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(54) **CERAMIC STEEL MATERIAL AND PREPARATION METHOD THEREOF**

(57) This invention discloses Cerasteel materials, which are composed of ceramic phase and metal phase. Thereinto, said ceramic phase is the boride consisted of Fe, Co, Ni, and one or more metal elements of IVB, VB and VIB of the fourth, fifth and sixth periodic metals. And said metal phase is an alloy composed of Mo and one or more metal elements of Fe, Co, Ni. Cerasteel materials in this invention have properties of high hardness, excellent wear resistance, corrosion resistance and high temperature resistance and can be used for producing

knives, cutting tools, and all kinds of wear resistant, corrosion resistant, high temperature resistant materials and all kinds of structural components composed of them. Moreover, Cerasteel materials have good weldability with steel and other metal materials, which can meet people's daily needs and application in industry, agriculture, machining and medical apparatus and instruments and so on. Moreover, the invention provides a method for preparing Cerasteel materials.

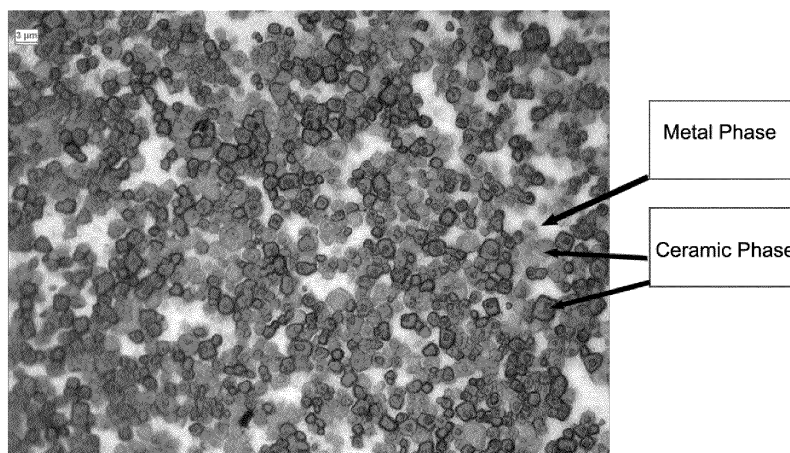


Fig. 1

Description**TECHNICAL FIELD**

5 **[0001]** The invention belongs to the technical field of composites, in particular to Cerasteel materials and their preparation method.

BACKGROUND TECHNIQUE

10 **[0002]** Under the development of social technology and the increase of people's living standards, people's demands for daily supplies are increasing. People put higher request forward aspects such as appearance of products, which is not limited to their qualities and functionalities. Knives, cutting tools, as one of the necessary equipment of kitchen, are perennially in the water, water vapor, salt, acid and other environment, this is a big challenge for corrosion resistance of materials; meanwhile, knives, cutting tools are used for cutting or cutting food, hence, the demand for strength and
15 hardness of materials are increasing.

[0003] At present, the common materials used for manufacturing knives and cutting tools on the market are usually those materials such as stainless steel, ceramics and so on. Stainless steel is well accepted due to its properties such as high toughness and corrosion resistance since the advent of it in 1913, which lays a foundation of the development of modern industry and improvement of technology. Therefore, it plays an important role in the production of knives and cutting tools. However, the blade is easy to be blunt and not sharp during use due to its low hardness, poor wear resistance, stainless steel usually needs frequent grinding. Zirconium ceramic knife and cutting tool is one of the new knives and cutting tools developed in recent years, which have properties of high hardness, wear resistance and high temperature resistance. But zirconium ceramic knife and cutting tool have some fatal flaws: High brittleness, poor impact resistance, thin edge of knife and cutting tool, easily chipping during use, which affects the useful life of zirconium ceramic
20 knives and cutting tools. Therefore, in order to better meet people's daily needs, the researchers are keen to research a kind of composite materials which have properties of high hardness, excellent wear resistance, corrosion resistance and high temperature resistance.

DISCLOSURE OF THE INVENTION

30 **[0004]** Given the above cited technical problems to be solved, this invention intends to provide Cerasteel materials and their preparation method, which have properties of high hardness, excellent wear resistance, corrosion resistance, high temperature resistance and good toughness.

