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• **Wang, Wenbin****Xi'an, Shaanxi 710077 (CN)**• **Wang, Xiaojun****Xi'an, Shaanxi 710077 (CN)**(74) Representative: **Gong, Jinping****CocreatelP****Engenfeldenerstraße 56****81929 München (DE)****(54) PREPARATION METHOD OF NOVEL CU-NANO WC COMPOSITE MATERIAL**

(57) The disclosure discloses a preparation method of a novel Cu-nano WC composite material, belonging to the technical field of Cu-WC composite material preparation. According to the disclosure, by utilizing a vacuum induction melting method, Cu powder and WC are uniformly mixed in a certain ratio, then the mixture is subjected to loose sintering, the Cu-nano WC body undergoing loose sintering and oxygen-free Cu blocks are burdened in a weight ratio of Cu to WC of 99:1~50:50 for vacuum induction melting, and finally the obtained prod-

uct is cooled. In the disclosure, the Cu-WC material is prepared by utilizing the vacuum induction melting method, and therefore gas content is low; the vacuum induction melting method is suitable for preparing the Cu-WC material having WC content of $\leq 50\%$; due to a cast structure, the Cu-WC material has a density of nearly 100%; furthermore, the raw material adopts nano WC powder, and the strength of this material can be greatly improved through a nano strengthening effect.

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Description**TECHNICAL FIELD**

5 **[0001]** The disclosure relates to the technical field of alloy material preparation, and particularly to a preparation method of a novel Cu-nano WC composite material.

BACKGROUND

10 **[0002]** At present, the Cu-WC material is prepared by widely adopting a ceramimetallurgical manner due to limitation from difference in melting points and other properties of Cu and WC two materials. The Cu-WC material prepared by the ceramimetallurgical manner is low in density, high in gas content and low in conductivity, and the ceramimetallurgical manner cannot be used for preparing a composite material having WC content of 50% or below, thereby greatly limiting the application field of Cu-WC materials.

15 **[0003]** The preparation process in the prior art is as follows:

Powder mixing: WC powder and powder mixed with a small amount of Cu powder and other added members are uniformly mixed through powder mixing equipment;

20 Pressing: the uniformly mixed powder is pressed through pressing equipment to obtain a green body with certain binding strength and porosity;

Sintering a skeleton: the pressed green body is sintered at a protective atmosphere or in vacuum to prepare an infiltrated skeleton;

25 Infiltration: liquid Cu is infiltrated into the sintered WC skeleton at a temperature larger than a melting point of Cu in vacuum.

30 **[0004]** The vacuum infiltration method is a powder metallurgy process. The prepared Cu-WC has low density and high gas content. Because the skeleton needs to be sintered, the WC particle is relatively large in size, and the WC content must be > 50%, and thus its conductivity is relatively low.

35 **[0005]** Based on the above existing problems, the disclosure has developed a Cu-WC material prepared by utilizing a vacuum induction melting method. The prepared Cu-WC material has low gas content and the vacuum induction melting method is suitable for preparing the Cu-WC composite material having WC content of $\leq 50\%$. Due to a cast structure, the Cu-WC material has a density of nearly 100%. The raw material adopts nano WC powder, so the strength of the material can be greatly improved through a nano strengthening effect.

SUMMARY

40 **[0006]** The technical problem to be solved by the disclosure is that the Cu-WC composite material prepared by the exiting technology is low in density, high in gas content and low in conductivity, and the composite material having WC content of 50% or below cannot be prepared, thereby greatly limiting the application field of Cu-WC materials.

[0007] The technical solution of the disclosure is as follows:

45 A preparation method of a novel Cu-nano WC composite material, wherein the Cu-nano WC composite material meets the following conditions:

in a weight ratio, Cu powder: WC powder =98:2~30:70;

the Cu powder is of -200 meshes and has a purity of $\geq 99.7\%$, and the WC powder is 500 nano and has a purity of $\geq 99.0\%$;

50 the process comprises the following steps:

S1) powder mixing process: Cu powder and WC are mixed in the above ratio and then the obtained mixed powder and steel balls are mixed for 3-10h in a weight ratio of mixed powder to steel balls of 100:100;

55 S2) loose sintering process: the uniformly mixed powder is loosened into a graphite crucible and subsequently subjected to vacuum sintering; the obtained product is preserved for 2h at 950-1050°C when a vacuum degree reaches 5×10^{-2} pa level or below so as to complete sintering, thereby obtaining a Cu-nano WC body; the raw materials are easy to form at the temperature of 950-1050°C, or else, they are difficultly sintered together if the temperature is low.

