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(54) **FUNCTIONALLY GRADED CEMENTED CARBIDE, AND PREPARATION METHOD THEREFOR AND USE THEREOF**

(57) The present invention relates to a functionally graded cemented carbide and a preparation method and application thereof. The carbide consists of a core portion and a surface layer of a cemented carbide matrix, the surface layer being a gradient layer. The structures of both the core portion and the gradient layer of the cemented carbide matrix are free of carbon-depleted phase and free graphite. The gradient layer has a thickness of greater than 2 mm, ranging from 2 mm to 6 mm, and the content of a binder phase within the gradient layer has a gradient distribution. The preparation method of the carbide adopts a two-step carbusintering technology of low-temperature deposition plus high-temperature carburization, the obtained functionally graded cemented carbide having good comprehensive performance, which meets the usage demand of a cemented carbide, especially a graded cemented carbide for mine rock drilling tools, the functionally graded cemented carbide having good market value and application prospect.

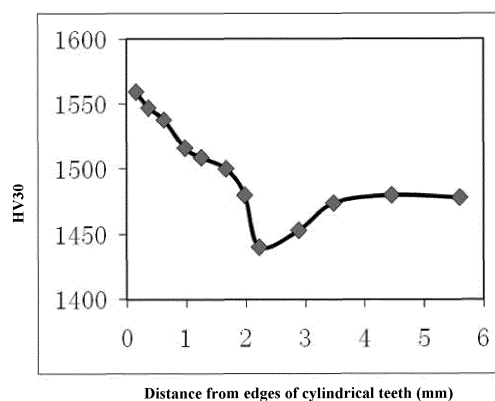


Fig. 1

Description

[0001] The present application claims the priority of the following patent application filed on July 2, 2021: Chinese patent application No. CN 202110751294.1 entitled "functionally graded cemented carbide and preparation method and application thereof, the entirety of which is incorporated herein by reference.

FIELD OF THE INVENTION

[0002] The present invention belongs to the technical field of cemented carbides and particularly relates to a functionally graded cemented carbide and a preparation method and application thereof.

BACKGROUND OF THE INVENTION

[0003] A functionally graded cemented carbide refers to a cemented carbide with a graded distribution of its composition or structure. The functionally graded cemented carbide has different properties in different parts due to its special gradient distribution changes in the structure or composition, and the product of the carbide has excellent comprehensive mechanical properties as a whole. The functionally graded cemented carbide can well resolve the conflict between wear resistance and toughness in a cemented carbide of a uniform structure, thus improving the comprehensive performance of the cemented carbide and prolonging the service life of the cemented carbide.

[0004] A high-surface-hardness/Co-depleted functionally graded cemented carbide has the advantages of a good wear resistance of the surface and a high strength and toughness of the core and can be used as one of the materials for mine rock drilling tools and machining tools. At present, researches on the preparation of such graded cemented carbide using a controlled atmosphere method are most active. One of the more common approaches is to first prepare a carbon-depleted (η -phase-containing) carbide matrix and then prepare a graded cemented carbide with a high surface hardness, a good wear resistance, and a good core impact toughness using a carburizing atmosphere sintering method. However, the graded cemented carbide prepared through this approach still contains a η phase in its core, which affects the overall performance improvement of the carbide. Another disclosed approach is to first prepare a cemented carbide material having a normal structure (which has a substoichiometric carbon content before sintering) and then prepare a graded cemented carbide containing no η phase and having a hardened surface layer using carburizing heat treatment (introducing a gas mixture of CH_4 and H_2), such as patent CN 101724760 B. Although this patent solves the problem of there being still a η phase in the core of the gradient cemented carbide, the surface layer of the gradient cemented carbide prepared using a one-step carburizing heat treatment method (introducing a gas mixture of CH_4 and H_2 , performing a carburizing heat treatment within the temperature range of 1260 to 1300°C where solid-phase tungsten carbide (WC), liquid-phase cobalt, and solid-phase cobalt coexist) has a relatively-low hardness value which is only at least 30 higher than the Vickers hardness value of the inner center of the material, and meanwhile has a very small thickness of only greater than 10 microns, which cannot meet the application requirements of a cemented carbide, especially a graded cemented carbide for mine rock drilling tools. Additionally, the gas mixture of CH_4 and H_2 , and especially H_2 , which are introduced by the above patent as the carburizing atmosphere, should be avoided as much as possible in the industrialized safety production of the cemented carbide industry.

SUMMARY OF THE INVENTION

[0005] In view of the defects of the prior art, the present invention provides a functionally graded cemented carbide, and a preparation method and application thereof. The functionally graded cemented carbide has the characteristics of high surface hardness, good wear resistance, and high core strength and toughness, the overall mechanical properties of the carbide being excellent. The functionally graded cemented carbide has a relatively-high surface layer hardness value and a relatively-large surface layer thickness, which meets the usage demand of a cemented carbide, especially a graded cemented carbide for mine rock drilling tools.

[0006] For this purpose, a first aspect of the invention provides a functionally graded cemented carbide, which consists of a core portion and a surface layer of a cemented carbide matrix, the surface layer being a gradient layer. Both the core portion and the gradient layer of the cemented carbide matrix are free of carbon-depleted phase and free graphite. The gradient layer has a thickness of from 2 to 6 mm, and a content of a binder phase in the gradient layer has a gradient distribution.

