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(54) **CEMENTED TUNGSTEN CARBIDE MATERIAL, METHOD OF MAKING SAME AND USE THEREOF**

ZEMENTIERTES WOLFRAMCARBIDMATERIAL, VERFAHREN ZU DESSEN HERSTELLUNG UND VERWENDUNG DAVON

MATÉRIAU EN CARBURE DE TUNGSTÈNE, SON PROCÉDÉ DE FABRICATION ET SON UTILISATION

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## Description

### Field

**[0001]** This disclosure is related to a cemented tungsten carbide material such as for use in high-pressure components for synthesis of diamond or c-BN or fabrication of poly-crystalline diamond or c-BN and a method of making same.

### Background

**[0002]** It is well known that cemented carbides employed for high-pressure high-temperature (HPHT) components used for diamond synthesis and production of polycrystalline diamond (PCD), including anvils and dies, are subjected to high pressures, temperatures and loads. Such unfavorable conditions lead to their deformation and, if the deformation exceeds a certain level, the HPHT components fail. In this respect it is very important to have a cemented carbide material with a high level of Young's modulus to reduce the deformation at high pressures and consequently improve the deformation resistance and lifetime of the HPHT components.

**[0003]** There is therefore a need for a cemented carbide material for use in the fabrication of high-pressure high-temperature components having improved resistance to deformation as well as high fracture toughness and strength.

**[0004]** JP 2011 235410 is directed to a cutting tool formed of WC-based cemented carbide, the content of Co as a binding phase component being 4 to 12 mass%. In the binding phase, 3-20 mass% of solid Re is soluble. On a surface of a WC particle of a hard phase, a diffusion thin layer of Re is formed.

**[0005]** US 2012/247028 is directed to a hard metal body comprising WC grains and a metal binder comprising cobalt. The body has a surface region and a core region and the mean binder fraction of the core region is greater than that of the surface region and the mean carbon concentration within the binder being higher in the surface region than in the core region.

**[0006]** US 2002/112896 is directed to a cutting tool insert having a WC based substrate and a coating. The hard metal consists of 4-15 wt% binder phase with FCC structure and 35-65wt% Fe and 35-65wt% Ni in addition to dissolved elements. FR 2350403 is directed to hard materials consisting of tungsten carbide, and a binder metal such as cobalt, for the manufacture of cutting tools. The hard material contains WC, Co, preferably an additional carbide such as TiC, TaC, NbC, HfC, VC or MoC and Re.

**[0007]** US 5649279 is directed to forming a coated carbide insert by enriching the binder phase for the cemented carbide material through dissolution of cubic phase to cause formation of stratified layers.

### Summary

**[0008]** Viewed from a first aspect the invention provides a cemented tungsten carbide material further comprising between 3 to 10 wt.% Co and between 0.5 to 8 wt.% Re; and optionally grain growth inhibitors comprising one or more of V, Cr, Ta, Ti, Mo, Zr, Nb and Hf or a carbide thereof;

the equivalent total carbon (ETC) content of the cemented tungsten carbide material with respect to the WC being between 6.3 wt.% to 6.9 wt.%;
the cemented tungsten carbide material being free of eta-phase and free carbon. Viewed from a second aspect, not part of the invention, there is provided a polycrystalline superhard construction comprising:

a substrate comprising the cemented tungsten carbide material defined above; and
a body of polycrystalline superhard material bonded to the substrate along an interface.

**[0009]** Viewed from a third aspect, not part of the invention, there is provided a cutter comprising a substrate comprising the cemented carbide material defined above bonded to a body of polycrystalline superhard material adapted for a rotary drill bit for boring into the earth.

**[0010]** Viewed from a fourth aspect**,** not part of the invention, there is provided a PCD element for a rotary shear bit for boring into the earth, for a percussion drill bit or for a pick for mining or asphalt degradation, comprising a cutter element comprising a body of superhard polycrystalline material bonded to a body of cemented tungsten carbide material as defined above.

**[0011]** Viewed from a fifth aspect**,** not part of the invention, there is provided a drill bit or a component of a drill bit for boring into the earth, comprising a PCD element as defined above.

**[0012]** Viewed from a sixth aspect the invention provides a method of producing the cemented tungsten carbide material defined above, the method comprising: milling a cemented carbide mixture containing WC and carbon with Re, Co, and optionally grain growth inhibitors comprising one or more of V, Cr, Ta, Ti, Mo, Zr, Nb and Hf or a carbide thereof;

pressing the cemented carbide article from the mixture; sintering the article at a temperature of above 1450°C in vacuum for between 1 to 10 minutes and a pressure of Ar (HIP) for 5 to 120 minutes; and cooling the article from said temperature to 1300 degrees Centigrade (°C); wherein the step of cooling the article comprises:

cooling the article in an atmosphere comprising one or more of an inert gas, nitrogen, hydrogen or a mixture thereof, at a cooling rate of 0.2 to 2 degrees per minute; or
cooling the article in a vacuum at a cooling rate of 0.2 to 2 degrees per minute. Viewed from a seventh aspect, not part of the invention, there is provided a method of recycling the cemented tungsten carbide material defined above, the method comprising melting the tungsten carbide material in a protective atmosphere with liquid Zn, evaporating the Zn to form a resultant product; and milling the resulting product to recover Re from the product.

**[0013]** Viewed from an eighth aspect, not part of the invention, there is provided a method of recycling the cemented tungsten carbide material defined above, the method comprising subjecting the cemented tungsten carbide material to an acid leaching mixture to remove the binder phase from the cemented tungsten carbide material; and chemically recovering Co and Re from the removed binder phase.

**[0014]** Viewed from a ninth aspect, not part of the invention, there is provided a method of recycling the cemented tungsten carbide material defined above, the method comprising oxidation of the cemented tungsten carbide material to dissolve the carbide, Re and Co, and recovering the Re.

**[0015]** Viewed from a tenth aspect the invention defines a use of a cemented tungsten carbide material in a high-pressure component for synthesis of diamond or c-BN, or in fabrication of polycrystalline diamond or c-BN operating at a pressure of above 5 GPa and a temperature of above 1100°C, wherein the cemented tungsten carbide material comprises:

a carbide of one or more metals in form of the second carbide phase, or dissolved in a binder phase in the material, said one or more metals comprising Ti, V, Cr, Mn, Zr, Nb, Mo, Hf and/or Ta;
between 0.5 to 8 wt.% Re and between 3 to 10 wt.% Co;
the equivalent total carbon (ETC) content of the cemented carbide material with respect to WC being between 6.3 wt.% to 6.9 wt.%
the cemented carbide material being free of eta-phase and free carbon.

## Brief description of the drawings

**[0016]** Embodiments will now be described by way of example and with reference to the accompanying drawings in which:

Figure 1 is an SEM image of a cemented carbide material according to a first example and comprising WC-Co-Re;
Figure 2 is an EBSD image of the WC-Co-Re cemented carbide material of Figure 1; and
Figure 3 is an EBSD image showing the microstructure of conventional WC-Co cemented carbide material.

## Detailed Description

**[0017]** It is well known that the equivalent total carbon (ETC) content with respect to WC of conventional WC-Co materials lies between roughly 6.0 and 6.3 wt.%. [see e.g. "Exner H., Gurland J. A review of parameters influencing some mechanical properties of tungsten carbide-cobalt alloy. Powder Met., 13 (1970) 13-31)"; and I. Konyashin, S. Hlawatschek , B. Ries, F. Lachmann, T. Weirich, F. Dorn, A. Sologubenko on the "Mechanism of WC Coarsening in WC-Co Hardmetals with Various Carbon Contents", International Journal of Refractory Metals and Hard Materials, 27 (2009) 234-243"]. When the carbon content is lower or higher than that of this range, additional phases (such as eta-phase or free carbon) appear in the carbide microstructure leading to a significant decrease in the mechanical properties of WC-Co materials, such as compressive strength, transverse rupture strength, and fracture toughness.

