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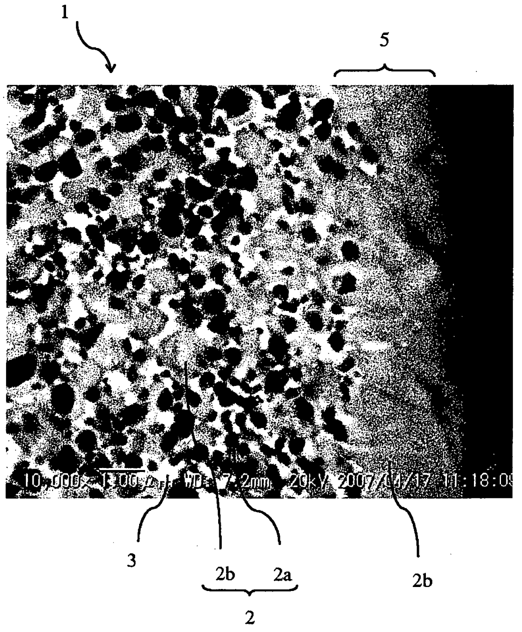
(54) TITANIUM-BASE CERMET, COATED CERMET, AND CUTTING TOOL

(57) There is provided a Ti-based cermet suitable for a cutting tool having high fracture resistance and wear resistance. The Ti-based cermet 1 is composed of at least one kind of element selected from Co and Ni, and one or more kinds of substances selected from carbides, nitrides, and carbonitrides of one or more kinds of metals selected from Group 4, Group 5, and Group 6 metals of the periodic table, each of which is composed mainly of Ti, and 0.1 to 0.5% by mass of Mn. In a scanning electron microscope (SEM) photograph of an arbitrary cross-section of the Ti-based cermet, a surface region is formed in which a hard phase 2 whose interior comprises a first hard phase 2a and a second hard phase 2b, and a binder phase 3 composed mainly of at least one kind of element selected from Co and Ni are observed, and the second hard phase 2b looks whiter than the first hard phase 2a, and the second hard phase 2b whose content percentage is not less than 90% by area is observed in a surface part.

Fig. 1



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Description

TECHNICAL FIELD

[0001] The present invention relates to a titanium (Ti)-based cermet, a coated cermet, and a cutting tool, particularly to a cutting tool whose cutting edge has enhanced wear resistance.

BACKGROUND ART

[0002] Sintered alloys such as cemented carbides composed mainly of WC, and Ti-based cermet composed mainly of Ti are currently widely used as members requiring wear resistance and sliding properties, as well as fracture resistance, such as cutting tools, wear-resistant members and sliding members. Developments of novel compositions for improving performance of these sintered alloys have been continued.

[0003] For example, patent document 1 discloses the technique of forming cemented carbide or a cermet by reaction sintering using microwaves, and describes that Mn or A1 is added in the proportion of 5% by mass or less into a metal binder phase such as Co.

[0004] Patent document 2 discloses the gradient composition sintered alloy made by adding 0.1 to 10% by mass of a specific metal element such as Mn, in addition to a hard phase composed mainly of carbides or nitrides of metals selected from Group 4, Group 5 and Group 6 metals of the periodic table, and mutual solid solutions of these, and 1 to 40% by mass of an iron-group metal. Ti-based cermets made by adding Mn are described in Samples No. 17 and No. 20 in Table 6. Table 8 indicates that the concentration of the Mn and the concentration of the binder phase in Sample No. 17 and No. 20 are increased in the interior of the cermet than the surface thereof.

Patent document 1: Japanese Unexamined Patent Publication No. 2000-503344
Patent document 2: Japanese Unexamined Patent Publication No. 2004-292905

DISCLOSURE OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0005] However, there is a limit to the improvements in the hardness and toughness of the cermet with the method in which Mn is added and then microwave sintered, as described in the patent document 1. Even in the gradient composition having the increased Mn concentration and the increased binder phase concentration in the interior of the sintered body, as described in the patent document 2, there is the problem that the effect in improving the hardness of the cermet surface remains insufficient, and the finish-machined surface of a work material becomes rough due to the welding of the work material onto the cutting edge, thus causing abnormal wear or fracture.

[0006] Therefore, the cutting tool of the present invention has been made to solve the above problems, and aims to enhance the wear resistance and welding resistance of the Ti-based cermet.

MEANS FOR SOLVING THE PROBLEMS

[0007] The Ti-based cermet of the invention is composed of at least one kind of element selected from Co and Ni; and one or more kinds of substances selected from carbides, nitrides, and carbonitrides of one or more kinds of metals selected from Group 4, Group 5 and Group 6 metals of the periodic table, each of which is composed mainly of Ti; and 0.1 to 0.5% by mass of Mn. In a scanning electron microscope (SEM) photograph of an arbitrary cross-section of the Ti-based cermet, a surface region is formed in which a hard phase whose interior comprises a first hard phase and a second hard phase, and a binder phase composed mainly of at least one kind of element selected from Co and Ni are observed. The second hard phase looks whiter than the first hard phase, and the second hard phase whose content percentage is not less than 90% by area is observed in a surface part.

[0008] The method of manufacturing the Ti-based cermet of the invention includes forming a mixed powder as a mixture of TiCN powder; at least one kind of powder selected from carbonate powder, nitride powder and carbonitride powder each containing one or more kinds of elements selected from W, Mo, Ta, V, Zr and Nb; at least one kind of powder selected from Co and Ni; and a total amount of 0.2 to 3.0% by mass in terms of Mn of a metal Mn powder or an Mn compound powder, followed by sintering under the following conditions: (a) increasing temperature under vacuum from room temperature to 1200°C; (b) increasing the temperature under vacuum at a temperature rising rate of 0.1 to 2°C/min from 1200°C to a sintering temperature T_1 of 1330 to 1380°C; (c) increasing the temperature at a temperature rising rate of 4 to 15°C/min from the sintering temperature T_1 to a sintering temperature T_2 of 1450 to 1600°C in an inert gas atmosphere of 30 to 2000 Pa; (d) retaining the sintering temperature T_2 in the inert gas atmosphere of 30 to 2000

Pa for 0.5 to 2 hours; and (e) decreasing the temperature.

[0009] The coated cermet of the invention is produced by using the above Ti-based cermet as a substrate, and coating a surface of the substrate with a coating layer. The content ratio of the binder phase in the surface region of the substrate is not more than 3% by mass, and the coating layer is formed by chemical vapor deposition.

[0010] The cutting tool of the invention is composed of the above Ti-based cermet or the above coated cermet, and a cutting edge is formed along a cross ridge part between a rake face and a flank face. In the residual stress measured by 2D method in the rake face which is exerted in a σ_{11} direction (a direction to connect between the center of the rake face and the center of the cutting edge nearmost the measured point), the second hard phase is preferably subjected to compressive stress of not less than 150 MPa ($\sigma_{11} \leq -150$ MPa).

EFFECT OF THE INVENTION

[0011] In accordance with the Ti-based cermet of the invention, 0.1 to 0.5% by mass of Mn is contained, and the surface region, in which the second hard phase whose content percentage is not less than 90% by area is observed, is formed in the surface of the cermet. This increases the toughness of the cermet as a whole, and enhances the hardness in the surface of the cermet, thereby improving wear resistance and also enhancing welding resistance.

PREFERRED EMBODIMENTS FOR CARRYING OUT THE INVENTION

<Ti-based Cermet>

[0012] An example of the Ti-based cermet of the invention will now be described based on the scanning electron microscope (SEM) photograph of the cross-section of the important parts including the surface region of the Ti-based cermet as shown in Fig. 1.

[0013] The Ti-based cermet (hereinafter referred to simply as "cermet") 1 in Fig. 1 is composed of at least one kind of element selected from Co and Ni; and one or more kinds of substances selected from carbides, nitrides, and carbonitrides of one or more kinds of metals selected from Group 4, Group 5, and Group 6 metals of the periodic table, each of which is composed mainly of Ti; and 0.1 to 0.5% by mass of Mn.

[0014] As shown in Fig. 1, in the scanning electron microscope (SEM) photograph of an arbitrary cross-section, a surface region 5 is formed in which a hard phase 2 whose interior comprises a black first hard phase 2a and a grayish white second hard phase 2b, and a binder phase 3 composed mainly of at least one kind of elements selected from Co and Ni are observed, and the second hard phase 2b whose content percentage is not less than 90% by area is observed in a surface part.

[0015] This increases the toughness of the cermet as a whole, and enhances the hardness in the surface of the cermet, thereby improving wear resistance and also enhancing welding resistance.

