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(54) **PREALLOYED IRON-BASED POWDER, A METHOD FOR THE MANUFACTURING AND USE THEREOF AND A SINTERED COMPONENT**

(57) The object of the invention is an easily sinterable prealloyed iron-based powder and the method for its manufacturing. The easily sinterable prealloyed iron-based powder comprises according to the invention at least 80% Fe by weight, Cu and P as alloying additives and inevitable impurities, particularly hardly reducible oxides. A method for producing the easily sinterable prealloyed iron-based powders according to the invention comprises the successive steps: preparing a reducible material; subjecting the said reducible material to mechanical processing by milling, including grinding, homogenization and activation of the reducible material; annealing the said ground homogenized and activated by milling reducible material in a reducing atmosphere; cooling the said reduced material to a temperature preventing its self-ignition; and grinding the said cooled material to a powder having a predetermined average particle size.

The invention further relates to the use of the easily sinterable prealloyed iron-based powder for the production of sintered structural and tool components, in particular sintered metal-diamond composites, and the sintered product, especially the sintered metal-diamond composite, wherein the total porosity of the sintered product at a temperature not higher than 950°C is lower than 5%.

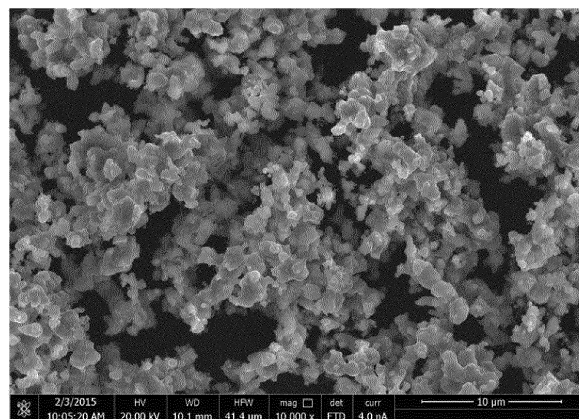


Fig. 1

Description

[0001] The invention relates to an easily sinterable prealloyed iron-based powder, a method for the manufacturing and use thereof and the sintered product.

[0002] The term "easily sinterable powder" as used in present application refers to a powder that after cold forming at pressure of 100-400 MPa and free sintering (at atmospheric pressure) in a reducing atmosphere for a time no longer than 60 minutes at a temperature not higher than 950° C allows to obtain sintered parts of the total porosity of less than 5% by volume.

[0003] Factors for rendering the easily sintering nature to powders are:

- finely-crystalline structure of the powder particles, in which the polycrystalline powder particles are composed of grains having an average size of about 2 µm or less,
- two- or multi-phase structure at the sintering temperature, which, while restraining grain growth, provides finely-crystalline structure of the material during sintering,
- presence of a liquid phase during sintering.

[0004] Low-alloy iron powders containing at least 90% Fe by weight and sintered without the liquid phase allow obtaining sintered parts of the total porosity of less than 5% by volume, while maintaining the fine-grained microstructure of the material. The two-phase microstructure of the material at the sintering temperature, composed of ferrite and austenite, is assured by the chemical composition of the alloy. Ferrite stabilizers, e.g.: P, W, Mo, Co, and austenite stabilizers, e.g.: Cu, Ni, are used in quantities and proportions assessed by means of experimental techniques (e.g. the high temperature X-ray diffraction phase analysis) or analytical techniques (e.g. the ThermoCalc software®) in order to obtain the ferrite-to-austenite volume ratio in the range from 2/5 to 3/5 within the possibly widest sintering temperature range. Furthermore, the increase in the phosphorus content of the powder contributes to the increase in the as-sintered hardness due to a strong solid solution strengthening effect.

[0005] The liquid phase sintered materials are characterized by a higher content of alloying elements such as Cu and Sn, which have to assure sufficient amount of persistent liquid phase at the sintering temperature in order to reach as-sintered porosity of less than 5% by volume. Liquid phase sintering of high-alloy iron powders containing at least 10% by weight of alloying elements makes it difficult to retain the fine-grained structure of the starting powder, but it promotes applicability of such powders whenever permanent bonding of the sintered part to another element must occur during sintering.

[0006] Easily sinterable iron-based powders are used for the production of sintered structural and tool products, in particular for the production of sintered metal-diamond composites obtained by the free sintering, but also by pressure sintering method. So far, the most commonly used material in these applications was a cobalt, high-alloy iron-based powders available on the market under the trade names Cobalite CNF® (Umicore, Belgium) and Next 400® (Eurotungstene, France) and mixtures thereof with prealloyed tin bronzes, iron, nickel and tungsten carbide (e.g.: MX4885, MX4380, MX4590, MX4940, etc.). Cobalite CNF® powder is described in the publication by B.J. Kamphuis, B. Serneels: "Cobalt and nickel free bond powder for diamond tools: Cobalite CNF" Industrial Diamond Review, No. 1, 2004, pp. 26-32. These raw materials, due to the high content of expensive alloying elements and the use of chemical production methods, are expensive to manufacture. They cause a serious health hazards to the persons vulnerable to prolonged exposure to fine powders containing cobalt and/or nickel, involving the frequent occurrence of cobalt lung, giant cell interstitial pneumonia, allergic and cancerous skin diseases. The above mentioned cost and environmental factors have caused a growing tendency to reduce the content of alloying elements, especially cobalt, in easily sinterable prealloyed iron-based powders, while maintaining their required technological and functional properties. Until recently research efforts have been directed toward seeking alternatives for cobalt, i.e. replacing it with other alloying elements, in consequence of that a total content of alloying elements still remained relatively high, for example in said powders Next400 and Cobalite CNF the total content of alloying elements is 50% by weight and 31.6% by weight, respectively.