[0005] Means for solving the technical problems by the invention is aimed to provide Cerasteel materials. Said Cerasteel materials in this invention are composed of ceramic phase and metal phase. Thereinto, said ceramic phase is the boride consisted of Fe, Co, Ni, and one or more metal elements of IVB, VB and VIB of the fourth, fifth and sixth periodic metals. And said metal phase is an alloy composed of Mo and one or more metal elements of Fe, Co, Ni.

[0006] Preferably, said Cerasteel materials further contain a few additives, said additives are C and one or more elements of V, Cr, Mn, Cu.

40 **[0007]** Preferably, of the said Cerasteel materials, the weight percentage of each chemical component is: B 5~10 wt.%, Ti 0~50 wt.%, V 0~50 wt.%, Cr 0~50 wt.%, Zr 0~50 wt.%, Nb 0~50 wt.%, Mo 20~60 wt.%, Fe 10~40 wt.%, Ni 0~15 wt.%, Co 0~20 wt.%. Element contents in said additives are no more than 5 wt.%.

[0008] Means for solving the other technical problems by the invention is to provide a preparation method of Cerasteel materials, characterized in that: Said preparation method of Cerasteel materials comprises the following steps of:

45 After exactly weighing raw materials powder (ceramic phase and metal phase raw materials), mixtures were processed by wet-ball-milled by one of cemented carbide ball, stainless steel ball and corundum ball, with milling media for 20~100h, 2~6 wt.% of forming agent were added, the ball-to-powder mass ratio was (3-10):1;
Mixed slurries were dried, sieved through 200 to 400 mesh, and then compressed under a pressure of 100~400 MPa.

50 **[0009]** Said blanks were prepared after sintering at 1200~1500°C. Then, the Cerasteel materials were obtained.

[0010] Preferably, the said milling medium described above is one of the following materials: anhydrous ethanol, gasoline, acetone, hexane, carbon tetrachloride and benzene.

[0011] Preferably, the said forming agent described above is one of the following materials: paraffin composed of n-alkanes, zinc stearate, polyvinyl butyral anhydrous ethanol solution and rubber oil solution.

55 **[0012]** Preferably, the said drying method described above is one of the following methods: vacuum drying, vapor drying and spray drying.

[0013] Preferably, the said sintering described above is one of the vacuum sintering, hot isostatic pressing sintering,

activated sintering and spark plasma sintering.

[0014] In comparison with prior art, the Cerasteel materials in this invention are composed of ceramic phase and metal phase. Thereinto, ceramic phase is the boride consisted of Fe, Co, Ni, and one or more metal elements of IVB, VB and VIB of the fourth, fifth and sixth periodic metals. Metal phase is an alloy composed of Mo and one or more metal elements of Fe, Co, Ni. Cerasteel materials in this invention have properties of high hardness, excellent wear resistance, corrosion resistance and high temperature resistance and can be used for producing knives, cutting tools, and all kinds of wear resistant, corrosion resistant, high temperature resistant materials and all kinds of structural components composed of them. Moreover, Cerasteel materials have good weldability with steel and other metal materials, which can meet people's daily needs and application in industry, agriculture, machining and medical apparatus and instruments and so on. Moreover, the invention provides a method for preparing Cerasteel materials.

[0015] The raw material reacted during sintering, boride and multiple boride were produced by in situ, which provides high hardness for Cerasteel materials using the above preparation method.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] Fig. 1 shows the microstructure of Cerasteel materials observed under a scanning electron microscope.

SPECIFIC EMBODIMENTS OF THE INVENTION

[0017] The present invention is further described with specific embodiments and tables as below, which will further clarify the aims, technical concept and advantages of this invention: It should be understood that the specific embodiment described above should only be used to explain the present invention, and not to limit it.

[0018] Thereinto, ceramic phase of the Cerasteel materials is the boride consisted of Fe, Co, Ni, and one or more metal elements of IVB, VB and VIB of the fourth, fifth and sixth periodic metals. Metal phase is an alloy composed of Mo and one or more metal elements of Fe, Co, Ni.

[0019] The Cerasteel materials further contain a few additives, the additives are C and one or more elements of V, Cr, Mn, Cu.

[0020] Alloy powders, compound powders and elementary powders can be selected as raw materials to prepare Cerasteel. After exactly weighing raw materials powder (ceramic phase and metal phase raw materials), mixtures were processed by wet-ball-milled by one of cemented carbide ball, stainless steel ball and corundum ball, with milling media for 20~100h, 2~6 wt.% of forming agent were added, the ball-to-powder mass ratio was (3-10):1;

Mixed slurries were dried, sieved through 200 to 400 mesh, and then compressed under a pressure of 100~400 MPa.