**[0018]** It has now been surprisingly appreciated that if WC-Co-Re cemented carbides have a significantly increased carbon content, which corresponds to the equivalent total carbon (ETC) content with respect to WC of between 6.3 wt.% and 6.9 wt.%, their mechanical properties such as compressive strength, transverse rupture strength, hardness, fracture toughness and hot hardness may be dramatically improved.

**[0019]** Whilst not wishing to be bound by theory, a possible reason for this may be the presence of residual compressive stresses in the binder phase of the WC-Co-Re cemented carbides in such materials. According to numerous publications on residual stresses in WC-Co cemented carbides, the binder phase in WC-Co is always under high residual tensile stresses resulting in decreased combinations of hardness and fracture toughness of conventional WC-Co materials [see for example the publication by Mari D, Clausen B, Bourke M A M, Buss K. entitled "Measurement of residual thermal

stress in WC-Co by neutron diffraction", Int. J. Refractory Met. Hard Mater., 2009; 27: 282-287", the publication by Krawitz A D, Venter A M, Drake E F, Luyckx S B, Clausen B entitled "Phase response in WC-Ni to cyclic compressive loading and its relation to roughness", Int. J. Refractory Met. Hard Mater., 2009; 27: 313-316", and the publication by Coats D I, Krawitz A D entitled "Effect of particle size on thermal residual stress in WC-Co composites", Mater. Sci. Engin., 2003; A359:338-342"].

**[0020]** As used herein, a "superhard material" is a material having a Vickers hardness of at least about 25GPa. Diamond and cubic boron nitride (cBN) material are examples of superhard materials.

**[0021]** As used herein, a "superhard construction" means a construction comprising polycrystalline superhard material or superhard composite material, or comprising polycrystalline superhard material and superhard composite material bonded to a cemented carbide substrate.

**[0022]** As used herein, polycrystalline diamond (PCD) is a PCS material comprising a mass of diamond grains, a substantial portion of which are directly inter-bonded with each other and in which the content of diamond is at least about 80 volume percent of the material. In one embodiment of PCD material, interstices between the diamond gains may be at least partly filled with a binder material comprising a catalyst for diamond. As used herein, "interstices" or "interstitial regions" are regions between the diamond grains of PCD material. In embodiments of PCD material, interstices or interstitial regions may be substantially or partially filled with a material other than diamond, or they may be substantially empty. Embodiments of PCD material may comprise at least a region from which catalyst material has been removed from the interstices, leaving interstitial voids between the diamond grains.

**[0023]** As used herein, polycrystalline cubic boron nitride (PCBN) material is a PCS material comprising a mass of cBN grains dispersed within a wear resistant matrix, which may comprise ceramic or metal material, or both, and in which the content of cBN is at least about 50 volume percent of the material. In some embodiments of PCBN material, the content of cBN grains is at least about 60 volume percent, at least about 70 volume percent or at least about 80 volume percent. Embodiments of superhard material may comprise grains of superhard materials dispersed within a hard matrix, wherein the hard matrix preferably comprises ceramic material as a major component, the ceramic material preferably being selected from silicon carbide, titanium nitride and titanium carbo-nitride.

**[0024]** With reference to Figure 1 and Figure 2, a cemented carbide material comprises a mass of grains of a hard material comprising a carbide phase and interstices between the hard grains which are filled with a binder material which constitutes the binder phase. In the embodiment shown in Figure 1, the carbide phase is WC and the binder phase comprises an alloy of Co and Re with some W and C dissolved in it.

**[0025]** Figure 3 shows, for comparison, a conventional cemented carbide material comprising WC as the carbide phase and Co as the binder phase.

**[0026]** In some embodiments, the cemented carbide material further comprises a carbide of one or more metals in the form of a second carbide phase or dissolved in the binder phase, the one or more metals comprising Ti, V, Cr, Mn, Zr, Nb, Mo, Hf and/or Ta. The cemented carbide material is free of eta-phase and free carbon.

**[0027]** According to the invention, the cemented carbide material comprises between 0.5 to 8 wt% Re.

**[0028]** According to the invention, the cemented carbide material comprises between 3 to 10 wt.% Co.

**[0029]** In other embodiments, the cemented carbide material comprises between 0.5 to around 6 wt.% Re.

**[0030]** The WC in the cemented carbide material may, for example, have a mean grain size below around 0.6 microns.

**[0031]** Furthermore, in some embodiments, the equivalent total carbon (ETC) content with respect to WC lies between 6.3 wt% to 6.9 wt%.

**[0032]** The magnetic properties of the cemented carbide material may be related to important structural and compositional characteristics and is understood to be an indication of the carbon content in the cemented carbide material. The most common technique for measuring the carbon content in cemented carbides is indirectly, by measuring the concentration of tungsten dissolved in the binder to which it is indirectly proportional. The higher the content of carbon dissolved in the binder the lower the concentration of tungsten dissolved in the binder. The magnetic saturation $4\pi\sigma$ or magnetic moment $\sigma$ of a hard metal, of which cemented tungsten carbide is an example, is defined as the magnetic moment or magnetic saturation per unit weight. The magnetic moment, $\sigma$, of pure Co is 16.1 micro-Tesla times cubic metre per kilogram ($\mu T.m^3/kg$), and the induction of saturation, also referred to as the magnetic saturation, $4\pi\sigma$, of pure Co is 201.9 $\mu T.m^3/kg$. The tungsten content within the binder may be determined from a measurement of the magnetic moment, $\sigma$, or magnetic saturation, $M_s = 4\pi\sigma$, these values having an inverse relationship with the tungsten content (Roebuck (1996), "Magnetic moment (saturation) measurements on cemented carbide materials", Int. J. Refractory Met., Vol. 14, pp. 419-424.).

**[0033]** The following formula may be used to relate magnetic saturation, Ms, to the concentrations of W and C in the binder:

$$M_s \propto [C]/[W] \times \text{wt.\% Co} \times 201.9 \text{ in units of } \mu T.m^3/kg$$

**[0034]** Some embodiments of the cemented carbide material have an associated magnetic saturation of at least around 40 percent to around 80 percent of the magnetic saturation of nominally pure Co.

**[0035]** The mean grain size of carbide grains, such as WC grains, may be determined by examination of micrographs obtained using a scanning electron microscope (SEM) or light microscopy images of metallurgically prepared cross-sections of a cemented carbide material body, applying the mean linear intercept technique, for example. Alternatively, the mean size of the WC grains may be estimated indirectly by measuring the magnetic coercivity of the cemented carbide material, which indicates the mean free path of Co intermediate the grains, from which the WC grain size may be calculated using a simple formula well known in the art. This formula quantifies the inverse relationship between magnetic coercivity of a Co-cemented WC cemented carbide material and the Co mean free path, and consequently the mean WC grain size. Magnetic coercivity has an inverse relationship with MFP.

**[0036]** As used herein, the "mean free path" (MFP) of a composite material such as cemented carbide is a measure of the mean distance between the aggregate carbide grains cemented within the binder material. The mean free path characteristic of a cemented carbide material may be measured using a micrograph of a polished section of the material. For example, the micrograph may have a magnification of about 1500x. The MFP may be determined by measuring the distance between each intersection of a line and a grain boundary on a uniform grid. The matrix line segments, Lm, are summed and the grain line segments, Lg, are summed. The mean matrix segment length using both axes is the "mean free path". Mixtures of multiple distributions of tungsten carbide particle sizes may result in a wide distribution of MFP values for the same matrix content.

**[0037]** As used herein, the grain sizes are expressed in terms of Equivalent Circle Diameter (ECD) according to the ISO FDIS 13067 standard. The ECD is obtained by measuring of the area A of each grain exposed at the polished surface and calculating the diameter of a circle that would have the same area A, according to the equation ECD = $(4A/\pi)^{1/2}$ (See section 3.3.2 of ISO FDIS 13067 "Microbeam analysis - Electron Backscatter Diffraction - Measurement of average grain size.", International Standards Organisation Geneva, Switzerland, 2011).