[0007] Specifically, the structures of both the core portion and the gradient layer of the cemented carbide matrix are free of carbon-depleted phase and free graphite.

[0008] In the invention, the term "carbon-depleted phase" is also referred to as " η phase".

[0009] In some implementations of the invention, the content of the binder phase within the gradient layer is gradually increased from the outside to the inside. Specifically, from the outside to the inside, the content of the binder phase

within the gradient layer is gradually increased from being lower than the content of a binder phase in the cemented carbide matrix.

[0010] In some implementations of the invention, the content of the binder phase in the functionally graded cemented carbide is firstly gradually increased from the outside to the inside from being lower than the content of the binder phase in the cemented carbide matrix and then decreased to the content of the binder phase in the core portion of the cemented carbide matrix.

[0011] In some implementations of the invention, the content of the binder phase on the surface of the gradient layer is lower than the content of the binder phase in the cemented carbide matrix by 85% or below.

[0012] In some implementations of the invention, the content of the binder phase in the cemented carbide matrix is from 2 to 20 wt%, and the balance is a carbide.

[0013] In some preferable implementations of the invention, the binder phase includes cobalt or a mixture of cobalt and at least one selected from a group consisting of nickel and ferrum.

[0014] In the invention, when the binder phase includes the mixture of cobalt and at least one selected from a group consisting of nickel and ferrum, that is, at least one selected from a group consisting of nickel and ferrum is used in place of part of cobalt.

[0015] In other implementations of the invention, the carbide includes tungsten carbide or a mixture of tungsten carbide and at least one selected from a group consisting of titanium carbide, tantalum carbide, chromium carbide, niobium carbide, and vanadium carbide.

[0016] In the invention, the term "content of the binder phase in the cemented carbide matrix" is the average content of the binder phase in the cemented carbide matrix, and is also referred to as "nominal composition average binder phase content of the cemented carbide matrix".

[0017] In the invention, the functionally graded cemented carbide has a high-hardness surface layer and a high-toughness core portion.

[0018] In some implementations of the invention, the surface layer of the functionally graded cemented carbide has a greater hardness than the core portion, and the core portion has a greater toughness than the surface layer.

[0019] In some preferable implementations of the invention, at a force load of 30 kg, the surface layer of the cemented carbide has a Vickers hardness value that is higher than that of the core portion by from 60 to 300.

[0020] A second aspect of the invention provides a preparation method of the cemented carbide according to the first aspect of the invention, which comprises: providing a cemented carbide and performing carburizing heat treatment on the cemented carbide in a furnace with a carburizing atmosphere to obtain a functionally graded cemented carbide; wherein, the carburizing heat treatment comprises the following steps:

S1, a carburizing atmosphere of methane is introduced into the furnace, a first heat treatment is performed on the cemented carbide to obtain a first heat treated cemented carbide;

S2, an inert gas is introduced into the furnace for gas replacement, a carburizing atmosphere of carbon dioxide is introduced after vacuumizing, and a second heat treatment is performed on the first heat treated cemented carbide to obtain the functionally graded cemented carbide.

[0021] In the invention, the above step S1 is referred to as a deposition process, and the above step S2 is referred to as a carburization process.

[0022] In some implementations of the invention, the inert gas may be argon (Ar).

[0023] In some implementations of the invention, in step S1, the first heat treatment is performed at a temperature of from 900°C to 1150°C for 60 to 180 mins with a gas partial pressure of from 500 to 1000 mbar.

[0024] In other implementations of the invention, in step S2, the second heat treatment is performed at a temperature of from 1150°C to 1500°C for 60 to 180 mins with a gas partial pressure of from 100 to 500 mbar.

[0025] In some specific implementations of the invention, the cemented carbide is provided by the following steps that:

T1, a carbide, a binder phase, and a pressing binder are mixed, wet-milled, and dried to obtain carbide-binder phase mixed powders;

T2, the carbide-binder phase mixed powders are pressed and sintered to obtain the cemented carbide.

[0026] In some implementations of the invention, the carbide-binder phase mixed powders have a substoichiometric carbon content. The carbon content is relatively high, so that the carbide-binder phase mixed powder is not only free of η phase but also free of free graphite at any temperature and time during or after the sintering step or the carburizing heat treatment step.

[0027] In other implementations of the invention, the carbide comprises tungsten carbide or a mixture of tungsten

carbide and at least one selected from a group consisting of titanium carbide, tantalum carbide, chromium carbide, niobium carbide, and vanadium carbide. The binder phase comprises cobalt or a mixture of cobalt and at least one selected from a group consisting of nickel and ferrum. The pressing binder is selected from any one of polyethylene glycol (PEG) and paraffin.

[0028] In some specific implementations of the invention, the usage amount of the pressing binder may be 1 to 3 wt% of the weight of raw materials.

[0029] In some specific implementations of the invention, in step T1, alcohol serves as a ball-milling medium of the wet milling, the adding amount of the alcohol being preferably 250 to 350 ml/kg.

[0030] In other specific implementations of the invention, in step T1, the wet milling is performed at a ratio of grinding media to material of 2:1 to 5:1 and a rotation speed of 50 to 100 rpm for 15 to 30 h.

[0031] In some implementations of the invention, the sintering and the carburizing heat treatment are carried out in a heat cycle of the same furnace, and a carbide blank does not need to be removed from the furnace after being sintered.

[0032] In other implementations of the invention, the sintering and the carburizing heat treatment are carried out in two separate furnaces, so that there are two separate heat cycles.