S3) burdening process: the Cu-nano WC body subjected to loose sintering and oxygen-free Cu blocks are burdened in a weight ratio of Cu to WC of 99:1-50:50; 50% of WC content is limit of the vacuum induction melting process; this ratio range can reach the effects of high temperature, high conductivity, wear resistance and low gas content;

S4) vacuum induction melting process: the prepared Cu-nano WC body and the oxygen-free Cu blocks are put in a ceramic crucible, a vacuum system of vacuum induction melting equipment is opened, the above reactants are subjected to gradient heating when the vacuum degree reaches 3×10^{-1} pa or below, the specific gradient heating process is as follows: 10-20 KW, 1-5 min; 20-30 KW, 1-5 min; 30-40 KW, 1-5 min; 40-50 KW, 1-5 min; subsequently, power is kept at 40-60kw, when the oxygen-free Cu blocks are gradually molten in the crucible, the vacuum system is closed, an inert protective gas is charged until the vacuum degree is -0.1~0.01 Mpa;

S5) cooling process: after all the Cu-nano WC bodies in the crucible are completely dissolved by liquid Cu and are uniform under the action of electromagnetic stirring, the molten liquid in the crucible is poured into a cooling mould to be cooled for 1 h.

[0008] According to the preparation method of the disclosure, preferably, the particle size of the used steel ball in the process of powder mixing is 5-20 mm, and the rotation speed of the powder mixing machine is 10-30 r/min.

[0009] According to the preparation method of the disclosure, preferably, the electromagnetic stirring frequency is 1000-3000 Hz.

[0010] According to the preparation method of the disclosure, preferably, the cooling manner is water cooling.

[0011] According to the preparation method of the disclosure, preferably, the material of the cooling mould is chromium-copper alloy, water is introduced into the outside of the mould for heat conduction, and the water flow direction is from bottom to top.

[0012] The disclosure has the beneficial effects:

First, in the preparation method of the disclosure, Cu is added twice, the first addition of Cu is to ensure that the Cu-nano WC body is easy to form and degas in the process of loose sintering, and to facilitate the uniform dispersion of WC and Cu in the process of subsequent vacuum induction melting. The second addition of copper blocks is to gradually dissolve the Cu-nano WC body undergoing loose sintering utilizing the feature of first melting caused by low melting point of copper blocks, and finally uniformly disperse Cu and nano WC without agglomeration.

Second, the Cu-nano WC composite copper alloy material is prepared by the process of first powder mixing, then loose sintering, and then adding oxygen-free copper blocks for vacuum induction melting; this process is suitable for application occasions where the WC content is less than 50% compared with the process of "mixing powder, pressing, sintering skeleton and infiltration" in the prior art; this process utilizes the nano strengthening technology and does not need a large amount of addition, and thus the conductivity is relatively high, and the gas content of the vacuum induction melting material is low. Because of the cast structure, the Cu-nano WC composite copper alloy material has a density of nearly 100%. And the raw material uses nano WC powder, so the strength of the material can be greatly improved through the nano strengthening effect.

DESCRIPTION OF THE EMBODIMENTS

[0013] The disclosure will be further described in combination with embodiments, but the protective scope of the disclosure is not limited thereto.

<Cu-nano WC composite material>

[0014] The Cu-nano WC composite material of the disclosure meets the following conditions:

in a weight ratio, Cu powder: WC powder =98:2~30:70;

the Cu powder is of -200 meshes and has a purity of $\geq 99.7\%$, and the WC powder is <500 nano and has a purity of $\geq 99.0\%$;

<preparation process of Cu-nano WC composite material>

[0015] The preparation process of the Cu-nano WC composite material of the disclosure comprises: loose sintering process S2) and vacuum induction melting process S4), preferably, the preparation method of the disclosure also comprises a power mixing process S1) and a burdening process S3).

<power mixing process S1)>

[0016] The preparation process of the disclosure preferably comprises the powder mixing process S1). In order that the uniformity of powder mixing is facilitated, the subsequent sintering is easy to exhaust and form and the uniformity of components of the final smelting process is facilitated, the preferable powder mixing process S1) of the disclosure comprises:

[0017] S1) powder mixing process: the copper powder and WC are mixed in a weight ratio of Cu powder to WC powder of 98:2~30:70, and the mixed powder and steel balls are mixed for 3-10 h in a weight ratio of mixed powder to steel balls of 100:100.