[0016] In the scanning electron microscope (SEM) photograph of the cross-sectional structure of the cermet 1 as shown in Fig. 1, the first hard phase 2a is observed as black particles, and the second hard phase 2b is observed as grayish white particles, or particles having a core-containing structure in which a grayish white peripheral part exists around a white core part. That is, the first hard phase 2a has a higher content ratio of a light element than the second hard phase 2b, and hence looks black. Although the first hard phase 2a corresponds to the black particles composed of TiCN, it may contain Co or Ni. Alternatively, other core-containing structure may be employed in which the grayish white second hard phase 2b exists as a peripheral part in the outer periphery of the first hard phase 2a. On the other hand, the binder phase 3 is observed as a white region, and Co and Ni constituting the binder phase 3 can be confirmed by energy dispersive spectroscopy (EMPA) annexed to the scanning electron microscope (SEM).

[0017] Unless not less than 0.1% by mass of Mn is contained in the cermet 1, the toughness of the cermet 1 is lowered. Conversely, if more than 0.5% by mass of Mn is contained in the cermet 1, the hardness of the cermet 1 is remarkably lowered. The suitable content of Mn is 0.2 to 0.5% by mass.

[0018] In the absence of the surface region 5 in the surface of the cermet 1, the hardness in the surface of the cermet 1 cannot be enhanced, thus leading to insufficient wear resistance of the cermet 1. If the percentage of presence of the second hard phase 2b in the surface region 5 is less than 90% by area, the wear resistance and welding resistance in the surface of the cermet 1 become insufficient. The suitable thickness of the surface region 5 is 0.8 to 3 μm. The preferable percentage of area Bus of the second hard phase 2b in the surface region 5 is 93 to 97% by area, in the interest of adhesion with respect to a coating layer 13.

[0019] Like the scanning electron microscope (SEM) photograph of the cross-section in the vicinity of the surface of the cermet 1 as shown in Fig. 1, the average particle diameter d_{1s} of the second hard phase 2b is preferably 0.5 to 3.0 μm, particularly 1.0 to 2.0 μm. The ratio (C_s/C_i) of the content ratio C_s of the binder phase 3 in the surface region 5 to the content ratio Ci of the binder phase 3 in the interior is preferably 0.01 to 0.1, with the view of enhancing the wear resistance in the surface of the cermet 1 and enhancing the welding resistance in the surface of the cermet 1.

[0020] When the cross-sectional structure in the interior of the cermet 1 is further observed, the average particle diameter of the second hard phase 2b is larger than the average particle diameter of the first hard phase 2a, preferably the ratio (b_i/a_i) of a_i and b_i is 2 to 8, where a_i is the average particle diameter of the first hard phase 2a in the interior, and b_i is the average particle diameter of the second hard phase 2b in the interior, in the point that the second hard phase 2b effectively contributes to thermal propagation thereby to improve the thermal conductivity of the cermet 1 and improve the thermal shock resistance of the cermet 1. The suitable ratio (b_i/a_i) of a_i and b_i is 3.5 to 7, with the view of maintaining the fracture resistance of the cermet 1.

[0021] In the present invention, the particle diameter of the hard phase 2 is measured according to the method of measuring the average particle diameter of cemented carbide as prescribed in CIS-019D-2005. Specifically, when the hard phase 2 has the core-containing structure, the region extending up to the outer edge of the peripheral part including the core part and the peripheral part is regarded as a single hard phase, and the particle diameter thereof is measured. When observing the cross-sectional structure in the interior of the cermet 1 of the invention, the region extending in a depth of not less than 1000 μm from the surface of the cermet 1 is observed.

[0022] Further in the cross-sectional structure of the interior of the cermet 1, the average area of the second hard phase 2b is larger than the average area of the first hard phase 2a, preferably the ratio (B_i/A_i) of A_1 and B_1 is 1.5 to 5, where A_i is the average area occupied by the first hard phase 2a, and B_i is the average area occupied by the second hard phase 2b, with respect to the entirety of the hard phase 2 in the interior, in the point that the second hard phase 2b more effectively contributes to thermal propagation thereby to improve the thermal conductivity of the cermet 1 and improve the thermal shock resistance of the cermet 1.

[0023] In the interior of the cermet 1, the total content ratio of nitrides or carbonitrides of Group 4, Group 5 and Group 6 metals of the periodic table, each of which constitutes the hard phase 2 and is composed mainly of Ti, is preferably 70 to 96% by mass, particularly 85 to 96% by mass, with the view of improving wear resistance. On the other hand, the content ratio of the binder phase 3 is preferably 4 to 30% by mass, particularly 4 to 15% by mass. This achieves excellent balance between the hardness and toughness of the cermet 1. The binder phase 3 preferably contains not less than 65% by mass of Co with respect to the total amount of iron-family metals with the view of enhancing the thermal shock resistance of a cutting tool. In order to maintain satisfactory sintering properties of the cermet 1 so that the baked surface of the cermet 1 becomes a smooth surface, it is preferable to contain 5 to 50% by mass of Ni, particularly 10 to 35% by mass of Ni with respect to the total amount of iron-family metals.

<Coated Cermet>

[0024] A coating layer can be formed on the surface of the above cermet 1. An example thereof will now be described based on Fig. 2, wherein (a) is a scanning electron microscope (SEM) photograph of important parts in a cross-section including a surface region of a coated cermet 10, and (b) is a scanning electron microscope (SEM) photograph of important parts of a ground surface before forming the coating layer of the coated cermet 10.

[0025] The coated cermet 10 of Fig. 2(a) has the structure that the surface of a substrate 12 composed of the above cermet 1 is coated with the coating layer 13.

[0026] In the present invention, as shown in Fig. 2, the coating layer 13 formed by chemical vapor deposition (CVD) method can also be formed. That is, conventional coated cermets generally employ physical vapor deposition (PVD) method carried out with the substrate heated to approximately 500°C. This is because if used CVD method that is carried out with a substrate heated to high temperatures of 700°C and above, the coating layer may cause partially abnormal particle growth and change into a needle shape due to Ni or Fe used as the binder phase of the Ti-based cermet, and the strength of the coating layer may be lowered, causing chipping or fracture. However, the cermet 1 as the substrate 12 of the invention is adapted to reduce the existence of Ni in the surface of the substrate 12, and hence the coating layer 13 does not cause any abnormal particle growth. It is also capable of preventing the hardness deterioration of the coating layer 13 due to a large amount of diffusion of the binder phase 3 into the coating layer 13. Consequently, the coating layer 13 has high hardness and high strength characteristics. Additionally, when the surface region 5 and the coating layer 13 are similar to each other in structural components and crystal structure, there is a slight difference in thermal expansion coefficients between the two, and hence separation due to thermal stress does not occur in the interface between the substrate 12 and the coating layer 13.

[0027] The surface region 5, in which the content ratio of the binder phase 3 is not more than 3% by mass, exists in the region extending 0.1 to 5 μm from the surface of the substrate 12, as shown in Fig. 2(b). The coating layer 13 is formed by CVD method. This enhances the adhesion of the coating layer 13 with respect to the substrate 12 without deteriorating the hardness of the coating layer 13, thereby enhancing the fracture resistance in the surface of the coated cermet 10.

[0028] That is, in the absence of the surface region 5 in the surface of the substrate 12, Ni exists in the surface of the substrate 12, and the coating layer 13 to be formed in the surface causes abnormal particle growth, thus deteriorating both hardness and toughness.

[0029] In the substrate 12, the thickness of the surface region 5 is preferably 0.8. to 3 μm, with the view of maintaining the shock resistance of the coated cermet 10. The percentage of area B_s of the second hard phase 2b in the surface region 5 is preferably 70 to 100% by area to the entirety of the hard phase 2, with the view of enhancing the adhesion with respect to the coating layer 13.

[0030] Preferably, a binder phase-rich region 8 exists in a region extending 1 to 10 μm from immediately below the surface region 5, at 1.1 to 2.0 in terms of the ratio (A/B) of A to B, where A is the content ratio of the binder phase 3, and B is the content ratio of the binder phase 3 in the interior of the substrate 12. Thus, even if the coating layer 13 is subjected to shock, the binder phase-rich region 8 relaxes the shock and reduces chipping or fracture in the coating layer 13.

[0031] In the coating layer 13, if the content of the binder phase 3 in the region extending up to 0.1 to 5 μm from the surface of the substrate 12 is larger than 3% by mass, the ingredients of the binder phase 3 diffuse into the coating layer 13, thus deteriorating the hardness of the coating layer 13.

[0032] In order to maintain satisfactory sintering properties for achieving a smooth burned surface of the substrate 12, and also enhance the thermal shock resistance of the substrate 12, it is preferable for the binder phase 3 that the content ratio of Ni in the interior of the substrate is 0.1 to 0.5 in terms of Ni/(Ni+Co) ratio.

