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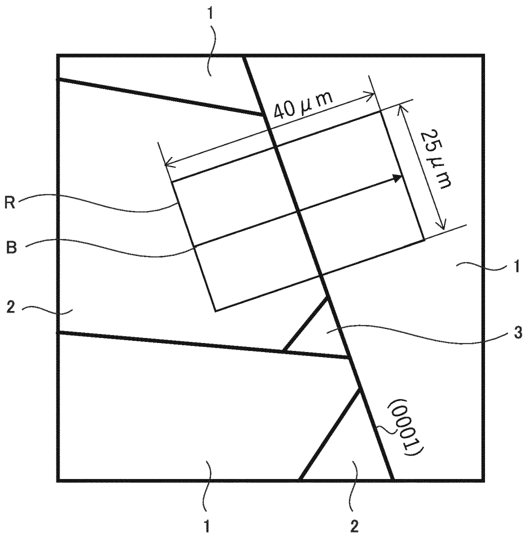
(54) CEMENTED CARBIDE AND CUTTING TOOL USING SAME

(57) The cemented carbide of the present disclosure is a cemented carbide comprising a first phase composed of a tungsten carbide particle and a second phase comprising cobalt as a main component, wherein a total content of the first phase and the second phase in the cemented carbide is 97% by volume or more, an average value of an equivalent circle diameter of the tungsten carbide particle is 0.8 μm or less, a cobalt content of the cemented carbide is 3% by mass or more and 10% by mass or less, a vanadium content of the cemented carbide is 0.01% by mass or more and 0.30% by mass or less, and a maximum value of the vanadium content in an interface region between a (0001) crystal plane of the tungsten carbide particle and the second phase is 15 atomic % or less.

FIG.1



Description

TECHNICAL FIELD

[0001] The present disclosure relates to a cemented carbide and a cutting tool using the same.

BACKGROUND ART

[0002] When a hole is drilled in a printed circuit board, it is common to drill a hole having a small diameter of φ 1 mm or less. Because of this, a so-called fine-grained cemented carbide, in which a hard phase consists of a tungsten carbide particle having an average particle diameter of 1 μm or less, is used as the cemented carbide used in a tool such as a small diameter drill (for example, PTL 1 to PTL 3).

CITATION LIST

PATENT LITERATURE

[0003]

PTL 1: Japanese Patent Laying-Open No. 2007-92090
PTL 2: Japanese Patent Laying-Open No. 2012-52237
PTL 3: Japanese Patent Laying-Open No. 2012-117100

SUMMARY OF INVENTION

[0004] The cemented carbide according to the present disclosure is
a cemented carbide comprising a first phase composed of a tungsten carbide particle and a second phase comprising cobalt as a main component, wherein

a total content of the first phase and the second phase in the cemented carbide is 97% by volume or more,
an average value of an equivalent circle diameter of the tungsten carbide particle is 0.8 μm or less,
a cobalt content of the cemented carbide is 3% by mass or more and 10% by mass or less,
a vanadium content of the cemented carbide is 0.01% by mass or more and 0.30% by mass or less, and
a maximum value of the vanadium content in an interface region between a (0001) crystal plane of the tungsten carbide particle and the second phase is 15 atomic % or less.

[0005] The cutting tool according to the present disclosure is a cutting tool including a cutting edge formed from the above cemented carbide.

BRIEF DESCRIPTION OF DRAWINGS

[0006]

Fig. 1 is a diagram for describing a method for measuring the vanadium content in a WC/second phase interface region.
Fig. 2 is a diagram showing an example of a cutting tool (small diameter drill) of the present embodiment.
Fig. 3 is a diagram for describing the width of a wear scar measured in Examples.

DETAILED DESCRIPTION

[Problem to be Solved by the Present Disclosure]

[0007] In recent years, with the expansion of 5G (fifth generation mobile communication system), efforts have been made to increase the capacity of information. Because of this, a printed circuit board is required to have higher heat resistance. In order to improve the heat resistance of a printed circuit board, a technique for improving the heat resistance of a resin or a glass filler that constitutes a printed circuit board has been developed. On the other hand, this has made it increasingly difficult to cut a printed circuit board. For this reason, in microfabrication of a printed circuit board, a cutting tool tends to wear out or break easily.

[0008] Therefore, an object of the present disclosure is to provide a cemented carbide that can provide a cutting tool that has a long tool life, particularly even when used as a material for a cutting tool used for microfabrication of a printed circuit board, and a cutting tool including the same.

[Advantageous Effect of the Present Disclosure]

[0009] According to the cemented carbide according to the present disclosure, it is possible to provide a cutting tool that has a long tool life, particularly even when used for microfabrication of a printed circuit board.

[Description of Embodiments of the Present Disclosure]

[0010] First, aspects of the present disclosure will be listed and described.

(1) The cemented carbide according to the present disclosure is a cemented carbide comprising a first phase composed of a tungsten carbide particle and a second phase comprising cobalt as a main component, wherein

a total content of the first phase and the second phase in the cemented carbide is 97% by volume or more,
an average value of an equivalent circle diameter of the tungsten carbide particle is 0.8 μm or less,
a cobalt content of the cemented carbide is 3% by mass or more and 10% by mass or less,
a vanadium content of the cemented carbide is 0.01% by mass or more and 0.30% by mass or less, and
a maximum value of the vanadium content in an interface region between a (0001) crystal plane of the tungsten carbide particle and the second phase is 15 atomic % or less.

[0011] According to the cemented carbide according to the present disclosure, it is possible to provide a cutting tool that has a long tool life, particularly even when used for microfabrication of a printed circuit board.
[0012] (2) In (1) above, preferably, the cemented carbide includes a third phase consisting of a third phase particle including 10 atomic % or more of vanadium,

a content of the third phase in the cemented carbide is more than 0% by volume and 1% by volume or less, and
a maximum value of an equivalent circle diameter of the third phase particle is 0.5 μm or less.

[0013] According to this, there is no coarse third phase particle having an equivalent circle diameter of more than 0.5 μm, which can become a starting point for breakage, and thus the breakage resistance of a cutting tool using the cemented carbide is improved.
[0014] (3) In (1) or (2) above, the maximum value of the chromium content in the interface region is preferably 20 atomic % or less.
[0015] According to this, a decrease in the interface strength between the WC particle and the Co particle due to the presence of chromium in the interface region is suppressed. Therefore, in the cemented carbide, the WC particle is unlikely to fall off because of a decrease in interface strength, and a cutting tool using the cemented carbide can have excellent wear resistance and breakage resistance.
[0016] (4) The cutting tool according to the present disclosure is a cutting tool including a cutting edge formed from the cemented carbide according to any of (1) to (3) above.
[0017] The cutting tool according to the present disclosure can have a long tool life, particularly even when used for microfabrication of a printed circuit board.

[Details of the Embodiments of the Present Disclosure]

[0018] With reference to the drawings, specific examples of the cemented carbide and the cutting tool according to the present disclosure will be described below. In the drawings of the present disclosure, the same reference signs represent the same portions or equivalent portions. In addition, a dimensional relationship such as length, width, thickness, or depth is appropriately changed for clarity and simplification of the drawings, and does not necessarily represent an actual dimensional relationship.
[0019] As used in the present disclosure, the expression of a range in the format "A to B" means the upper limit and the lower limit of the range (that is, A or more and B or less), and when no unit is written in A and a unit is only written in B, the unit for A and the unit for B are the same.
[0020] As used in the present disclosure, when one or more numerical values are written as each of the lower limit and the upper limit of a numerical range, a combination of any one numerical value written as the lower limit and any

one numerical value written as the upper limit shall also be disclosed. For example, when a1 or more, b1 or more, and c1 or more are written as the lower limit, and a2 or less, b2 or less, and c2 or less are written as the upper limit, a1 or more and a2 or less, a1 or more and b2 or less, a1 or more and c2 or less, b1 or more and a2 or less, b1 or more and b2 or less, b1 or more and c2 or less, c1 or more and a2 or less, c1 or more and b2 or less, and c1 or more and c2 or less shall be disclosed.

[0021] As used in the present disclosure, when a compound or the like is represented by a chemical formula, if the atomic ratio is not particularly limited, the chemical formula shall include all conventionally known atomic ratios, and should not necessarily be limited only to those within the stoichiometric range.

[0022] In the crystallographic description in the present disclosure, an individual orientation is indicated by [], a family of orientations are indicated by <>, an individual plane is indicated by (), and a family of planes are indicated by { }. In addition, a crystallographic index that is negative is usually expressed by adding a "-" (bar) above the number, but in the present disclosure, a negative sign is added in front of the number.

[Embodiment 1: Cemented Carbide]

[0023] The cemented carbide according to one embodiment of the present disclosure (hereinafter also referred to as "the present embodiment") is

> a cemented carbide comprising a first phase composed of a tungsten carbide particle and a second phase comprising cobalt as a main component, wherein
> a total content of the first phase and the second phase in the cemented carbide is 97% by volume or more,
> an average value of an equivalent circle diameter of the tungsten carbide particle is 0.8 μm or less,
> a cobalt content of the cemented carbide is 3% by mass or more and 10% by mass or less,
> a vanadium content of the cemented carbide is 0.01% by mass or more and 0.30% by mass or less, and
> a maximum value of the vanadium content in an interface region between a (0001) crystal plane of the tungsten carbide particle and the second phase is 15 atomic % or less.

[0024] According to the cemented carbide according to the present embodiment, it is possible to provide a cutting tool that has a long tool life, particularly even when used for microfabrication of a printed circuit board. Although the reason for this is not clear, it is presumed as described in (i) to (v) below.