**[0038]** In some embodiments, the carbide phase of the cemented carbide material is formed of carbide grains having a mean grain size of at least around 0.1 μm to at most around 10 μm and the cemented carbide material may have an associated magnetic coercive force varying from around 2kA/m to around 70 kA/m.

**[0039]** In some embodiments, the carbide phase comprises WC and the cemented carbide material has a coercive force Hc in kA/m as a function of the WC mean grain size $D_{wc}$ in μm determined on the basis of EBSD images of the carbide microstructure equal to or less than values given by the equation:

$$Hc = 10 \times D_{wc}^{-0.62}$$

**[0040]** In some embodiments, the carbide phase comprises WC and the binder phase comprises Co and Re.

**[0041]** The binder phase of the cemented carbide material may, for example, be a solid solution of Re, carbon and W and one of more of Fe, Co, and Ni. In some embodiments, the binder phase comprises at least about 0.1 weight percent to at most about 5 weight percent of one or more of V, Cr, Ta, Ti, Mo, Zr, Nb and Hf in solid solution and/or in the form of carbide compounds. In some other embodiments, the material comprises at least about 0.01 weight percent and at most about 2 weight percent of one or more of Ru, Rh, Pd, Os, Ir and Pt.

**[0042]** The cemented carbide has an associated hardness and, in some embodiments, the hardness decrease at 300°C is at most 20%, or, in some other embodiments, is at most 17%. Hardness measurements were carried out according to the DIN ISO 3878 on metallurgical cross-sections at a load of 30 kgf at room temperature as well as at 300°C, 500°C and 800°C in an Ar atmosphere. After achieving the elevated temperatures the cross-section was annealed for 10 min, after which a Vickers indentation was made under the load of 30 kgf and the load was applied for 15 sec. The hardness values of both a conventional cemented carbide material containing a Co binder and an embodiment of cemented carbide material containing the Co-Re binder were measured, and a decrease of hardness at the elevated temperatures compared to that at room temperature was calculated for both the conventional material and embodiment material.

**[0043]** The cemented carbide material may, for example, have a hardness decrease at 500°C of at most 30% or, in some other embodiments, at most 27%.

**[0044]** The hardness-toughness coefficient may be calculated by multiplying the Vickers hardness in GPa and indentation fracture toughness in MPa $m^{1/2}$, and, in some embodiments, this is above 150. In some emboidments, the cemented carbide material has a Vickers hardness

**[0045]** In some embodiments, the binder phase of the cemented carbide material has one or more residual compressive stresses and these may, for example, be between around -5 MPa to around 100 MPa.

**[0046]** An embodiment of a cemented carbide material may be made by a method including milling a cemented carbide mixture containing carbides with Re, Co, Ni and/or Fe and optionally grain growth inhibitors including V, Cr, Ta, Ti, Mo,

Zr,, Nb and Hf or their carbides and then pressing a cemented carbide article from the mixture. The article is then sintered at temperatures of above 1450°C in vacuum for 1 to 10 min and afterwards under pressure of Ar (HIP) for 5 to 120 min. The article is then cooled from the sintering temperatures to 1300 degrees Centigrade (°C) in an atmosphere comprising inert gases, nitrogen, hydrogen or a mixture thereof, or in a vacuum, at a cooling rate of approximately 0.2 to 2 degrees per minute.

**[0047]** Some embodiments are now described in more detail with reference to the following example below, which is not intended to be limiting.

**Example**

**[0048]** Tungsten carbide powder, wherein the WC grains had an average grain size of about 0.6 μm with carbon content of 6.13 wt.%, was milled with 5.5%Re powder and 3.7%Co powder. The Co grains had an average grain size of about 1 μm. The powder mixture was produced by milling the powders together for 24 hours using a ball mill in a milling medium comprising hexane with 2 wt.% paraffin wax, and using a powder-to-ball ratio of 1:6. After milling 0.35 wt.% carbon black was added and additional milling was performed for 1 hr resulting in the fact that the equivalent total carbon (ETC) content with respect to WC of the mixture was equal to 6.51 wt.%. After drying the mixture, green bodies were pressed and sintered at 1540°C for 60 min (30 min vacuum + 30 min HIP in Ar at a pressure of 50 Bar). After the sintering at 1540°C the bodies were cooled down to 1300°C at a rate of 0.5 degrees per min and afterwards at an uncontrolled rate down to room temperature. The carbon content was measured on the sintered samples after their crushing by hand with the aid of of the LECO WC600 instrument and determined to be equal to 5.85 wt.% providing evidence that the equivalent total carbon (ETC) content with respect to WC is equal to 6.44 wt%.

**[0049]** A control batch of conventional WC-Co cemented carbides without Re was made from the same WC powder batch and 6 wt.% Co, which corresponds to the same volume percentage of binder as in the WC-Co-Re material, without adding carbon black. The batch was milled in the same way as the WC-Co-Re carbide and sintered at 1440°C for 1 hr including 30 sintering vacuum and 30 min sintering under pressure (HIP). The carbon content was measured on sintered samples in the same way as for the WC-Co-Re cemented carbides and found to be equal to 5.77 wt.% providing evidence that the equivalent total carbon (ETC) content with respect to WC is equal to 6.13 wt%.

**[0050]** Metallurgical cross-sections of the WC-Co-Re and WC-Co cemented carbides were made and examined by optical microscopy and SEM. The hardness (HV20), indentation fracture toughness ($K_{1C}$), transverse rupture strength (TRS), compressive strength and Young's modulus as well as coercive force and magnetic moment (saturation) of the sintered bodies were examined.

**[0051]** The WC mean grain size was measured on the basis of the EBSD image of the cross-sections according to the procedure described in: K.P. Mingard, B. Roebuck a, E.G. Bennett, M.G. Gee, H. Nordenstrom, G. Sweetman, P. Chan . Comparison of EBSD and conventional methods of grain size measurement of hard metals. Int. Journal of Refractory Metals & Hard Materials 27 (2009) 213-223.

**[0052]** Figures 1 and 2 show SEM and EBSD images respectively of the WC-Co-Re cemented carbide formed according to Example 1, and Figure 3 shows the microstructure of the conventional WC-Co cemented carbides without Re and having the Equivalent Total Carbon content with respect to WC of 6.13 wt.%. The WC-Co-Re carbide shown in Figure 1 and Figure 2 has a WC mean grain size of 0.44 μm. It will be seen that there is neither eta-phase nor free carbon nor porosity in the microstructure of both carbide materials shown in Figures 1 and 2. Table 1 shows the grain size distribution in the microstructure of the WC-Co-Re cemented carbide shown in Figures 1 and 2.

Table 1

| Grain size distribution in the microstructure of the WC-Co-Re cemented carbide. | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Grain Size | 0.05-0.2 μm | 0.2-0.4 μm | 0.4-0.6 μm | 0.6-0.8 μm | 0.8-1 μm | 1-1.5 μm | 1.5-2 μm | 2-6 μm |
| % | 20.2 | 29.4 | 28.5 | 13.5 | 5.3 | 2.7 | 0.4 | 0 |

**[0053]** The magnetic moment of the WC-Co-Re carbide material of Figure 1 and Figure 2 was equal to 4.7 $Gcm^3/g$, which is 64% of the theoretical value for cemented carbide with 3.7 % of nominally pure Co providing evidence for its specific magnetic saturation in per cent (SMS). The coercive force of the WC-Co-Re material was determined to be 284 Oe. Its mechanical properties were determined to be HV20=1860 or 18.6 GPa, $K_{1C}$= 10.5 MPa $m^{½}$, and TRS=3700 MPa. The hardness-toughness coefficient calculated by multiplying the Vickers hardness in GPa and fracture toughness in MPa $m^{1/2}$ was therefore equal to 195. The compressive strength of the WC-Co-Re cemented carbide was determined to be 6020 MPa and its Young's modules to be equal to 712 GPa. Its hot hardness was found to be equal to 16.9 GPa at 300°C and 14.9 GPa at 500°C providing evidence that the hardness decrease at the elevated temperatures was about 9.1% and 19.8% correspondingly. The compressive strength almost did not change when increasing the temperatures

from room temperature to 300°C and 500°C.