[0033] In some implementations of the invention, the sintering may be performed at 1400 to 1500°C.

[0034] In some specific implementations of the invention, the functionally graded cemented carbide is prepared specifically by the following steps:

(1) after being mixed, a carbide (tungsten carbide or a mixture of tungsten carbide with carbides of other metals), a binder phase (cobalt powder or a mixture of cobalt powder with nickel/ferrum powder), and a pressing binder are ball-milled with alcohol and dried to obtain uniform carbide-binder phase mixed powders;

(2) the uniform carbide-binder phase mixed powders are pressed to obtain a molded compact;

(3) the molded compact is sintered to obtain a uniform-structure (compact) cemented carbide, which is free of free graphite and carbon-depleted phase (η phase);

(4) carburizing heat treatment is performed on the uniform-structure cemented carbide in a furnace with a carburizing atmosphere to obtain the functionally graded cemented carbide; the carburizing heat treatment specifically comprises two main steps, which are respectively: the first step: deposition, that is, introducing a carburizing atmosphere of methane (CH_4) in the furnace for heat treatment within a temperature range from 900°C to 1150°C for 60 to 180 mins with a gas partial pressure of 500 to 1000 mbar; and the second step: carburization, that is, introducing argon (Ar) in the furnace for gas replacement at the end of the first step, introducing a carburizing atmosphere of carbon dioxide (CO_2) after vacuum pumping, and performing heat treatment within a temperature range from 1150°C to 1500°C for 60 to 180 mins with a gas partial pressure of 100 to 500 mbar. Subsequently the furnace is cooled to room temperature.

[0035] The functionally graded cemented carbide obtained after undergoing two steps of carburizing heat treatment has a cobalt-depleted (binder phase) surface layer with a cobalt content (binder phase content) being lower than the cobalt content of a nominal composition value of a cemented carbide matrix, and the functionally graded cemented carbide is not only free of free graphite but also free of η phase.

[0036] A third aspect of the invention provides an application of the functionally graded cemented carbide according to the first aspect of the invention or the functionally graded cemented carbide prepared by the method according to the second aspect in mine rock drilling tools and machining tools.

[0037] The invention has the beneficial effects that the preparation method of the functionally graded cemented carbide described in the invention avoids H_2 from the perspective of safety production and introduces a carburizing atmosphere of CO_2 , the carburizing atmosphere being in a form of a combination of CH_4 plus Ar plus CO_2 , which is more suitable for popularization and application of industrialized safety production of the cemented carbide industry; and the method adopts a two-step carbusintering technology of low-temperature deposition plus high-temperature carburization, that is, the carbusintering technology is divided into two main steps (deposition plus carburization), with the carburizing atmosphere of CH_4 selected for the low-temperature deposition process before the appearance of a liquid phase point (900°C to 1150°C) and the carburizing atmosphere of CO_2 selected for the high-temperature carburization process, by charging CO_2 within a temperature interval from 1150°C to 1500°C, carbon atoms with higher activity may be generated in a high-temperature reaction, which is conducive to performing the carburization process and increasing the thickness of gradient layer. The functionally graded cemented carbide of the invention prepared by the two-step carburization method is not only free of η phase but also free of graphite phase, and has good comprehensive performance (at a force load of 30 kg, the high-hardness surface layer of the functionally graded cemented carbide has a Vickers hardness value from 60 to 300 higher than that of the core portion, and the surface layer has a thickness of from 2 to 6 mm; the service life of

the carbide is prolonged by 30% or above), which meets the usage demand of a cemented carbide, especially a graded cemented carbide for mine rock drilling tools, the functionally graded cemented carbide having good market value and application prospect.

BRIEF DESCRIPTION OF DRAWINGS

[0038] The present invention will be further described below in conjunction with accompanying drawings.

Fig. 1 is a Vickers hardness distribution diagram of a functionally graded cemented carbide obtained according to Embodiment 1 of the present invention;

Fig. 2 is a cobalt content distribution diagram of the functionally graded cemented carbide obtained according to Embodiment 1 of the present invention.

DETAILED DESCRIPTION

[0039] In order to make the invention easier to understand, the invention will be further described below in detail with reference to embodiments, which are illustrative only and are not limited to the scope of application of the invention. Raw materials or compositions used in the invention can be prepared by commercial means or conventional methods unless otherwise specified.

Embodiment 1: preparation of a functionally graded cemented carbide spherical shape bits with a cobalt content of 6% of the whole material of a carbide matrix

[0040] Commercially available tungsten carbide (having the Fss of about 4.0 μm) and cobalt powders were adopted as raw materials, 2 wt% of a pressing binder PEG being doped therein, the mixture being ball-milled with alcohol (with the adding amount of the alcohol being 250 ml/kg, the ratio of grinding media to material being 3:1, the rotation speed being 80 rpm; and with the wet-milling time being 20 h) and dried to prepare uniform tungsten carbide-cobalt mixed powders (with the content of cobalt being 6 wt%, the balance being tungsten carbide, the substoichiometric carbon content being 5.75%). A cemented carbide of a uniform structure was manufactured by pressing and sinter-hip (with the sintering temperature being 1450°C), there being no free graphite and η phase in the carbide.