[0007] The previously known methods for manufacturing fine grain, especially easily sinterable prealloyed iron-based powders, using co-precipitation technology of metal hydroxides or oxalates from aqueous salt solutions, which, after filtration and calcination, are subjected to reduction with hydrogen, also proved unsatisfactory due to cost and environmental aspects. Such methods are known e.g. from the patent specifications US 6,554,885 B1, US 6,613,122 B1, US 6,312,497 B1, US 7,077,883 B2, EP 0 865 511 B1, EP 1 492 897 B1. Disadvantages of the known methods based on co-precipitation of hydroxides or salts are both their high cost as well as disposal problems with environmentally harmful wastes inevitable in those processes.

[0008] The object of the invention is to provide easily sinterable prealloyed iron-based powders that do not demonstrate the prior art disadvantages resulting from the high content of alloying elements. They are therefore more environmentally friendly, cheaper and easier to manufacture, while maintaining very good properties, both technological as well as functional.

[0009] The object of the invention is also to propose a method for manufacturing easily sinterable prealloyed iron-based powders, which method eliminates the disadvantages occurring in the prior art, namely it is environmentally friendly, less expensive to implement and demonstrates flexibility allowing the better adjustment of the properties of the resulting powder to a particular application.

[0010] The easily sinterable prealloyed iron-based powder according to the invention is characterized in that it comprises at least 80% Fe by weight, Cu and P as alloying additives and inevitable impurities, particularly hardly reducible oxides.

[0011] Preferably the easily sinterable prealloyed iron-based powder comprises at least 90% Fe by weight, 1- 9,8% Cu by weight and 0.2-2% P by weight.

[0012] Preferably, the easily sinterable prealloyed iron-based powder further comprises at least one alloying element selected from the group consisting of Sn, Co, Ni, W, Mo.

[0013] Preferably the easily sinterable prealloyed iron-based powder comprises at least 1-18% Cu by weight, 0,5-4% Sn by weight and 0.2-2% P by weight.

[0014] Preferably, the total content of Co and/or Ni and/or W and/or Mo is not more than 5% by weight.

[0015] Preferably, the hydrogen loss of the powder annealed in a reducing atmosphere is less than 1.5% by weight.

[0016] Preferably, the average particle size of the powder determined by the Fisher apparatus is not more than 10 μm .

[0017] Preferably, the powder comprises polycrystalline particles constituted of grains having average size not greater than 2 μm .

[0018] A method for producing the easily sinterable prealloyed iron-based powder according to claims 1 to 8, comprising the successive steps:

- preparing a reducible material;
- subjecting the said reducible material to mechanical processing by milling, including grinding, homogenization and activation of the reducible material;
- annealing the said ground homogenized and activated by milling reducible material in a reducing atmosphere;
- cooling the said reduced material to a temperature preventing its self-ignition; and
- grinding the said cooled material to a powder having a predetermined average particle size.

[0019] Preferably, the annealing is carried out at a temperature of 550-750°C, for a time of 1-8 hours, in a reducing atmosphere, which is hydrogen or a gas mixture containing hydrogen.

[0020] Preferably, the reducible material comprises oxides, carbonates, nitrates, metals and metal alloys and mixtures thereof, reducible by technical purity hydrogen at a temperature not higher than 750°C.

[0021] Preferably, the mechanical processing of the reducible material is performed in dry or wet condition.

[0022] Preferably, further drying is carried out after the mechanical processing in wet condition.

[0023] The easily sinterable prealloyed iron-based powder as described above is used for the manufacturing of sintered structural and tool components, in particular sintered metal-diamond composites.

[0024] The sintered product, especially the sintered metal-diamond composite, prepared from the easily sinterable prealloyed iron-based powder according to the invention is characterized in that the easily sinterable prealloyed iron-based powder is the powder as described above, wherein the total porosity of the sintered product at a temperature not higher than 950°C is lower than 5%.

[0025] Thus, the invention allows in a surprisingly simple and inexpensive manner to produce the easily sinterable prealloyed iron-based powder comprising at least 80% of iron by weight, copper and phosphorus, and optionally at least one from the group of alloying elements including tin, cobalt, nickel, tungsten and molybdenum, as well as impurities, mainly in the form of hardly reducible oxides such, for example SiO_2 . The total content of alloying elements and impurities in the powders produced according to the invention does not exceed 20% by weight, wherein the powders in which the minimum content of alloying elements is 10% by weight are intended for applications in which it is required that permanent bonding of the sintered part to another element or elements, made of iron or its alloys, must occur during sintering, e.g. by brazing.