<loose sintering process S2)>

[0018] The preparation method of the disclosure comprises the loose sintering process S2). Because the materials are easily formed at the temperature of 950-1050 °C, or else they are difficultly sintered together due to low temperature; therefore, the loose sintering process S2) of the disclosure is preferably as follows: the uniformly mixed powder is loosened into a graphite crucible, and then subjected to vacuum sintering. When the vacuum degree reaches 5×10^{-2} pa level or below, the above product is preserved for 2 h at 950-1050 °C to obtain a Cu-nano WC body;

<burdening process S3) >

[0019] The preparation method of the disclosure preferably comprises a burdening process S3). In order to achieve the effect of high temperature, high conductivity, wear resistance and low gas content, the burdening process S3) of the disclosure preferably comprises the following steps: the Cu-nano WC body subjected to loose sintering and free-oxygen copper blocks are burdened in a weight ratio of Cu to WC of 99:1-50:50;

< vacuum induction melting process S4) >

[0020] The preparation method of the disclosure comprises the vacuum induction smelting process S4). In the preparation method of the disclosure, copper is added twice, first addition of copper powder is to ensure that the Cu-nano WC body is easy to form and degas in the process of loose sintering and the uniform dispersion of WC and Cu is facilitated in the process of subsequent vacuum induction sintering, second addition of copper blocks is to allow copper blocks to be gradually molten to dissolve the Cu-nano WC body subjected to loose sintering by utilizing the characteristic that the copper blocks are molten firstly due to low melting point and then to finally uniformly disperse Cu and nano WC without agglomeration; therefore, the vacuum induction melting process S4) of the disclosure is preferably as follows: the prepared Cu-nano WC body and the free-oxygen copper blocks are put into the ceramic crucible, the vacuum system of the vacuum induction melting equipment is opened, and the reactants are subjected to gradient heating when the vacuum degree reaches 3×10^{-1} pa or below, and the specific process of gradient heating is: 10-20 KW, 1-5 min; 20-30 KW, 1-5 min; 30-40 KW, 1-5 min; 40-50 KW, 1-5 min; subsequently, the power is kept at 40-60kw, when the oxygen-free copper blocks in the crucible are gradually molten, the vacuum system is closed, and the inert protective gas is charged until the vacuum degree is - 0.1 ~ 0.01 Mpa;

< cooling process S5) >

[0021] As a preferred process, the preparation process of the disclosure also comprises the cooling process S5): after all the Cu-nano WC bodies in the crucible are dissolved by liquid Cu, and are uniformly stirred under the action of an electromagnetic force, the molten liquid in the crucible is poured into a cooling mold to be cooled for 1 h.

Example 1: preparation of CuWC4

[0022] Copper powder (- 200 meshes) having a purity $\geq 99.7\%$ and WC (< 500 nm) having purity of $> 99.0\%$ were selected as raw materials. First, copper powder and WC were mixed in a weight ratio of Cu powder to WC powder of 75:25, and then mixed for 3 h in a weight ratio of mixed powder to steel balls of 100:100; the diameter of the steel ball was 5 mm, and the rotation speed of a powder mixing machine was 10 r/min; when the uniformly mixed powder was loosened into the graphite crucible and subsequently subjected to vacuum sintering, and when the vacuum degree was 5×10^{-2} pa or below, the obtained product was preserved for 2h at 950 °C to complete sintering so as to obtain a Cu-nano WC body; the Cu-nano WC body subjected to loose sintering and oxygen-free copper blocks were burdened in a weight ratio of Cu to WC of 96:4;

the prepared Cu-nano WC body and oxygen-free copper blocks were put into the ceramic crucible, the vacuum system of the vacuum induction smelting equipment was opened, and the reactants were subjected to gradient heating when the vacuum degree reached below 3×10^{-1} pa: 10 KW, 1 min; 20 KW, 1 min; 30 KW, 1min; 40 KW, 1 min; then the power was kept at 40 KW; when the oxygen-free copper blocks in the crucible were molten gradually, the vacuum system

was closed, and the inert protective gas was charged until the vacuum degree was -0.1 Mpa; When all the Cu-nano WC bodies in the crucible were dissolved by liquid Cu and uniformly stirred under the action of an electromagnetic force at the frequency of 3000 Hz, then the molten liquid in the crucible was poured into the cooling mould to be subjected to water cooling for 1 h. The material of the cooling mould was low chromium copper alloy, and water was charged into the outside of the mold for heat conduction, and the water flow direction was from top to bottom.