[0041] The cemented carbide of the uniform structure underwent carburizing heat treatment in a sintering furnace with a carburizing atmosphere, the sintering step and the carburizing heat treatment step in the preparation process of the aforementioned cemented carbide of the uniform structure being carried out in two separate furnaces. The carburizing atmosphere introduced in the first step of carburizing heat treatment was methane (CH_4), heat treatment being performed at 900°C for 100 mins with a gas partial pressure of 600 mbar; the second step was to introduce argon (Ar) for gas replacement at the end of the first step, the carburizing atmosphere introduced after vacuum pumping being carbon dioxide (CO_2), and heat treatment being performed at 1200°C for 90 mins with a gas partial pressure of 300 mbar. The cemented carbide undergoing two steps of carburizing heat treatment had a gradient layer of a cobalt-depleted surface layer, the gradient layer having a surface cobalt content of 85% lower than a nominal composition average cobalt content of a cemented carbide matrix. There was neither free graphite nor η phase in the finally heat-treated functionally graded cemented carbide, the high-hardness surface layer of the cemented carbide having a Vickers hardness value that is higher than that of the core portion of the material by 80 at a force load of 30 kg, and the gradient layer of the surface layer having a thickness of about 2.2 mm. The Vickers hardness distribution diagram of the finally obtained functionally graded cemented carbide was shown in Fig. 1, the cobalt content distribution diagram of the same was shown in Fig. 2. Properties of the carbide before and after carburizing heat treatment were shown in Table 1. The functionally graded cemented carbide spherical shape bits were mainly applicable to high-air-pressure drill bits for rock drilling.

Table 1: Properties of the carbide before and after carburizing heat treatment

Nominal composition average cobalt content	Cobalt magnetization Com, % (before treatment)	Coercive force Hc, KA/m (before treatment)	Cobalt magnetization Com, % (after treatment)	Coercive force Hc, KA/m (after treatment)
6%	5.7	13.1	5.95	11.7

Embodiment 2: preparation of a functionally graded cemented carbide spherical shape bits with a cobalt content of 11.5% of the whole material of a carbide matrix

[0042] Commercially available tungsten carbide (having the Fss of about 4.0 μm) and cobalt powders were adopted as raw materials, 2 wt% of a pressing binder paraffin being doped therein, the mixture being ball-milled with alcohol (with the adding amount of the alcohol being 300 ml/kg, the ratio of grinding media to material being 3:1, the rotation speed being 80 rpm; and with the wet-milling time being 22 h) and dried to prepare uniform tungsten carbide-cobalt mixed powders (with the content of cobalt being 11.5 wt%, the balance being tungsten carbide, the substoichiometric carbon content being 5.42%). A cemented carbide of a uniform structure was manufactured by pressing and sinter-hip (with the sintering temperature being 1450°C), there being no free graphite and η phase in the carbide.

[0043] The cemented carbide of the uniform structure underwent carburizing heat treatment in a sintering furnace with a carburizing atmosphere, the sintering step and the carburizing heat treatment step in the preparation process of the aforementioned cemented carbide of the uniform structure being carried out in a heat cycle of the same furnace. The carburizing atmosphere introduced in the first step of carburizing heat treatment was methane (CH_4), heat treatment being performed at 1000°C for 120 mins with a gas partial pressure of 800 mbar; the second step was to introduce argon (Ar) for gas replacement at the end of the first step, the carburizing atmosphere introduced after vacuum pumping being carbon dioxide (CO_2), and heat treatment being performed at 1300°C for 100 mins with a gas partial pressure of 400 mbar. The cemented carbide undergoing two steps of carburizing heat treatment had a gradient layer of a cobalt-depleted surface layer, the gradient layer having a surface cobalt content of 85% lower than a nominal composition average cobalt content of a cemented carbide matrix. There is neither free graphite nor η phase in the finally heat-treated functionally graded cemented carbide, the high-hardness surface layer of the cemented carbide having a Vickers hardness value that is higher than that of the core portion of the material by 180 at a force load of 30 kg, and the gradient layer of the surface layer having a thickness of 3.1 mm. Properties of the carbide before and after carburizing heat treatment were shown in Table 2. The functionally graded cemented carbide spherical shape bits were mainly applicable to roller bits for mines and oil fields.

Table 2: Properties of the carbide before and after carburizing heat treatment

Nominal composition average cobalt content	Cobalt magnetization Com, % (before treatment)	Coercive force Hc, KA/m (before treatment)	Cobalt magnetization Com, % (after treatment)	Coercive force Hc, KA/m (after treatment)
11.5%	10.3	9.5	10.8	7.8

Embodiment 3: preparation of a graded cemented carbide spherical shape bits with a cobalt content of 13% of the whole material of a carbide matrix

[0044] Commercially available tungsten carbide (having the Fss of about 2.0 μm) and cobalt powders were adopted as raw materials, 2 wt% of a pressing binder PEG being doped therein, the mixture being ball-milled with alcohol (with the adding amount of the alcohol being 300 ml/kg, the ratio of grinding media to material being 3:1, the rotation speed being 80 rpm; and with the wet-milling time being 26 h) and dried to prepare uniform tungsten carbide-cobalt mixed powders (with the content of cobalt being 13%, the balance being tungsten carbide, the substoichiometric carbon content being 5.34%). A cemented carbide of a uniform structure was manufactured by pressing and sinter-hip (with the sintering temperature being 1450°C), there being no free graphite and η phase in the carbide.