**[0054]** The residual stress in the Co-Re binder phase of the WC-Co-Re cemented carbide was measured using a Bruker D8 Discover diffractometer using the Cu-K$\alpha$ radiation. This wavelength of X-ray typically obtained diffraction information from a depth of around 5 $\mu$m. The diffracted beam was collected using a Braun Position Sensivite Detector with a bin size of 0.01059°. The residual stress measurement was performed by use of the Co (211) peak at an angle of 146.6° using a step size of 0.01059° and a count time of 10 sec. per step. The residual stress measurements were performed using the standard iso.inclination $\sin^2\psi$ technique in accordance with the ref. "Fitzpatrick M, Fry T, Holdway P, et al. NPL Good Practice Guide No. 52: Determination of Residual Stresses by X-ray Diffraction - Issue 2. September 2005".

**[0055]** Two measurements of the WC-Co-Re cemented carbide were made which provided data with the compressive stress being -11MPa in the Phi = 0 direction and -8MPa in the Phi =90 direction for the first measurement; and -9MPa in the Phi = 0 direction and -31MPa in the Phi =90 direction for the second measurement. Therefore, in all the cases the binder phase of the WC-Co-Re materials was under residual compressive stresses.

**[0056]** The magnetic moment of the conventional WC-6%Co carbide material, having the same volume proportion of the binder phase as the WC-Co-Re cemented carbide was found to be equal to 9.2 $Gcm^3/g$, which is 95.2% of the theoretical value for the cemented carbide with 6% nominally pure Co, the coercive force was 270 Oe, HV20=1610 or 16.1 GPa, $K_{1C}$= 9.5 $MPam^{½}$, TRS=2900 MPa, compressive strength was 5200 GPa and Young's modulus of 640 GPa. Its WC mean grain size was determined to be equal to 0.59 $\mu$m. Its hot hardness was found to be equal to 12.1 GPa at 300°C and 8.1 GPa at 500°C providing evidence that the hardness decrease was about 25% and 49% correspondingly.

**[0057]** Young's modulus is a type of elastic modulus and is a measure of the uni-axial strain in response to a uni-axial stress, within the range of stress for which the material behaves elastically. A method of measuring the Young's modulus E is by means of measuring the transverse and longitudinal components of the speed of sound through the material using ultrasonic waves. In particular, a preferred method of measuring the Young's modulus $E$ is by means of measuring the transverse and longitudinal components of the speed of sound through the material, according to the equation $E = 2\rho.C_T^2(1 + \upsilon)$, where $\upsilon = (1 - 2(C_T/C_L)^2)/(2 - 2(C_T/C_L)^2)$, $C_L$ and $C_T$ are respectively the measured longitudinal and transverse speeds of sound through it and $\rho$ is the density of the material. The longitudinal and transverse speeds of sound may be measured using ultrasonic waves, as is well known in the art. Where a material is a composite of different materials, the mean Young's modulus may be estimated by means of one of three formulas, namely the harmonic, geometric and rule of mixtures formulas as follows: $E = 1 / (f_1 / E_1 + f_2 / E_2))$; $E = E_1^{f1} + E_1^{f2}$; and $E = f_1 E_1 + f_2 E_2$; in which the different materials are divided into two portions with respective volume fractions of $f_1$ and $f_2$, which sum to one.

**[0058]** The cemented carbide material of one or more embodiments may find particular application in use in high-pressure components for synthesis of diamond or c-BN, or in fabrication of polycrystalline diamond or c-BN operating at pressures of above 5 GPa and temperatures of above 1100°C.

**[0059]** In such applications, PCD composite compact elements may comprise a PCD structure bonded along an interface to an embodiment of a cemented carbide substrate comprising particles of a metal carbide and the binder material described above.

**[0060]** An embodiment of a PCD composite compact element may be made by a method including providing the cemented carbide substrate, contacting an aggregated, substantially unbonded mass of diamond particles against a surface of the substrate to form an pre-sinter assembly, encapsulating the pre-sinter assembly in a capsule for an ultra-high pressure furnace and subjecting the pre-sinter assembly to a pressure of at least about 5.5 GPa and a temperature of at least about 1,250 degrees centigrade, and sintering the diamond particles to form a PCD composite compact element comprising a PCD structure integrally formed on and joined to the cemented carbide substrate. In some embodiments of the invention, the pre-sinter assembly may be subjected to a pressure of at least about 6 GPa, at least about 6.5 GPa, at least about 7 GPa or even at least about 7.5 GPa.

**[0061]** The hardness of cemented tungsten carbide substrate may be enhanced by subjecting the substrate to an ultra-high pressure and high temperature, particularly at a pressure and temperature at which diamond is thermodynamically stable. The magnitude of the enhancement of the hardness may depend on the pressure and temperature conditions. In particular, the hardness enhancement may increase the higher the pressure. Whilst not wishing to be bound by a particular theory, this is considered to be related to the Co drift from the substrate into the PCD during press sintering, as the extent of the hardness increase is directly dependent on the decrease of Co content in the substrate.

**[0062]** In some embodiments, as described above, the cemented carbide material forming the substrate may comprise between 2 to 8 wt.% Re, and 3 to 9 wt.%Co, with the remainder being WC.

**[0063]** The working temperature on the surface of the high-pressure components may be at least around 200°C and at most around 800°C.

**[0064]** In connection with the present invention, it has now been surprising found out that if the cemented carbide contains cobalt (Co) and rhenium (Re) and the proportion of Re and Co lies in a certain range it may be possible to improve significantly the Young's modulus of the cemented carbide material. At the same time it may be possible to improve the cemented carbide hot hardness at temperatures dramatically of up to 800°C. As a result, it may be possible

to employ embodiments of the WC-Co-Re cemented carbide materials as HPHT components.

**[0065]** Furthermore, it may be possible to recycle used embodiments of cemented carbide materials. This has clear environmental and economic benefits. The recycling procedure may comprise melting the cemented carbide material in a protective atmosphere with liquid Zn with consequent evaporation of Zn from the mixture, and milling the resulting product.

**[0066]** Alternatively, the cemented carbide material may be subjected to an acid leaching treatment to remove the binder phase of the cemented carbide article and chemically recover the Co and Re. A further method of recycling the cemented carbide material may comprise oxidation of the cemented carbides articles with consequent dissolution of carbides, Re and Co and their recovery.

## Claims

1. A cemented tungsten carbide (WC) material further comprising between 3 to 10 wt.% Co and between 0.5 to 8 wt.% Re; and optionally grain growth inhibitors comprising one or more of V, Cr, Ta, Ti, Mo, Zr, Nb and Hf or a carbide thereof;

   the equivalent total carbon (ETC) content of the cemented tungsten carbide (WC) material with respect to the WC, as defined in the description, being between 6.3 wt.% to 6.9 wt.%;
   the cemented tungsten carbide material being free of eta-phase and free carbon.

2. The cemented tungsten carbide material of claim 1, wherein the cemented tungsten carbide material comprises between 0.5 to 6 wt% Re; and/or

   the WC in the material has a mean grain size less than 0.6 μm; and/or
   the cemented tungsten carbide material has a magnetic saturation of at least 40 percent to 80 percent of the magnetic saturation of nominally pure Co; and/or
   the tungsten carbide phase is formed of tungsten carbide grains having a mean grain size of at least 0.1 μm to at most 10 μm; and/or
   the cemented tungsten carbide material has an associated magnetic coercive force varying from 2kA/m to 70 kA/m; and/or
   the cemented tungsten carbide comprising a carbide of one or more metals in form of the second carbide phase, or dissolved in a binder phase in the material, said one or more metals comprising Ti, V, Cr, Mn, Zr, Nb, Mo, Hf and/or Ta.