> (i) The cemented carbide according to the present embodiment includes a first phase composed of a plurality of tungsten carbide particles (hereinafter also referred to as "WC particles") and a second phase including cobalt as a main component, wherein the total content of the first phase and the second phase in the cemented carbide is 97% by volume or more. According to this, the cemented carbide has high hardness and strength, and a cutting tool using the cemented carbide can have excellent wear resistance and breakage resistance.
> (ii) In the cemented carbide according to the present embodiment, the average value of the equivalent circle diameters of the WC particles is 0.8 μm or less. According to this, the cemented carbide has high hardness, and a cutting tool using the cemented carbide can have excellent wear resistance. In addition, the cemented carbide has excellent strength, and the cutting tool using the cemented carbide can have excellent breakage resistance.
> (iii) The cobalt content of the cemented carbide according to the present embodiment is 3% by mass or more and 10% by mass or less. According to this, the cemented carbide has high hardness and strength. A cutting tool using the cemented carbide can have excellent wear resistance and breakage resistance.
> (iv) The vanadium content of the cemented carbide according to the present embodiment is 0.01% by mass or more and 0.30% by mass or less. According to this, the generation of a coarse WC particle is suppressed, and the structure of the cemented carbide is densified. Therefore, the cemented carbide has excellent hardness and strength, and a cutting tool using the cemented carbide can have excellent wear resistance and breakage resistance.
> (v) In the cemented carbide according to the present embodiment, the maximum value of the vanadium content in an interface region between a (0001) crystal plane of a tungsten carbide particle and a second phase is 15 atomic % or less. According to this, the formation of a vanadium concentrated layer in which vanadium is present in a concentrated manner is suppressed in the interface region. Because of this, a decrease in the interface strength between the WC particle and the second phase due to the vanadium concentrated layer is suppressed. Therefore, in the cemented carbide, the WC particle is unlikely to fall off because of a decrease in interface strength, and a cutting tool using the cemented carbide can have excellent wear resistance and breakage resistance.

<Composition of Cemented Carbide>

<<Content of First phase, Second Phase, and Third Phase>>

[0025] The cemented carbide according to the present embodiment includes a first phase composed of a tungsten carbide particle and a second phase including cobalt as a main component. The total content of the first phase and the second phase in the cemented carbide is 97% by volume or more. According to this, the cemented carbide has high hardness and strength, and a cutting tool using the cemented carbide can have excellent wear resistance and breakage resistance.

[0026] The lower limit of the total content of the first phase and the second phase in the cemented carbide is 97% by volume or more, preferably 98% by volume or more, and more preferably 99% by volume or more. The upper limit of the total content of the first phase and the second phase in the cemented carbide is preferably 100% by volume or less. The total content of the first phase and the second phase in the cemented carbide is preferably 97% by volume or more and 100% by volume or less, more preferably 98% by volume or more and 100% by volume or less, and further preferably 99% by volume or more and 100% by volume or less. The cemented carbide preferably consists of a first phase and a second phase.

[0027] From the viewpoint of improving the hardness, the lower limit of the content of the first phase in the cemented carbide is preferably 82% by volume or more, more preferably 85% by volume or more, and further preferably 87% by volume or more. The upper limit of the content of the first phase in the cemented carbide is less than 100% by volume, and from the viewpoint of improving the breakage resistance, the upper limit is preferably 95% by volume or less, more preferably 94% by volume or less, further preferably 93% by volume or less, and more further preferably 90% by volume or less. The content of the first phase in the cemented carbide is preferably 82% by volume or more and 95% by volume or less, more preferably 85% by volume or more and 93% by volume or less, and further preferably 87% by volume or more and 90% by volume or less.

[0028] From the viewpoint of improving the breakage resistance, the lower limit of the content of the second phase in the cemented carbide is preferably 5% by volume or more, more preferably 7% by volume or more, and further preferably 9% by volume or more. From the viewpoint of improving the hardness, the upper limit of the content of the second phase in the cemented carbide is preferably 18% by volume or less, more preferably 16% by volume or less, and further preferably 14% by volume or less. The content of the second phase in the cemented carbide is preferably 5% by volume or more and 18% by volume or less, more preferably 7% by volume or more and 16% by volume or less, and further preferably 9% by volume or more and 14% by volume or less.

[0029] In addition to the first phase and the second phase, the cemented carbide according to the present embodiment can include a third phase consisting of a third phase particle including 10 atomic % or more of vanadium.

[0030] When the cemented carbide includes a third phase, the content of the third phase in the cemented carbide is preferably more than 0% by volume and 1% by volume or less. According to this, a decrease in the breakage resistance of the cemented carbide due to the presence of the third phase is suppressed. The lower limit of the content of the third phase in the cemented carbide is more than 0% by volume. The upper limit of the content of the third phase in the cemented carbide is preferably 1% by volume or less, more preferably 0.8% by volume or less, and further preferably 0.7% by volume or less. When the cemented carbide includes a third phase, the content of the third phase in the cemented carbide is preferably more than 0% by volume and 1% by volume or less, more preferably more than 0% by volume and 0.8% by volume or less, and further preferably more than 0% by volume and 0.7% by volume or less.

[0031] The cemented carbide according to the present embodiment can include an unavoidable impurity in addition to the first phase, the second phase, and the third phase as long as the effect of the present disclosure is exhibited. Examples of the unavoidable impurity include iron, molybdenum, and sulfur. The content of the unavoidable impurity in the cemented carbide is preferably less than 0.1% by mass. The content of the unavoidable impurity in the cemented carbide is measured by ICP emission spectroscopy (Inductively Coupled Plasma) Emission Spectroscopy (measuring apparatus: "ICPS-8100" (trademark) of Shimadzu Corporation).

[0032] The content of each of the first phase, the second phase, and the third phase in the cemented carbide is measured according to the following procedures (A1) to (D1).

[0033] (A1) A thin sample having a thickness of 50 nm or less is cut out from the cemented carbide by using an ion slicer or the like, and the surface of the thin sample is mirror-finished. Examples of a mirror finishing method include a method involving polishing with a diamond paste, a method involving using a focused ion beam apparatus (FIB apparatus), a method involving using a cross section polisher apparatus (CP apparatus), and a method combining these.

[0034] (B1) Elemental mapping of tungsten (W), cobalt (Co), chromium (Cr), and vanadium (V) is carried out on the mirror-finished surface of the thin sample by EDX (Energy Dispersive X-ray Spectroscopy) accompanying Transmission Electron Microscopy (TEM) to obtain a mapping image of each element. The measurement conditions are an observation magnification of 100,000 times and an acceleration voltage of 200 kV. The number of pixels for element mapping is 125 × 125. The elemental mapping images in five fields of view are prepared. The photographing regions of the elemental mapping images in the five fields of view are different from each other. The photographing regions can be set arbitrarily.

[0035] In the above elemental mapping images, a region including 70 atomic % or more of tungsten based on the sum of the numbers of atoms of tungsten (W), cobalt (Co), chromium (Cr), and vanadium (V) corresponds to a region in which a first phase is present. In the above elemental mapping images, a region including 70 atomic % or more of cobalt based on the sum of the numbers of atoms of tungsten, cobalt, chromium, and vanadium corresponds to a region in which a second phase is present. In the above elemental mapping images, a region including 10 atomic % or more of vanadium based on the sum of the numbers of atoms of tungsten, cobalt, chromium, and vanadium corresponds to a region in which a third phase is present. The vanadium concentrated layer present in an interface region between a tungsten carbide particle and a second phase and the vanadium concentrated layer present in the interface region between second phases are each in the form of a layer having a constant thickness on the order of several atoms (for example, about 1 to 5 atoms), and thus are not detected at an observation magnification of 100,000 times.

[0036] (C1) Image analysis software (ImageJ, version 1.51j8: https://imagej.nih.gov/ij/) is used on the elemental mapping images of each element in the five fields of view obtained in (B1) above to measure the area % of each of the first phase, the second phase, and the third phase with all the fields of view as the denominator.

[0037] (D1) The average value of the area % of the first phase obtained in the five fields of view is calculated. The average value corresponds to the content (% by volume) of the first phase in the cemented carbide. The average value of the area % of the second phase obtained in the five fields of view is calculated. The average value corresponds to the content (% by volume) of the second phase in the cemented carbide. The average value of the area % of the third phase obtained in the five fields of view is calculated. The average value corresponds to the content (% by volume) of the third phase in the cemented carbide.

[0038] As long as the applicant has carried out the measurement, it has been confirmed that as long as the measurement is carried out on the same sample, even if a selected location of a measurement region is changed to carry out the measurement a plurality of times, there is little variation in the measurement results, and that even if a measurement field of view is arbitrarily set, it is not contrived.

<First Phase>

<<Composition of First Phase>>

[0039] The first phase is composed of tungsten carbide particles. Here, the tungsten carbide particles include not only "pure WC particles (including WC containing no impurity element and also WC in which the content of an impurity element is below the detection limit)" but also "WC particles inside which an impurity element is intentionally or unavoidably contained as long as the effect of the present disclosure is not impaired." The content of an impurity in the first phase (when two or more elements constitute the impurity, the total concentration of the elements) is less than 0.1% by mass. The content of the impurity element in the first phase is measured by ICP emission spectrometry.

<<Average Value of Equivalent Circle Diameter of Tungsten Carbide Particles>>

[0040] In the present embodiment, the average value of the equivalent circle diameter of the tungsten carbide particles (hereinafter also referred to as the "average particle diameter of the WC particles") is 0.8 μm or less. According to this, the cemented carbide has high hardness, and a cutting tool using the cemented carbide can have excellent wear resistance. In addition, the cemented carbide has excellent strength, and the cutting tool using the cemented carbide can have excellent breakage resistance. In the present disclosure, the average value of the equivalent circle diameter of the tungsten carbide particles means the number-based arithmetic mean of the equivalent circle diameter of the WC particles measured on a cross section of the cemented carbide.