[0033] When the content ratio of N in the surface region 5 is larger than that in the interior of the sintered body, the surface region 5 has excellent toughness characteristic. Therefore, when the coating layer 13 having a higher hardness than the surface region 5 is formed immediately above the surface region 5, the high-hard and brittle coating layer 13 causes neither chipping nor separation even under shock exerted during cutting or the like, thereby achieving satisfactory wear resistance and fracture resistance. The distribution of the content ratio of N can be compared by X-ray photoelectron spectroscopic analysis in a depth direction from the surface of the cermet 1 toward the interior thereof.

[0034] On the other hand, the coating layer 13 is composed of a columnar crystal extending vertically with respect to the surface of the substrate 12. The coating layer 13 preferably includes a columnar crystal coating layer in which the columnar crystal has an average crystal width of 0.1 to 1 μm, in the interest of high fracture resistance and excellent wear resistance of the coating layer 13. As the columnar crystal coating layer, a TiCN layer is suitable in the interest of easy manufacture of the above-mentioned structure. In this case, the coating layer is capable of producing the above effect irrespective of whether the coating layer is a single columnar crystal coating layer, or a multilayer structure made up of one or more columnar crystal coating layers and other layer. The TiCN layer composed of the TiCN columnar crystal included in the coating layer 13 preferably has its strongest peak in (422) plane in an X-ray diffraction measurement, in the interest of high wear resistance of the coating layer 13 and excellent adhesion with respect to the substrate 12.

<Cutting Tool>

[0035] An example of the cutting tool of the invention will now be described with reference to Figs. 3(a) and 3(b), which are schematic perspective views thereof.

[0036] Referring to Fig. 3, the cutting tool 20 of the invention is constructed to have a rake face 21 on the main surface thereof, a flank face 22 on the side surface thereof, and cutting edges 23 (23a to 23d) along a cross ridge line between the rake face 21 and the flank face 22. As shown in Fig. 3, a recessed part 25 including a breaker 24 is formed in the rake face 21. A screw hole 26 for mounting the cutting tool 20 onto a holder (not shown) is formed at the center of the rake face 21.

[0037] The method of machining a work material includes the following three steps. In the first step, the cutting tool 20 made of the cermet 1 or the coated cermet 10 and provided with the cutting edges 23 is prepared. In the next step, the cutting edge 23 of the cutting tool 20 is brought into contact with the work material. In the last step, the work material is subjected to cutting by using the cutting tool 20.

[0038] According to the present invention, in the residual stress exerted in the σ_{11} direction (a direction to connect between the center of the rake face 21 and the cutting edge 23a nearmost the measured point) measured by 2D method in a portion P other than the recessed part of the rake face 21, the second hard phase 2b is preferably subjected to compressive stress of not less than 150 MPa ($\sigma_{11} \leq$ -150 MPa). This improves the fracture resistance in the cutting edges 23.

<Manufacturing Method>

[0039] An example of the method of manufacturing the above cermet will be described below.

[0040] Firstly, a mixed powder is prepared by mixing TiCN powder having an average particle diameter of 0.1 to 2 μm, preferably 0.2 to 1.2 μm, one kind of powder selected from carbonate powder, nitride powder and carbonitride powder of the above-mentioned other metal having an average particle diameter of 0.1 to 2 μm, Co powder or Ni powder, metal Mn powder or Mn compound powder having an average particle diameter of 0.5 to 10 μm, wherein a total amount in terms of Mn is 0.2 to 3.0% by mass.

[0041] Subsequently, a binder is added to the mixed powder and formed into a predetermined shape by any known forming method such as press forming, extrusion forming, injection forming, or the like.

[0042] According to the present invention, the cermet having the predetermined structure described above can be manufactured by performing sintering steps under the following conditions. The sintering conditions are as follows: (a) Temperature is increased under vacuum from room temperature to 1200°C; (b) The temperature is increased under vacuum at a temperature rising rate r_1 of 0.1 to 2°C/min from 1200°C to a sintering temperature T_1 of 1330 to 1380 °C; (c) The temperature is increased in an inert gas atmosphere of 30 to 2000 Pa at a temperature rising rate r_2 of 4 to 15°C/min from the sintering temperature T_1 to a sintering temperature T_2 of 1450 to 1600°C; (d) The sintering temperature T_2 is retained for 0.5 to 2 hours in an inert gas atmosphere of 30 to 2000 Pa; and (e) The temperature is decreased.

[0043] That is, among the above sintering conditions, if the sintering atmosphere in the step (b) is an inert gas atmosphere instead of under vacuum, the volatilization of Mn is reduced, and the content of Mn in the cermet after sintering cannot be controlled, and the above surface region is not formed. The surface region is also not formed if the temperature rising rate in the step (b) is higher than 2°C/min. If the atmosphere in the step (c) is under vacuum or an inert gas atmosphere of less than 30 Pa, more than 0.5% by mass of Mn remains in the interior of the cermet 1, and the surface region is not formed. Conversely, if it is a high inert gas atmosphere exceeding 2000 Pa, the surface region is not formed. If the sintering temperature T_2 in the step (d) is below 1450°C, the surface region is not formed. If the sintering temperature T_2 exceeds 1600°C, the surface region of not less than 5 μm is formed, resulting in poor toughness.

[0044] The surface region 5 having high hardness and high welding resistance is achieved by performing the temperature decreasing step (e) in a vacuum atmosphere. If the temperature decreasing step (e) is performed in an inert gas atmosphere, the content ratio of N in the surface region 5 becomes larger than that in the interior of the cermet 1, thereby forming the surface region having high toughness.

[0045] Preferably, a coating layer is coated onto the surface of the substrate composed of the above cermet at 800 to 1100°C by CVD method. Specific film forming conditions are as follows. Firstly, a titanium nitride (TiN) layer is formed by preparing in a CVD furnace a mixed gas composed of, for example, 0.1 to 10% by volume of titanium chloride ($TiCl_4$), 10 to 60% by volume of nitrogen (N_2) gas, and the rest that is hydrogen (H_2) gas, and by admitting the mixed gas into a reaction chamber, followed by controlling the inside of the chamber in the range of 800 to 1100°C and 50 to 85 kPa.

[0046] Subsequently, with so-called MT-CVD method, a titanium carbonitride (TiCN) layer is formed on the titanium nitride (TiN) layer by admitting a mixed gas prepared so that titanium chloride ($TiCl_4$) is 0.5 to 5.0% by volume, acetonitrile (CH_3CN) is 0.3 to 1.5% by volume, nitrogen (N_2) is 10 to 40% by volume, and the rest is hydrogen (H_2), at a reaction temperature of 800 to 900°C.

[0047] With regard to the above film forming conditions, by adjusting the proportion of acetonitrile gas in the gas to the above-mentioned range, the structure of the titanium carbonitride (TiCN) in the titanium carbonitride (TiCN) layer can be surely grown within the above-mentioned range. The titanium carbonitride (TiCN) layer composed of the columnar crystal having an average crystal width of 0.1 to 1 μm can be formed by setting the film forming temperature to 800°C to 850°C, and by controlling, in the titanium carbonitride (TiCN) crystal growth step in the early period of forming the titanium carbonitride (TiCN) layer, the proportion V_A of the acetonitrile (CH_3CN) gas in the range of 0.3 to 1.5% by volume, and also controlling the ratio (V_A/V_H) of the proportion V_H of the hydrogen gas (H_2) as carrier gas and the proportion V_A of the acetonitrile (CH_3CN) gas at a low concentration of not more than 0.03. The TiCN layer has a film thickness of not less than 2 μm, and (422) peak becomes the strongest in an XRD diffraction.

[0048] Next, a titanium oxycarbonitride (TiCNO) layer is formed by preparing and admitting a mixed gas composed of 0.1 to 3% by volume of titanium chloride ($TiCl_4$) gas, 0.1 to 10% by volume of methane (CH_4) gas, 0.01 to 5% by volume of carbon dioxide (CO_2) gas, 0.1 to 60% by volume of nitrogen (N_2) gas, and the rest that is hydrogen (H_2) gas, into the reaction chamber, and by controlling the conditions within the chamber in the range of 800 to 1100°C and 5 to 30 kPa.

[0049] Subsequently, an aluminum oxide (Al_2O_3) layer is formed by using a mixed gas composed of 3 to 20% by volume of aluminum chloride ($AlCl_3$) gas, 0.5 to 3.5% by volume of hydrogen chloride (HCl) gas, 0.01 to 5% by volume of carbon dioxide (CO_2) gas, 0 to 0.01% by volume of hydrogen sulfide (H_2S) gas, and the rest that is hydrogen (H_2) gas, and by controlling in the range of 900 to 1100°C and 5 to 10 kPa.