3. The cemented tungsten carbide material of any one of the preceding claims, wherein the material comprises a binder phase having one or more residual compressive stresses.

4. The cemented tungsten carbide material of claim 3, wherein

   the binder phase comprises a binder material comprising Co, Re, W and C; or
   the binder phase comprises a binder material, the binder material comprising a solid solution of Re, carbon and W and one of more of Fe, Co, and Ni.

5. The cemented tungsten carbide material as claimed in any one of the preceding claims, wherein the cemented tungsten carbide material has a coercive force Hc in kA/m as a function of the WC mean grain size $D_{wc}$ in μm determined on the basis of EBSD images of the carbide microstructure equal to or less than values given by the equation:

$$Hc = 10 \times D_{wc}^{-0.62}$$

6. The cemented tungsten carbide material as claimed in any one of the preceding claims, wherein the material has a compression strength above 5500 MPa at room temperature and at an elevated temperature of up to 500°C.

7. The cemented tungsten carbide material of claim 6, wherein the material has a Vickers hardness, and the hardness decrease at 300°C is at most 12%.

**8.** The cemented tungsten carbide material as claimed in any one of the preceding claims, wherein the material has a Vickers hardness, and wherein the hardness decrease at 500°C is at most 21% ; and/or

the Young's Modulus of said material is above 700 GPa; and/or
the hardness-toughness coefficient calculated by multiplying the Vickers hardness in GPa and fracture toughness in MPa $m^{1/2}$ is above 190; and/or
the cemented tungsten carbide material comprises a binder phase having a binder material comprising at least 0.1 weight percent to at most 5 weight percent of one or more of V, Cr, Ta, Ti, Mo, Zr, Nb and Hf in solid solution and/or in the form of carbide compounds; and/or
the material comprises at least about 0.01 weight percent and at most 2 weight percent of one or more of Ru, Rh, Pd, Os, Ir and Pt.

**9.** A polycrystalline superhard construction comprising:

a substrate comprising the cemented tungsten carbide material of any one of claims 1 to 8; and
a body of polycrystalline superhard material bonded to the substrate along an interface.

**10.** The polycrystalline superhard construction of claim 9, wherein the body of polycrystalline superhard material comprises polycrystalline diamond (PCD) material; or the body of polycrystalline superhard material comprises PCBN.

**11.** A method of producing the cemented tungsten carbide material of any one of claims 1 to 8, the method comprising:

- milling a cemented carbide mixture containing WC and carbon with Re, Co, and optionally grain growth inhibitors comprising one or more of V, Cr, Ta, Ti, Mo, Zr, Nb and Hf or a carbide thereof;
- pressing the cemented carbide article from the mixture;
- sintering the article at a temperature of above 1450°C in vacuum for between 1 to 10 minutes and a pressure of Ar (HIP) for 5 to 120 minutes; and
- cooling the article from said temperature to 1300 degrees Centigrade (°C), wherein:
the step of cooling the article comprises:

cooling the article in an atmosphere comprising one or more of an inert gas, nitrogen, hydrogen or a mixture thereof, at a cooling rate of 0.2 to 2 degrees per minute; or
cooling the article in a vacuum at a cooling rate of 0.2 to 2 degrees per minute.

**12.** Use of a cemented tungsten carbide material in a high-pressure component for synthesis of diamond or c-BN, or in fabrication of polycrystalline diamond or c-BN operating at a pressure of above 5 GPa and a temperature of above 1100°C, wherein the cemented tungsten carbide material comprises:

a carbide of one or more metals in form of the second carbide phase, or dissolved in a binder phase in the material, said one or more metals comprising Ti, V, Cr, Mn, Zr, Nb, Mo, Hf and/or Ta;
between 0.5 to 8 wt.% Re and between 3 to 10 wt.% Co;
the equivalent total carbon (ETC) content of the cemented carbide material with respect to WC being between 6.3 wt.% to 6.9 wt.%
the cemented tungsten carbide material being free of eta-phase and free carbon.

**13.** Use of the cemented tungsten carbide material as claimed in claim 12, wherein:

the cemented tungsten carbide material comprises between 0.5 to 6 wt.% Re; and/or
the WC in the material has a mean grain size less than 0.6 μm; and/or
the cemented tungsten carbide material has a magnetic saturation of at least 40 percent to 80 percent of the magnetic saturation of nominally pure Co; and/or
the tungsten carbide phase is formed of carbide grains having a mean grain size of at least 0.1 μm to at most 10 μm; and/or
the cemented tungsten carbide material has an associated magnetic coercive force varying from 2kA/m to 70 kA/m; and/or
the cemented tungsten carbide material comprises a binder phase having a binder material comprising Co, Re, W and C; or
the cemented tungsten carbide material comprises a binder phase having a binder material, the binder material

comprising a solid solution of Re, carbon and W and one of more of Fe, Co, and Ni; and/or
the cemented tungsten carbide material has a coercive force Hc in kA/m as a function of the WC mean grain size $D_{wc}$ in μm determined on the basis of EBSD images of the carbide microstructure equal to or less than values given by the equation: $Hc = 10 \times D_{wc}^{-0.62}$ ; and/or
the material has a Vickers hardness, and wherein the hardness decrease at 300°C compared to that at room temperature is at most 20%, preferably the hardness decrease at 300°C is at most 17%; and/or
the material has a Vickers hardness, and wherein the hardness decrease at 500°C is at most 30%, preferably the hardness decrease at 500°C is at most 27%; and/or
the hardness-toughness coefficient calculated by multiplying the Vickers hardness in GPa and fracture toughness in MPa $m^{1/2}$ is above 150; and/or
the material comprises a binder phase having a binder material comprising at least 0.1 weight percent to at most 5 weight percent of one or more of V, Cr, Ta, Ti, Mo, Zr, Nb and Hf in solid solution and/or in the form of carbide compounds; and/or the material comprises at least 0.01 weight percent and at most 2 weight percent of one or more of Ru, Rh, Pd, Os, Ir and Pt.

**14.** The method of claim 11, wherein the step of milling further comprises:

milling the cemented carbide mixture with Ni and/or Fe in addition to the WC, Co and Re; and/or
milling the one or more carbides with between 0.5 to 8 wt % Re to form the cemented carbide material comprising between 0.5 to 8 wt% Re.

**Patentansprüche**

**1.** Zementiertes Wolframcarbid- (WC)-Material, das des Weiteren zwischen 3 und 10 Gew.% Co und zwischen 0,5 und 8 Gew.% Re und gegebenenfalls Kornwachstumsinhibitoren umfasst, die ein oder mehrere von V, Cr, Ta, Ti, Mo, Zr, Nb und Hf oder Carbid davon umfassen,
wobei der Gehalt des zementierten Wolframcarbid- (WC)-Materials an äquivalentem Gesamtkohlenstoff (ETC) in Bezug auf das WC, wie in der Beschreibung definiert, zwischen 6,3 Gew.% und 6,9 Gew.% liegt,
wobei das zementierte Wolframcarbidmaterial frei von eta-Phase und freiem Kohlenstoff ist.

**2.** Zementiertes Wolframcarbidmaterial nach Anspruch 1, das zwischen 0,5 und 6 Gew.% Re umfasst, und/oder
wobei das WC in dem Material eine mittlere Korngröße von weniger als 0,6 μm aufweist, und/oder
das zementierte Wolframcarbidmaterial eine magnetische Sättigung von mindestens 40 Prozent bis 80 Prozent der magnetischen Sättigung von nominell reinem Co aufweist, und/oder
die Wolframcarbidphase aus Wolframcarbidkörnern mit einer mittleren Korngröße von mindestens 0,1 μm bis höchstens 10 μm gebildet ist, und/oder
das zementierte Wolframcarbidmaterial eine damit verbundene magnetische Koerzitivkraft aufweist, die von 2 kA/m bis 70 kA/m variiert, und/oder
das zementierte Wolframcarbid Carbid von einem oder mehreren Metallen in Form der zweiten Carbidphase oder gelöst in einer Bindemittelphase in dem Material umfasst, wobei das eine oder die mehreren Metalle Ti, V, Cr, Mn, Zr, Nb, Mo, Hf und/oder Ta umfasst bzw. umfassen.