[0041] From the viewpoint of improving the wear resistance, the lower limit of the average particle diameter of the WC particles is preferably 0.2 μm or more, more preferably 0.3 μm or more, and further preferably 0.4 μm or more. From the viewpoint of improving the wear resistance and the breakage resistance, the upper limit of the average particle diameter of the WC particles is 0.8 μm or less, preferably 0.5 μm or less, more preferably 0.6 μm or less, and further preferably 0.4 μm or less. The average particle diameter of the WC particles is preferably 0.2 μm or more and 0.8 μm or less, more preferably 0.2 μm or more and 0.6 μm or less, and further preferably 0.2 μm or more and 0.5 μm or less.

[0042] The average value of the equivalent circle diameter of the tungsten carbide particles is measured by the following procedures (A2) to (D2).

[0043] (A2) An arbitrary cross section of the cemented carbide is mirror-finished. Examples of a mirror finishing method include a method involving polishing with a diamond paste, a method involving using a focused ion beam apparatus (FIB apparatus), a method involving using a cross section polisher apparatus (CP apparatus), and a method combining these.

[0044] (B2) A worked surface of the cemented carbide is photographed by using a scanning electron microscope ("S-

3400N" manufactured by Hitachi High-Technologies Corporation). Three photographed images are prepared. The photographing regions of the three photographed images are different from each other. The photographing regions can be set arbitrarily. The conditions are an observation magnification of 10,000 times, an acceleration voltage of 10 kV, and a backscattered electron image.

[0045] (C2) The three backscattered electron images obtained in (B2) above were imported into a computer and subjected to binarization processing by using image analysis software (ImageJ, version 1.51j8: https://imagej.nih.gov/ij/). The binarization processing is executed under the conditions preset in the image analysis software by pressing the "Make Binary" display on the computer screen after the images are imported. In an image after binarization processing, the first phase and the second phase can be distinguished by color shading. For example, in an image after binarization processing, the first phase is shown as a black region, and the second phase is shown as a white region. When the cemented carbide includes a third phase, the third phase is shown in the same color tone (white) as the second phase in an image after binarization processing.

[0046] (D2) The above image analysis software is used on the three obtained photographing images to measure the equivalent circle diameter (Heywood diameter: equal area equivalent circle diameter) of each of all tungsten carbide particles (black regions) in the three photographing images. The number-based arithmetic mean value of the equivalent circle diameter of all tungsten carbide particles in three measurement fields of view is calculated. In the present disclosure, the arithmetic mean value corresponds to the average value of the equivalent circle diameter of the WC particles.

[0047] As long as the applicant has carried out the measurement, it has been confirmed that as long as the measurement is carried out on the same sample, even if a selected location of a measurement region is changed to carry out the measurement a plurality of times, there is little variation in the measurement results, and that even if a measurement field of view is arbitrarily set, it is not contrived.

<Second Phase>

[0048] The second phase includes cobalt as a main component. The second phase is a binder phase that binds the tungsten carbide particles in the first phase to each other.

[0049] In the present disclosure, the "second phase including cobalt as a main component" means that in the second phase, the percentage of cobalt to all of tungsten, chromium, vanadium, and cobalt is 70% by mass or more. In the second phase, the lower limit of the percentage of cobalt to all of tungsten, chromium, vanadium, and cobalt can be 70% by mass or more, 80% by mass or more, or 90% by mass or more. The upper limit of the percentage can be less than 100% by mass. The percentage can be 70% by mass or more and less than 100% by mass, 80% by mass or more and less than 100% by mass, or 90% by mass or more and less than 100% by mass.

[0050] It has been confirmed that in the second phase in the cemented carbide according to the present disclosure, as long as the percentage of cobalt to all of tungsten, chromium, vanadium, and cobalt is 70% by mass or more, the second phase functions as a binder phase, and the effect of the present disclosure is not impaired.

[0051] The percentage of cobalt to all of tungsten, chromium, vanadium, and cobalt in the second phase can be measured by ICP emission spectrometry (equipment used: "ICPS-8100" (trademark) manufactured by Shimadzu Corporation).

[0052] In addition to cobalt, the second phase can include chromium (Cr), tungsten (W), vanadium (V), iron (Fe), nickel (Ni), carbon (C), and the like. The second phase can consist of cobalt and at least one selected from the group consisting of chromium, tungsten, vanadium, iron, nickel, and carbon. The second phase can consist of cobalt, at least one selected from the group consisting of chromium, tungsten, vanadium, iron, nickel, and carbon, and an impurity. Examples of the impurity include manganese (Mn), magnesium (Mg), calcium (Ca), molybdenum (Mo), sulfur (S), titanium (Ti), and aluminum (Al). When the second phase includes vanadium, it is assumed that the vanadium content of the second phase does not exceed 5 atomic %. That is, the vanadium content of the second phase can be 5 at % or less.

<Third Phase>

<<Composition of Third Phase>>

[0053] Preferably, the cemented carbide according to the present embodiment includes a third phase consisting of a third phase particle including 10 atomic % or more of vanadium, the content of the third phase in the cemented carbide is more than 0% by volume and 1% by volume or less, and the maximum value of the equivalent circle diameter of the third phase particle is 0.5 μm or less. According to this, there is no coarse third phase particle having an equivalent circle diameter of more than 0.5 μm, which can become a starting point for breakage, and thus the breakage resistance of a cutting tool using the cemented carbide is improved.

[0054] The third phase consists of a third phase particle including 10 atomic % or more of vanadium. It is presumed that the third phase is a fine precipitation phase of vanadium (V) derived from vanadium carbide (VC) added as a grain growth inhibitor in a step of manufacturing a cemented carbide. In the present disclosure, a vanadium concentrated layer having a constant thickness on the order of several atoms does not correspond to the third phase.

[0055] In the present disclosure, the "third phase particle including 10 atomic % or more of vanadium" means that in the third phase particle, the percentage of vanadium to all of tungsten, chromium, vanadium, and cobalt is 10% by mass or more.

[0056] In addition to vanadium, the third phase particle can include tungsten, cobalt, chromium, carbon, and the like. The third phase particle can consist of vanadium and at least one selected from the group consisting of tungsten, cobalt, chromium, and carbon. The third phase particle can consist of vanadium, at least one selected from the group consisting of tungsten, cobalt, chromium, and carbon, and an impurity. Examples of the impurity include iron, nickel, manganese, niobium, magnesium, calcium, molybdenum, sulfur, titanium, and aluminum.

[0057] In the third phase particle, the lower limit of the percentage of vanadium to all of tungsten, chromium, vanadium, and cobalt is 10 atomic % or more, and can be 20 atomic % or more, or 30 atomic % or more. The upper limit of the percentage can be 100 atomic % or less. The percentage can be 10 atomic % or more and 100 atomic % or less, 20 atomic % or more and 100 atomic % or less, or 30 atomic % or more and 100 atomic % or less.

[0058] The method for measuring the percentage of vanadium to all of tungsten, chromium, vanadium, and cobalt in the third phase particle is as follows.

[0059] First, elemental mapping analysis is carried out according to the same procedures as (A1) to (B 1) in the method for measuring the content of each of the first phase, the second phase, and the third phase in the cemented carbide, to obtain elemental mapping images in five fields of view. In each of the elemental mapping images, a region including 10 atomic % or more of vanadium based on the sum of the numbers of atoms of tungsten, cobalt, chromium, and vanadium is identified. This region corresponds to a third phase particle.

[0060] The identified third phase particle is magnified to an observation magnification of 2,000,000 times, and the percentage of the number of atoms of vanadium to the sum of the numbers of atoms of tungsten, cobalt, chromium, and vanadium in the third phase particle (hereinafter also referred to as the "vanadium content of the third phase particle) is measured by EDX point analysis. The measurement is carried out on five third phase particles. The average value of the vanadium content of the five third phase particles is calculated. The average value corresponds to the percentage of vanadium to all of tungsten, chromium, vanadium, and cobalt in the third phase particle in the present disclosure.

[0061] As long as the applicant has carried out the measurement, it has been confirmed that as long as the measurement is carried out on the same sample, even if a selected location of a measurement region is changed to carry out the measurement a plurality of times, there is little variation in the measurement results, and that even if a measurement field of view is arbitrarily set, it is not contrived.

<<Maximum Value of Equivalent Circle Diameter of Third Phase Particle>>

[0062] In the present embodiment, the maximum value of the equivalent circle diameter of the third phase particle (hereinafter also referred to as the "maximum value of the third phase particle") is preferably 0.5 μm or less.

[0063] When the cemented carbide includes a third phase, the upper limit of the maximum value of the third phase particle is preferably 0.5 μm or less, preferably 0.4 μm or less, preferably 0.3 μm or less, more preferably 0.2 μm or less, and further preferably 0.1 μm or less. The lower limit of the maximum value of the equivalent circle diameter of the third phase particle is not particularly limited, and can be more than 0 μm. The maximum value of the equivalent circle diameter of the third phase is preferably more than 0 μm and 0.5 μm or less, preferably more than 0 μm and 0.4 μm or less, preferably more than 0 μm and 0.3 μm or less, more preferably more than 0 μm and 0.2 μm or less, and further preferably more than 0 μm and 0.1 μm or less.

[0064] The maximum value of the equivalent circle diameter of the third phase particle is measured by the following procedures (A3) to (B3).

[0065] (A3) Elemental mapping images in five fields of view are analyzed by using the above image analysis software (ImageJ) according to the same procedures as (A1) to (C1) in the method for measuring the content of each of the first phase, the second phase, and the third phase in the cemented carbide described above, to identify the third phase.

[0066] (B3) The equivalent circle diameter (Heywood diameter: equal area equivalent circle diameter) of each of all third phase particles in the five measurement regions is measured by using the above image analysis software. The maximum value of the equivalent circle diameter of all the third phase particles in the five measurement fields of view corresponds to the maximum value of the equivalent circle diameter of the third phase particle in the present disclosure.