[0050] Further, a titanium nitride (TiN) layer is formed by preparing and admitting a mixed gas composed of 0.1 to 10% by volume of titanium chloride ($TiCl_4$) gas, 10 to 60% by volume of nitrogen (N_2) gas, and the rest that is hydrogen (H_2) gas, into the reaction chamber, and by controlling the conditions within the chamber in the range of 800 to 1100°C and 50 to 85 kPa.

[0051] Thereafter, as required, a predetermined portion of the surface of the formed coating layer 8 is subjected to mechanical grinding by means of brush, elastic grinding, or blast method. This grinding adjusts the residual stress generated during film formations and remaining in the coating layer.

Example 1

[0052] A mixed powder was prepared by blending, in the proportions shown in Table 1, TiCN powder having an average particle diameter of 0.6 μm, WC powder having an average particle diameter of 1.1 μm, TiN powder having an average particle diameter of 1.5 μm, TaC powder having an average particle diameter of 2 μm, MoC powder having an average particle diameter of 1.5 μm, NbC powder having an average particle diameter of 1.5 μm, ZrC powder having an average particle diameter of 1.8 μm, VC powder having an average particle diameter of 1.0 μm, Ni powder having an average particle diameter of 2.4 μm, Co powder having an average particle diameter of 1.9 μm, and $MnCO_3$ powder having an average particle diameter of 5.0 μm. These average particle diameters (d_{50} values) were measured by microtrack method. The mixed powder was then wet mixed while adding isopropyl alcohol (IPA), and then 3% by mass of paraffin was added and mixed together by using a ball mill and carbide balls made of stainless steel. Subsequently, this mixed powder was press-formed into a throw-away tip tool shape of CNMG120408 at an applied pressure of 200 MPa. Thereafter, throw-away tips made of the cermets of Samples Nos. 1 to 11, respectively, were obtained through the following steps: (a) Temperature was increased under vacuum from room temperature to 1200°C at 10°C/min; (b) The temperature was increased in the sintering atmosphere and at the temperature rising rate r_1 (°C/min) shown in Table 2, from 1200°C to the sintering temperature T_1 shown in Table 2; (c) The temperature was increased in the sintering atmosphere shown in Table 2, at the temperature rising rate r_2 (°C/min) shown in Table 2, from the sintering temperature T_1 to the sintering temperature T_2 shown in Table 2; (d) Sintering was carried out in the sintering atmosphere at the sintering temperature and the sintering time shown in Table 2; and (e) The temperature was decreased in the sintering atmosphere shown in Table 2.

[0053]

[Table 1]

Sample No.	Material composition (% by mass)										
	TiCN	WC	TiN	TaC	MoC	NbC	ZrC	VC	Ni	Co	$MnCO_3$
1	51.5	17	10	3	0	10	1	1	2	3	1.5
2	63.5	10	5	1	1	8	2	1	2	6	0.5
3	57	15	8	0	1	5	2	1	3	6	2
4	58	12	7	0	2	8	1	2	2	7	1
5	53.5	10	12	3	0	6	1	1	4	7	2.5
6	54.5	15	3	0	0	9	1	2	2	12	1.5
7	58	13	7	2	0	10	1	1	2	5	1
* 8	49	14.	12	3	0	8	2	2	4	6	-
* 9	49	14	12	3	0	8	2	2	4	6	1
* 10	48	17	10	1	1	9	2	1	3	7	1
* 11	48	17	10	1	1	9	2	1	3	7	1
The samples marked "*" are out of the scope of the present invention.											

[0054]

[Table 2]

Sample No.	Sintering condition												
	Step (b)				Step (c)				Step (d)			Step (e)	
	Temperature rising rate r_1 (°C/min)	Sintering temperature T_1 (°C)	Sintering atmosphere		Temperature rising rate r_2 (°C/min)	Sintering temperature T_2 (°C)	Sintering atmosphere		Sintering time (hr)	Sintering atmosphere		Sintering atmosphere	
1	1.5	1350	Vacuum		5	1550	N_2	500Pa	1.5	N_2	500Pa	Vacuum	
2	0.7	1350	Vacuum		10	1525	Ar	80Pa	1	Ar	80Pa	Vacuum	
3	0.5	1350	Vacuum		7	1600	N_2	800Pa	0.5	N_2	800Pa	Vacuum	
4	0.7	1360	Vacuum		8	1575	N_2	1000Pa	1	N_2	1000Pa	Vacuum	
5	1	1380	Vacuum		4	1450	N_2	300Pa	2	N_2	300Pa	Vacuum	
6	0.3	1330	Vacuum		15	1550	N_2	700Pa	1	N_2	700Pa	Vacuum	
7	0.7	1340	Vacuum		10	1575	He	1000Pa	1	He	1000Pa	Vacuum	
* 8	1	1350	Vacuum		10	1550	He	1200Pa	1	He	1200Pa	He	1200Pa
* 9	5	1350	Vacuum		5	1550	He	1200Pa	1	He	1200Pa	He	1200Pa
* 10	1.0	1350	N_2	800Pa	2	1650	N_2	800Pa	1	N_2	800Pa	N_2	800Pa
* 11	1.0	1350	N_2	800Pa	8	1550	Vacuum		1	Vacuum		Vacuum	

The samples marked "*" are out of the scope of the present invention.

[0055] Each of the obtained cermets was subjected to a scanning electron microscope (SEM) observation, and an image analysis was performed using commercially available image analysis software onto arbitrary five points in the surface and the interior thereof, respectively, at a region of 8 μm × 8 μm in a photograph taken at 10000 magnification. Then, it was confirmed whether or not the surface region existed by observing the existing states of the hard phase and the binder phase, and the structure states in the interior and the surface. In all the individual samples, it was confirmed that the binder phase was composed mainly of Co and Ni, based on the energy dispersive spectroscopic analysis (EMPA) annexed to the scanning electron microscope (SEM). Subsequently, the average particle diameter of the hard phase in the above region of each sample was measured, and the ratio thereof was calculated. The results were shown in Table 3. Further, the content ratio of the metal Mn ingredient in the interior of the cermet substrate of each sample was determined by ICP analysis. The results were shown in Table 3.

[0056] Next, these cutting tools made of the obtained cermets were subjected to a cutting test under the following cutting conditions. The results were also shown in Table 3.

Work material: SCM435
Cutting speed: 200m/min
Feed rate: 0.20mm/rev
Depth of cut: 1.0mm
Cutting state: Wet (using water-soluble cutting fluid)
Evaluation method: Time (min) elapsed until the amount of wear reached 0.2mm

[0057]

[Table 3]

Sample No.	Interior							Mn ratio (% by mass)	Surface region					Cutting performances$^{9)}$
	$d_i^{1)}$	$a_i^{2)}$	$b_i^{3)}$	b_i/a_i	$A_i^{4)}$	$B_i^{5)}$	B_i/A_i		$\mathbf{b}_s^{6)}$	b_s/b_i	$B_s^{7)}$	$C_s/c_i^{8)}$	Thickness (μm)	
1	0.44	0.40	1.26	3.15	26	74	2.85	0.25	1.85	1.47	93	0.05	2.1	53
2	0.50	0.26	0.90	3.46	38	62	1.63	0.12	1.20	1.33	92	0.08	0.8	46
3	0.45	0.37	1.38	3.73	25	75	3.00	0.30	2.13	1.54	91	0.10	3.9	55
4	0.50	0.21	1.05	5.00	37	63	1.70	0.20	1.58	1.50	94	0.07	2.8	57
5	0.49	0.18	0.95	5.28	40	60	1.50	0.40	1.27	1.34	96	0.02	2.5	50
6	0.45	0.35	1.26	3.60	27	73	2.70	0.15	1.95	1.55	91	0.08	4.5	52
7	0.40	0.49	1.75	3.57	18	82	4.56	0.12	2.11	1.21	93	0.03	1.5	48
* 8	0.41	0.28	1.21	4.32	27	73	2.70	<0.05	Absence					32
* 9	0.57	0.28	1.21	4.32	35	65	1.86	1.00	Absence					35
* 10	0.34	0.37	1.42	3.84	19	81	4.26	0.07	2.21	1.56	91	0.1	8	39
* 11	033	0.35	1.25	3.57	21	79	3.76	0.13	Absence					37

The samples marked "*" are out of the scope of the present invention.