[0026] The easily sinterable prealloyed iron-based powder according to the invention, while maintaining properties similar to the known powders of this kind, has in comparison to them a number of economic, environmental and technological advantages such as:

- very low, limited to 20% by weight, total content of alloying elements and impurities;
- very low, limited to 5% by weight, total content of expensive, deficient and/or harmful alloying elements such as Co,

Ni, W, Mo, rare earth metals, etc.;

- possibility of manufacturing sintered parts having a hardness greater than 200 HV;
- possibility of heat treatment of sintered parts and further increase in hardness above 300 HV;
- possibility of manufacturing by means of mechanochemical methods.

[0027] The method of the invention for producing the new prealloyed iron-based powders eliminates the expensive chemical method for obtaining mixtures of hydroxides, oxalates or other metal compounds hardly soluble in water, in which environmentally harmful waste (salts), that require utilization, are formed, and their later thermal decomposition to oxides occurs. It is replaced by a cheaper, mechanochemical synthesis of oxides, which, in comparison with the chemical method, gives greater freedom in selection the chemical composition of the powder. Mechanochemical synthesis consists in inducing chemical reactions preceded by grinding and mechanical activation of substrates. It enables receiving new materials characterized by a low level of chemical and structural heterogeneity, fine-grained microstructure and the most often desirable complex phase composition.

[0028] In the method according to the invention a reducible material is thus prepared through mechanical processing by milling, resulting in grinding, homogenization and activation of the reducible material. The crushed, homogenized and activated by grinding reducible material thus obtained is annealed in a reducing atmosphere, and then cooled to a temperature which prevents self-ignition of the material. Finally, the annealed and cooled material is ground to a powder having a predetermined average particle size. The application of mechanochemical processes, due to milling reagents in ball mills, simplifies synthesis procedures and eliminates the need of expensive waste utilization, which in turn significantly improves the ecology of producing high performance functional materials, thus meeting the principles of so called "Green Chemistry".

[0029] The method according to the invention has the following advantages in comparison to the traditional method of co-precipitation hydroxides or oxalates:

- environmental performance;
- lower material and equipment costs;
- possibility of flexible selection of chemical composition of the powders enabling direct influence on the properties of the final product;
- shortening the milling time due to the use of a more energetic mill.

[0030] The powders produced by the mechanochemical method of oxides synthesis are free of drawbacks, which intrinsically characterise commercial powders, while maintaining similar to them technological properties. For this reason, the presented invention has tremendous application potential.

[0031] The object of the invention is illustrated hereinafter in the embodiment and shown in the accompanying drawing, in which:

Figure 1 is a scanning electron microscope micrograph showing the structure of the powdered metal sponge obtained in Example 1;

Figure 2 is a graph obtained by X-ray diffraction phase analysis illustrating the prealloyed nature of the powder according to Example 1;

Figure 3 is a scanning electron microscope micrograph showing the structure of the powdered metal sponge obtained according to Example 3;

Figure 4 is a scanning electron microscope micrograph showing the structure of the powdered metal sponge obtained according to Example 5;

Figure 5 is the graph obtained by X-ray diffraction phase analysis illustrating the prealloyed nature of the powder according to Example 5; and

Figure 6 is a metallographic light microscope micrograph illustrating the joint between the sintered part of Example 7 and the steel substrate.

Example 1

[0032] A powder mixture containing 92.86 g Fe_2O_3 ; 3.57 g CuO and 3.57 g of prealloyed Fe-P powder containing 10% phosphorus by weight was prepared by mixing the ingredients in a Turbula type mixer for 10 minutes. The powders were

EP 3 124 634 A1

placed together with grinding media in a 1.25 dm³ roller ball mill drum. 12 mm diameter 100Cr6 bearing steel balls were used as the grinding media. The degree of filling of the mill was 50% by volume, and the ball-to-powder weight ratio was 20:1. Ethyl alcohol was poured into the drum in an amount required for the complete immersion of the grinding media together with the powder in the liquid. The drum was turned on to rotate at 65% of the critical speed. After milling for 72 hours, the charge of the mill was dried in a laboratory drier at 130°C. The powder was then subjected to reducing annealing for 180 minutes at 700°C in a hydrogen atmosphere and cooled to below 30°C in order to avoid self-ignition. The thus obtained metal sponge was ground in a ceramic mortar to powder (Figure 1) with a nominal content of 95.5% Fe by weight, 4% Cu by weight and 0.5% P by weight, the hydrogen loss of 1.1% by weight

[0033] (determined in accordance with PN-EN ISO 4491-3: 2006) and Fisher sub-sieve size of 1.3 µm. The prealloyed nature of the powder was verified by X-ray diffraction phase analysis (Figure 2).

Example 2

[0034] 5 g portions of the powder obtained according to the procedure described in Example 1 were cold-pressed under 200 MPa in a carbide die having cavity dimensions 15.5 x 15.5 mm. The green densities of compacts was determined using the geometric method (Table 1). The powder compacts were sintered in a laboratory tube furnace for 60 minutes at 890, 900, 910, 920 and 925°C in a hydrogen atmosphere. During heating the compacts were held for 60 minutes at 700°C before proceeding to the sintering temperature. After sintering the samples were furnace cooled to room temperature. The sintered samples were tested for density by the water immersion technique (Table 1).