[0021] Blanks were prepared after sintering at 1200~1500°C. Then, the Cerasteel materials were obtained.

[0022] The raw material reacted during sintering, boride and multiple boride were produced by in situ, which provides high hardness for Cerasteel materials using the above preparation method. The ceramic phase and metal phase precipitated in situ have high bonding strength, so the Cerasteel had high toughness. Therefore, the Cerasteel has excellent mechanical properties.

[0023] The hardness of the Cerasteel in the present invention can be up to 50~75 HRC, comparable to zirconium ceramic, while flexural strength can be up to 1200~2300 MPa, much higher than zirconium ceramic. In comparison with the widely used stainless steel, Cerasteel has higher hardness, more than doubled wear resistance. Moreover, Cerasteel has excellent chemical stability. Therefore, Cerasteel is suitable for preparing knives, cutting tools, and all kinds of wear resistant, corrosion resistant, high temperature resistant materials and all kinds of structural components composed of them, which are supposed to be used perennially in the water, water vapor, salt, acid, alkali and other work environment. Moreover, Cerasteel has good weldability with steel, hence, it is possible to prepare Cerasteel knives, cutting tools and all kinds of wear resistant, corrosion resistant, high temperature resistant materials and all kinds of structural components composed of them at low costs and easier to achieve large-scale promotion with only a few Cerasteel welding to the stainless steel.

[0024] Cerasteel materials of this invention have properties of high hardness, excellent wear resistance, corrosion resistance and high temperature resistance and can be used for producing knives, cutting tools, and all kinds of wear resistant, corrosion resistant, high temperature resistant materials and all kinds of structural components composed of them. Moreover, Cerasteel materials have good weldability with steel and other metal materials, which can meet people's daily needs, and are suitable for application in industry, agriculture, machining and medical apparatus and instruments and so on.

[0025] Cerasteel materials in this invention are composed of ceramic phase and metal phase. Thereinto, ceramic phase is the boride consisted of Fe, Co, Ni, and one or more metal elements of IVB, VB and VIB of the fourth, fifth and sixth periodic metals. Metal phase is an alloy composed of Mo and one or more metal elements of Fe, Co, Ni.

[0026] Alloy powders, compound powders and elementary powders can be selected as raw materials to prepare Cerasteel. After exactly weighing raw materials powder, mixtures were processed by ball milling, drying, sieving, pressing

and sintering. Then, Cerasteel materials were obtained.

[0027] Knives and cutting tools made of Cerasteel materials have the advantages of stainless steel knives and cutting tools and zirconium ceramic knives and cutting tools without their shortcomings. Therefore, Cerasteel knives and cutting tools can be used to replace existing stainless steel knives and cutting tools and zirconium ceramic knives and cutting tools, which are not only durable, but also cost-effective and easy to realize promotion in application on a large scale.

[0028] The specific embodiments and tables described below will further clarify the said technical concept of this invention:

Example 1: A preparation method of Cerasteel materials: 20 wt.% of NiB, 40 wt.% of Mo, 5 wt.% of Cr, 10 wt.% of Ni, 1 wt.% of C and Fe powder (the balance), and 2.5 wt.% of paraffin were wet-milled in a ball milling machine for 100h. The cemented carbide ball-to-powder: (NiB, Mo, Cr, Ni, C and Fe powder) mass ratio was 8:1, anhydrous ethanol were added as milling media. The slurry mixtures were vacuum dried for 7h at the temperature of 70°C, sieved through 325 mesh, and then compressed. Finally, Cerasteel materials were obtained after vacuum sintering at 1220°C for 15h.

Example 2: A preparation method of Cerasteel materials: 20 wt.% of FeB, 60 wt.% of Mo, 5 wt.% of Cr, 10 wt.% of Ni, 1 wt.% of C and Fe powder (the balance), and 2.2 wt.% of paraffin were wet-milled in a ball milling machine for 85h. The cemented carbide ball-to-powder: (FeB, Mo, Cr, Ni, C and Fe powder) mass ratio was 6:1, acetone were added as milling media. The slurry mixtures were vacuum dried for 6h at the temperature of 80°C, sieved through 325 mesh, and then compressed. Finally, Cerasteel materials were obtained after vacuum sintering at 1250°C for 14h.