1) d_i: Average particle diameter (μ m) of whole hard phase in interior

2) $a_{i:}$ Average particle diameter (μ m) of first hard phase in interior

3) b_i: Average particle diameter (μ m) of second hard phase in interior

4) A_i: Percentage of area (% by area) of first hard phase in interior

5) B_i: Percentage of area (% by area) of second hard phase in interior

6) b_s: Average particle diameter (μ m) of second hard phase in surface region

7) B_s: Percentage of area (% by area) of second hard phase in surface region

8) c_s/c_i: Content ratio c_s of binder phase in surface region / content ratio c_i of binder phase in interior

9) Cutting performance: Time (min) elapsed until amount of wear reached 0.2mm

[0058] The followings will be noted from Tables 1 to 3. That is, in Sample No. 8 without Mn addition, the surface region was not formed and wear occurred early. In Sample No. 10 in which the sintering temperature was higher than 1600°C and the content of Mn is less than 0.1% by mass, the wear resistance thereof was deteriorated due to the occurrence of chipping. Also in Sample No. 9 in which the content of Mn exceeded 0.5% by mass, the wear resistance thereof was poor. In Sample No. 11 in which the surface region was not formed due to the mismatched sintering conditions, the wear resistance thereof was lowered.

[0059] On the contrary, all Samples Nos. 1 to 7, which were the cermets having the structures within the scope of the invention, exhibited excellent wear resistance and satisfactory wear resistance, thereby achieving a long tool life.

[0060] The residual stress in the rake face of each of Samples Nos. 4, 7 and 11 was measured by 2D method (an X-ray diffraction apparatus manufactured by Bruker AXS Inc., D8 DISCOVER with GADDS Super Speed, Ray source: CuK_α, Collimater diameter: 0.3mmΦ, Measured diffraction line: TiN (422) plane). In the residual stress exerted in the σ_{11} direction (the direction to connect between the center of the rake face and the center of the cutting edge nearmost the measured point), the individual second hard phases were subjected to compressive stress of 250 MPa (σ_{11} = -250 MPa), 150 MPa (σ_{11} = -150 MPa), 100 MPa (σ_{11} = -100 MPa), respectively.

Example 2

[0061] Cermets were manufactured under the same manufacturing conditions as in the throw-away tips made of the cermets of Samples Nos. 1 to 11 in Example 1, except for changing the atmosphere in the temperature decreasing step (e) into the atmospheres shown in Table 4. Similarly to Example 1, the structures of the obtained cermets were observed and the results thereof were shown in Table 5. In each of these cermets, the content of N in the interior of the cermet and that in the surface region thereof were compared by performing the X-ray photoelectron spectroscopic analysis in a depth direction from the surface of the sintered body to the interior thereof. Then, the ratio of the content of N in the surface region to the content of N in the interior was shown in Table 6. Thereafter, throw-away tips of Samples Nos. 12 to 18 were obtained by forming the coating layers of Table 6 on these cermets, respectively. The obtained throw-away tips made of the cermets were subjected to a cutting test under the same cutting conditions as Example 1. The results were also shown in Table 6.

[0062]

[Table 4]

Sample No.	Material composition No. for substrates	Sintering condition										
		Step (b)			Step (c)				Step (d)			Step (e)	
		Temperature rising rate r_1 (°C/min)	Sintering temperature T_1 (°C)	Sintering atmosphere	Temperature rising rate r_2 (°C/min)	Sintering temperature T_2 (°C)	Sintering atmosphere		Sintering time (hr)	Sintering atmosphere		Sintering atmosphere	
12	1	1.5	1350	Vacuum	5	1550	N_2	500Pa	1	N_2	500Pa	N_2	100Pa
13	2	0.7	1350	Vacuum	10	1525	Ar	80Pa	0.5	Ar	80Pa	N_2	500Pa
14	3	0.5	1350	Vacuum	7	1600	N_2	800Pa	1.5	N_2	800Pa	N_2	1000Pa
15	4	0.7	1360	Vacuum	8	1575	N_2	1000Pa	1	N_2	1000Pa	N_2	1500Pa
16	5	1	1380	Vacuum	4	1450	N_2	600Pa	2	N_2	600Pa	N_2	900Pa
17	6	0.3	1330	Vacuum	15	1550	N_2	700Pa	1	N_2	700Pa	N_2	1200Pa
18	7	0.7	1340	Vacuum	10	1575	He	1000Pa	1.5	He	1000Pa	N_2	1000Pa

The samples marked "*" are out of the scope of the present invention.

[0063]

[Table 5]

Sample No.	Interior							Mn ratio (% by mass)	Surface region				
	d_i 1)	a_i 2)	b_i 3)	b_i/a_i	A_i 4)	B_i 5)	B_i/A_i		b_s 6)	b_s/b_i	B_s 7)	c_s/c_i 8)	Thickness (μm)
12	0.45	0.35	1.25	3.57	27	73	2.70	0.24	1.75	1.40	94	0.05	2.1
13	0.52	0.26	0.85	3.27	40	60	1.50	0.15	1.30	1.53	92	0.03	1.2
14	0.43	0.41	1.45	3.54	23	77	3.35	0.25	2.10	1.45	93	0.07	4.2
15	0.50	0.21	1.05	5.00	37	63	1.70	0.20	1.78	1.70	95	0.06	3
16	0.43	0.20	0.95	4.75	35	65	1.86	0.38	1.57	1.65	94	0.04	2.8
17	0.45	0.35	1.26	3.60	27	73	2.70	0.17	1.95	1.55	91	0.08	4.5
18	0.39	0.51	1.80	3.53	17	83	4.88	0.14	2.35	1.31	92	0.02	2

The samples marked "*" are out of the scope of the present invention.

1) d_i: Average particle diameter (μm) of whole hard phase in interior

2) a_i: Average particle diameter (μm) of first hard phase in interior

3) b_i: Average particle diameter (μm) of second hard phase in interior

4) A_i: Percentage of area (% by area) of first hard phase in interior

5) B_i: Percentage of area (% by area) of second hard phase in interior

6) b_s: Average particle diameter (μm) of second hard phase in surface region

7) B_s: Percentage of area (% by area) of second hard phase in surface region

8) c_s/c_i: Content ratio c_s of binder phase in surface region / content ratio c_i of binder phase in interior

[0064]

[Table 6]

Sample No.	Content percentage of N in surface region of cermets (Surface region / interior)	Coating layer Film thicknesses (μm) are shown in parentheses.	Cutting performance[1)]
12	1.9	$TiCN(3.5)+Al_2O_3(4)+TiN(0.5)$	80
13	2	$TiCN(4)Al_2O_3(2)$	71
14	2.3	$TiAlN(3)$	65
15	1.8	$TiCN(3.5)+Al_2O_3(4)+TiN(0.5)$	85
16	1.7	$TiCN(4)+Al_2O_3(2)$	74
17	1.5	$Al_2O_3(4)$	68
18	1.2	$TiCN(3)$	63
The samples marked "*" are out of the scope of the present invention. 1) Cutting performance: Time (min) elapsed until amount of wear reached 0.2mm			

[0065] It will be noted from Tables 4 to 6 that in each of Samples Nos. 12 to 18, the surface region having a higher content of N than that in the interior thereof was formed, and the throw-away tip with the coating layer formed thereon exhibited excellent wear resistance and had satisfactory wear resistance.

Example 3

[0066] The cermet substrates of Samples Nos. 19 to 31 were obtained under the same conditions as Example 1, except for the material compositions in Table 7 and the sintering conditions in Table 8.

[0067]

[Table 7]

Sample No.	Material composition [1)]											
	TiCN	WC	TiN	TaC	MoC	NbC	ZrC	VC	Ni	Co	Ni/ (Co+Ni)	$MnCO_3$
19	55	18	5	0	0	10	1	1	2	8	0.20	3
20	50	15	10	2	0	12	1	1	2	7	0.22	3
21	63	18	3	1	1	3	1	1	4	5	0.44	2
22	50	18	11	0	0	9	0	2	2	8	0.20	4
23	48	18	10	4	1	8	1	2	1	7	0.13	2
24	48	15	13	0	4	10	1	1	3	5	0.38	3
25	60	20	10	1	0	1	1	1	4	2	0.67	4
* 26	51	10	18	5	0	0	2	2	4	8	0.33	3
* 27	50	5	17	3	1	12	3	0	4	5	0.44	3
* 28	52	12	9	1	5	10	1	0	7	3	0.70	0
* 29	49	10	14	0	5	10	1	1	3	7	0.30	3
* 30	44	18	12	0	5	10	1	0	6	4	0.60	3
* 31	52	10	10	1	5	10	1	1	0	10	0.00	0
The samples marked "*" are out of the scope of the present invention. 1) Material composition: The unit of materials other than $MnCO_3$ is "% by mass." MnCO3 is represented in "parts by mass" to 100 parts by mass of the total amount of the other materials.												