Table 1

Green density [g/cm ³]	Sintering temperature [°C]	As-sintered density [g/cm ³]
4.53	890	7.53
4.52	900	7.69
4.50	910	7.66
4.52	920	7.65
4.50	925	7.57

Example 3

[0035] A powder mixture containing 92.86 g Fe₂O₃; 3.57 g CuO and 3.57 g of prealloyed Fe-P powder containing 10% phosphorus by weight was prepared by mixing the ingredients in a Turbula type mixer for 10 minutes. The powders were placed together with grinding media in a 1.25 dm³ roller ball mill drum. 12 mm diameter 100Cr6 bearing steel balls were used as the grinding media. The degree of filling of the mill was 50% by volume, and the ball-to-powder weight ratio was 20:1. Distilled water was poured into the drum in an amount required for the complete immersion of the grinding media together with the powder in the liquid. The drum was turned on to rotate at 65% of the critical speed. After milling for 24 hours, the charge of the mill was dried in a laboratory drier at 130°C. The powder was then subjected to reducing annealing for 180 minutes at 700°C in a hydrogen atmosphere. After cooling to below 30°C the obtained metal sponge was ground in a ceramic mortar to powder (Figure 3) with a nominal content of 95.5% Fe by weight, 4% Cu by weight and 0.5% P by weight, the hydrogen loss of 1.2% by weight and Fisher sub-sieve size of 2.15 µm.

Example 4

[0036] 5 g portions of the powder obtained according to the procedure described in Example 3 were cold-pressed under 200 MPa in a carbide die having cavity dimensions 15.5x15.5 mm. The green densities of compacts was determined using the geometric method (Table 2). The powder compacts were sintered in a laboratory tube furnace for 60 minutes at 900°C in a hydrogen atmosphere. During heating the compacts were held for 60 minutes at 700°C before proceeding to the sintering temperature. After sintering the samples were furnace cooled to room temperature. The sintered samples were tested for density by the water immersion technique (Table 2). Selected sintered samples were then solution treated by re-heating to 900°C, holding for 30 minutes in nitrogen and quenching in water. Then they were aged for 60 minutes at 400, 450, 475, 500, 550 and 600°C. The sintered parts were re tested for a Vickers hardness determined at a 1 kgf load (Table 2).

Table 2

Green density [g/cm ³]	As-sintered density [g/cm ³]	Variant of the heat treatment	HV1 ⁽¹⁾
4.63	7.74	as-sintered condition	212 ± 5
4.63	7.74	solution treated	209 ± 7
4.65	7.71	solution treated and aged at 400°C	228 ± 7
4.66	7.72	solution treated and aged at 450°C	297 ± 10
4.64	7.72	solution treated and aged at 475°C	312 ± 8
4.65	7.71	solution treated and aged at 500°C	304 ± 8
4.64	7.72	solution treated and aged at 550°C	286 ± 6
4.66	7.72	solution treated and aged at 600°C	240 ± 11
⁽¹⁾ The confidence intervals were estimated for a confidence level 1- α = 0.9			

Example 5

[0037] 10 g of dry powder mixture comprising 8.82 g Fe₂O₃; 0.68 g CuO; 0.36 g of prealloyed Fe-P powder containing 10% phosphorus by weight and 0.14 g Sn was placed together with 100 g of 10 mm diameter steel balls in a 0.25 dm³ steel reactor of a laboratory, planetary ball mill (Activator 2S, Novosibirsk Corp.). The charge was then subjected to high-energy milling for 2 hours at a rotational speed of 700 rpm in air atmosphere. During the milling process the reactor was water-cooled. In this manner, the composite oxide powder having a modified crystalline microstructure and characterized by a high susceptibility to reduction in hydrogen was obtained. The powder was then subjected to reducing annealing for 180 minutes at 700°C in a hydrogen atmosphere and cooled to below 30°C in order to avoid self-ignition. The metal sponge thus obtained was ground in a ceramic mortar to a powder (Figure 4) with a nominal content of 90% Fe by weight, 7.5% Cu by weight, 2% Sn by weight and 0.5% P by weight, the hydrogen loss of 0.6% by weight and Fisher sub-sieve size of 8 μ m. The prealloyed nature of the powder was verified by X-ray diffraction phase analysis (Figure 5).

Example 6

[0038] 5 g portions of the powder obtained according to the procedure described in Example 5 were cold-pressed under 200 MPa, in a carbide die having cavity dimensions 15.5x15.5 mm. The green densities of compacts was determined using the geometric method (Table 3). The powder compacts were sintered in a laboratory tube furnace for 60 minutes at a temperature 900°C in a hydrogen atmosphere. During heating the compacts were held for 60 minutes at 700°C before proceeding to the sintering temperature. After sintering the samples were furnace cooled to room temperature. The sintered parts were tested for density by the water immersion technique (Table 1) and for Vickers hardness determined at a 1 kgf load (Table 3).