Example 2: preparation of CuWC6

[0023] Copper powder (- 200 meshes) having a purity of $\geq 99.7\%$ and WC (< 500 nm) having a purity of $> 99.0\%$ were selected as raw materials. First, copper powder and WC were mixed in a weight ratio of Cu powder to WC powder of 90:10, and then mixed for 5 h in a weight ratio of mixed powder to steel balls of 100:100; the diameter of the steel ball was 12 mm, and the rotation speed of a powder mixing machine was 13 r/min;

when the uniformly mixed powder was loosened into the graphite crucible and subsequently subjected to vacuum sintering, when the vacuum degree was 5×10^{-2} pa or below, the obtained product was preserved for 2 h at 980 °C to complete sintering so as to obtain a Cu-nano WC body;

the Cu-nano WC body subjected to loose sintering and oxygen-free copper blocks were burdened in a weight ratio of Cu to WC of 94:6;

the prepared Cu-nano WC body and oxygen-free copper blocks were put into the ceramic crucible, the vacuum system of the vacuum induction smelting equipment was opened, and the reactants were subjected to gradient heating when the vacuum degree reached below 3×10^{-1} pa: 12 KW, 2 min; 24 KW, 2 min; 33 KW, 3 min; 42 KW, 2 min; subsequently, the power was kept at 46 KW; when the oxygen-free copper blocks in the crucible were molten gradually, the vacuum system was closed, and the inert protective gas was charged until the vacuum degree was - 0.06 Mpa;

When all the Cu-nano WC bodies in the crucible were dissolved by liquid Cu and uniformly stirred under the action of an electromagnetic force at the frequency of 2400 Hz, then the molten liquid in the crucible was poured into the cooling mould to be subjected to water cooling for 1h. The material of the cooling mold was low chromium copper alloy, and water was charged into the outside of the mould for heat conduction, and the water flow direction was from top to bottom.

Example 3 preparation of CuWC8

[0024] Copper powder (- 200 meshes) having a purity of $\geq 99.7\%$ and WC (< 500 nm) having a purity of $> 99.0\%$ were selected as raw materials. First, copper powder and WC were mixed in a weight ratio of Cu powder to WC powder of 80:20, and then mixed for 5 h in a weight ratio of mixed powder to steel ball of 100:100; the diameter of the steel ball was 16 mm, and the rotation speed of a powder mixing machine was 22 r/min;

when the uniformly mixed powder was loosened into the graphite crucible and subsequently subjected to vacuum sintering, when the vacuum degree was 5×10^{-2} pa or below, the obtained product was preserved for 2h at 1000 °C to complete sintering so as to obtain a Cu-nano WC body;

the Cu-nano WC body subjected to loose sintering and oxygen-free copper blocks were burdened in a weight ratio of Cu to WC of 92:8;

the prepared Cu-nano WC body and oxygen-free copper blocks were put into the ceramic crucible, the vacuum system of the vacuum induction smelting equipment was opened, and the reactants were subjected to gradient heating when the vacuum degree reached below 3×10^{-1} pa: 18 KW, 5 min; 26 KW, 3 min; 35 KW, 4 min; 45 KW, 3 min; then the power was kept at 48 KW; when the oxygen-free copper blocks in the crucible were molten gradually, the vacuum system was closed, and the inert protective gas was charged until the vacuum degree was -0.05 Mpa;

When all the Cu-nano WC bodies in the crucible were dissolved by liquid Cu and uniformly stirred under the action of an electromagnetic force at the frequency of 1900 Hz, then the molten liquid in the crucible was poured into the cooling mould to be subjected to water cooling for 1 h. The material of the cooling mould was low chromium copper alloy, and water was charged into the outside of the mould for heat conduction, and the water flow direction was from top to bottom.

Example 4 preparation of CuWC30

[0025] Copper powder (- 200 meshes) having a purity of $\geq 99.7\%$ and WC (< 500 nm) having a purity of $\geq 99.0\%$ were selected as raw materials. First, copper powder and WC were mixed in a weight ratio of Cu powder to WC powder of 40:60, and then mixed for 8 h in a weight ratio of mixed powder to steel balls of 100:100; the diameter of the steel ball was 20 mm, and the rotation speed of a powder mixing machine was 25 r/min;

when the uniformly mixed powder was loosened into the graphite crucible and subsequently subjected to vacuum sintering, when the vacuum degree was 5×10^{-2} pa or below, the obtained product was preserved for 2 h at 1020 °C to complete sintering so as to obtain a Cu-nano WC body;

the Cu-nano WC body subjected to loose sintering and oxygen-free copper blocks were burdened in a weight ratio of Cu to WC of 70:30;

the prepared Cu-nano WC body and oxygen-free copper blocks were put into the ceramic crucible, the vacuum system of the vacuum induction smelting equipment was opened, and the reactants were subjected to gradient heating when the vacuum degree reached below 3×10^{-1} pa: 18 KW, 4 min; 22 KW, 5 min; 37 KW, 5 min; 50 KW, 5 min; then the power was kept at 50kW; when the oxygen-free copper blocks in the crucible were molten gradually, the vacuum system was closed, and the inert protective gas was charged until the vacuum degree was -0.01 Mpa;