Example 3: A preparation method of Cerasteel materials: 20 wt.% of CoB, 40 wt.% of W, 20 wt.% of Co, 10 wt.% of Ni, 1 wt.% of C and Fe powder (the balance), and 2 wt.% of rubber oil solution were wet-milled in a ball milling machine for 65h. The stainless steel ball-to-powder: (CoB, W, Co, Ni, C and Fe powder) mass ratio was 5:1, hexane were added as milling media. The slurry mixtures were vacuum dried for 10h at the temperature of 60°C, sieved through 300 mesh, and then compressed. Finally, Cerasteel materials were obtained after hot isostatic pressing sintering at 1280°C for 12h.

Example 4: A preparation method of Cerasteel materials: 50 wt.% of TiB₂, 20 wt.% of Mo, 5 wt.% of Cr, 15 wt.% of Ni, 1 wt.% of C and Fe powder (the balance), and 2.5 wt.% of rubber oil solution were wet-milled in a ball milling machine for 80h. The stainless steel ball-to-powder: (TiB₂, Mo, Cr, Ni, C and Fe powder) mass ratio was 3:1, carbon tetrachloride were added as milling media. The slurry mixtures were spray dried for 8h at the temperature of 90°C, sieved through 200 mesh, and then compressed. Finally, Cerasteel materials were obtained after hot isostatic pressing sintering at 1300°C for 12h.

Example 5: A preparation method of Cerasteel materials: 50 wt.% of ZrB₂, 20 wt.% of Mo, 5 wt.% of Cr, 15 wt.% of Ni, 1 wt.% of C and Fe powder (the balance), and 3 wt.% of zinc stearate were wet-milled in a ball milling machine for 90h. The corundum ball-to-powder: (ZrB₂, Mo, Cr, Ni, C, and Fe powder) mass ratio was 5:1, benzene were added as milling media. The slurry mixtures were spray dried for 5h at the temperature of 70°C, sieved through 400 mesh, and then compressed. Finally, Cerasteel materials were obtained after spark plasma sintering at 1280°C for 2h.

Example 6: A preparation method of Cerasteel materials: 50 wt.% of NbB₂, 20 wt.% of Mo, 5 wt.% of Cr, 15 wt.% of Ni, 1 wt.% of C and Fe powder (the balance), and 3 wt.% of polyvinyl butyral anhydrous ethanol solution were wet-milled in a ball milling machine for 75h. The corundum ball-to-powder: (NbB₂, Mo, Cr, Ni, C and Fe powder) mass ratio was 5:1, gasoline were added as milling media. The slurry mixtures were vapor dried for 8h at the temperature of 90°C, sieved through 400 mesh, and then compressed. Finally, Cerasteel materials were obtained after activated sintering at 1250°C for 15h.

Example 7: A preparation method of Cerasteel materials: 25 wt.% of FeB, 35 wt.% of Mo, 10 wt.% of Cr, 5 wt.% of Ni, 0.6 wt.% of C, 2 wt.% of V, 5 wt.% of Cu and Fe powder (the balance), and 3 wt.% of paraffin were wet-milled in a ball milling machine for 60h. The corundum ball-to-powder: (FeB, Mo, Cr, Ni, C, V, Cu and Fe powder) mass ratio was 6:1, gasoline were added as milling media. The slurry mixtures were vacuum dried for 8h at the temperature of 90°C, sieved through 400 mesh, and then compressed. Finally, Cerasteel materials were obtained after activated sintering at 1300°C for 15h.

Table 1: Hardness and Flexural Strength of Cerasteel Materials

Example	Hardness (HRC)	Flexural Strength (MPa)
1	65	2017
2	68	2278
3	67	1882
4	72	1635
5	75	1340
6	71	1390

(continued)

Example	Hardness (HRC)	Flexural Strength (MPa)
7	70	1720

[0029] The above mentioned description applies solely to the ideal embodiment as offered by preparation methods of Cerasteel materials, and should not serve to restrict its application. Any amendments, equivalent substitutions and improvements that are implemented in the scope of spirit and principles of Cerasteel materials will be protected by this invention document.