[0045] The cemented carbide of the uniform structure underwent carburizing heat treatment in a sintering furnace with a carburizing atmosphere, the sintering step and the carburizing heat treatment step in the preparation process of the aforementioned cemented carbide of the uniform structure being carried out in two separate furnaces. The carburizing atmosphere introduced in the first step of carburizing heat treatment was methane (CH_4), heat treatment being performed at 1100°C for 160 mins with a gas partial pressure of 1000 mbar; the second step was to introduce argon (Ar) for gas replacement at the end of the first step, the carburizing atmosphere introduced after vacuum pumping being carbon dioxide (CO_2), and heat treatment being performed at 1390°C for 150 mins with a gas partial pressure of 500 mbar. The cemented carbide undergoing two steps of carburizing heat treatment had a gradient layer of a cobalt-depleted surface layer, the gradient layer having a surface cobalt content of 85% lower than a nominal composition average cobalt content of a cemented carbide matrix. There was neither free graphite nor η phase in the finally heat-treated functionally graded cemented carbide, the high-hardness surface layer of the cemented carbide having a Vickers hardness value that is higher than that of the core portion of the material by 220 at a force load of 30 kg, and the gradient layer of the surface layer having a thickness of about 4.3 mm. Properties of the carbide before and after carburizing heat treatment were

shown in Table 3. The functionally graded cemented carbide spherical shape bits were mainly applicable to roller bits for oil fields.

Table 3: Properties of the carbide before and after carburizing heat treatment

Nominal composition average cobalt content	Cobalt magnetization Com, % (before treatment)	Coercive force Hc, KA/m (before treatment)	Cobalt magnetization Com, % (after treatment)	Coercive force Hc, KA/m (after treatment)
13%	11.8	10.5	12.3	8.8

Embodiment 4: preparation of a graded cemented carbide spherical shape bits with a cobalt plus nickel content of 8% of the whole material of a carbide matrix

[0046] Commercially available tungsten carbide (having the Fss of about 1.5 μm), tantalum carbide, niobium carbide (having the Fss of about 2.0 μm), cobalt powders, and nickel powders were adopted as raw materials, 3 wt% of a pressing binder PEG being doped therein, the mixture being ball-milled with alcohol (with the adding amount of the alcohol being 280 ml/kg, the ratio of grinding media to material being 4:1, the rotation speed being 90 rpm; and with the wet-milling time being 30 h) and dried to prepare uniform tungsten carbide-tantalum carbide-niobium carbide-cobalt-nickel mixed powders (with the content of cobalt being 6%, the content of nickel being 2%, the content of tantalum carbide being 0.5%, the content of niobium carbide being 0.3%, the balance being tungsten carbide, the substoichiometric carbon content being 5.64%). A cemented carbide of a uniform structure was manufactured by pressing and sinter-hip (with the sintering temperature being 1410°C), there being no free graphite and η phase in the carbide.

[0047] The cemented carbide of the uniform structure underwent carburizing heat treatment in a sintering furnace with a carburizing atmosphere, the sintering step and the carburizing heat treatment step in the preparation process of the aforementioned cemented carbide of the uniform structure being carried out in a heat cycle of the same furnace. The carburizing atmosphere introduced in the first step of carburizing heat treatment was methane (CH_4), heat treatment being performed at 1000°C for 70 mins with a gas partial pressure of 500 mbar; the second step was to introduce argon (Ar) for gas replacement at the end of the first step, the carburizing atmosphere introduced after vacuum pumping being carbon dioxide (CO_2), and heat treatment being performed at 1350°C for 70 mins with a gas partial pressure of 200 mbar. The cemented carbide undergoing two steps of carburizing heat treatment had a gradient layer of a cobalt-depleted surface layer, the gradient layer having a surface cobalt content of 85% lower than a nominal composition average cobalt content of a cemented carbide matrix. There was neither free graphite nor η phase in the finally heat-treated functionally graded cemented carbide, the high-hardness surface layer of the cemented carbide having a Vickers hardness value that is higher than that of the core portion of the material by 150 at a force load of 30 kg, and the gradient layer of the surface layer having a thickness of about 2.8 mm. Properties of the carbide before and after carburizing heat treatment were shown in Table 4. The functionally graded cemented carbide spherical shape bits were mainly applicable to high-air-pressure drill bits for rock drilling.

Table 4: Properties of the carbide before and after carburizing heat treatment

Nominal composition average cobalt plus nickel content	Cobalt magnetization Com, % (before treatment)	Coercive force Hc, KA/m (before treatment)	Cobalt magnetization Com, % (after treatment)	Coercive force Hc, KA/m (after treatment)
8%	5.5	19.4	6.0	17.2

Embodiment 5: preparation of a graded cemented carbide spherical shape bits with a cobalt plus ferrum content of 20% of the whole material of a carbide matrix

[0048] Commercially available tungsten carbide (having the Fss of about 12 μm), titanium carbide (having the Fss of about 3.0 μm), cobalt powders, and ferrum powders were adopted as raw materials, 2.3 wt% of a pressing binder paraffin being doped therein, the mixture being ball-milled with alcohol (with the adding amount of the alcohol being 350 ml/kg, the ratio of grinding media to material being 3.5:1, the rotation speed being 36 rpm; and with the wet-milling time being 24 h) and dried to prepare uniform tungsten carbide-titanium carbide-cobalt-ferrum mixed powders (with the content of cobalt being 19%, the content of ferrum being 1%, the content of titanium carbide being 2%, the balance being tungsten carbide, the substoichiometric carbon content being 5.10%). A cemented carbide of a uniform structure was manufactured by pressing and sinter-hip (with the sintering temperature being 1480°C), there being no free graphite and η phase in

the carbide.