When all the Cu-nano WC bodies in the crucible were dissolved by liquid Cu and uniformly stirred under the action of an electromagnetic force at the frequency of 1500 Hz, and then the molten liquid in the crucible was poured into the cooling mould to be subjected to water cooling for 1 h. The material of the cooling mould was low chromium copper alloy, and water was charged into the outside of the mould for heat conduction, and the water flow direction was from top to bottom.

Example 5 preparation of CuWC35

[0026] Copper powder (- 200 meshes) having a purity of $\geq 99.7\%$ and WC (< 500 nm) having a purity of $> 99.0\%$ were selected as raw materials. First, copper powder and WC were mixed in a weight ratio of Cu powder to WC powder of 50:50, and then mixed for 9 h in a weight ratio of mixed powder to steel ball of 100:100; the diameter of the steel ball was 18 mm, and the rotation speed of a powder mixing machine was 24 r/min;

when the uniformly mixed powder was loosened into the graphite crucible and subsequently subjected to vacuum sintering, when the vacuum degree was 5×10^{-2} pa or below, the obtained product was preserved for 2 h at 1050 °C to complete sintering so as to obtain a Cu-nano WC body;

the Cu-nano WC body subjected to loose sintering and oxygen-free copper blocks were burdened in a weight ratio of Cu to WC of 65:35;

the prepared Cu-nano WC body and oxygen-free copper blocks were put into the ceramic crucible, the vacuum system of the vacuum induction smelting equipment was opened, and the reactants were subjected to gradient heating when the vacuum degree reached below 3×10^{-1} pa: 20 KW, 5 min; 20 KW, 2 min; 30 KW, 1 min; 40 KW, 1 min; then the power was kept at 42 KW; when the oxygen-free copper blocks in the crucible were molten gradually, the vacuum system was closed, and the inert protective gas was charged until the vacuum degree was 0.01 Mpa;

When all the Cu-nano WC bodies in the crucible were dissolved by liquid Cu and uniformly stirred under the action of an electromagnetic force at the frequency of 1300 Hz, then the molten liquid in the crucible was poured into the cooling mould to be subjected to water cooling for 1 h. The material of the cooling mould was low chromium copper alloy, and water was charged into the outside of the mould for heat conduction, and the water flow direction was from top to bottom.

Example 6 preparation of CuWC50

[0027] Copper powder (- 200 meshes) having a purity of $\geq 99.7\%$ and WC (< 500 nm) having a purity of $\geq 99.0\%$ were selected as raw materials. First, copper powder and WC were mixed in a weight ratio of Cu powder to WC powder of 30:70, and then mixed for 10 h in a weight ratio of mixed powder to steel balls of 100:100; the diameter of the steel ball was 19 mm, and the rotation speed of a powder mixing machine was 26 r/min;

when the uniformly mixed powder was loosened into the graphite crucible and subsequently subjected to vacuum sintering, when the vacuum degree was 5×10^{-2} pa or below, the obtained product was preserved for 2 h at 1050 °C to complete sintering so as to obtain a Cu-nano WC body;

the Cu-nano WC body subjected to loose sintering and oxygen-free copper blocks were burdened in a weight ratio of Cu to WC of 50:50;

the prepared Cu-nano WC body and oxygen-free copper blocks were put into the ceramic crucible, the vacuum system of the vacuum induction smelting equipment was opened, and the reactants were subjected to gradient heating when the vacuum degree reached below 3×10^{-1} pa: 20 KW, 5 min; 22 KW, 4 min; 40 KW, 5 min; 41 KW, 5 min; then the power was kept at 60kW; when the oxygen-free copper blocks in the crucible were molten gradually, the vacuum system was closed, and the inert protective gas was charged until the vacuum degree was -0.01 Mpa;

When all the Cu-nano WC bodies in the crucible were dissolved by liquid Cu and uniformly stirred under the action of an electromagnetic force at the frequency of 1000 Hz, then the molten liquid in the crucible was poured into the cooling mould to be subjected to water cooling for 1 h. The material of the cooling mould was low chromium copper alloy, and water was charged into the outside of the mould for heat conduction, and the water flow direction was from top to bottom.

