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(54) Title: METHOD FOR MANUFACTURING COMPOSITE MATERIALS, AND A COMPOSITE MATERIAL MANUFAC-  
TURED WITH THE METHOD

(57) Abstract: A method for manufacturing powder metallurgical composite material and a material manufactured with said method,  
whereby in said method at least one steel powder including alloying materials forming nitrides and carbides is used, and in said  
method the powder is compacted by means of pressure and temperature into a solid product. The amount of the alloying materials  
forming nitrides and carbides in the steel powder to be used in the method is more than 10 percent by weight, and the carbon or  
nitrogen content of the steel powder is increased in the manufacturing steps following the atomizing.



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## METHOD FOR MANUFACTURING COMPOSITE MATERIALS, AND A COMPOSITE MATERIAL MANUFACTURED WITH THE METHOD

The present invention relates to manufacturing of composite material manufactured of a plurality of different powder materials by using different powder metallurgical manufacturing methods. More precisely, the invention relates to optimizing of the composition of the different powder qualities, so as to manufacture higher alloyed materials than possible with the methods of prior art, and to adjust the wear resistance and toughness of the structure.

### Background

In order to improve the wear resistance of the material as well against the abrasion and the erosion, it is in the most cases necessary to bring to the structure in different ways ceramic particles harder than the metallic matrix metal itself, such as carbides, nitrides and oxides, the hardness of which exceeds that of many particles causing wearing, and which consequently are able to prevent the wearing of the material having mainly a metallic structure and to protect it. There are many different ways to bring to the structure these particles increasing the wear resistance, like alloying and heat treatment. In casting processes it is possible, with certain conditions, add ceramic particles to the material to be cast, but the controllability of this method is not yet very good, at least in large components.

With powder metallurgic methods it is possible to add ceramic particles to the composite structure naturally by means of alloying and heat treatment. The amount of these ceramic particles can be increased clearly higher than in cast or worked materials, due to the elimination of the segregation problems of the alloying materials in the manufacturing of a water or gas atomized powder. So, it is possible with the powder metallurgic methods to manufacture the highest alloyed tool-making steels. Even the powder metallurgic manufacturing has, however, restrictions with respect to the amount of the alloying materials that can be brought to the structure, due to, for example, a high content of carbon and simultaneously to the formation of carbides into the melt caused by the increasing amount of the alloying materials forming carbides, like vanadium and niobe, which results in clogging of the atomizing nozzles.

In materials manufactured with powder metallurgical methods, different ceramic particles can be mixed to the metal powder in order to produce, after the compacting of the powder, a structure having a desired distribution of ceramic particles in a metallic matrix. An advantage of the powder metallurgic methods is the more controllable distribution of the ceramic particles in the metallic matrix, as well as the higher content of ceramic particles to be achieved. Treatment of the ceramic particles and the metal powder, however, is a demanding technology due to their different density and form in many cases and the resulting tendency of segregation.

In addition, it is possible with powder metallurgic manufacturing to combine the methods of adding ceramic particles to the metal powder by alloying and of separately admixing the ceramic particles with the metal powder, providing a percentage of even more than 40 % of ceramic particles by volume.

A problem with the admixing of ceramic particles with the metallic powder is that in order to avoid the segregation of the ceramic particles onto the powder particle boundary surfaces, the size distributions of the metallic and ceramic particles must be compatible. Especially the situation must be avoided, where the ceramic particles to be separately admixed have a prominently smaller size than the metallic powder particles, having a risk of continuous ceramic particle stripes formed by the ceramic particles to the boundary surfaces of the powder particles weakening the toughness and the fatigue durability. On the other hand, it is known, that there is an optimized carbide size for certain wearing conditions depending on the size, surface pressure and hardness of the wear particles in the wear system, providing edge conditions to the size of the ceramic particles to be alloyed. In order to avoid the use of metallic powder with small particles having a high price, the size of the carbides must be big enough, which means a compromise with respect to the properties to be achieved, the manufacturability and the manufacturing costs. So, the traditional manufacturing of materials including ceramic particles has plenty of restrictions.

### **Description of the Invention**

In the method in accordance with the present invention, the material is manufactured of one or a plurality of powder-like metallic materials by compacting. The material can in connection with the compacting be joined to a solid material to form a so-called combination structure, and other solid materials can be combined inside it or partly inside it.

In addition to metallic powders also ceramic or partly ceramic particles (like for instance WC-Co) can be admixed to the material before compacting to increase the wear resistance in certain conditions.

5 More precisely, the method in accordance with the invention is characterized by what is stated in the characterizing part of Claim 1 and the material manufactured with the method in accordance with the invention is characterized by what is stated in the characterizing part of Claim 11.