[0068]

[Table 8]

Sample No.	Step (b)		Step (c)(d)				Step (e)
	Temperature T_1 (°C)	Temperature rising rate a (°C/min)	Step (c) gas pressure (Pa)	Temperature T_2 (°C)	Step (d) gas pressure (Pa)	Time (hr)	Gas pressure (MPa)
19	1350	1	800	1525	800	1	0.2
20	1380	0.6	800	1575	500	1	0.1
21	1330	0.1	500	1525	1000	1	0.1
22	1350	0.1	2000	1575	1000	0.5	0.1
23	1330	2	500	1575	800	2	0.1
24	1300	0.6	500	1575	500	1.5	0.3
25	1400	1	9×10^5	1600	9×10^6,	1.5	0.6
* 26	1450	3	800	1550	800	1	0.1
* 27	1150	1	800	1550	500	1	0.1
* 28	1350	1	500	1550	500	1	0.1
* 29	1350	1	500	1575	Vacuum	1	0.1
* 30	1350	1	3000	1525	800	1	Vacuum
* 31	1350	1	3000	1525	800	1	0.1
The samples marked "*" are out of the scope of the present invention.							

[0069] Each of the obtained cermets was subjected to a scanning electron microscope (SEM) observation, and an image analysis was performed using commercially available image analysis software onto arbitrary five points in the surface and the interior thereof, respectively, at a region of 8 μm × 8 μm in a photograph taken at 10000 magnification. Then, it was confirmed whether or not the surface region existed and the binder phase-rich region existed by observing the existing states of the hard phase, and the structure states in the interior and the surface. Subsequently, the average particle diameter of each of these regions was measured, and the ratio thereof was calculated. Further, the content ratio of the Mn ingredient in the cermet substrate of each sample was determined by ICP analysis. The results were shown in Table 9.

[0070]

[Table 9]

Sample No.	Interior structure			Binder phase-rich region			Surface region		
	Average particle diameter of hard phase (μm)	Mn ratio (% by mass)	Content ratio B of binder phase (% by mass)	Content ratio A of binder phase (% by mass)	A/B	Thickness (μm)	Ratio of binder phase (% by mass)	Thickness (μm)	Nb ratio (% by mass)
19	0.7	0.2	10	18	1.5	2.5	1.5	2.1	15
20	0.8	0.1	9	9.9	1.3	4.7	1.2	1.5	21.6
21	0.6	0.2	9	9.9	1.2	3.9	1.7	2.3	7.2
22	1	0.3	10	13	1.7	2.3	0.9	1.7	16.2
23	0.9	0.4	8	12	1.8	1.8	2.5	5	17.6

(continued)

Sample No.	Interior structure			Binder phase-rich region			Surface region		
	Average particle diameter of hard phase (μm)	Mn ratio (% by mass)	Content ratio B of binder phase (% by mass)	Content ratio A of binder phase (% by mass)	A/B	Thickness (μm)	Ratio of binder phase (% by mass)	Thickness (μm)	Nb ratio (% by mass)
24	1.5	0.4	8	16	2	2.1	2.8	2.7	21
25	2	0.5	6	6.6	2.1	3.5	3	1.5	2.8
* 26	0.8	0.1	12	35	2.9	7.9	-		
* 27	0.8	1.5	9	9.9	1.1	3.6	5.4	8.3	21.6
* 28	0.8	<0.05	10	-			-		
* 29	0.8	0.1	10	-			-		
* 30	0.8	2.2	10	2.3	0.2	1.2	-		
* 31	0.8	<0.05	10	-			-		
The samples marked "*" are out of the scope of the present invention.									

[0071] Next, the coating layers having the structures shown in Table 11 were formed on the above cermet substrates by CVD method under the film forming conditions shown in Table 10, respectively. As shown in Table 11, in the scanning electron microscopic observations of Samples Nos. 19 to 22 and 24 in which a TiCN layer having a film thickness of not less than 2 μm was formed, it was confirmed that these samples were composed of the columnar crystal having an average crystal width of 0.1 to 1 μm extending vertically with respect to the surface of the cermet substrate, as shown in the photograph of Sample No. 24 in Figs. 2(a) and 2(b). In each of their respective X-ray diffraction measurements, the peak of (422) plane was the strongest.

[0072]

[Table 10]

Coating layer	Mixed gas composition (% by volume)	Mixed gas flow rate (ℓ/min)	Film forming temperature (°C)	Pressure (kPa)
TiN	$TiCl_4$:0.5, N_2:33, H_2:The rest	80	900	16
TiCN	$TiCl_4$:1.0, N_2:30, CH_3CN:0.4, H_2:The rest	70	820	9
TiCNO	$TiCl_4$:0.7, CH_4:4, N_2:5. CO_2:1.0, H_2:The rest	35	1010	10
TiNO	$TiCl_4$:0.7, CH_4:4, N_2:5, CO_2:1.1, H_2:The rest	35	1010	10
TiC	$TiCl_4$:1.0, CH4:6, H2: The rest	65	1000	10
Al_2O_3	$AlCl_3$:15, HCl:2, CO_2:4, H_2S:0.01, H_2:The rest	35	1005	6
ZrN	$ZrCl_4$:2.0, N_2:20, H_2:The rest	70	1010	16

[0073] Next, the obtained cutting tools made of the cermets were subjected to cutting tests under the following cutting conditions. The results were shown in Table 11.

<Wear resistance test>

[0074] Work material: SCM435
Cutting speed: 200m/min
Feed rate: 0.20mm/rev
Depth of cut: 1.0mm
Cutting state: Wet (using water-soluble cutting fluid)
Evaluation method: Time (min) elapsed until the amount of wear reached 0.2mm

<Fracture resistance test>

[0075] Work material: SCM440
Cutting speed: 100m/min
Feed rate: 0.05mm/rev (increased by 0.05mm/rev at 10 seconds intervals, a maximum of 0.50mm/rev)
[0076] Depth of cut: 1.5mm
Cutting state: Dry
Evaluation method: Time measured until the cutting edge was fractured (a maximum of 100 seconds)
[0077]

[Table 11]

Sample No.	Structure of coating layers Film thicknesses (μ m) are shown in parentheses.						Wear resistance (Cutting time) (min)	Fracture resistance (Cutting time) (sec)
	First layer	Second layer	Third layer	Fourth layer	Fifth layer	Nb diffusion[1)]		
19	TiCN (4)	TiCNO (0.5)	Al_2O_3 (2)	TiN (0.5)	-	Yes	88	100
20	TiCN (4)	TiCNO (0.2)	Al_2O_3 (2)	-	-	Yes	82	94
21	TiCN (5)	TiCNO (0.5)	Al_2O_3 (2)	ZrN (1)	-	Yes	76	88
22	TiN (0.5)	TiCN (4)	TiCNO (0.5)	Al_2O_3 (3)	TiN (0.5)	Yes	69	85
23	TiC (3)	Al_2O_3 (2)	TiN (0.5)	-	-	Yes	68	84
24	TiCN (3.5)	-	-	-	-	Yes	71	79
25	Al_2O_3 (4)	-	-	-	-	No	73	73
* 26	TiCN (4)	-	-	-	-	No	38	66
* 27	TiCN (4)	TiCNO (0.5)	Al_2O_3 (3)	TiN (0.5)	-	Yes	46	43
* 28	TiCN (4)	TiCNO (0.5)	Al_2O_3 (3)	TiN (0.5)	-	No	36	48
* 29	TiCN (4)	TiCNO (0.5)	Al_2O_3 (2)	TiN (0.5)	-	No	43	36
* 30	TiN (1)	TiCN (4)	TiCNO (0.5)	Al_2O_3 (2)	TiN (0.5)	Yes	48	65

(continued)

Sample No.	Structure of coating layers Film thicknesses (μ m) are shown in parentheses.						Wear resistance (Cutting time) (min)	Fracture resistance (Cutting time) (sec)
	First layer	Second layer	Third layer	Fourth layer	Fifth layer	Nb diffusion[1)]		
* 31	TiN (0.5)	TiCN (5)	TiCNO (0.1)	Al_2O_3 (2)	TiN (0.5)	No	44	25

The samples marked "*" are out of the scope of the present invention.
1) Nb diffusion: "yews" indicates that the ratio of a content ratio of Nb in the region extending 0.5 μm from the surface of the cermet substrate to a content ratio of Nb in the surface of the cermet substrate, in the coating layer, is 10% or more. "No." indicates that the ratio of a content ratio of Nb in the region extending 0.5 μm from the surface of the cermet substrate to a content ratio of Nb in the surface of the cermet substrate, in the coating layer, is less than 10%.