[0028] Various property parameters of Cu-nano WC composite copper alloy materials prepared in the above examples 1-6 are shown in Table 1.

Table 1: Table of property parameters of various models of Cu-nano WC composite cupper alloy materials in examples 1-6

Group	Name	WC content %	Cu content %	Vacuum sintering temperature °C	Oxygen content ppm	Nitrogen content ppm	Conductivity MS/m	Hardness (cast) HB	Hardness (900°C annealing) HB
Example 1	CuWC4	4	Residue	950	<20	<20	>52	58-70	58-70
Example 2	CuWC6	6	Residue	980	<30	<20	>49	63-75	63-75
Example 3	CuWC8	8	Residue	1000	<40	<20	>45	70-85	70-85
Example 4	CuWC30	30	Residue	1020	<100	<50	>37	190-220	190-220
Example 5	CuWC35	35	Residue	1050	<120	<50	>33	220-240	220-240
Example 6	CuWC50	50	Residue	1050	<150	<50	>25	270-300	270-300
900°C annealing without softness									

[0029] It can be seen from the above data that the method of the disclosure can prepare the Cu-WC composite material having WC content of $\leq 50\%$, and the material is high in strength, low in gas content, high in conductivity and high in density, and has significant advantages compared with the prior art.

Experimental example

1. Study on effect of a ratio of Cu powder to WC powder on properties of composite material

[0030] A powder mixing ratio where copper powder and WC were mixed in a weight ratio of Cu powder to WC powder of 99:1 was used as a comparative example 1, a powder mixing ratio where copper powder and WC were mixed in a weight ratio of Cu powder to WC powder of 28:72 was used as a comparative example 2, a powder mixing ratio where copper powder and WC were mixed in a weight ratio of Cu powder to WC powder of 90:10 was used as a comparative example 3, a powder mixing ratio where copper powder and WC were mixed in a weight ratio of Cu powder to WC powder of 80:20 was used as a comparative example 4, a powder mixing ratio where copper powder and WC were mixed in a weight ratio of Cu powder to WC powder of 50:50 was used as a comparative example 5, a powder mixing ratio where copper powder and WC were mixed in a weight ratio of Cu powder to WC powder of 40:60 was used as a comparative example 6, and various comparative examples performed preparation of composite materials according to the preparation method of example 1. In comparative example 1, oxygen-free copper blocks were not added in step (3), and other parameters are the same as those in example 1 except that the ratio of Cu powder to WC powder when in primary powder mixing was different. The property parameters of the obtained composite material are shown in Table 2:

Table 2: Table of property parameters of Cu-nano WC composite cupper alloy materials prepared in comparative examples 1-2

Group	Name	WC content %	Cu content %	Ratio of Cu powder to WC powder during the powder mixing	Oxygen content ppm	Nitrogen content ppm	Conductivity MS/m	Hardness (cast) HB	Hardness (900 °C annealing) HB
Comparative example 1	CuWC1	1	Residue	99:1	<150	<150	<20	8-20	8-20
Comparative example 2	CuWC4	4	Residue	28:72	>160	>40	<45	35-66	35-66
Comparative example 3	CuWC4	4	Residue	90: 10	<18	<18	>53	58-70	58-70
Comparative example 4	CuWC4	4	Residue	80: 20	<10	<10	>56	62-80	62-80
Comparative example 5	CuWC4	4	Residue	50: 50	<20	<20	>55	60-70	60-70
Comparative example 6	CuWC4	4	Residue	40: 60	<20	<20	>53	58-73	58-73
Example 1	CuWC4	4	Residue	75:25	<20	<20	>52	58-70	58-70

[0031] It can be seen from the above data that when the ratio of Cu powder to WC powder is greater than 98:2 or less than 30:70 in the process of powder mixing, it is not conducive to uniform powder mixing, exhausting and forming, and is not conducive to the uniformity of components in the process of final smelting, thereby resulting in a fact that the prepared Cu-WC composite material is high in gas content, low in electrical conductivity and greatly reduced material strength and wear resistance, and does not meet the use requirement.

[0032] **Conclusion 1:** under the condition that all the parameters are the same (the main control parameters are: the melting ratio is Cu: WC = 96:4; the vacuum sintering temperature is 950 °C), when the mixing ratio of Cu powder to WC powder is 80:20, it is conducive to the uniform powder mixing, easy to exhaust and form in the next sintering, and is also conducive to the uniformity of components in the process of final smelting. The prepared composite material is low in gas content, and relatively high in material strength and hardness and conductivity.