10 Essential for the selection and manufacturing of powder materials is that at least for the part of one metal powder, the amount of the alloying materials forming ceramic particles (for example carbides and nitrides) is such, that not all of it are bound to carbides and nitrides, and that the final amount and distribution of the ceramic particles in one or in a plurality of metal powder particles forming the microstructure is determined as a result of the diffusion and reactions occurring in connection with the compacting among the different powder qualities and the alloying materials including nitrogen and carbon, added to the powder  
15 mixture.

Alloying materials including nitrogen and carbon can be added to the metal powders before compacting, or for example graphite or chrome nitride. This is a way to increase the amount of carbides and nitrides in the material, if the metal powders have enough alloying materials (V, Nb, W, Mo, Cr, Ti etc.) forming carbides and nitrides added before atomizing. Thereby  
20 the problems can be avoided, occurring as a result of the strong precipitation of the carbides and nitrides to the melt before atomizing, caused by the increase of the amount of the alloying materials, and of the clogging of the nozzles caused by that.

As an alternative for adding alloying materials as solid materials to the powder mix prior to the compacting, in addition one or a plurality of metal powders can be nitrided or carbonized  
25 after the atomizing as a solid state prior to the mixing, and thus higher amounts of carbides and nitrides can be achieved than what would be possible by alloying to the melt.

In the material manufactured with the method in accordance with the invention, by selection of the powders to be used, a structure can be produced, wherein a certain portion of the materials includes less ceramic materials like carbides and nitrides, being a more tough  
30 material, and a certain portion of the structure includes more ceramic particles, being better

from the point of view of the wear resistance. With this kind of a structure it is possible to produce microstructures having the best possible combination of toughness and wear resistance.

- In the method in accordance with the present invention it is also possible to use powder materials so, that one of the used materials includes very much alloying materials including carbides and nitrides, and carbon and nitrogen only that much that free carbides and nitrides, free from alloying materials remain in the structure. In the other metal powder the situation is the contrary, in other words it has more free carbon and nitrogen alloyed, whereas the amount of alloying materials including carbides and nitrides is smaller than what is needed for binding the whole carbon and nitrogen content into carbides and nitrides. During the compacting and heat treatments and workings after that, the free carbon and nitrogen diffuses to the powder having alloying materials left with free carbides and nitrides, whereby a higher carbide and nitride percentage is formed there, compared to what would have been possible to produce directly to the atomized powder.
- If the amount of alloying materials including carbides and nitrides of a powder originally including free carbon and nitrogen is low, the structure will be formed so that it includes less carbides and nitrides, in other words more tough, thus being able to prevent for example the proceeding of a crack.

The manufacturing method in accordance with the present invention comprises the following steps:

- I. By means of gas or water atomizing one or a plurality of different metal powders are prepared, including a desired amount of alloying materials forming carbides and nitrides and other ceramic particles, and naturally carbon and nitrogen.
- II. The one or plurality of the metallic powders can be carbonized or nitrided to the desired carbon and nitride content prior to the mixing of the powders with each other.
- III. The metallic powders are mixed with each other and with other substantially ceramic particles to be eventually separately alloyed, and with eventual alloying materials including nitrogen and carbon.

IV. The powders are compacted by means of temperature and/or pressure for example by sintering, hot isostatic compression or hot extrusion.

V. After the compacting, the material can be further hot worked by forging or rolling to achieve the desired microstructure or form or the better density.

5 VI. The billet is subjected to necessary after-treatments like machining and thermal treatments, depending on the requirements set by the used materials.

VII. The after-treated, wear resistant material is joined to the desired point of the component by soldering, mechanical joining, gluing or welding.

10 The parameters of the compacting, forming and heat treatment must be chosen so that the alloying materials of the material after the diffusion and phase transitions form a desired distribution in the structure.

The powder comprising a different amount of alloying materials forming carbides and nitrides can also be mixed with the material to be fusion-layered, whereby it is injected in connection with the fusion-layering to the atomizing jet and it reacts during the fusion-  
15 layering and the following process steps like hot working, hot isostatic pressing or heat treatment with the other material thus forming a composite structure.

The material to be manufactured with the method in accordance with the invention has the following advantages:

- 20 1. The amount of ceramic particles improving the wear resistance in the material can be increased higher than when manufacturing the material traditionally (in other words prealloying the molten metal and by atomizing it to powder), and thus a better wear resistance can be achieved.
- 25 2. A good combination of wear resistance and toughness can be achieved with the material, because in addition to the metallic powders including plenty of ceramic particles, the structure can include metal particles including less ceramic particles, whereby it is possible to affect the toughness of the microstructure by adjusting their amount and distribution.