[0067] As long as the applicant has carried out the measurement, it has been confirmed that as long as the measurement is carried out on the same sample, even if a selected location of a measurement region is changed to carry out the measurement a plurality of times, there is little variation in the measurement results, and that even if a measurement field of view is arbitrarily set, it is not contrived.

<<Cobalt Content>>

[0068] The cobalt content of the cemented carbide according to the present embodiment is 3% by mass or more and 10% by mass or less. According to this, the cemented carbide has high hardness and strength. A cutting tool using the cemented carbide can have excellent wear resistance and breakage resistance.

[0069] From the viewpoint of improving the breakage resistance, the lower limit of the cobalt content of the cemented carbide is 3% by mass or more, and preferably 4% by mass or more. From the viewpoint of improving the hardness, the upper limit of the cobalt content of the cemented carbide is 10% by mass or less, preferably 9% by mass or less, and more preferably 8% by mass or less. The cobalt content of the cemented carbide is preferably 4% by mass or more and 10% by mass or less, more preferably 3% by mass or more and 9% by mass or less, and further preferably 3% by mass or more and 8% by mass or less.

[0070] The cobalt content of the cemented carbide is measured by ICP emission spectrometry.

<<Vanadium Content>>

[0071] The vanadium content of the cemented carbide according to the present embodiment is 0.01% by mass or more and 0.30% by mass or less. According to this, the generation of a coarse WC particle is suppressed, and the structure of the cemented carbide is densified. Therefore, the cemented carbide has excellent hardness and strength, and a cutting tool using the cemented carbide can have excellent wear resistance and breakage resistance.

[0072] From the viewpoint of suppressing the generation of a coarse WC particle, the lower limit of the vanadium content of the cemented carbide is 0.01% by mass or more, preferably 0.05% by mass or more, and more preferably 0.10% by mass or more. From the viewpoint of suppressing a decrease in interface strength, the upper limit of the vanadium content of the cemented carbide is 0.30% by mass or less, and preferably 0.20% by mass or less. The vanadium content of the cemented carbide is preferably 0.01% by mass or more and 0.20% by mass or less, and further preferably 0.10% by mass or more and 0.20% by mass or less.

[0073] The vanadium content of the cemented carbide is measured by ICP emission spectrometry.

<<Chromium Content>>

[0074] The cemented carbide according to the present embodiment can include chromium (Cr). The chromium content of the cemented carbide according to the present embodiment is preferably 0.2% by mass or more and 0.8% by mass or less. Chromium has the action of suppressing grain growth of a tungsten carbide particle. When the chromium content of the cemented carbide is in the above range, it is possible to effectively suppress a fine-grained tungsten carbide particle of the raw material remaining as it is in the obtained cemented carbide, and it is possible to effectively suppress the generation of a coarse grain, and the tool life is improved.

[0075] The lower limit of the chromium content of the cemented carbide is preferably 0.2% by mass or more, and more preferably 0.3% by mass or more. The upper limit of the chromium content of the cemented carbide is preferably 0.8% by mass or less, and more preferably 0.5% by mass or less. The chromium content of the cemented carbide is preferably 0.2% by mass or more and 0.8% by mass or less, and further preferably 0.3% by mass or more and 0.5% by mass or less.

[0076] The chromium content of the cemented carbide is measured by ICP emission spectrometry.

<Vanadium Content in Interface Region>

[0077] In the cemented carbide according to the present embodiment, the maximum value of the vanadium content in an interface region between the (0001) crystal plane of a tungsten carbide particle and a second phase (hereinafter also referred to as a "WC/second phase interface region") is 15 atomic % or less. According to this, the formation of a vanadium concentrated layer in which vanadium is present in a concentrated manner is suppressed in the interface region. Because of this, a decrease in the interface strength between the WC particle and the second phase due to the vanadium concentrated layer is suppressed. Therefore, in the cemented carbide, the WC particle is unlikely to fall off because of a decrease in interface strength, and a cutting tool using the cemented carbide can have excellent wear resistance and breakage resistance. A conventional cemented carbide has a large amount of a vanadium concentrated layer at the interface, which tends to reduce the interface strength.

[0078] In the cemented carbide, when a vanadium concentrated layer is present in the WC/second phase interface region, there is a possibility that a vanadium concentrated layer is also present in an interface region between the (0001) crystal plane of a WC particle and a further WC particle adjacent to the (0001) crystal plane of the WC particle (hereinafter also referred to as a "WC/WC interface region"). It has been confirmed that in the cemented carbide according to the present embodiment, when the maximum value of the vanadium content in the WC/second phase interface region is 15 atomic % or less, the maximum value of the vanadium content in the WC/WC interface region is also 15 atomic % or less. Therefore, if the maximum value of the vanadium content in the WC/second phase interface region is 15 atomic % or less, the maximum value of the vanadium content in the WC/WC interface region is also 15 atomic % or less, and the formation of a vanadium concentrated layer is suppressed in the WC/WC interface region. Because of this, a decrease in the interface strength between WC particles due to the vanadium concentrated layer is also suppressed.

[0079] The upper limit of the maximum value of the vanadium content in the WC/second phase interface region is preferably 15 atomic % or less, preferably 14 atomic % or less, more preferably 13 atomic % or less, further preferably 12 atomic % or less, and more further preferably 11 atomic % or less. The lower limit of the maximum value of the vanadium content in the WC/second phase interface region is not particularly limited, and can be, for example, 1 atomic % or more, or 2 atomic % or more. The maximum value of the vanadium content in the WC/second phase interface region is preferably 1 atomic % or more and 15 atomic % or less, more preferably 1 atomic % or more and 12 atomic % or less, further preferably 2 atomic % or more and 15 atomic % or less, and more further preferably 2 atomic % or more and 12 atomic % or less.

[0080] The maximum value of the vanadium content in the WC/second phase interface region is measured by the following procedures (A4) to (D4).

[0081] (A4) A thin sample having a thickness of 50 nm or less is cut out from the cemented carbide by using an ion slicer or the like. The surface of the thin sample is mirror-finished. Examples of a mirror finishing method include a method involving polishing with a diamond paste, a method involving using a focused ion beam apparatus (FIB apparatus), a method involving using a cross section polisher apparatus (CP apparatus), and a method combining these.

[0082] (B4) The mirror-finished surface of the thin sample is observed with a transmission electron microscope (TEM) to obtain an electron diffraction image of WC particles. The observation magnification is 2,000,000 times.

[0083] (C4) In the electron diffraction image, the (0001) crystal plane of a WC particle is identified. By using EDX (Energy Dispersive X-ray Spectroscopy) accompanying TEM, line analysis is carried out on an interface region between the (0001) crystal plane of the WC particle and a second phase adjacent to the WC particle when observed from the [11-20] or [10-10] orientation of the WC particle for which the (0001) crystal plane has been identified. In the line analysis, the percentage of the number of atoms (atomic %) of each of tungsten (W), cobalt (Co), chromium (Cr), and vanadium (V) is measured. The percentage of the number of atoms means the percentage of the number of atoms of each element when the sum of the numbers of atoms of W, Co, Cr, and V is 100 atomic %.

[0084] With reference to Fig. 1, the specific procedure for the line analysis will be described. Fig. 1 schematically shows a transmission electron microscope (TEM) image of the thin sample. In Fig. 1, a measurement region R for the line analysis is a rectangular region indicated by a sign R.

[0085] As shown in Fig. 1, a portion of the interface between the (0001) crystal plane of a WC particle 1 and a second phase 2 adjacent to the (0001) crystal plane of WC particle 1 which is approximately straight and in which the length of the approximately straight portion is 25 nm or more is selected. The line analysis is carried out in a direction perpendicular to the approximately straight portion (direction of an arrow B in Fig. 1). The distance for the line analysis is 20 nm from the approximately straight portion as the center to each of the WC particle side and the second phase side. The width for the line analysis is 25 nm, and the step interval is 0.4 nm. As shown in Fig. 1, measurement region R for the line analysis is set such that a third phase particle 3 is not included.

[0086] Based on the line analysis results, the maximum value of the percentage (atomic %) of vanadium is calculated when the sum of the numbers of atoms of W, Cr, V, and Co is 100 atomic %. The maximum value is defined as the maximum value of the vanadium content in the interface region between the (0001) crystal plane of the WC particle and the second phase.

[0087] (D4) The measurement in (C4) above is carried out in an interface region between the (0001) crystal plane of each of five different WC particles and a second phase. The average value of the vanadium content in the five interface regions is calculated. The average value corresponds to the maximum value of the vanadium content in the interface region between the (0001) crystal plane of the tungsten carbide particle and the second phase in the cemented carbide according to the present disclosure. Therefore, when the average value of the vanadium content in the five interface regions is 15 atomic % or less in a cemented carbide, the maximum value of the vanadium content in the interface region between the (0001) crystal plane of the tungsten carbide particle and the second phase is 15 atomic % or less in the cemented carbide.

[0088] As long as the applicant has carried out the measurement, it has been confirmed that as long as the measurement is carried out on the same sample, even if a selected location of a measurement region is changed to carry out the measurement a plurality of times, there is little variation in the measurement results, and that even if a measurement field of view is arbitrarily set, it is not contrived.

[0089] It has been confirmed that as long as the maximum value of the percentage of vanadium to all of tungsten, chromium, vanadium, and cobalt is 15 atomic % or less in the interface region between the (0001) crystal plane of the tungsten carbide particle and the second phase in the cemented carbide according to the present disclosure, a decrease in interface strength is suppressed, and the effect of the present disclosure is not impaired.