Table 3

Green density [g/cm ³]	As-sintered density [g/cm ³]	HV1 ⁽¹⁾
4.57	7.94	230 ± 8
⁽¹⁾ The confidence intervals were estimated for a confidence level 1- α = 0.9		

Example 7

[0039] 5 g portions of the powder obtained according to the procedure described in Example 5 were cold-pressed under 200 MPa in a carbide die having cavity dimensions 15.5x15.5 mm. The green compacts were placed on a plain low-carbon steel sheet and sintered in a laboratory tube furnace for 60 minutes at 900°C in a hydrogen atmosphere. During heating the compacts were held for 60 minutes at 700°C before proceeding to the sintering temperature. After sintering the samples were furnace cooled to room temperature. After sintering, metallographic specimens were prepared to make a qualitative evaluation of the joint between the sintered part and the steel substrate. A light microscope was used to the analysis (Figure 6).

Claims

1. The easily sinterable prealloyed iron-based powder **characterized in that** it comprises at least 80% Fe by weight, Cu and P as alloying additives and inevitable impurities, particularly hardly reducible oxides.
2. The easily sinterable prealloyed iron-based powder according to claim 1, **characterized in that** it comprises at least 90% Fe by weight, 1 - 9,8% Cu by weight and 0.2 - 2% P by weight.
3. The easily sinterable prealloyed iron-based powder according to claim 1 or 2, **characterized in that** it further comprises at least one alloying element selected from the group consisting of Sn, Co, Ni, W, and Mo.
4. The easily sinterable prealloyed iron-based powder according to claim 1 or 3, **characterized in that** it comprises 1-18% Cu by weight, 0,5 - 4% Sn by weight and 0.2 - 2% P by weight.
5. The easily sinterable prealloyed iron-based powder according to any one of the preceding claims, **characterized in that** the total content of Co and/or Ni and/or W and/or Mo is not more than 5% by weight.
6. The easily sinterable prealloyed iron-based powder according to any one of the preceding claims, **characterized in that** the hydrogen loss of the powder annealed in a reducing atmosphere is less than 1.5% by weight.
7. The easily sinterable prealloyed iron-based powder according to any one of the preceding claims, **characterized in that** the average particle size of the powder determined by the Fisher apparatus is not more than 10 μm .
8. The easily sinterable prealloyed iron-based powder according to any one of the preceding claims, **characterized in that** the powder comprises polycrystalline particles containing grains having average size not greater than 2 μm .
9. A method for producing the easily sinterable prealloyed iron-based powder according to claims 1 to 8, comprising the successive steps:
 - preparing a reducible material;
 - subjecting the said reducible material to mechanical processing by milling, including grinding, homogenization and activation of the reducible material;
 - annealing the said ground homogenized and activated by milling reducible material in a reducing atmosphere;
 - cooling the said annealed material to a temperature preventing its self-ignition; and
 - grinding the said cooled material to a powder having a predetermined average particle size.
10. The method according to claim 9, **characterized in that** the annealing is carried out at a temperature of 550-750°C, for a time of 1-8 hours, in a reducing atmosphere, which is hydrogen or gas mixture containing hydrogen.
11. The method according to claim 9, **characterized in that** the reducible material comprises oxides, carbonates, nitrates, metals and metal alloys and mixtures thereof, reducible by a technical purity hydrogen at a temperature not higher than 750°C.
12. The method according to any one of the preceding claims, **characterized in that** the mechanical processing of the reducible material is performed in dry or wet condition.
13. The method according to claim 9, **characterized in that** further drying is carried out after the mechanical processing in wet condition.
14. Use of the easily sinterable prealloyed iron-based powder according to any one of the claims 1 to 8 for the manufacturing of sintered structural and tool components, in particular sintered metal-diamond composites.
15. A sintered product, especially the sintered metal-diamond composite, prepared from the easily sinterable prealloyed iron-based powder **characterized in that** the easily sinterable prealloyed iron-based powder is the easily sinterable prealloyed iron-based powder according to any one of preceding claims 1 to 8, and the total porosity of the sintered product at a temperature not higher than 950°C is lower than 5%.