2. Study on effect of vacuum sintering temperature on properties of composite material

[0033] 930 °C vacuum sintering temperature was used as comparative example 7, 1080 °C vacuum sintering temperature was used as comparative example 8, 970 °C vacuum sintering temperature was used as comparative example 9, 1010 °C vacuum sintering temperature was used as comparative example 10, and 1040 °C vacuum sintering temperature was used as comparative example 11. The composite material is prepared according to the preparation method of example 3. Other parameters were the same as those in example 3 except the vacuum sintering temperature was different. The property parameters of the obtained composite material are shown in Table 3:

Table 3: Table of property parameters of Cu-nano WC composite copper alloy materials prepared in comparative examples 3-4

Group	Name	WC content %	Cu content %	Vacuum sintering temperature °C	Oxygen content ppm	Nitrogen content ppm	Conductivity MS/m	Hardness (cast) HB	Hardness (900 °C annealing) HB
Comparative example 7	CuWC8	8	Residue	930	<65	<30	>15	40-70	40-70
Comparative example 8	CuWC8	8	Residue	1080	<50	<30	>12	45-73	45-73
Comparative example 9	CuWC8	8	Residue	970	<40	<30	>45	72-85	72-85
Comparative example 10	CuWC8	8	Residue	1010	<40	<20	>50	70-80	70-80
Comparative example 11	CuWC8	8	Residue	1040	<40	<20	>48	70-80	70-80
Example 3	CuWC8	8	Residue	1000	<40	<20	>45	70-85	70-85

[0034] It can be seen from the above data that when the vacuum sintering temperature is less than 950°C or greater than 1050 °C, relatively, the prepared Cu-WC composite material becomes high in gas content and becomes poor in conductivity, especially, when the temperature is less than 950°C, the material is not easy to form and is difficultly sintered together, so as to cause difficult subsequent smelting, resulting in greatly reduced strength and wear resistance of the material, which does not meet the use requirement. Thus, it is suitable to control the vacuum sintering temperature to be between 950°C and 1050°C, and the prepared material is good in various properties.

[0035] **Conclusion 2:** under the condition that all the parameters are the same (the main control parameters are: the ratio of Cu powder to WC powder is 80:20; when in smelting, Cu : WC is 92:8), when the vacuum sintering temperature is 1010°C, the material is easy to form and conducive to sintering, and it is also conducive to the uniformity of components in the process of final smelting. The prepared composite material is low in gas content, and relatively high in material strength and hardness and conductivity.

3. Study on effect of WC content on properties of composite material

[0036] Example 3 was used as reference, WC content of 0.8% was used as comparative example 12, WC content of 53 % was used as comparative example 13, WC content of 2% was used as comparative example 13, WC content of 15% was used as comparative example 15, WC content of 25% was used as a comparative example 16, and WC content of 50% was used as comparative example 17. The composite material was prepared according to the preparation method in example 3. Other parameters were the same as those in example 3 except the vacuum sintering temperature was different. The property parameters of the obtained composite materials are shown in Table 4:

Table 4: Table of property parameters of Cu-nano WC composite copper alloy materials prepared in comparative examples 5-6

Group	Name	WC content %	Cu content %	Vacuum sintering temperature	Oxygen content ppm	Nitrogen content ppm	Conductivity MS/m	Hardness (cast) HB	Hardness (900°C annealing) HB
Comparative example 12	CuWC0.8	0.8	Residue	<30	<20	>55	35-45	35-45	<30
Comparative example 13	CuWC53	53	Residue	< 170	<80	>20	70-85	70-85	< 170
Comparative example 14	CuWC2	2	Residue	<20	<20	>57	40-50	40-50	<20
Comparative example 15	CuWC15	15	Residue	<45	<20	>43	60-180	60-180	<45
Comparative example 16	CuWC25	25	Residue	<50	<20	>41	70-185	70-185	<50
Comparative example 17	CuWC50	50		< 140	<40	>32	150-185	150-185	< 140
Example 3	CuWC8	8	Residue	<40	<20	>45	70-85	70-85	<40

[0037] It can be seen from the above data that when the WC content is less than 1%, the prepared Cu-WC composite material has low gas content and high conductivity, but its material strength and wear resistance are greatly reduced. When the WC content is higher than 50%, the prepared Cu-WC composite material has good strength and wear resistance, but has high gas content and poor conductivity, so it does not meet the user requirement. Therefore, it is suitable to control the WC content within the range from 1% to 50%, and the prepared material is good in various properties.

[0038] Conclusion 3: under the condition that all the parameters are the same (the main control parameters are: when in powder mixing, Cu powder: WC powder = 80:20; vacuum sintering temperature is 1000 °C), when the WC content is 15%, the prepared composite material has excellent properties in the aspects of gas content, material strength, hardness and conductivity.