<Chromium Content in Interface Region>

[0090] In the cemented carbide according to the present embodiment, the maximum value of the chromium content in the interface region between the (0001) crystal place of the tungsten carbide particle and the second phase is preferably 20 atomic % or less. According to this, the formation of a chromium concentrated layer in which chromium is present in a concentrated manner is suppressed in the interface region. Because of this, a decrease in the interface strength between the WC particle and the second phase due to the chromium concentrated layer is suppressed. Therefore, in the cemented carbide, the WC particle is unlikely to fall off because of a decrease in interface strength, and a cutting tool using the cemented carbide can have excellent wear resistance and breakage resistance.

[0091] In the cemented carbide, when a chromium concentrated layer is present in the WC/second phase interface region, there is a possibility that a chromium concentrated layer is also present in an interface region between the (0001) crystal place of a WC particle and a further WC particle adjacent to the (0001) crystal plane of the WC particle (WC/WC interface region). It has been confirmed that in the cemented carbide according to the present embodiment, when the maximum value of the chromium content in the WC/second phase interface region is 20 atomic % or less, the maximum value of the chromium content in the WC/WC interface region is also 20 atomic % or less. Therefore, if the maximum value of the chromium content in the WC/second phase interface region is 20 atomic % or less, the maximum value of the chromium content in the WC/WC interface region is also 20 atomic % or less, and the formation of a chromium concentrated layer in which chromium is present in a concentrated manner is suppressed in the WC/WC interface region. Because of this, a decrease in the interface strength between WC particles due to the chromium concentrated layer is also suppressed.

[0092] The upper limit of the maximum value of the chromium content in the WC/second phase interface region is preferably 20 atomic % or less, preferably 18 atomic % or less, more preferably 16 atomic % or less, further preferably 15 atomic % or less, and more further preferably 14 atomic % or less. The lower limit of the maximum value of the chromium content in the WC/second phase interface region is not particularly limited, and can be, for example, 1 atomic % or more, or 2 atomic % or more. The maximum value of the chromium content in the WC/second phase interface region is preferably 1 atomic % or more and 20 atomic % or less, more preferably 1 atomic % or more and 15 atomic % or less, further preferably 2 atomic % or more and 20 atomic % or less, and more further preferably 2 atomic % or more and 15 atomic % or less.

[0093] The maximum value of the chromium content in the WC/second phase interface region is obtained by calculating the percentage (atomic %) of chromium when the sum of the numbers of atoms of W, Cr, V, and Co is 100 atomic % instead of the percentage (atomic %) of vanadium when the sum of the numbers of atoms of W, Cr, V, and Co is 100 atomic % in (A4) to (D4) in the method for measuring the vanadium content in the WC/second phase interface region described above.

[0094] As long as the applicant has carried out the measurement, it has been confirmed that as long as the measurement is carried out on the same sample, even if a selected location of a measurement region is changed to carry out the measurement a plurality of times, there is little variation in the measurement results, and that even if a measurement field of view is arbitrarily set, it is not contrived.

[0095] It has been confirmed that as long as the maximum value of the percentage of chromium to all of tungsten, chromium, vanadium, and cobalt is 20 atomic % or less in the interface region between the (0001) crystal plane of the tungsten carbide particle and the second phase in the cemented carbide according to the present disclosure, a decrease in interface strength is suppressed, and the effect of the present disclosure is not impaired.

<Method for Manufacturing Cemented Carbide>

[0096] In order to reduce the vanadium content in the interface region between the (0001) crystal plane of the tungsten carbide particle and the second phase in the cemented carbide, the amount of vanadium added as a grain growth inhibitor may be reduced. However, when the amount of vanadium added is reduced, the effect of suppressing grain growth is insufficient and the WC particle undergoes abnormal grain growth. This causes a decrease in the strength of the cemented carbide. The present inventors have carried out extensive studies and as a result have newly found a method for manufacturing a cemented carbide that can reduce the vanadium content in the interface region while adding a sufficient amount of vanadium in order to suppress the generation of coarse WC particles. The details of the method for manufacturing a cemented carbide according to the present embodiment will be described below.

[0097] The cemented carbide according to the present embodiment can typically be manufactured by carrying out a raw material powder preparing step, a mixing step, a compacting step, a sintering step (including a preliminary sintering step and a main sintering step), a repeated heat treatment step, and a cooling step in presented order. Hereinafter, each step will be described.

<<Preparing Step>>

[0098] The preparing step is a step for preparing all raw material powders of materials that constitute the cemented carbide. Examples of the raw material powders include a tungsten carbide powder (hereinafter also referred to as a "WC powder"), which is a raw material for the first phase, a cobalt powder (hereinafter also referred to as a "Co powder"), which is a raw material for the second phase, and a vanadium carbide powder (hereinafter also referred to as a "VC powder"), which is a grain growth inhibitor. In addition, a chromium carbide powder (hereinafter also referred to as a "Cr_3C_2 powder"), which is a grain growth inhibitor, can be prepared as needed. As the tungsten carbide powder, the cobalt powder, the vanadium carbide powder, and the chromium carbide powder, commercially available ones can be used.

[0099] The average particle diameter of the tungsten carbide powder can be 0.2 μm or more and 1.0 μm or less. The WC powder preferably has a ratio of the 20% cumulative volume particle diameter d20 thereof to the 80% cumulative volume particle diameter d80 thereof, d20/d80, of 0.2 or more and 1 or less. Such a WC powder has a uniform particle diameter and has a low content of a fine-grained WC particle. Because of this, when a cemented carbide is produced by using the WC powder, the generation of a coarse WC particle due to dissolution and reprecipitation is suppressed in the sintering step. The term "20% cumulative volume particle diameter d20" means the particle diameter at which the cumulative percentage from the smaller diameter side in the volume-based cumulative particle size distribution of crystal grains reaches 20%. The term "80% cumulative volume particle diameter d80" means the particle diameter at which the cumulative percentage from the smaller diameter side in the volume-based cumulative particle size distribution of crystal grains reaches 80%.

[0100] The average particle diameter of the cobalt powder can be 0.5 μm or more and 1.5 μm or less. The average particle diameter of the vanadium carbide powder can be 0.1 μm or more and 0.5 μm or less. By using a fine VC powder, the VC powder can be sufficiently diffused into the mixed powder in the subsequent preliminary sintering step. The average particle diameter of the chromium carbide powder can be 1.0 μm or more and 2.0 μm or less.

[0101] As used herein, the average particle diameter of a raw material powder described above means the average particle diameter measured by an FSSS (Fisher Sub-Sieve Sizer) method. The average particle diameter is measured by using "Sub-Sieve Sizer Model 95" (trademark) manufactured by Fisher Scientific. The particle diameter distribution of the WC powder is measured by using a particle size distribution measuring apparatus (trade name: MT3300EX) manufactured by Microtrac.

<<Mixing Step>>

[0102] The mixing step is a step of mixing the raw material powders prepared in the preparing step. A mixed powder in which the raw material powders are mixed is obtained by the mixing step. The content of each raw material powder in the mixed powder is appropriately adjusted in consideration of the content of each component such as the first phase, the second phase, and the third phase in the cemented carbide.

[0103] The content of the tungsten carbide powder in the mixed powder can be, for example, 88.85% by mass or more and 99.83% by mass or less.

[0104] The content of the cobalt powder in the mixed powder can be, for example, 3% by mass or more and 10% by mass or less.

[0105] The content of the vanadium carbide powder in the mixed powder can be, for example, 0.01% by mass or more and 0.37% by mass or less.

[0106] The content of the chromium carbide powder in the mixed powder can be, for example, 0.20% by mass or more and 0.92% by mass or less.

[0107] A ball mill is used for mixing. The mixing time can be 15 hours or more and 36 hours or less. According to this, pulverization of the raw material powders can be suppressed, and the VC powder can be sufficiently dispersed into the mixed powder while maintaining the particle diameters of the raw material powders.

[0108] After the mixing step, the mixed powder may be granulated as needed. By granulating the mixed powder, it is easy to fill a die or a mold with the mixed powder during the compacting step described later. A known granulation method can be applied to the granulation, and for example, a commercially available granulator such as a spray dryer can be used.

<<Compacting Step>>

[0109] The compacting step is a step of compacting the mixed powder obtained in the mixing step into a predetermined shape to obtain a compact. As the compacting method and the compacting conditions in the compacting step, a general method and general conditions may be adopted, and these are not particularly limited. Examples of the predetermined shape include a cutting tool shape (for example, the shape of a small diameter drill).

<<Sintering Step>>

[0110] The sintering step includes a preliminary sintering step and a main sintering step. In the preliminary sintering step, the compact is held at a sintering temperature of 800 to 1000°C for 2 hours. The atmosphere is a vacuum. A sintering temperature of 800 to 1000°C is a temperature range in which no grain growth of WC occurs. By holding in a temperature range in which no grain growth of WC occurs for 2 hours, VC in the mixed powder can be diffused throughout cobalt. Thereby, in the main sintering step, VC exhibits a uniform grain growth suppressing effect throughout the cemented carbide, and the generation of a coarse WC particle is suppressed.

[0111] Subsequently, the main sintering step is carried out. In the main sintering step, the compact after the preliminary sintering step is held at a sintering temperature of 1350 to 1450°C for 1 to 2 hours in an argon (Ar) atmosphere to obtain a cemented carbide. According to this, the generation of a coarse WC particle is suppressed. In addition, the content of a fine-grained WC particle in the obtained cemented carbide can be reduced.

[0112] By carrying out the preliminary sintering step and the main sintering step, vanadium can be sufficiently solid-dissolved in cobalt.