Claims

1. Cerasteel materials which **characterized in that**: Said Cerasteel materials composed of ceramic phase and metal phase. Said ceramic phase is the boride consisted of Fe, Co, Ni, and one or more metal elements of IVB, VB and VIB of the fourth, fifth and sixth periodic metals. And said metal phase is an alloy composed of Mo and one or more metal elements of Fe, Co, Ni.
2. Cerasteel materials according to Claim 1, **characterized in that**: Said Cerasteel materials further contain a few additives, said additives are C and one or more elements of V, Cr, Mn, Cu.
3. Cerasteel materials according to Claim 1 or 2, **characterized in that**: The weight percentage of each chemical component of said Cerasteel materials is: B 5~10 wt.%, Ti 0~50 wt.%, V 0~50 wt.%, Cr 0~50 wt.%, Zr 0~50 wt.%, Nb 0~50 wt.%, Mo 20~60 wt.%, Fe 10~40 wt.%, Ni 0~15 wt.%, Co 0~20 wt.%. Element contents in said additives are no more than 5 wt.%.
4. Method for preparing Cerasteel materials according to one of the preceding claims, which can be used for producing knives, cutting tools, and all kinds of wear resistant, corrosion resistant, high temperature resistant materials and all kinds of structural components composed of them.

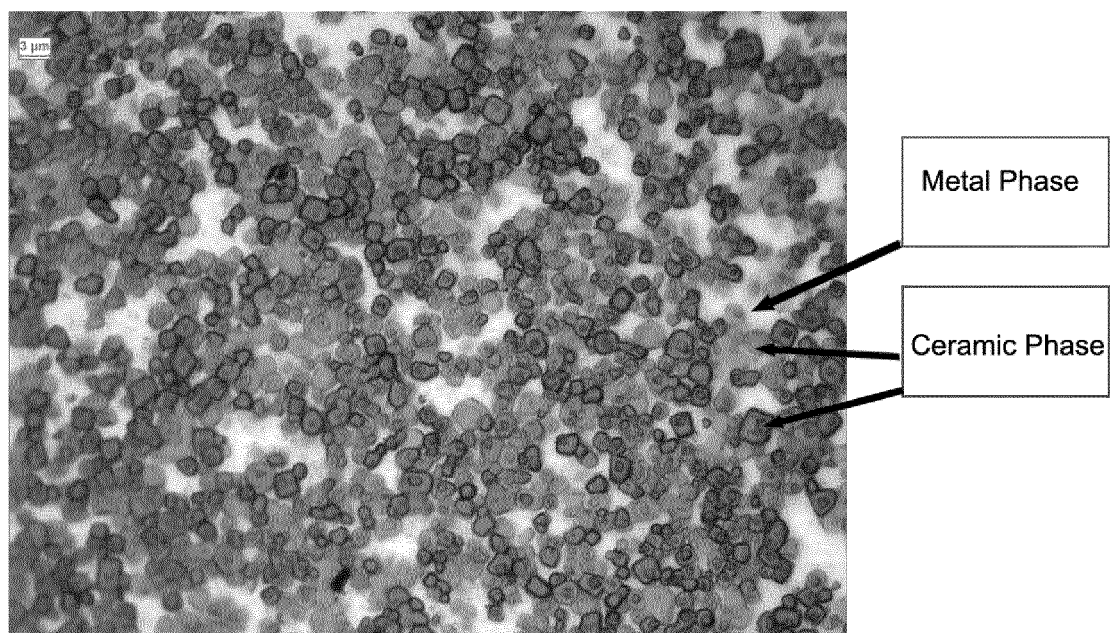


Fig. 1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2014/094719

A. CLASSIFICATION OF SUBJECT MATTER

C22C 29/14 (2006.01) i; C22C 27/04 (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)

C22C

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

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

DWPI, CNABS, CNTXT, CNKI: boring, adhesive, boride?, ceramic, metal, hard w alloy?, composit+, mo, molybdenum, fe, iron, nickel, ni, co, cobalt, binder+, phase+

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	CN 102787267 A (SICHUAN UNIVERSITY), 21 November 2012 (21.11.2012), claims 1-3	1-4
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X	GB 1404734 A (NIPPON TUNGSTEN K. K.), 03 September 1975 (03.09.1975), description, page 1, left-hand column, line 30 to right-hand column, line 42	1-4
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X	US 4194900 A (TOYO KOHAN CO., LTD.), 25 March 1980 (25.03.1980), description, column 2, lines 18-24 and 43-47	1-4

☒ 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	

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2014/094719

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP S634617 B2 (HITACHI METALS LTD.), 29 January 1988 (29.01.1988), claim 1	1-4
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Form PCT/ISA/210 (continuation of second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/CN2014/094719

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