[0049] The cemented carbide of the uniform structure underwent carburizing heat treatment in a sintering furnace with a carburizing atmosphere, the sintering step and the carburizing heat treatment step in the preparation process of the aforementioned cemented carbide of the uniform structure being carried out in a heat cycle of the same furnace. The carburizing atmosphere introduced in the first step of carburizing heat treatment was methane (CH_4), heat treatment being performed at 1150°C for 180 mins with a partial pressure of 1000 mbar; the second step was to introduce argon (Ar) for gas replacement at the end of the first step, the carburizing atmosphere introduced after vacuum pumping being carbon dioxide (CO_2), and heat treatment being performed at 1450°C for 180 mins with a partial pressure of 500 mbar. The cemented carbide undergoing two steps of carburizing heat treatment had a gradient layer of a cobalt-depleted surface layer, the gradient layer having a surface cobalt content of 85% lower than a nominal composition average cobalt content of a cemented carbide matrix. There was neither free graphite nor η phase in the finally heat-treated functionally graded cemented carbide, the high-hardness surface layer of the cemented carbide having a Vickers hardness value that is higher than that of the core portion of the material by 260 at a force load of 30 kg, and the gradient layer of the surface layer having a thickness of 5.8 mm. Properties of the carbide before and after carburizing heat treatment were shown in Table 5. The functionally graded cemented carbide spherical shape bits were mainly applicable to tools for shield tunneling machines.

Table 5: Properties of the carbide before and after carburizing heat treatment

Nominal composition average cobalt plus ferrum content	Cobalt magnetization Com, % (before treatment)	Coercive force Hc, KA/m (before treatment)	Cobalt magnetization Com, % (after treatment)	Coercive force Hc, KA/m (after treatment)
20%	17.5	7.4	18.8	6.0

Comparative example 1

[0050] The preparation process was basically the same as that of Embodiment 1, except that a carburizing atmosphere introduced in the first step of carburizing heat treatment was methane (CH_4), heat treatment being performed at 1200°C for 100 mins with a gas partial pressure of 600 mbar.

[0051] There was neither free graphite nor η phase in the functionally graded cemented carbide underwent two steps of carburizing heat treatment, the surface layer of the cemented carbide having a Vickers hardness value that is higher than that of the core portion of the material by 30 at a force load of 30 kg, and the gradient layer of the surface layer having a thickness of about 2.3 mm. Properties of the carbide before and after carburizing heat treatment were shown in Table 6.

Table 6: Properties of the carbide before and after carburizing heat treatment

Nominal composition average cobalt content	Cobalt magnetization Com, % (before treatment)	Coercive force Hc, KA/m (before treatment)	Cobalt magnetization Com, % (after treatment)	Coercive force Hc, KA/m (after treatment)
6%	5.7	13.1	5.97	11.5

Comparative example 2

[0052] The preparation process was basically the same as that of Embodiment 1, except that the second step of carburizing heat treatment was to introduce argon (Ar) for gas replacement at the end of the first step, a carburizing atmosphere introduced after vacuum pumping being carbon dioxide (CO_2), and heat treatment being performed at 900°C for 90 mins with a gas partial pressure of 300 mbar.

[0053] There was neither free graphite nor η phase in the cemented carbide underwent two steps of carburizing heat treatment; the surface layer of the carbide having a Vickers hardness value that is higher than that of the core portion of the material by 20 at a force load of 30 kg, and there being no obvious gradient layer in the carbide. Properties of the carbide before and after carburizing heat treatment were shown in Table 7.

Table 7: Properties of the carbide before and after carburizing heat treatment

Nominal composition average cobalt content	Cobalt magnetization Com, % (before treatment)	Coercive force Hc, KA/m (before treatment)	Cobalt magnetization Com, % (after treatment)	Coercive force Hc, KA/m (after treatment)
6%	5.7	13.1	5.76	12.7

[0054] It is to be noted that, the aforementioned embodiments are intended to explain the invention only and do not constitute any limitation to the invention. The invention is described with reference to exemplary embodiments, but it is to be understood that the words used therein are descriptive and explanatory rather than restrictive. The invention may be modified within the scope of the claims of the invention as specified, and may be amended without departing from the scope and spirit of the invention. Although the invention described therein relates to specific methods, materials, and embodiments, it is not intended that the invention is limited to the particular examples disclosed therein; rather, the invention can be extended to all other methods and applications having the same function.