«Repeated Heat Treatment Step»

[0113] Subsequently, the cemented carbide obtained in the sintering step is rapidly cooled. The cemented carbide is rapidly cooled at a cooling rate of -60°C/min or more from the temperature in the main sintering step to 1100°C at which VC precipitates as a solid phase, and held at 1100°C for 30 minutes. Such rapid cooling suppresses the movement of vanadium dissolved in cobalt, which is likely to occur during cooling. Therefore, a region having a high vanadium content in an interface region between a WC particle and a second phase (WC/second phase interface region) or an interface region between WC particles (WC/WC interface region) (corresponding to a "vanadium concentrated layer") and/or a fine precipitation phase of VC (hereinafter also referred to as a "VC fine precipitation phase") are/is uniformly formed in the cemented carbide. Hereinafter, the step of rapidly cooling the cemented carbide to 1100°C at a cooling rate of -60°C/min or more and holding the cemented carbide at 1100°C for 30 minutes will also be referred to as a "rapid cooling step."

[0114] Subsequently, the cemented carbide is heated to 1250°C and held at 1250°C for 10 to 20 minutes. By setting the holding time at 1250°C to 20 minutes or less, vanadium in the vanadium concentrated layer having a large surface area can be preferentially solid-dissolved in cobalt. On the other hand, solid dissolution of vanadium in the VC fine precipitation phase in cobalt is suppressed, and at least a part of the VC fine precipitation phase can remain in the alloy. Hereinafter, the step of heating the cemented carbide to 1250°C and holding the cemented carbide at 1250°C for 10 to 20 minutes will also be referred to as a "heat treatment step."

[0115] Subsequently, the cemented carbide is rapidly cooled to 1100°C at a cooling rate of -60°C/min or more and held at 1100°C for 30 minutes (corresponding to the rapid cooling step). This suppresses the movement of vanadium solid-dissolved in cobalt in the heat treatment step. Therefore, a vanadium concentrated layer and/or a VC fine precipitation phase are/is uniformly formed in the cemented carbide.

[0116] The above rapid cooling step and heat treatment step are alternately repeated two or more times each. Thereby, the maximum value of the vanadium concentration in the vanadium concentrated layer present in each of the WC/second phase interface region and the WC/WC interface region is finally reduced. That is, the vanadium content in an interface region between the (0001) crystal plane of a tungsten carbide particle and a second phase in the cemented carbide, and the vanadium content in an interface region between the (0001) crystal plane of a WC particle and a WC particle adjacent to the (0001) crystal plane of the WC particle are reduced. Furthermore, even when the cemented carbide includes a VC particle, the VC particle is fine and uniformly dispersed in the cemented carbide.

«Cooling Step»

[0117] Subsequently, the cemented carbide after the repeated heat treatment step is cooled. As the cooling conditions, general conditions may be adopted, and these are not particularly limited.

[0118] According to the above method for manufacturing a cemented carbide, a cemented carbide that does not include a coarse WC particle because abnormal grain growth of a WC particle is suppressed and that has a reduced vanadium content in an interface region can be obtained. The cemented carbide has excellent wear resistance and breakage resistance.

[Embodiment 2: Cutting Tool]

[0119] The cutting tool of the present embodiment includes a cutting edge formed from the cemented carbide of Embodiment 1. In the present disclosure, the cutting edge means a portion involved in cutting, and means a region surrounded by a cutting edge ridgeline thereof and a virtual plane at a distance of 2 mm along a line perpendicular to the tangent to the cutting edge ridgeline from the cutting edge ridgeline toward the cemented carbide side, in the cemented carbide.

[0120] Examples of the cutting tool include a cutting bit, a drill, an end mill, an indexable cutting insert for milling working, an indexable cutting insert for turning working, a metal saw, a gear cutting tool, a reamer, and a tap. In particular, as shown in Fig. 2, a cutting tool 10 of the present embodiment can exhibit an excellent effect in the case of a small diameter drill for working a printed circuit board. A cutting edge 11 of cutting tool 10 shown in Fig. 2 is formed from the cemented carbide of Embodiment 1.

[0121] The cemented carbide according to the present embodiment may constitute the whole of each of these tools, or a part thereof. Here, the term "constituting a part" refers to, for example, a mode of forming a cutting edge portion by brazing the cemented carbide according to the present embodiment at a predetermined position of an arbitrary base material.

<<Hard Film>>

[0122] The cutting tool according to the present embodiment may further include a hard film that coats at least a part of the surface of a base material formed from the cemented carbide. For example, diamond-like carbon or diamond can be used as the hard film.

[Appendix 1]

[0123] The total content of the first phase and the second phase in the cemented carbide according to the present disclosure is preferably 97% by volume or more and 100% by volume or less.

[0124] The content of the first phase in the cemented carbide according to the present disclosure is preferably 82% by volume or more and 95% by volume or less.

[0125] The content of the second phase in the cemented carbide according to the present disclosure is preferably 5% by volume or more and 18% by volume or less.

[0126] The content of the third phase in the cemented carbide according to the present disclosure is preferably more than 0% by volume and 0.8% by volume or less.

[Appendix 2]

[0127] In the cemented carbide according to the present disclosure, the average value of the equivalent circle diameter of the tungsten carbide particle is preferably 0.2 μm or more and 0.8 μm or less.

[0128] In the cemented carbide according to the present disclosure, the average value of the equivalent circle diameter of the tungsten carbide particle is preferably 0.2 μm or more and 0.6 μm or less.

[Appendix 3]

[0129] In the second phase in the cemented carbide according to the present disclosure, the percentage of cobalt to all of tungsten, chromium, vanadium, and cobalt is preferably 70% by mass or more.

[Appendix 4]

[0130] The cobalt content of the cemented carbide according to the present disclosure is preferably 4% by mass or more and 10% by mass or less.

[0131] The cobalt content of the cemented carbide according to the present disclosure is preferably 3% by mass or more and 9% by mass or less.

[Appendix 5]

[0132] The chromium content of the cemented carbide according to the present disclosure is preferably 0.2% by mass or more and 0.8% by mass or less.

[0133] The chromium content of the cemented carbide according to the present disclosure is preferably 0.3% by mass or more and 0.5% by mass or less.

[Appendix 6]

[0134] In the cemented carbide according to the present disclosure, the maximum value of vanadium content in the interface region between the (0001) crystal plane of the tungsten carbide particle and the second phase is preferably 1 atomic % or more and 15 atomic % or less.

[0135] In the cemented carbide according to the present disclosure, the maximum value of vanadium content in the interface region between the (0001) crystal plane of the tungsten carbide particle and the second phase is preferably 1 atomic % or more and 12 atomic % or less.

[Appendix 7]

[0136] The maximum value of the chromium content in the interface region between the (0001) crystal plane of the tungsten carbide particle and the second phase is preferably 1 atomic % or more and 20 atomic % or less.

[0137] The maximum value of the chromium content in the interface region between the (0001) crystal plane of the tungsten carbide particle and the second phase is preferably 1 atomic % or more and 15 atomic % or less.

Examples

[0138] The present embodiment will be described more specifically with reference to Examples. However, the present embodiment is not limited by these Examples.

[0139] In the present Examples, cemented carbides of sample 1 to sample 12 and sample 1-1 to sample 1-10 were produced by changing the blending ratio of raw material powders and manufacturing conditions. A small diameter drill having a cutting edge formed from each of the cemented carbides was fabricated and evaluated.

<Production of Samples>

«Preparing Step»

[0140] Powders having the compositions shown in the "Mixed powder" column of Table 1 were prepared as the raw material powders. The average particle diameter of the WC powder is 0.4 μm, and d20/d80 is 0.3 or more. The average particle diameter of the Co powder is 1 μm, the average particle diameter of the VC powder is 0.3 μm, and the average particle diameter of the Cr_3C_2 powder is 1 μm. The WC powder, the Co powder, the Cr_3C_2 powder, and the VC powder are commercially available products.

<<Mixing Step>>

[0141] Each raw material powder was mixed in the amount blended shown in "% by mass" in "Mixed powder" of Table 1 to produce a mixed powder. "% by mass" in the "Mixed powder" column of Table 1 indicates the proportion of the mass of each raw material powder to the total mass of the raw material powders. Mixing was carried out in a ball mill for 15 hours. The obtained mixed powder was dried by using a spray dryer to obtain a granulated powder.

<<Compacting Step>>

[0142] The obtained granulated powder was pressed to fabricate a round bar-shaped compact having φ 3.4 mm.

<<Sintering Step>>

[0143] Subsequently, the compact was subjected to a preliminary sintering step. The compact was placed in a sintering furnace and held in vacuum for 2 hours at the temperature shown in the "Temperature" column in "Preliminary sintering" of Table 1. The description of "No" in the "Preliminary Sintering" column of Table 1 indicates that the preliminary sintering step was not carried out.

[0144] Subsequently, the main sintering step was carried out. The compact after the preliminary sintering step was held in an Ar atmosphere for 1 hour at the temperature shown in the "Temperature" column in "Main sintering" of Table 1 to obtain a cemented carbide.

«Repeated Heat Treatment Step»

[0145] Subsequently, the cemented carbide obtained in the sintering step was alternately subjected to a rapid cooling step and a heat treatment step twice each. That is, the rapid cooling step, the heat treatment step, the rapid cooling step, and the heat treatment step were carried out in presented order.

[0146] In the rapid cooling step, the cemented carbide was rapidly cooled to 1100°C at a cooling rate of -60°C/min or more and held at 1100°C for 30 minutes. In the heat treatment step, the cemented carbide was heated to 1250°C and held at 1250°C for 20 minutes.

[0147] The description of "No" in the "Repeated heat treatment" column of Table 1 indicates that the repeated heat treatment step was not carried out.

«Cooling Step»

[0148] Subsequently, the cemented carbides after the repeated heat treatment step were slowly cooled in an argon (Ar) gas atmosphere to obtain a cemented carbide of each sample.