[0078] The followings will be noted from Tables 7 to 11. That is, in Sample No. 31 in which neither Ni nor Mn was added and the content of Mn was less than 0.1% by mass, a large amount of the binder phase was dispersed into the coating layer to thereby deteriorate the hardness of the coating layer, and the sintering properties of the cermet substrate was poor, thus being susceptible to chipping. In Sample No. 28 in which Mn was not added and the content of Mn was less than 0.1% by mass, the surface region was not formed and needle-shaped abnormal particles were grown in the coating layer, thus causing severe wear and fracture. In Sample No. 26 in which the sintering temperature T_1 in the step (b) was higher than 1380°C and the temperature rising rate r_1 was higher than 2°C/min in the temperature range from 1200°C to 1300-1380°C, and in Sample No. 29 in which the sintering atmosphere in the step (e) was under vacuum, and in Sample No. 30 in which the sintering atmosphere in the step (e) was under vacuum, the surface region was not formed, and needle-shaped abnormal particles were grown in the coating layer, thus deteriorating wear resistance and fracture resistance. In Sample No. 27 in which the sintering temperature T_1 in the step (b) was below 1300°C, exceeding 3% by mass of Mn remained in the cermet substrate after sintering, thus deteriorating wear resistance.

[0079] On the contrary, all Samples Nos. 19 to 25, which were the cermets having the structures within the scope of the invention, exhibited excellent wear resistance and satisfactory wear resistance, thereby achieving a long tool life.

Explanation of marks

BRIEF DESCRIPTION OF DRAWINGS

[0080]

Fig. 1 is a scanning electron microscope (SEM) photograph showing an example of the Ti-based cermet of the invention, specifically a cross-section of important parts including a surface region thereof;
Figs. 2(a) and 2(b) are scanning electron microscope (SEM) photographs showing an example of the coated cermet of the invention, specifically cross-sections of important parts including a surface region thereof, respectively; and
Figs. 3(a) and 3(b) are schematic diagrams of an example of the cutting tool of the invention.

EXPLANATION OF REFERENCE

[0081]

1	Cermet(Ti-based cermet)
2	Hard phase
	2a First hard phase
	2b Second hard phase
3	Binder phase
5	Surface region
8	Binder phase-rich region
10	Coated cermet
12	Substrate
13	Coating layer
20	Cutting tool

21	Rake face
22	Flank face
23	Cutting edge
24	Breaker
25	Recessed part
26	Screw hole

Claims

1. A Ti-based cermet comprising at least one kind of element selected from Co and Ni; one or more kinds of substances selected from carbides, nitrides, and carbonitrides of one or more kinds of metals selected from Group 4, Group 5, and Group 6 metals of the periodic table, each of which is composed mainly of Ti; and 0.1 to 0.5% by mass of Mn, wherein in a scanning electron microscope (SEM) photograph of an arbitrary cross-section of the Ti-based cermet, a surface region is formed in which a hard phase whose interior comprises a first hard phase and a second hard phase, and a binder phase composed mainly of at least one kind of element selected from Co and Ni are observed, and the second hard phase looks whiter than the first hard phase, and the second hard phase whose content percentage is not less than 90% by area is observed in a surface part.

2. The Ti-based cermet according to claim 1 wherein the surface region has a thickness of 0.5 to 5 μm.

3. The Ti-based cermet according to claim 1 or 2 wherein Nb is dissolved in the second hard phase to form a solid solution, and the proportion of Nb dissolved in the second hard phase to form solid solution in the surface region is larger than the proportion of Nb dissolved in the second hard phase to form solid solution in the interior.

4. A method of manufacturing a Ti-based cermet comprising the steps of:

   forming a mixed powder as a mixture of TiCN powder; at least one kind of powder selected from carbonate powder, nitride powder and carbonitride powder each containing one or more kinds of elements selected from W, Mo, Ta, V, Zr and Nb; at least one kind of powder selected from Co and Ni; and a total amount of 0.2 to 3.0% by mass in terms of Mn of a metal Mn powder or an Mn compound powder; and
   sintering the mixed powder under the following conditions:

   (a) temperature is increased under vacuum from room temperature to 1200°C;
   (b) the temperature is increased under vacuum at a temperature rising rate of 0.1 to 2°C/min from 1200°C to a sintering temperature T_1 of 1330°C to 1380°C;
   (c) the temperature is increased at a temperature rising rate of 4 to 15°C/min from the sintering temperature T_1 to a sintering temperature T_2 of 1450 to 1600°C in an inert gas atmosphere of 30 to 2000 Pa;
   (d) the sintering temperature T_2 is retained in the inert gas atmosphere of 30 to 2000 Pa for 0.5 to 2 hours; and
   (e) the temperature is decreased.

5. A coated cermet comprising a substrate comprising the Ti-based cermet according to any one of claims 1 to 3, and a coating layer coating a surface of the substrate, wherein the content ratio of the binder phase in the surface region of the substrate is not more than 3% by mass, and the coating layer is formed by chemical vapor deposition.

6. The coated cermet according to claim 5 wherein a binder phase-rich region exists in a region extending 1 to 10 μm from immediately below the surface region, at 1.1 to 2.0 in terms of a ratio (A/B) of a content ratio A of the binder phase to a content ratio B of the binder phase in the interior of the substrate.

7. The coated cermet according to claim 5 or 6 wherein the content ratio of Ni in the interior of the substrate is 0.1 to 0.5 in terms of Ni/(Ni+Co) ratio.

8. The coated cermet according to any one of claims 5 to 7 wherein the content percentage of N in the surface region is larger than that of the interior of a sintered body.

9. The coated cermet according to any one of claims 5 to 8 wherein the coating layer is composed of a columnar crystal extending vertically with respect to the surface of the substrate, and the columnar crystal has an average crystal width of 0.1 to 1 μm.

10. The coated cermet according to claim 9 wherein the columnar crystal is TiCN.

11. The coated cermet according to claim 10 wherein the coating layer has its strongest peak in (422) plane in an X-ray diffraction measurement.

12. A cutting tool comprising the Ti-based cermet according to any one of claims 1 to 3, or the coated cermet according to any one of claims 5 to 11, wherein a cutting edge is formed along a cross ridge part between a rake face and a flank face.

13. The cutting tool according to claim 12 wherein in the residual stress exerted in a σ_{11} direction (namely, a direction to connect between the center of the rake face and the center of the cutting edge nearmost a measured point) measured in the rake face by 2D method, the second hard phase is subjected to compressive stress of not less than 150 MPa ($\sigma_{11} \leq -150$ MPa).