Claims

1. A functionally graded cemented carbide, consisting of a core portion and a surface layer of a cemented carbide matrix, the surface layer being a gradient layer, both the core portion and the gradient layer of the cemented carbide matrix being substantially free of carbon-depleted phase and free graphite, the gradient layer having a thickness of from about 2 mm to about 6 mm, and a content of a binder phase in the gradient layer having a gradient distribution.
2. The functionally graded cemented carbide according to claim 1, **characterized in that**, from outside to inside, a content of a binder phase in the functionally graded cemented carbide is first gradually increased from being lower than a content of a binder phase in the cemented carbide matrix and then decreased to a content of a binder phase in the core portion of the cemented carbide matrix.
3. The functionally graded cemented carbide according to claim 1 or 2, **characterized in that** the content of the binder phase on the surface of the gradient layer is lower than the content of the binder phase in the cemented carbide matrix by about 85% or below;

preferably, the content of the binder phase in the cemented carbide matrix is from about 2 wt% to about 20 wt%, and the balance is a carbide;
more preferably, the binder phase comprises cobalt or a mixture of cobalt and at least one selected from a group consisting of nickel and ferrum; and/or the carbide comprises tungsten carbide or a mixture of tungsten carbide and at least one selected from a group consisting of titanium carbide, tantalum carbide, chromium carbide, niobium carbide, and vanadium carbide.
4. The functionally graded cemented carbide according to any one of claims 1 to 3, **characterized in that** the surface layer of the functionally graded cemented carbide has a greater hardness than the core portion, and the core portion has a greater toughness than the surface layer; preferably, at a force load of 30 kg, the surface layer of the cemented carbide has a Vickers hardness value that is higher than that of the core portion by from about 60 to about 300.
5. A preparation method of the functionally graded cemented carbide according to any one of claims 1 to 4, comprising: providing a cemented carbide, and performing a carburizing heat treatment on the cemented carbide in a furnace with a carburizing atmosphere to obtain a functionally graded cemented carbide;
wherein, the carburizing heat treatment comprises the following steps:

S1, a carburizing atmosphere of methane is introduced into the furnace, a first heat treatment is performed on the cemented carbide to obtain a first heat treated cemented carbide;
S2, an inert gas is introduced into the furnace for gas replacement, a carburizing atmosphere of carbon dioxide is introduced after vacuumizing, and a second heat treatment is performed on the first heat treated cemented carbide to obtain the functionally graded cemented carbide.
6. The method according to claim 5, **characterized in that** in step S1, the first heat treatment is performed at a

temperature of from about 900°C to about 1150°C for about 60 mins to about 180 mins with a gas partial pressure of from about 500 mbar to about 1000 mbar; and/or
in step S2, the second heat treatment is performed at a temperature of about 1150°C to about 1500°C for about 60 mins to about 180 mins with a gas partial pressure of 100 mbar to about 500 mbar.

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7. The method according to claim 5 or 6, **characterized in that** the cemented carbide is provided by the following steps that:

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T1, a carbide, a binder phase, and a pressing binder are mixed, wet-milled and dried to obtain carbide-binder phase mixed powders;
T2, the carbide-binder phase mixed powders are pressed and sintered to obtain the cemented carbide.

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8. The method according to claim 7, **characterized in that** the carbide-binder phase mixed powders have a substoichiometric carbon content; and/or
the carbide comprises tungsten carbide or a mixture of tungsten carbide and at least one selected from a group consisting of titanium carbide, tantalum carbide, chromium carbide, niobium carbide, and vanadium carbide; the binder phase comprises cobalt or a mixture of cobalt and at least one selected from a group consisting of nickel and ferrum; the pressing binder is selected from any one of polyethylene glycol and paraffin.

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9. The method according to claim 7 or 8, **characterized in that** the sintering and the carburizing heat treatment are carried out in the same furnace or in two separate furnaces.

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10. An application of the functionally graded cemented carbide according to any one of claims 1 to 4 or the functionally graded cemented carbide prepared by the method according to any one of claims 5 to 9 in mine rock drilling tools and machining tools.