[Table 1]

[0149]

Table 1

Sample No.	Mixed powder				Mixing step	Preliminary sintering		Main sintering		Repeated heat treatment
	WC powder	Co powder	VC powder	Cr_3C_2 powder	Time	Temperature	Time	Temperature	Time	Yes/No
	% by mass	% by mass	% by mass	% by mass	hr	°C	hr	°C	hr	
1	89.53	10.00	0.01	0.46	15	1000	2	1420	1	Yes
2	96.17	3.00	0.37	0.46	15	1000	2	1420	1	Yes
3	96.30	3.00	0.24	0.46	15	1000	2	1420	1	Yes
4	91.30	8.00	0.24	0.46	15	1000	2	1420	1	Yes
5	91.17	8.00	0.37	0.46	15	1000	2	1420	1	Yes
6	96.30	3.00	0.24	0.46	15	800	2	1420	1	Yes
7	89.17	10.00	0.37	0.46	15	1000	2	1420	1	Yes
8	91.30	8.00	0.24	0.46	15	1000	2	1420	1	Yes
9	95.84	3.00	0.24	0.92	15	1000	2	1420	1	Yes
10	96.17	3.00	0.37	0.46	15	800	2	1420	1	Yes
11	91.30	3.00	0.24	0.69	15	1000	2	1420	1	Yes
12	96.17	3.00	0.01	0.46	15	1000	2	1420	1	Yes
1-1	96.17	3.00	0.37	0.46	15	No	-	1420	1	Yes
1-2	98.17	1.00	0.37	0.46	15	1000	2	1420	1	Yes
1-3	87.17	12.00	0.37	0.46	15	1000	2	1420	1	Yes
1-4	96.54	3.00	0	0.46	15	1000	2	1420	1	Yes
1-5	96.05	3.00	0.49	0.46	15	1000	2	1420	1	Yes
1-6	96.17	3.00	0.37	0.46	15	1000	2	1500	1	Yes
1-7	96.17	3.00	0.37	0.46	15	1000	2	1420	1	No
1-8	96.17	3.00	0.37	0.46	15	No	-	1420	1	No
1-9	89.53	10.00	0.01	0.46	15	No	-	1420	1	Yes
1-10	96.17	3.00	0.01	0.46	15	1000	2	1420	1	No

<Evaluation of Cemented Carbide>

[0150] The cemented carbide of each sample was measured for the content of the first phase, the second phase, and the third phase in the cemented carbide (shown the "First phase (% by volume)," "Second phase (% by volume)," and "Third phase (% by volume)" columns, respectively, in Table 2), the cobalt content of the cemented carbide (shown in the "Co (% by mass)" column in Table 2), the vanadium content of the cemented carbide (shown in the "V (% by mass)" column in Table 2), the percentage of cobalt to all of tungsten, chromium, vanadium, and cobalt in the second phase (shown in the "Co/second phase (% by mass)" column in Table 2), the average value of the equivalent circle diameter of the WC particle (shown in the "WC particle Average particle diameter (μm)" column in Table 2), the maximum value of the equivalent circle diameter of the third phase particle (shown in the "Third phase Maximum particle diameter (μm)" column in Table 2), the maximum value of the vanadium content in the interface region between the (0001) crystal plane of the tungsten carbide particle and the second phase (shown in the "V maximum (atomic %)" column in the "WC/second phase interface region" in Table 2), and the maximum value of the chromium content in the interface region (shown in the "Cr maximum (atomic %)" column in "Interface region" in Table 2). The method for measuring each item is as shown in Embodiment 1. Results thereof are shown in Table 2.

<Cutting Test>

[0151] The round bar of each sample was worked to fabricate a small diameter drill (rotating tool for working a printed circuit board) having a cutting edge diameter φ of 0.2 mm. Currently, it is common to form a drill by press-fitting only a cutting edge portion into a stainless steel shank, but for an evaluation purpose, a drill was fabricated by subjecting the tip of a φ 3.4 mm round bar to sharpening working. By using the drill, a commercially available in-vehicle printed circuit board was subjected to drill working.

[0152] In a wear resistance evaluation test, the drill working conditions were a rotation speed of 160 krpm and a feed speed of 2.7 m/min. After drilling 10,000 holes, the width (μm) of a wear scar on the drill was measured. With reference to Fig. 3, the width of the wear scar in the present Examples will be described. Fig. 3 is a diagram of a small diameter drill fabricated in the present Examples when viewed from the tip side thereof. The width of the wear scar means a width L1 of a wear scar W at a location at a distance of 0.08 mm from a drill center C, as shown in Fig. 3. Results thereof are shown in the "Wear resistance (μm) in Cutting test" column of Table 2. In the present Examples, when the width of the wear scar is 22 μm or less, it is determined that the wear resistance is good, and when the width of the wear scar is 20 μm or less, it is determined that the wear resistance is better.

[0153] In a breakage resistance evaluation test, the drill working conditions were a rotation speed of 100 krpm and a feed speed of 3.6 m/min. A maximum of 5000 holes were drilled, and the number of times a hole had been drilled until breakage was measured. Results thereof are shown in the "Breakage resistance (times) in Cutting test" column of Table 2. A result of 5000 times means that no breakage occurred when a hole was drilled 5000 times. In the present Examples, when the number of times a hole is drilled until breakage is 3000 times or more, it is determined that the breakage resistance is good, and when the number of times a hole is drilled until breakage is 5000 times, it is determined that the breakage resistance is better.

[Table 2]

[0154]

Table 2

Sample No.	Cemented carbide							WC particle	Third phase	WC/second phase interface region		Cutting test	
	First phase	Second phase	Third phase	First phase + second phase	Co	V	Co/ second phase	Average particle diameter	Maximum particle diameter	V maximum	Cr maximum	Wear resistance	Breakage resistance
	% by volume	% by volume	% by volume	% by volume	% by mass	% by mass	% by mass	µm	µm	Atomic %	Atomic %	µm	Times
1	82.0	18.0	0.0	100.0	10	0.01	93	0.8	0	2	15	21.8	5000
2	94.0	5.0	0.8	99.0	3	0.30	90	0.3	0.5	12	15	19.3	3790
3	94.0	5.0	0.0	99.0	3	0.20	86	0.3	0.4	10	15	19.2	5000
4	85.0	15.0	0.0	100.0	8	0.20	85	0.4	0.2	10	15	19.6	5000
5	84.0	15.0	0.5	99.0	8	0.30	92	0.2	0.2	9	14	19.9	5000
6	94.0	5.0	0.5	99.0	3	0.20	90	0.3	0.5	9	15	19.2	3852
7	82.0	18.0	0.0	100.0	10	0.30	90	0.3	0.3	10	14	21.2	5000
8	84.0	15.0	0.6	99.0	8	0.20	93	0.5	0.4	11	15	19.5	4501
9	94.0	5.0	0.3	99.0	3	0.20	83	0.4	0.2	11	22	21	4167
10	94.0	5.0	0.7	99.0	3	0.30	90	0.3	0.5	15	16	20.3	3548
11	94.0	5.0	0.3	99.0	3	0.20	83	0.4	0.2	11	20	19.6	4088
12	94.0	5.0	0.6	99.0	3	0.01	88	0.3	0.4	10	15	19.2	3804
1-1	91.0	5.0	1.3	96.0	3	0.30	96	0.3	1.0	13	15	20.8	1657
1-2	95.0	2.0	1.0	97.0	1	0.30	85	0.3	0.7	4	9	Breakage	1
1-3	78.0	22.0	0.0	100.0	12	0.30	93	0.3	0.4	10	12	23.1	5000
1-4	95.0	5.0	0.0	100.0	3	0	91	0.9	0	0	14	21.9	2523
1-5	93.0	5.0	0.6	98.0	3	0.40	89	0.3	0.9	17	0	22.3	947
1-6	94.0	5.0	0.5	99.0	3	0.30	90	1.0	0.9	12	14	19.5	1095
1-7	94.0	5.0	0.6	99.0	3	0.30	92	0.3	0.2	17	16	22.4	2874

(continued)

Sample No.	Cemented carbide							WC particle	Third phase	WC/second phase interface region		Cutting test	
	First phase	Second phase	Third phase	First phase + second phase	Co	V	Co/ second phase	Average particle diameter	Maximum particle diameter	V maximum	Cr maximum	Wear resistance	Breakage resistance
	% by volume	% by volume	% by volume	% by volume	% by mass	% by mass	% by mass	µm	µm	Atomic %	Atomic %	µm	Times
1-8	92.0	5.0	1.0	97.0	3	0.30	90	0.6	0.9	18	21	22.6	761
1-9	82.0	18.0	0.0	100.0	10	0.01	93	0.9	0	2	20	22.1	1382
1-10	94.0	5.0	0.6	99.0	3	0.01	89	0.3	0.3	16	24	22.1	2020

<Discussion>

[0155] The cemented carbides and the cutting tools of sample 1 to sample 12 correspond to the Examples. It was confirmed that these samples had excellent wear resistance and breakage resistance.

[0156] The cemented carbides and the cutting tools of sample 1-1 to sample 1-10 correspond to the Comparative Examples. It was confirmed that these samples had insufficient wear resistance and/or breakage resistance.

[0157] The embodiments and the Examples of the present disclosure have been described as above, and it is also planned from the beginning to appropriately combine the configurations of the embodiments and the Examples described above and to modify these in various ways.

[0158] The embodiments and the Examples disclosed this time should be considered to be illustrative in all respects and non-limiting. The scope of the present invention is defined by the Claims, not by the above embodiments and Examples, and is intended to include all modifications within the meaning and scope equivalent to the Claims.