Fig. 1

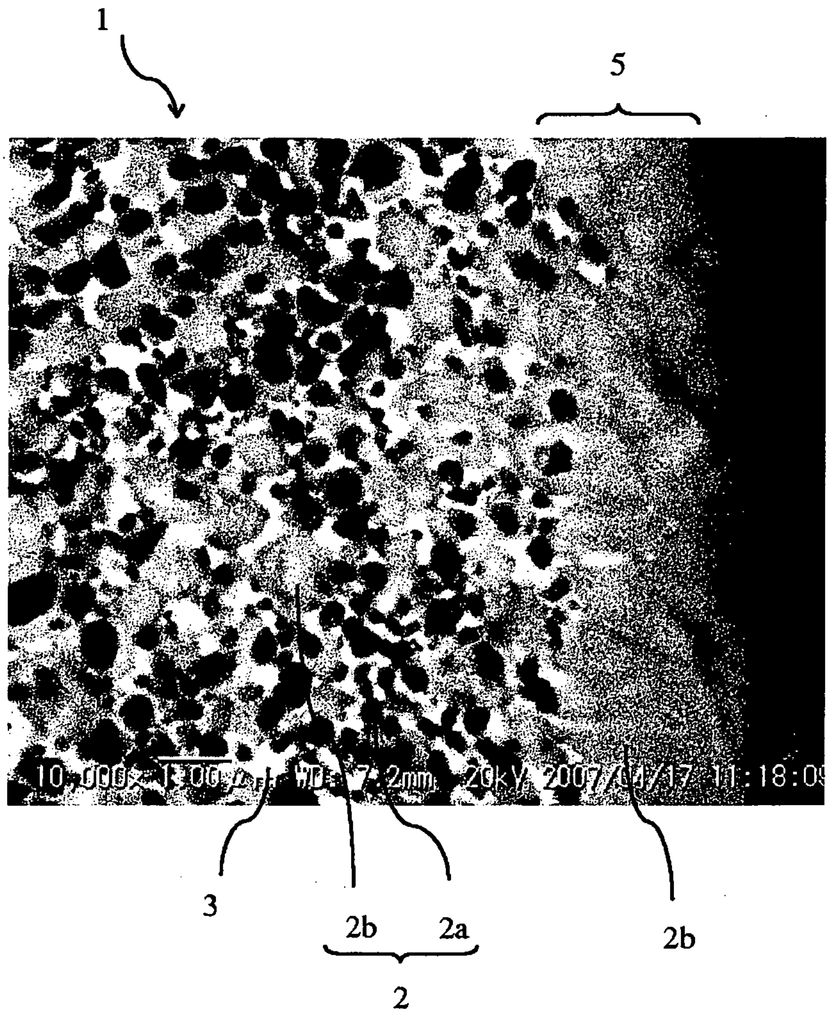
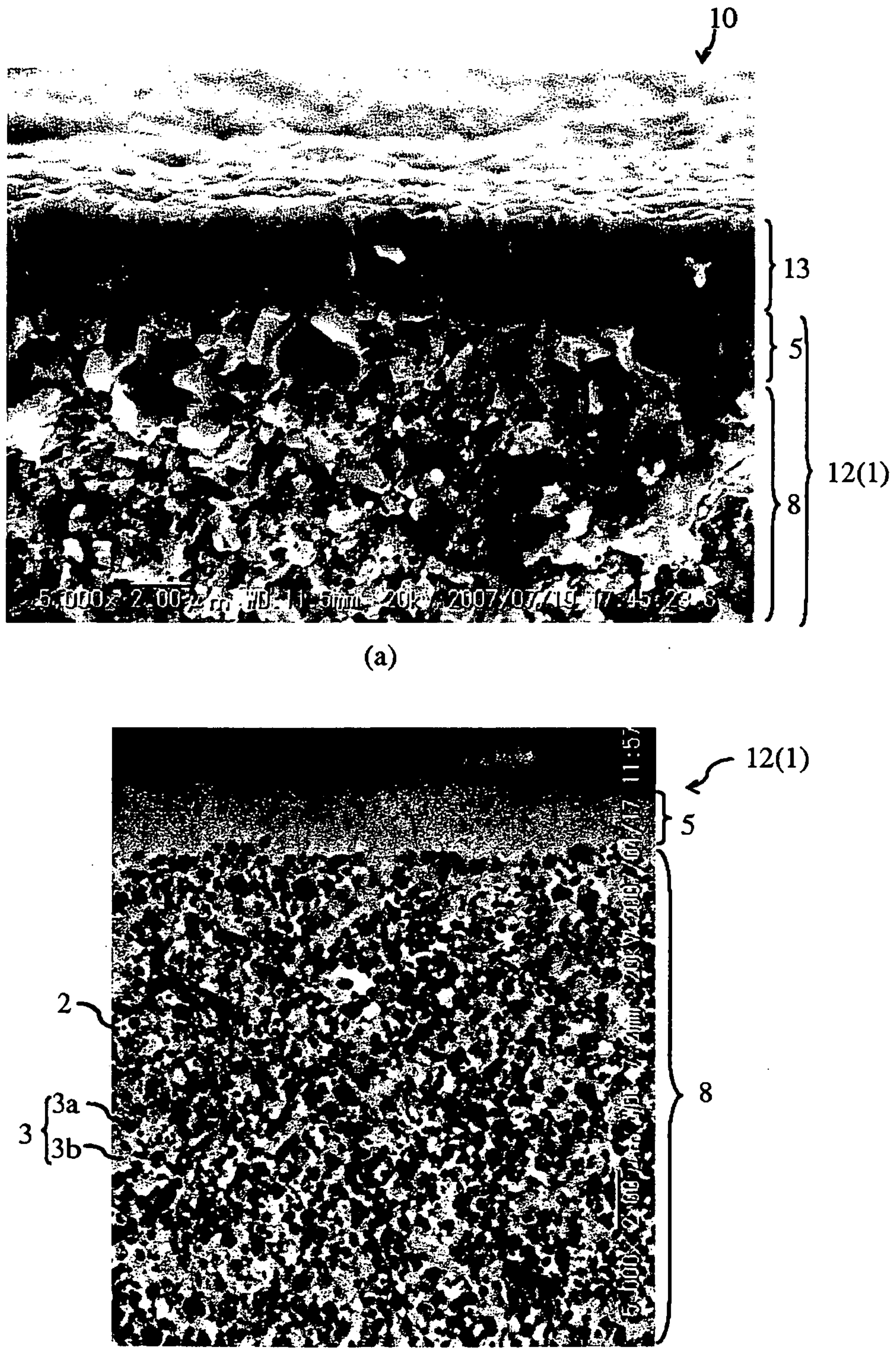


Fig. 2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3
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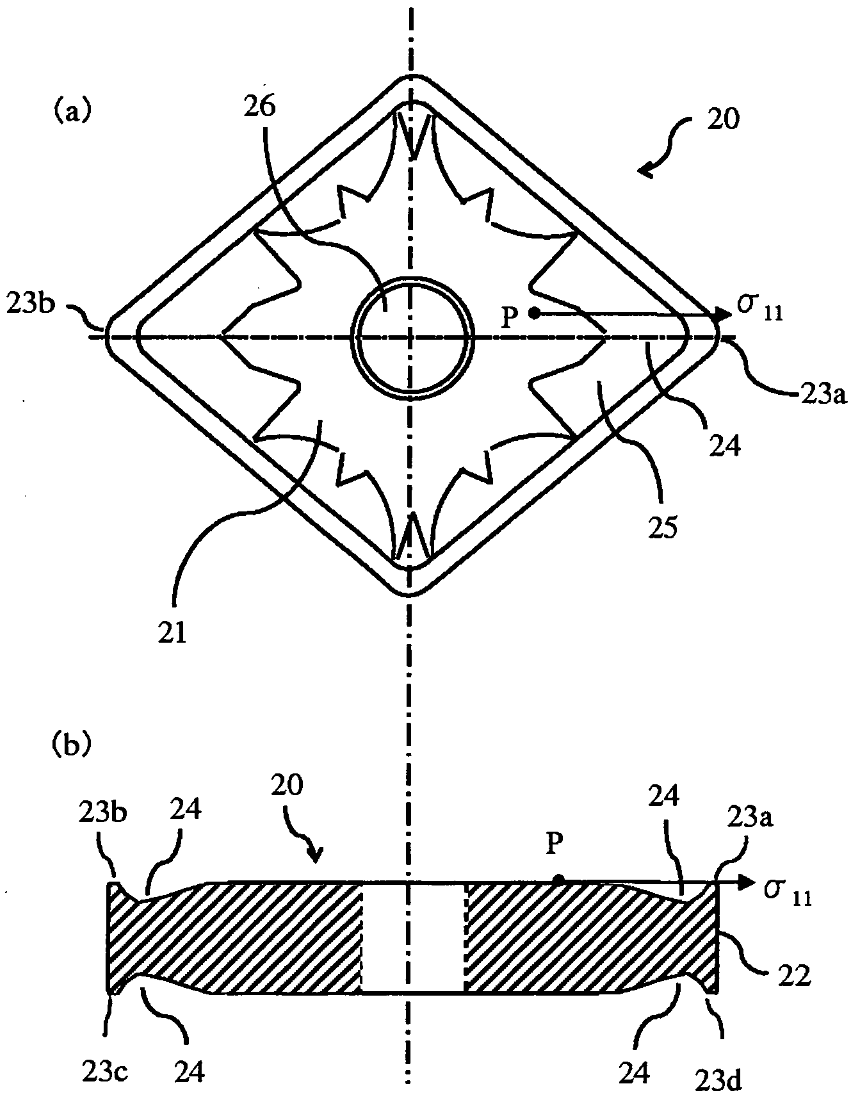
(a)

(b)

Fig. 3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INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER
C22C29/04(2006.01)i, *B23B27/14*(2006.01)i, *C22C1/05*(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)
C22C29/04, B23B27/14, C22C1/05

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2008
Kokai Jitsuyo Shinan Koho	1971-2008	Toroku Jitsuyo Shinan Koho	1994-2008

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2004-115881 A (Kyocera Corp.), 15 April, 2004 (15.04.04), Claims (Family: none)	1-13
A	JP 2004-292905 A (Tungaloy Corp.), 21 October, 2004 (21.10.04), Claims & US 2004/187639 A1 & EP 1462534 A1 & KR 2004/085050 A & CN 1534100 A	1-13

☐ 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
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"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 17 October, 2008 (17.10.08)	Date of mailing of the international search report 28 October, 2008 (28.10.08)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

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REFERENCES CITED IN THE DESCRIPTION

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