**3.** Zementiertes Wolframcarbidmaterial nach einem der vorhergehenden Ansprüche, bei dem das Material Bindemittelphase mit einer oder mehreren Druckeigenspannungen umfasst.

**4.** Zementiertes Wolframcarbidmaterial nach Anspruch 3, bei dem die Bindemittelphase Bindemittelmaterial umfasst, welches Co, Re, W und C umfasst, oder
die Bindemittelphase Bindemittelmaterial umfasst, wobei das Bindemittelmaterial eine feste Lösung von Re, Kohlenstoff und W und einem oder mehreren von Fe, Co und Ni umfasst.

**5.** Zementiertes Wolframcarbidmaterial nach einem der vorhergehenden Ansprüche, bei dem das zementierte Wolframcarbidmaterial eine Koerzitivkraft Hc in kA/m als Funktion der mittleren Korngröße von WC, $D_{WC}$, in μm, bestimmt auf Grundlage der EBSD-Bilder der Carbidmikrostruktur, gleich oder kleiner als Werte hat, die durch die folgende Gleichung gegeben sind:

$$Hc = 10 \times D_{WC}^{-0,62}.$$

6. Zementiertes Wolframcarbidmaterial nach einem der vorhergehenden Ansprüche, bei dem das Material eine Druckfestigkeit von mehr als 5500 MPa bei Raumtemperatur und bei erhöhter Temperatur von bis zu 500°C aufweist.

7. Zementiertes Wolframcarbidmaterial nach Anspruch 6, bei dem das Material eine Vickers-Härte aufweist und die Abnahme der Härte bei 300°C höchstens 12 % beträgt.

8. Zementiertes Wolframcarbidmaterial nach einem der vorhergehenden Ansprüche, bei dem das Material eine Vickers-Härte aufweist und die Abnahme der Härte bei 500°C höchstens 21 % beträgt, und/oder
der Youngsche Modul des Materials über 700 GPa liegt, und/oder der Härte-Zähigkeitkoeffizient, der berechnet wird, indem die Vickers-Härte in GPa mit der Bruchzähigkeit in MPa $m^{1/2}$ multipliziert wird, über 190 liegt, und/oder das zementierte Wolframcarbidmaterial Bindemittelphase mit einem Bindemittelmaterial umfasst, das mindestens 0,1 Gewichtsprozent bis höchstens 5 Gewichtsprozent von einem oder mehreren von V, Cr, Ta, Ti, Mo, Zr, Nb und Hf in fester Lösung und/oder in Form von Carbidverbindungen umfasst, und/oder das Material mindestens etwa 0,01 Gewichtsprozent und höchstens 2 Gewichtsprozent von einem oder mehreren von Ru, Rh, Pd, Os, Ir und Pt umfasst.

9. Polykristalline superharte Konstruktion, die
ein Substrat, welches das zementierte Wolframcarbidmaterial gemäß einem der Ansprüche 1 bis 8 umfasst, und einen Körper aus polykristallinem superhartem Material umfasst, der entlang einer Grenzfläche an das Substrat gebunden ist.

10. Polykristalline superharte Konstruktion nach Anspruch 9, bei der der Körper aus polykristallinem superhartem Material polykristallines Diamant- (PCD)-Material umfasst, oder der Körper aus polykristallinem superhartem Material PCBN umfasst.

11. Verfahren zur Herstellung des zementierten Wolframcarbidmaterials nach einem der Ansprüche 1 bis 8, bei dem

- eine zementierte Carbidmischung, die WC und Kohlenstoff mit Re, Co und gegebenenfalls Kornwachstumsinhibitoren enthält, die ein oder mehrere von V, Cr, Ta, Ti, Mo, Zr, Nb und Hf oder Carbid davon umfassen, gemahlen wird,
- der zementierte Carbidartikel aus der Mischung gepresst wird,
- der Artikel bei einer Temperatur von mehr als 1450°C im Vakuum zwischen 1 und 10 Minuten und mit einem Druck von Ar (HIP) 5 bis 120 Minuten lang gesintert wird, und
- der Artikel von der Temperatur bis auf 1300 Grad Celsius (°C) abgekühlt wird, wobei
der Schritt des Kühlens des Artikels umfasst, dass

der Artikel in einer Atmosphäre, die ein oder mehrere von Inertgas, Stickstoff, Wasserstoff oder eine Mischung davon umfasst, mit einer Kühlrate von 0,2 bis 2 Grad pro Minute abgekühlt wird, oder
der Artikel im Vakuum mit einer Kühlrate von 0,2 bis 2 Grad pro Minute abgekühlt wird.

12. Verwendung von zementiertem Wolframcarbidmaterial in einer Hochdruckkomponente zur Synthese von Diamant oder c-BN oder in der Fertigung von polykristallinem Diamant oder c-BN, wobei mit einem Druck von mehr als 5 GPa und einer Temperatur von mehr als 1100°C gearbeitet wird, wobei das zementierte Wolframcarbidmaterial Carbid von einem oder mehreren Metallen in Form der zweiten Carbidphase oder gelöst in einer Bindemittelphase in dem Material, wobei das eine oder die mehreren Metalle Ti, V, Cr, Mn, Zr, Nb, Mo, Hf und/oder Ta umfasst bzw. umfassen,
zwischen 0,5 und 8 Gew.% Re und zwischen 3 und 10 Gew.% Co umfasst,
wobei der Gehalt des zementierten Carbidmaterials an äquivalentem Gesamtkohlenstoff (ETC) in Bezug auf WC zwischen 6,3 Gew.% und 6,9 Gew.% liegt,
wobei das zementierte Wolframcarbidmaterial frei von eta-Phase und freiem Kohlenstoff ist.

13. Verwendung des zementierten Wolframcarbidmaterials nach Anspruch 12, bei der
das zementierte Wolframcarbidmaterial zwischen 0,5 und 6 Gew.% Re umfasst, und/oder
das WC in dem Material eine mittlere Korngröße von weniger als 0,6 μm aufweist, und/oder

das zementierte Wolframcarbidmaterial eine magnetische Sättigung von mindestens 40 Prozent bis 80 Prozent der magnetischen Sättigung von nominell reinem Co aufweist, und/oder
die Wolframcarbidphase aus Carbidkörnern mit einer mittleren Korngröße von mindestens 0,1 μm bis höchstens 10 μm gebildet ist, und/oder
das zementierte Wolframcarbidmaterial eine damit verbundene magnetische Koerzitivkraft aufweist, die von 2 kA/m bis 70 kA/m variiert, und/oder
das zementierte Wolframcarbidmaterial Bindemittelphase mit Bindemittelmaterial umfasst, welches Co, Re, W und C umfasst, oder
das zementierte Wolframcarbidmaterial Bindemittelphase mit Bindemittelmaterial umfasst, wobei das Bindemittelmaterial eine feste Lösung von Re, Kohlenstoff und W und einem oder mehreren von Fe, Co und Ni umfasst, und/oder
das zementierte Wolframcarbidmaterial eine Koerzitivkraft Hc in kA/m als Funktion der mittleren Korngröße von WC, $D_{WC}$, in μm, bestimmt auf Grundlage der EBSD-Bilder der Carbidmikrostruktur, gleich oder kleiner als Werte hat, die durch die folgende Gleichung gegeben sind: $Hc = 10 \times D_{WC}^{-0,62}$ und/oder
das Material eine Vickers-Härte aufweist, und wobei die Abnahme der Härte bei 300°C, verglichen mit derjenigen bei Raumtemperatur, höchstens 20 % beträgt, wobei die Abnahme der Härte bei 300°C vorzugsweise höchstens 17 % beträgt, und/oder das Material eine Vickers-Härte aufweist, und wobei die Abnahme der Härte bei 500°C höchstens 30 % beträgt, wobei vorzugsweise die Abnahme der Härte bei 500°C höchstens 27 % beträgt, und/oder der Härte-Zähigkeitkoeffizient, der berechnet wird, indem die Vickers-Härte in GPa mit der Bruchzähigkeit in MPa $m^{1/2}$ multipliziert wird, über 150 liegt, und/oder
das Material Bindemittelphase mit Bindemittelmaterial umfasst, das mindestens 0,1 Gew.% bis höchstens 5 Gewichtsprozent von einem oder mehreren von V, Cr, Ta, Ti, Mo, Zr, Nb und Hf in fester Lösung und/oder in Form von Carbidverbindungen umfasst, und/oder das Material mindestens 0,01 Gew.% und höchstens 2 Gewichtsprozent von einem oder mehreren von Ru, Rh, Pd, Os, Ir und Pt umfasst.