REFERENCE SIGNS LIST

[0159] 1 Tungsten carbide particle; 2 Second phase; 3 Third phase particle; R Measurement region; 10 Cutting tool; 11 Cutting edge; C Drill center; W Wear scar

Claims

1. A cemented carbide comprising a first phase composed of a tungsten carbide particle and a second phase comprising cobalt as a main component, wherein

   a total content of the first phase and the second phase in the cemented carbide is 97% by volume or more,
   an average value of an equivalent circle diameter of the tungsten carbide particle is 0.8 μm or less,
   a cobalt content of the cemented carbide is 3% by mass or more and 10% by mass or less,
   a vanadium content of the cemented carbide is 0.01% by mass or more and 0.30% by mass or less, and
   a maximum value of the vanadium content in an interface region between a (0001) crystal plane of the tungsten carbide particle and the second phase is 15 atomic % or less.

2. The cemented carbide according to claim 1, wherein

   the cemented carbide comprises a third phase consisting of a third phase particle including 10 atomic % or more of vanadium,
   a content of the third phase in the cemented carbide is more than 0% by volume and 1% by volume or less, and
   a maximum value of an equivalent circle diameter of the third phase particle is 0.5 μm or less.

3. The cemented carbide according to claim 1 or 2, wherein a maximum value of a chromium content in the interface region is 20 atomic % or less.

4. A cutting tool comprising a cutting edge formed from the cemented carbide according to any one of claim 1 to claim 3.

FIG.1

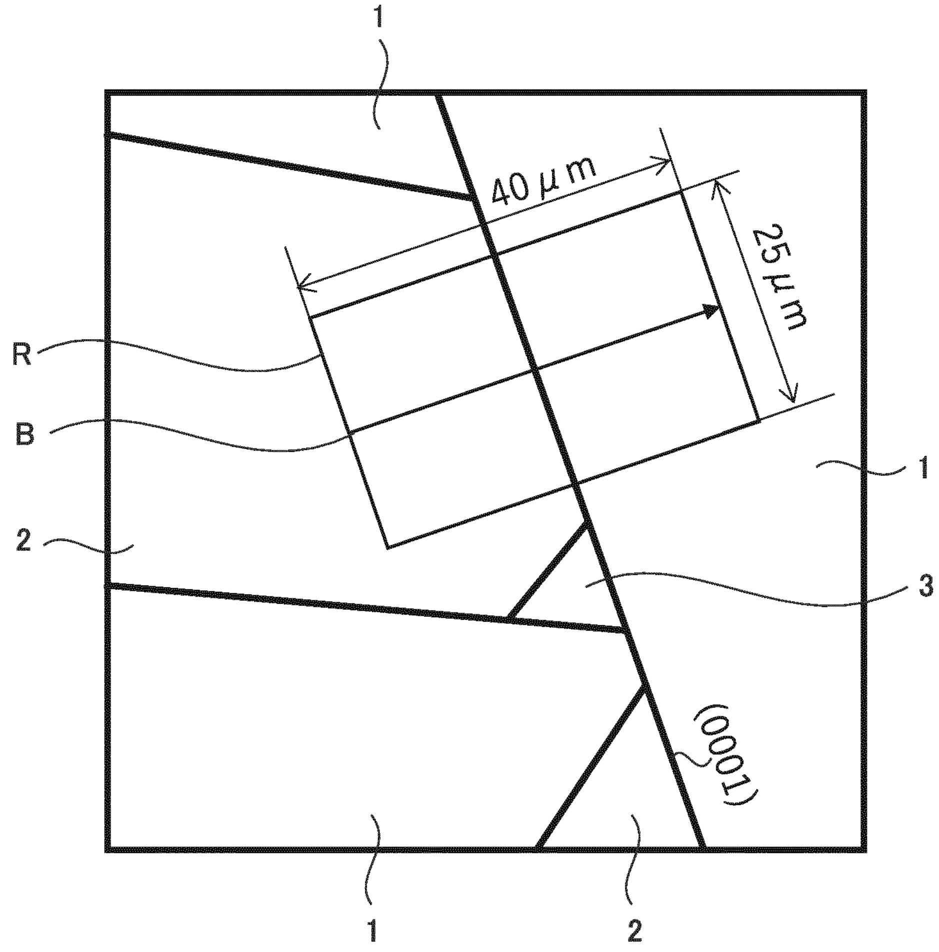


FIG.2

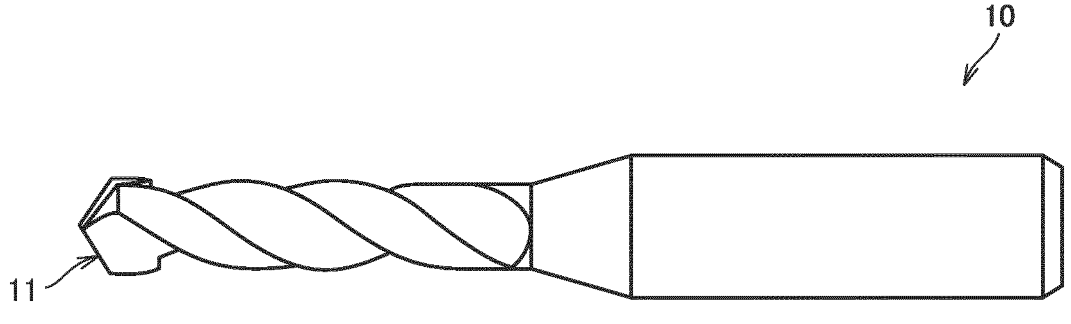
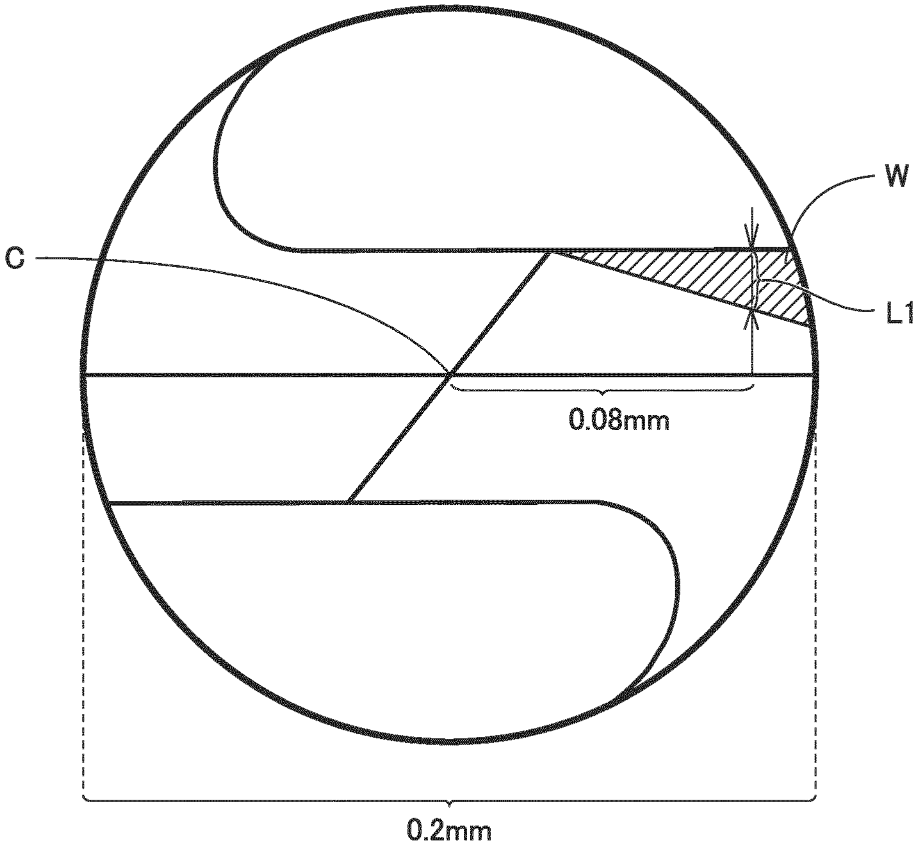


FIG.3



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2022/021423

A. CLASSIFICATION OF SUBJECT MATTER

C22C 29/08(2006.01)i; ***B22F 1/00***(2022.01)i
FI: C22C29/08; B22F1/00 Q

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)

C22C29/08; B22F1/00

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

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2022
Registered utility model specifications of Japan 1996-2022
Published registered utility model applications of Japan 1994-2022

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

JSTPlus/JST7580 (JDreamIII) &　キーワード：ＷＣ(0001)、バナジウム、偏析等

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	KAWAKAMI, Masaru. TERADA, Osamu. HAYASHI, Koji. Effect of Sintering Cooling Rate on V Segregation Amount at WC/Co Interface in VC-doped WC-Co Fine-Grained Hardmetal. 粉体および粉末冶金, vol. 51. no. 8. 2004, pp. 576-585, https://doi.org/10.2497/jjspm.51.576 p. 576, left column, lines 1-11, p. 578, right column to p. 584, right column, line 13, (Journal of the Japan Society of Powder and Powder Metallurgy)	1, 3-4
A	JP 2008-38242 A (FUJI DIES KK) 21 February 2008 (2008-02-21) claims, paragraphs [0012]-[0031]	1-4
A	JP 2011-208268 A (HITACHI TOOL ENGINEERING LTD) 20 October 2011 (2011-10-20) claims, paragraphs [0013]-[0036]	1-4
A	JP 2001-239411 A (MITSUBISHI MATERIALS CORP) 04 September 2001 (2001-09-04) claims, paragraphs [0012]-[0022], fig. 1	1-4

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

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Date of the actual completion of the international search **08 August 2022**	Date of mailing of the international search report **16 August 2022**
Name and mailing address of the ISA/JP **Japan Patent Office (ISA/JP)** **3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915** **Japan**	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2022/021423

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	JP 2004-162080 A (HITACHI TOOL ENGINEERING LTD) 10 June 2004 (2004-06-10) abstract, claims, paragraphs [0004]-[0015]	1-4

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2022/021423

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JP 2011-208268 A	20 October 2011	(Family: none)	
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- JP 2012052237 A **[0003]**
- JP 2012117100 A **[0003]**