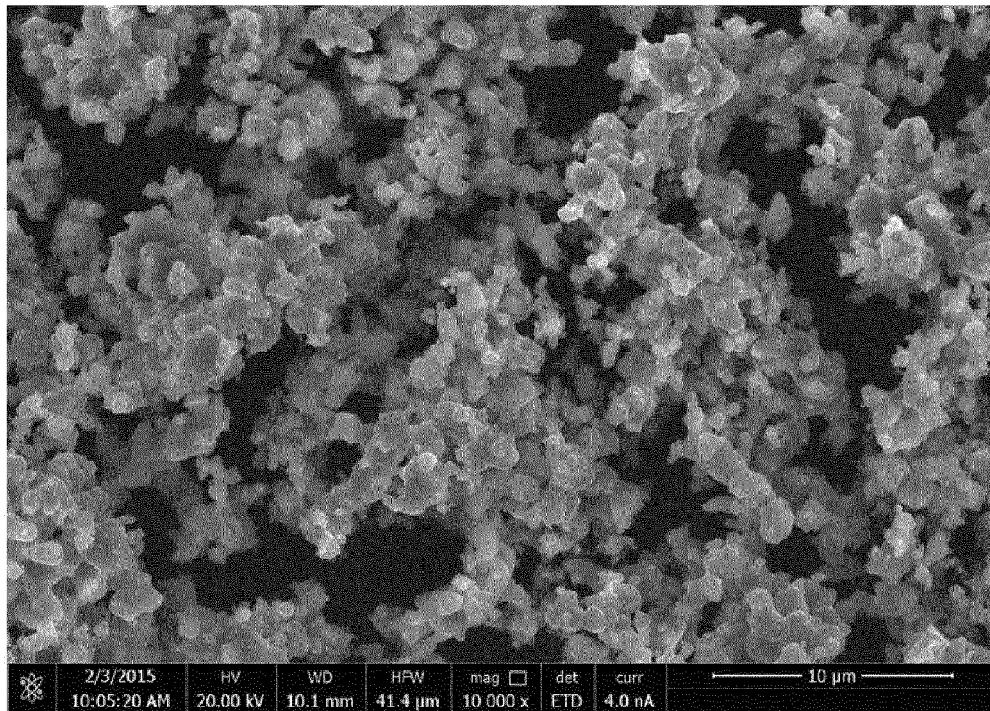


Fig. 1

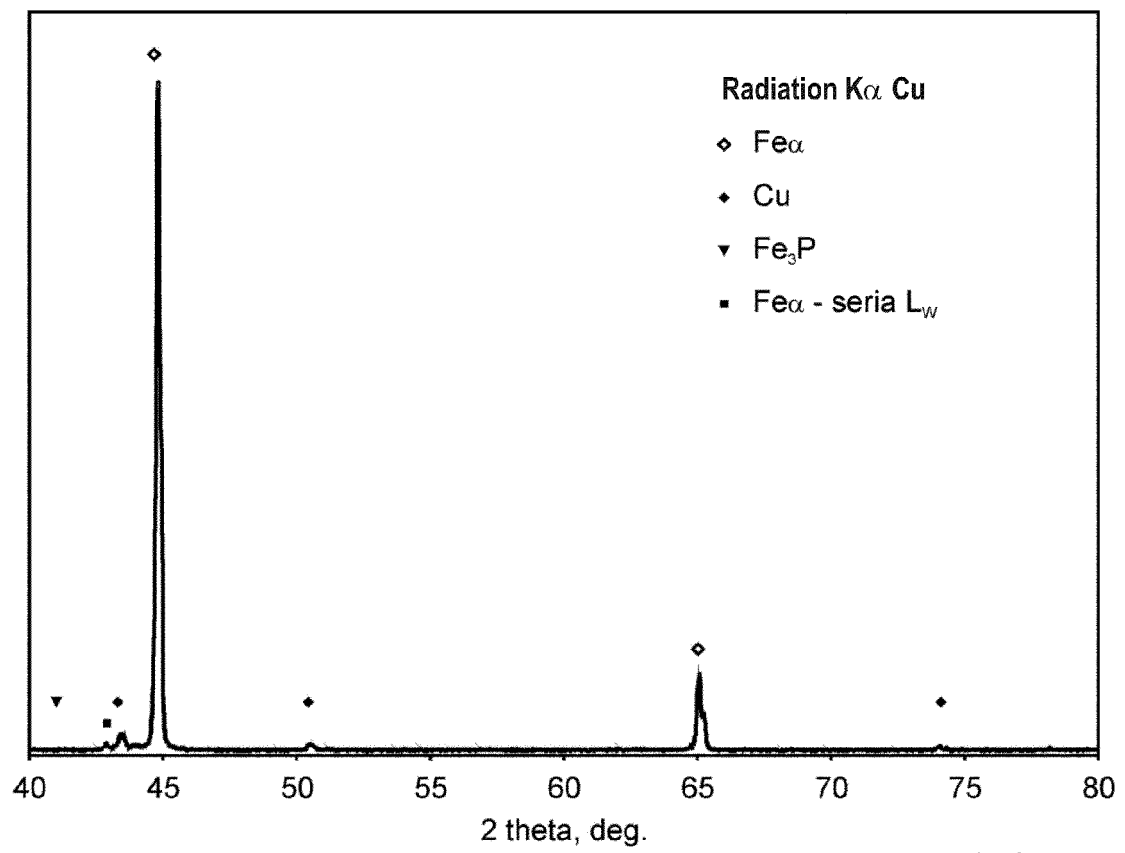


Fig. 2

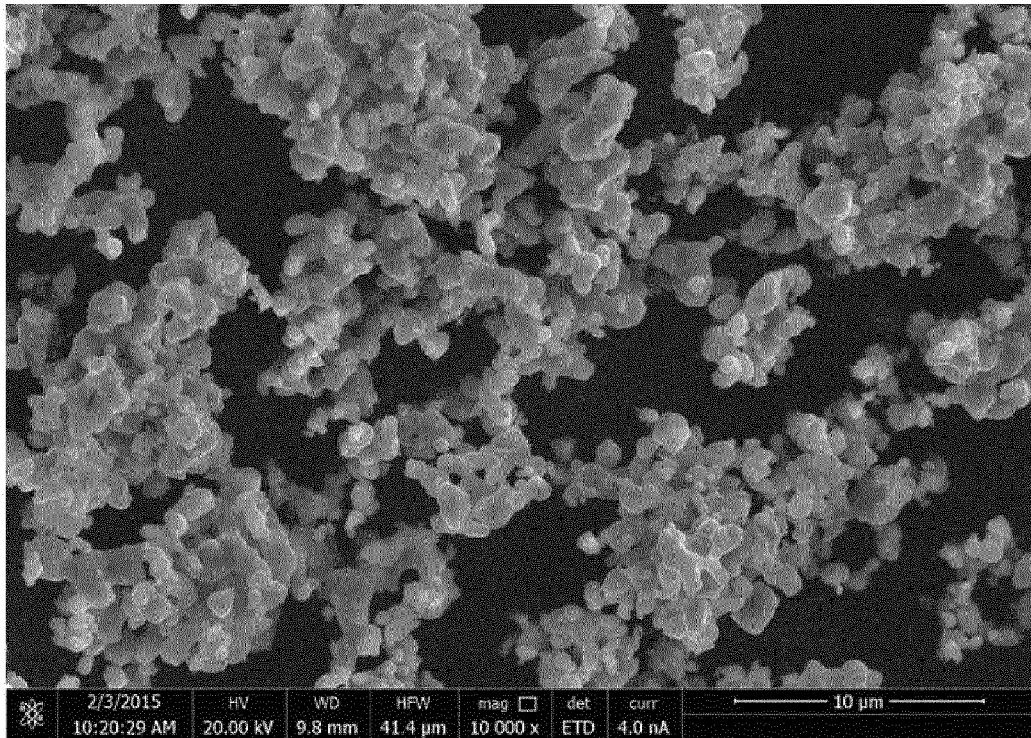


Fig. 3

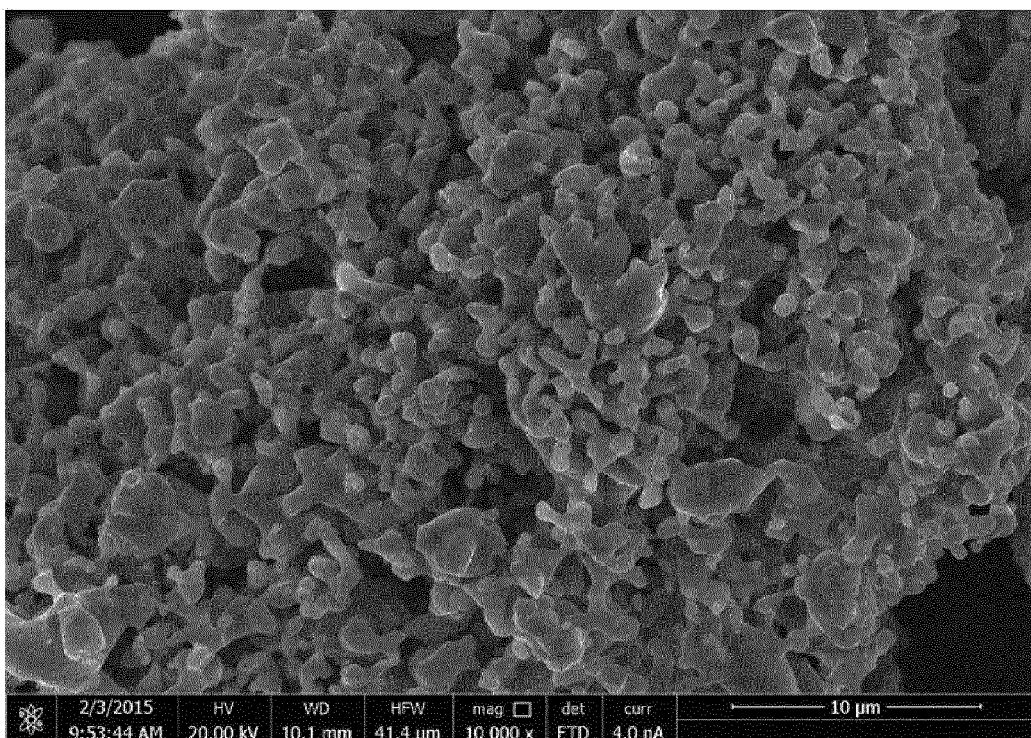


Fig. 4

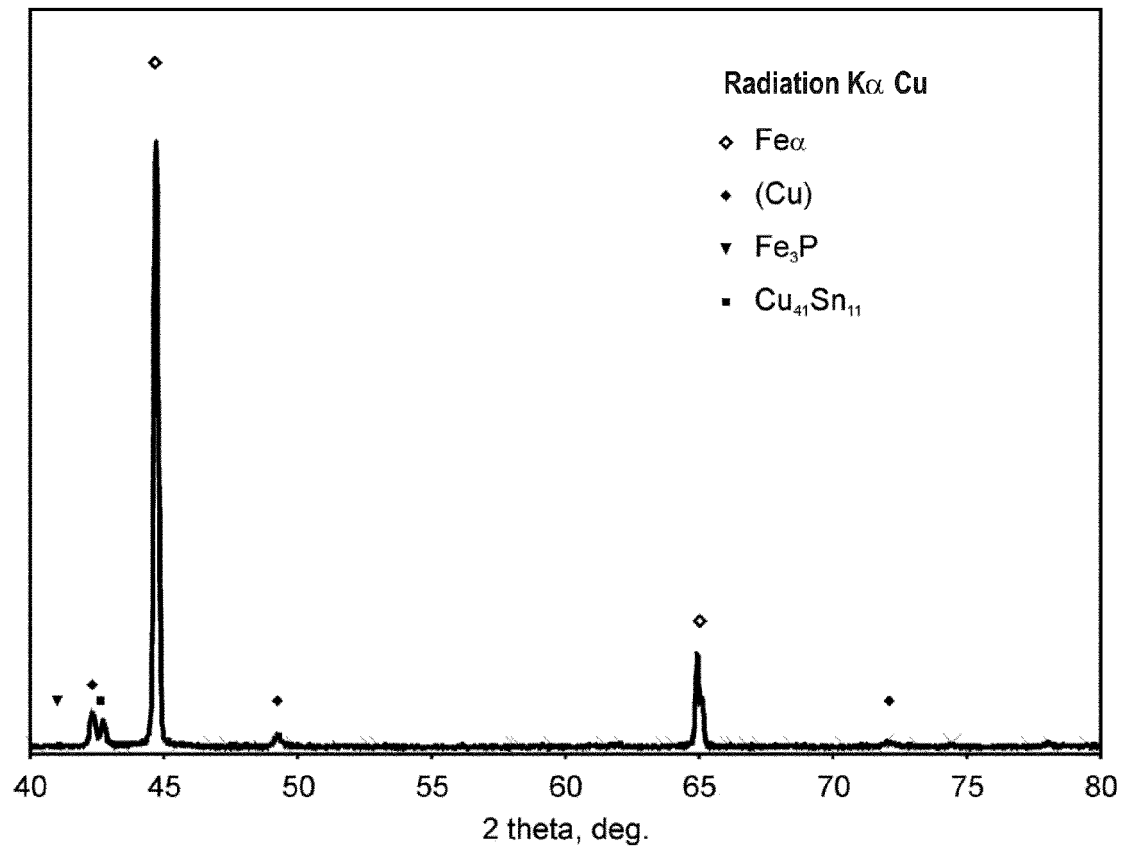


Fig. 5

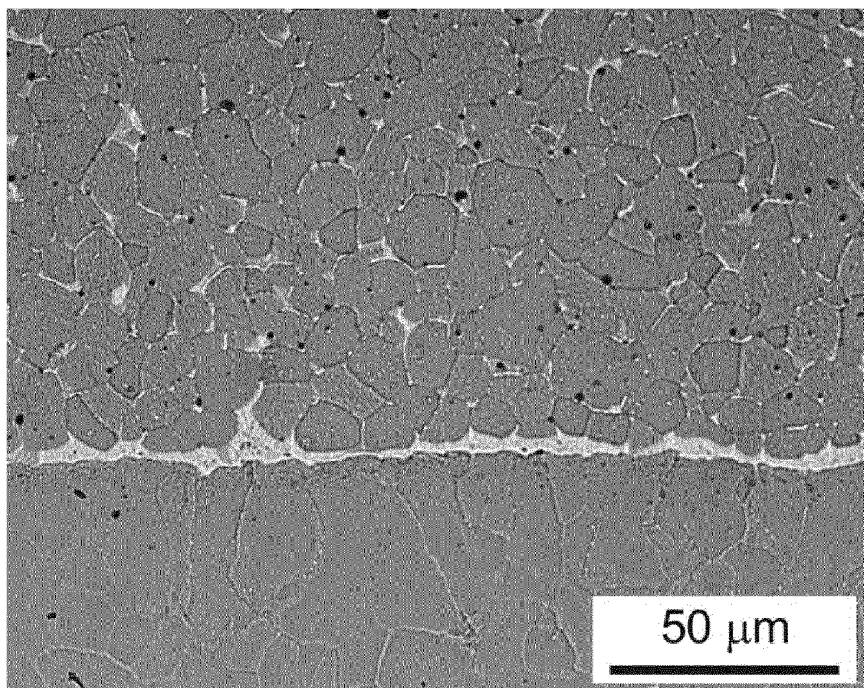


Fig. 6



EUROPEAN SEARCH REPORT

 Application Number
 EP 15 18 3275

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DOCUMENTS CONSIDERED TO BE RELEVANT			
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X A	US 4 518 563 A (SUGANUMA TETSUYA [JP] ET AL) 21 May 1985 (1985-05-21) * column 2, line 18 - line 25 * * examples *	1-3,5,6,14,15 4,7-13	INV. C22C33/02 C22C38/00 C22C38/16 B22F9/22
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			TECHNICAL FIELDS SEARCHED (IPC)
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The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 16 December 2016	Examiner Morra, Valentina
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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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 15 18 3275

5 This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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