**14.** Verfahren nach Anspruch 11, bei dem in dem Schritt des Mahlens des Weiteren
die zementierte Carbidmischung mit Ni und/oder Fe zusätzlich zu dem WC, Co und Re gemahlen wird, und/oder
das eine oder die mehreren Carbide mit zwischen 0,5 und 8 Gew.% Re gemahlen wird bzw. werden, um das zementierte Carbidmaterial zu bilden, welches zwischen 0,5 und 8 Gew.% Re umfasst.

**Revendications**

**1.** Matériau en carbure de tungstène (WC) cémenté comprenant en outre entre 3 et 10 % en poids de Co et entre 0,5 et 8 % en poids de Re ; et éventuellement des inhibiteurs de croissance de grain comprenant un ou plusieurs parmi V, Cr, Ta, Ti, Mo, Zr, Nb et Hf, ainsi que leurs carbures ;
la teneur en carbone total équivalent (ETC) du matériau en carbure de tungstène (WC) cémenté par rapport au WC, telle que définie dans la description, étant comprise entre 6,3 % en poids et 6,9 % en poids ;
le matériau en carbure de tungstène cémenté étant exempt de phase êta et de carbone libre.

**2.** Matériau en carbure de tungstène cémenté selon la revendication 1, lequel matériau en carbure de tungstène cémenté comprend entre 0,5 et 6 % en poids de Re ; et/ou
dans lequel le WC dans le matériau a une granulométrie moyenne inférieure à 0,6 μm ; et/ou
lequel matériau en carbure de tungstène cémenté a une saturation magnétique d'au moins 40 % à 80 % de la saturation magnétique du Co nominalement pur ; et/ou
dans lequel la phase de carbure de tungstène est formée de grains de carbure de tungstène ayant une granulométrie moyenne d'au moins 0,1 μm à au plus 10 μm ; et/ou
lequel matériau en carbure de tungstène cémenté a une force coercitive magnétique associée variant de 2 kA/m à 70 kA/m ; et/ou
dans lequel le carbure de tungstène cémenté comprend un carbure d'un ou plusieurs métaux sous forme de deuxième phase de carbure, ou dissous dans une phase de liant dans le matériau, lesdits un ou plusieurs métaux comprenant Ti, V, Cr, Mn, Zr, Nb, Mo, Hf et/ou Ta.

**3.** Matériau en carbure de tungstène cémenté selon l'une quelconque des revendications précédentes, lequel matériau comprend une phase de liant ayant une ou plusieurs contraintes de compression résiduelles.

**4.** Matériau en carbure de tungstène cémenté selon la revendication 3, dans lequel
la phase de liant comprend un matériau liant comprenant Co, Re, W et C ; ou
la phase de liant comprend un matériau liant, le matériau liant comprenant une solution solide de Re, carbone et

W et un ou plusieurs parmi Fe, Co et Ni.

**5.** Matériau en carbure de tungstène cémenté selon l'une quelconque des revendications précédentes, lequel matériau en carbure de tungstène cémenté a une force coercitive Hc en kA/m qui est fonction de la granulométrie moyenne $D_{WC}$ du WC en $\mu$m, déterminée sur la base d'images EBSD de la microstructure du carbure, égale ou inférieure aux valeurs données par l'équation :

$$Hc = 10 \times D_{WC}^{-0,62}$$

**6.** Matériau en carbure de tungstène cémenté selon l'une quelconque des revendications précédentes, lequel matériau a une résistance à la compression supérieure à 5500 MPa à la température ambiante et à une température élevée allant jusqu'à 500°C.

**7.** Matériau en carbure de tungstène cémenté selon la revendication 6, lequel matériau a une dureté Vickers, et la diminution de dureté à 300°C est d'au plus 12 %.

**8.** Matériau en carbure de tungstène cémenté selon l'une quelconque des revendications précédentes, lequel matériau a une dureté Vickers, dans lequel la diminution de dureté à 500°C est d'au plus 21 % ; et/ou
dans lequel le module de Young dudit matériau est supérieur à 700 GPa ; et/ou
dans lequel le coefficient de dureté-ténacité, calculé par multiplication de la dureté Vickers en GPa par la ténacité à la fracture en MPa $m^{1/2}$ est supérieur à 190 ; et/ou
lequel matériau en carbure de tungstène cémenté comprend une phase de liant ayant un matériau liant comprenant au moins 0,1 % en poids à au plus 5 % en poids d'un ou plusieurs parmi V, Cr, Ta, Ti, Mo, Zr, Nb et Hf en solution solide et/ou sous la forme de composés carbures ; et/ou
lequel matériau comprend au moins environ 0,01 % en poids et au plus 2 % en poids d'un ou plusieurs parmi Ru, Rh, Pd, Os, Ir et Pt.

**9.** Construction superdure polycristalline comprenant :

un substrat comprenant le matériau en carbure de tungstène cémenté de l'une quelconque des revendications 1 à 8 ; et
un corps de matériau superdur polycristallin lié au substrat le long d'une interface.

**10.** Construction superdure polycristalline selon la revendication 9, dans laquelle le corps de matériau superdur polycristallin comprend un matériau en diamant polycristallin (PCD) ; ou le corps de matériau superdur polycristallin comprend du PCBN.

**11.** Procédé de production du matériau en carbure de tungstène cémenté de l'une quelconque des revendications 1 à 8, le procédé comprenant :

- le broyage d'un mélange de carbure cémenté contenant du WC et du carbone avec Re, Co et éventuellement des inhibiteurs de croissance de grain comprenant un ou plusieurs parmi V, Cr, Ta, Ti, Mo, Zr, Nb et Hf ainsi que leurs carbures ;
- le pressage de l'article en carbure cémenté à partir du mélange ;
- le frittage de l'article à une température supérieure à 1450°C sous vide pendant 1 à 10 minutes et sous une pression d'Ar (HIP) pendant 5 à 120 minutes ; et
- le refroidissement de l'article de ladite température à 1300 degrés Celsius (°C),

dans lequel l'étape de refroidissement de l'article comprend :

le refroidissement de l'article dans une atmosphère comprenant un ou plusieurs parmi un gaz inerte, l'azote, l'hydrogène et leurs mélanges, à une vitesse de refroidissement de 0,2 à 2 degrés par minute ; ou
le refroidissement de l'article sous vide à une vitesse de refroidissement de 0,2 à 2 degrés par minute.