[0039] It is worth noting that those skilled in the art can directly derive or associate some deformations from the contents of the disclosure and common senses under the enlightenment of the concept and specific embodiments of the disclosure. Those of ordinary skill in the art will appreciate that other methods or the common known technologies in the prior art can be replaced, as well as different combinations of features and other non-substantive modifications can also be adopted. Similarly, the functions and effects described in the disclosure can also be realized, which are not described in detail one by one, and belong to the protective scope of the disclosure.

Claims

1. A preparation method of a novel Cu-nano WC composite material, wherein the Cu-nano WC composite material meets the following conditions:

in a weight ratio, Cu powder: WC powder=98:2~30: 70;

the Cu powder is of -200 meshes and has a purity of $\geq 99.7\%$, and the WC is <500 nano and has a purity of $\geq 99.0\%$;

the process comprises the following steps:

S1) powder mixing process: Cu powder and WC are mixed in the above ratio and then the obtained mixed powder and steel balls are mixed for 3-10 h in a weight ratio of mixed powder to steel balls of 100:100;

S2) loose sintering process: the uniformly mixed powder is loosened into a graphite crucible and subsequently subjected to vacuum sintering; when a vacuum degree reaches 5×10^{-2} pa level or below, the obtained product is preserved for 2 h at 950-1050 °C so as to complete sintering, thereby obtaining a Cu-nano WC body;

S3) burdening process: the Cu-nano WC body subjected to loose sintering and oxygen-free Cu blocks are burdened in a weight ratio of Cu to WC of 99:1-50:50;

S4) vacuum induction melting process: the prepared Cu-nano WC body and the oxygen-free Cu blocks are put in a ceramic crucible, a vacuum system of vacuum induction melting equipment is opened, the above reactants are subjected to gradient heating when the vacuum degree reaches 3×10^{-1} pa or below, the specific gradient heating process is as follows: 10-20 KW, 1-5 min; 20-30 KW, 1-5 min; 30-40 KW, 1-5 min; 40-50 KW, 1-5 min; subsequently, power is kept at 40-60kw, when the oxygen-free Cu blocks are gradually molten in the crucible, the vacuum system is closed, an inert protective gas is charged until the vacuum degree is -0.1~0.01 Mpa;

S5) cooling process: after all the Cu-nano WC bodies in the crucible are completely dissolved by liquid Cu and are uniform under the action of electromagnetic stirring, the molten liquid in the crucible is poured into a cooling mould to be cooled for 1 h.

2. The preparation method of the novel Cu-nano WC composite material according to claim 1, wherein in the process of ball milling and powder mixing, the particle size of the used steel ball is 5-20 mm, and the rotation speed of a powder mixing machine is 10-30 r/min.

3. The preparation method of the novel Cu-nano WC composite material according to claim 1, wherein the electromagnetic stirring frequency is 1000-3000 Hz.

4. The preparation method of the novel Cu-nano WC composite material according to claim 1, wherein the cooling manner is water cooling.

5. The preparation method of the novel Cu-nano WC composite material according to claim 4, wherein the material of the cooling mould is chromium-copper alloy, water is introduced into the outside of the mould for heat conduction, and the water flow direction is from bottom to top.



EUROPEAN SEARCH REPORT

Application Number
EP 20 16 5731

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	YAO GONGCHENG ET AL: "High-performance copper reinforced with dispersed nanoparticles", JOURNAL OF MATERIALS SCIENCE, KLUWER ACADEMIC PUBLISHERS, DORDRECHT, vol. 54, no. 5, 26 November 2018 (2018-11-26), pages 4423-4432, XP036709861, ISSN: 0022-2461, DOI: 10.1007/S10853-018-3152-0 [retrieved on 2018-11-26] * page 4424; "nanocomposite fabrication" * * page 4429; "comparison with other fabrication methods for MMNCs" * * figure 1 *	1-5	INV. C22C1/02 C22C1/04 C22C1/05 C22C1/10 C22C32/00
A	----- Srinath Viswanathan ET AL: "Vacuum Induction Melting" In: "ASM Handbook; Volume 15 Casting", 1 December 2008 (2008-12-01), ASM International, XP055694695, pages 116-123, DOI: 10.1361/asmhba0005200, * page 116; "process description" * * page 118, right column, 2nd paragraph * * figure 2 * -----	1-5	TECHNICAL FIELDS SEARCHED (IPC) C22C B22D
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 13 May 2020	Examiner Momeni, Mohammad
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	

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