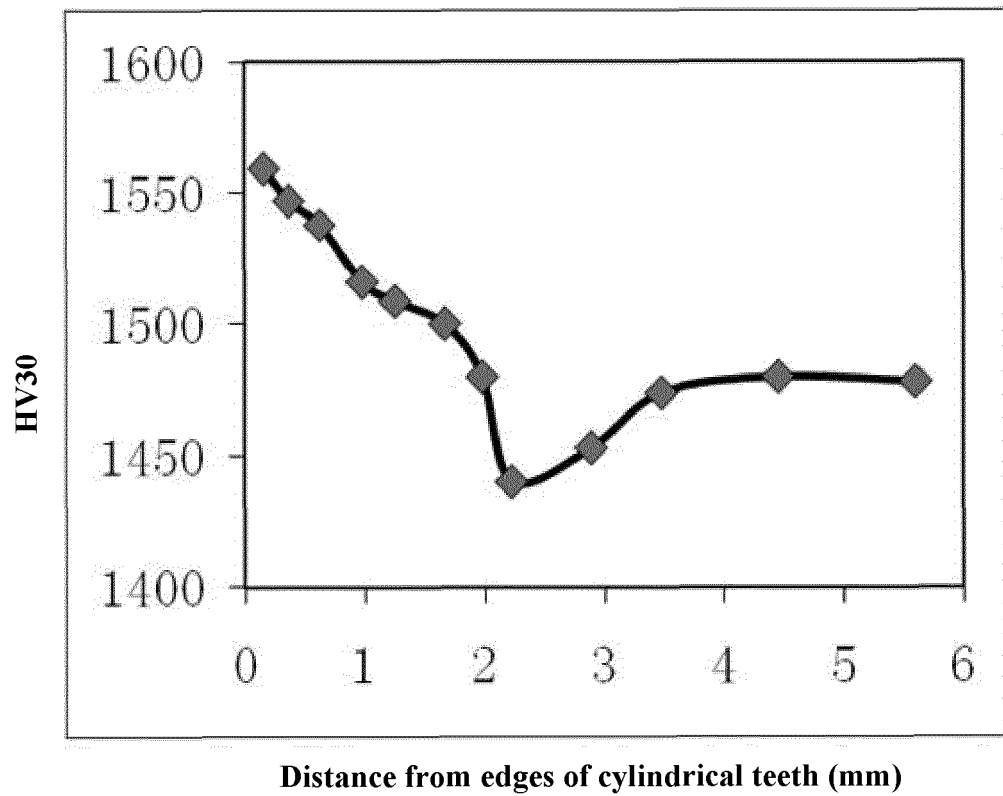


Fig. 1

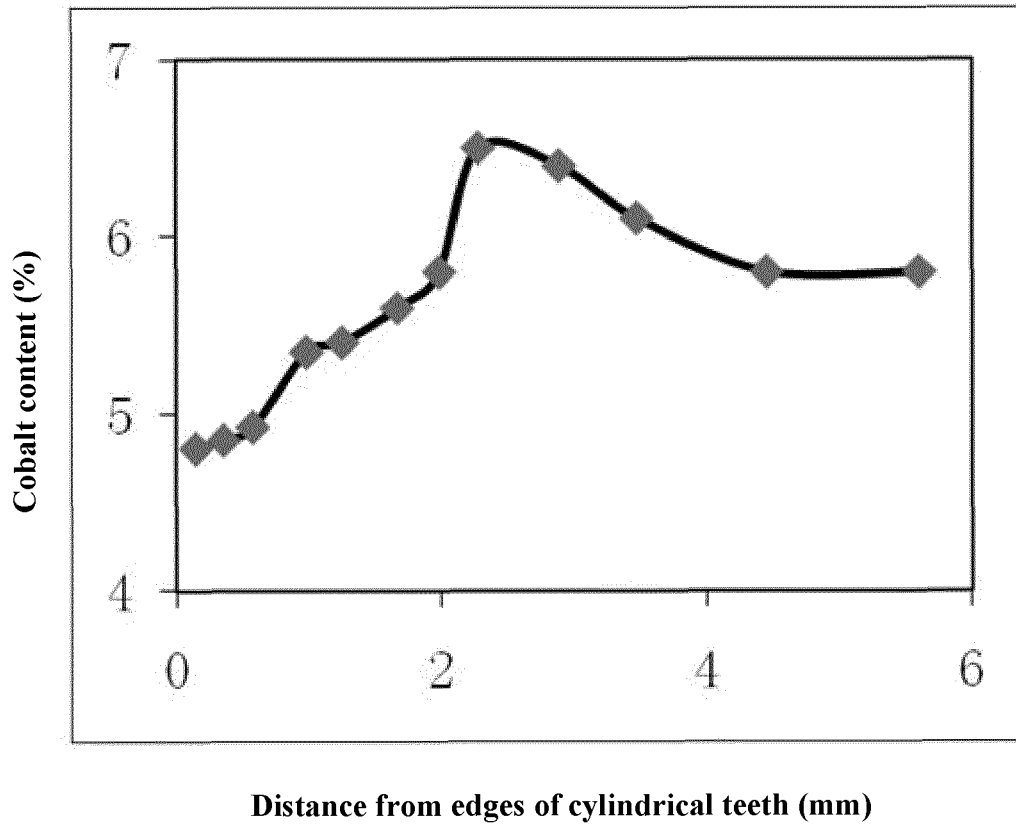


Fig. 2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2022/103430

A. CLASSIFICATION OF SUBJECT MATTER

C23C 8/20(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CNTXT; CJFD; ENTXTC; VEN; CNKI; ELSEVIER: 株洲硬质合金集团, 张颢, 赵玉玲, 徐涛, 郭建中, 硬质合金, 梯度, 游离石墨, 游离碳, 缺碳相, 渗碳, 甲烷, 二氧化碳, 碳化钨, 钴, 两步, 热处理, WC-Co, CO₂, free carbon, two step, free graphite, tungsten carbide, η相, Eta phase, gradient, heat treatment, CH₄, η phase, Carburizing, carburiz+

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
PX	CN 113652629 A (ZHUZHOU CEMENTED CARBIDE GROUP CO., LTD.) 16 November 2021 (2021-11-16) claims 1-10	1-10
X	US 2013118308 A1 (FANG, Z. Z. et al.) 16 May 2013 (2013-05-16) description, paragraphs 11-89, and figures 1-4	1-4, 10
X	CN 108149183 A (SINOPEC OILFIELD EQUIPMENT CORPORATION et al.) 12 June 2018 (2018-06-12) description, paragraphs 6-25	1-4, 10
A	CN 107267837 A (WUHAN SHAREATE TOOLS CO., LTD.) 20 October 2017 (2017-10-20) entire document	1-10

☐ Further documents are listed in the continuation of Box C.
 ☒ See patent family annex.

* Special categories of cited documents:	"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
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier application or patent but published on or after the international filing date	"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
"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)	"&" document member of the same patent family
"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	

Date of the actual completion of the international search

15 August 2022

Date of mailing of the international search report

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Form PCT/ISA/210 (second sheet) (January 2015)

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2022/103430

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CN	113652629	A	16 November 2021	None			
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CN	108149183	A	12 June 2018	CN	108149183	B	26 February 2021
CN	107267837	A	20 October 2017	CN	107267837	B	11 January 2019

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REFERENCES CITED IN THE DESCRIPTION

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- CN 101724760 B [0004]