**12.** Utilisation d'un matériau en carbure de tungstène cémenté dans un composant haute pression pour la synthèse de diamant ou de c-BN, ou dans la fabrication de diamant polycristallin ou de c-BN fonctionnant sous une pression supérieure à 5 GPa et à une température supérieure à 1100°C, lequel matériau en carbure de tungstène cémenté

comprend :

un carbure d'un ou plusieurs métaux sous forme de deuxième phase de carbure, ou dissous dans une phase de liant dans le matériau, lesdits un ou plusieurs métaux comprenant Ti, V, Cr, Mn, Zr, Nb, Mo, Hf et/ou Ta ;
entre 0,5 et 8 % en poids de Re et entre 3 et 10 % en poids de Co ;
la teneur en carbone total équivalent (ETC) du matériau en carbure cémenté par rapport au WC étant comprise entre 6,3 % en poids et 6,9 % en poids ;
le matériau en carbure de tungstène cémenté étant exempt de phase êta et de carbone libre.

**13.** Utilisation d'un matériau en carbure de tungstène cémenté selon la revendication 12, dans laquelle :

le matériau en carbure de tungstène cémenté comprend entre 0,5 et 6 % en poids de Re ; et/ou
le WC dans le matériau a une granulométrie moyenne inférieure à 0,6 μm ; et/ou
le matériau en carbure de tungstène cémenté a une saturation magnétique d'au moins 40 % à 80 % de la saturation magnétique du Co nominalement pur ; et/ou
la phase de carbure de tungstène est formée de grains de carbure de tungstène ayant une granulométrie moyenne d'au moins 0,1 μm à au plus 10 μm ; et/ou
le matériau en carbure de tungstène cémenté a une force coercitive magnétique associée variant de 2 kA/m à 70 kA/m ; et/ou
le matériau en carbure de tungstène cémenté comprend une phase de liant ayant un matériau liant comprenant Co, Re, W et C ; ou
le matériau en carbure de tungstène cémenté comprend une phase de liant ayant un matériau liant, le matériau liant comprenant une solution solide de Re, carbone et W et un ou plusieurs parmi Fe, Co et Ni ; et/ou
le matériau en carbure de tungstène cémenté a une force coercitive Hc en kA/m qui est fonction de la granulométrie moyenne $D_{WC}$ du WC en μm, déterminée sur la base d'images EBSD de la microstructure du carbure, égale ou inférieure aux valeurs données par l'équation : $Hc = 10 \times D_{WC}^{-0,62}$ ; et/ou
le matériau a une dureté Vickers, et la diminution de dureté à 300°C comparativement à celle de la température ambiante est d'au plus 20 %, de préférence la diminution de dureté à 300°C est d'au plus 17 % ; et/ou
le matériau a une dureté Vickers, et la diminution de dureté à 500°C est d'au plus 30 %, de préférence la diminution de dureté à 500°C est d'au plus 27 % ; et/ou
le coefficient de dureté-ténacité, calculé par multiplication de la dureté Vickers en GPa par la ténacité à la fracture en MPa $m^{1/2}$ est supérieur à 150 ; et/ou
le matériau comprend une phase de liant ayant un matériau liant comprenant au moins 0,1 % en poids à au plus 5 % en poids d'un ou plusieurs parmi V, Cr, Ta, Ti, Mo, Zr, Nb et Hf en solution solide et/ou sous la forme de composés carbures ; et/ou le matériau comprend au moins environ 0,01 % en poids et au plus 2 % en poids d'un ou plusieurs parmi Ru, Rh, Pd, Os, Ir et Pt.

**14.** Procédé selon la revendication 11, dans lequel l'étape de broyage comprend en outre :

le broyage du mélange de carbure cémenté avec Ni et/ou Fe en plus des WC, Co et Re ; et/ou
le broyage du ou des carbures avec 0,5 à 8 % en poids de Re pour former le matériau en carbure cémenté comprenant entre 0,5 et 8 % en poids de Re.

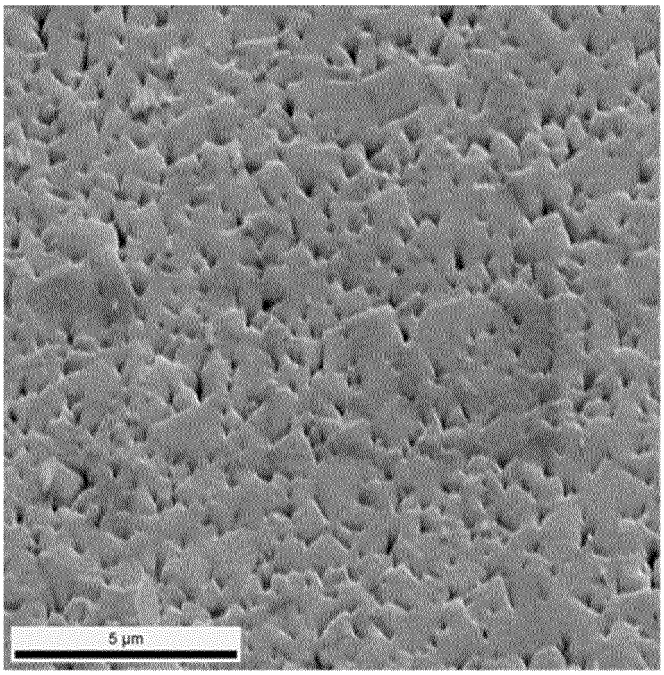



Figure 1

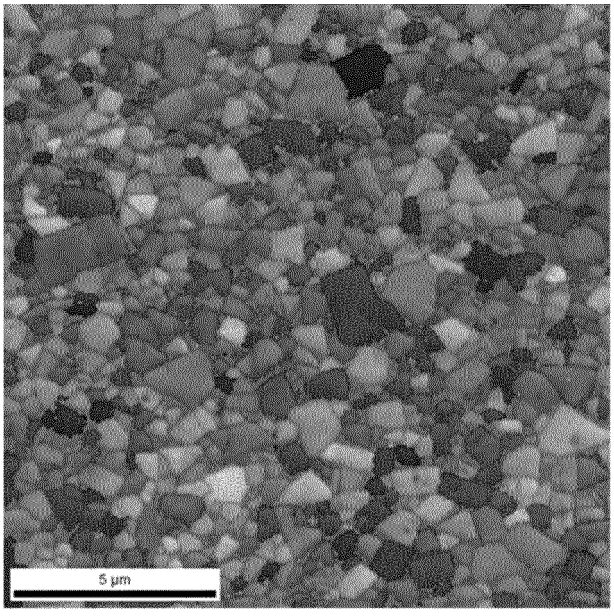



Figure 2

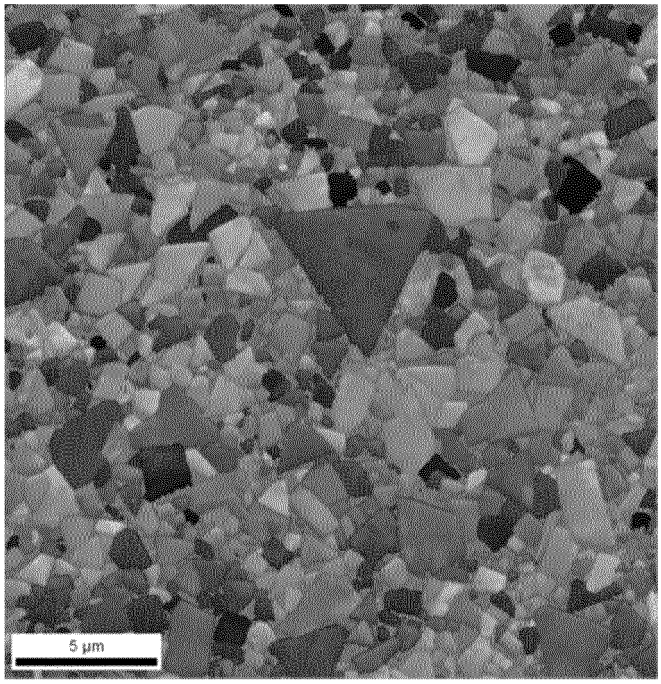



Figure 3

## REFERENCES CITED IN THE DESCRIPTION

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