, see the whole document --	20-23
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A	--	1-19
A	SE, B, 415783 (FANSTEEL INC) 27 October 1980, see page 1, line 1 - page 2, line 16; page 5, line 20 - line 28; page 8, line 13 - line 21 --	1-8,13, 15-26
A	EP, A1, 0286164 (NORDDEUTSCHE AFFINERIE AG) 12 October 1988, see the whole document --	1-5,9, 10
A	EP, A2, 0477685 (HITACHI METALS, LTD) 1 April 1992, see page 4, line 50 - line 55; page 5, line 9 - line 37 --	1-23
A	Ullmanns Encyklopädie der technischen Chemie, Vol. 10, 4th ed., Verlag Chemie, Weinheim/Bergstr.: "Dentalchemie bis Erdölverarbeitung", page 413 - page 415 -- -----	

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. ☒ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE¹

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers....., because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claim numbers 20-23, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

See further information continued.

3. ☐ Claim numbers....., because they are dependent claims and are not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING²

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the the claims. It is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM THE FIRST SHEET

Claims 20-23 are difficult to evaluate for novelty and inventive step in comparison with the state of the art described in documents searched. The parameters stated as characterising features only refer to structural properties of the material, which are results of the method according to claim 1. Moreover, these properties may be accomplished by means not mentioned in the application. Thus, when evaluating a method according to the state of the art, the result of it must be considered.

Therefore, it is not possible to carry out a meaningful and complete search for the features of claims 20-23.

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.PCT/SE 92/00234**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the Swedish Patent Office EDP file on 29/05/92
The Swedish Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		JP-A- 59173206	84-10-01
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		GB-A- 1266966	72-03-15
		US-A- 3480410	69-11-25
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		JP-A- 1025910	89-01-27
		US-A- 4818280	89-04-04

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A2- 0477685	92-04-01	NONE	