3. A higher amount of ceramic particles can be achieved with the material than what can be produced with normal alloying, without separate adding of ceramic particles, thus facilitating the manufacturing.

5 The material in accordance with the invention is suitable for use in components exposed to wearing and very high loading like for example in wear parts of rock crushers, linings of stone mills, hammer crushers, shredders, rollers and in other tools, cutters and rams of metallurgy industry.

10 Preferably the material manufactured with the method in accordance with the present invention has the total amount of ceramic particles of the material at least 10 % by volume after the compacting and thermal treatments. In addition, the manufactured material is preferably iron based ( $\text{Fe} > 50\%$  by weight).

The composition of the powder to be used in the method in accordance with the invention in percentage by weight can be for example the following:

|    | C   | Si  | Mn  | Cr  | Mo  | V  |
|----|-----|-----|-----|-----|-----|----|
| 15 | 2,0 | 0,7 | 0,8 | 7,1 | 1,0 | 13 |
|    | Nb  | N   |     |     |     |    |
|    | 1,0 | 0,1 |     |     |     |    |

20 The powder can be carbonized in a fluidized bed furnace to a carbon content of 3,1 % by weight, whereby the carbide and nitride content of the steel can be increased higher and a better wear resistance can be achieved in the compacted material compressed with hot isostatic pressing.

Alternatively the steel powder can be nitrided in a fluidized bed furnace, whereby a bigger amount of nitrides is formed to the steel.

## CLAIMS

1. A method for manufacturing powder metallurgic composite material, at least one steel powder including alloying materials forming nitrides and carbides being used in said method, and powder being compacted in said method by means of pressure and temperature into a solid product, **characterized** in that
- the amount of the alloying materials (V, Nb, W, Cr, Mo etc.) forming nitrides and carbides in the steel powder is more than 10 percent by weight, and
  - the carbon and nitrogen content of the steel powder is increased in the manufacturing steps following the atomizing.
2. A method in accordance with Claim 1, **characterized** in that in the manufacturing of the material at least two metal powders are used, having a different amount of alloying materials forming carbides and nitrides and a different amount of nitrogen and carbon.
3. A method in accordance with Claim 1 or 2, **characterized** in that at least one of the powders has been before mixing nitrated or carbonized in a solid state in order to achieve to the material a higher carbon or nitrogen content than in the state after atomizing, thus providing higher carbide and/or nitride contents.
4. A method in accordance with any of the Claims from 1 to 3, **characterized** in that before compacting alloying materials including nitrogen and/or carbon have been admixed to the compound powder prior to the compacting in order to increase the carbon or nitrogen content in the diffusion in connection with the compacting, thus providing higher carbide and/or nitrogen contents.
5. A method in accordance with any of the Claims from 1 to 4, **characterized** in that ceramic particles or particles including ceramic material more than 50 percent by weight are admixed to the compound powder prior to the compacting.



6. A method in accordance with any of the Claims from 1 to 5, **characterized** in that the compacting of the powder is performed by means of hot isostatic pressing, hot isostatic pressing and hot working, sintering or sintering and hot working.
- 5 7. A method in accordance with any of the Claims from 1 to 6, **characterized** in that at least one of the powder qualities is gas-atomized.
8. A method in accordance with any of the Claims from 1 to 7, **characterized** in that a powder including a differing amount of alloying materials forming nitrides and/or carbides, than the rest of the structure, is injected in melt layering to the atomizing jet, whereby it is mixed with the powder material comprising a different amount of  
10 ceramic particles to be melt layered.
9. A method in accordance with any of the Claims from 1 to 8, **characterized** in that solid materials for maximum 70 percent by volume are set inside or around the powder material prior to the compacting of the powder, and that the total amount of carbides and nitrides of said used solid materials is less than 5 percent by volume.
- 15 10. A method in accordance with any of the Claims from 1 to 9, **characterized** in that the manufactured material is joined with another solid material to produce a combination structure.
11. A material manufactured with a method in accordance with any of the Claims from 1 to 10, **characterized** in that the total amount of ceramic particles of the material is  
20 at least 10 percent by volume after the compacting and thermal treatment.
12. A material in accordance with Claim 11, **characterized** in that the manufactured material is iron based ( $\text{Fe} > 50$  percent by weight).

## INTERNATIONAL SEARCH REPORT

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## A. CLASSIFICATION OF SUBJECT MATTER

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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)

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
FI, SE, DK, NO, classes as above

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

Epodoc, PAJ, WPI, TXTE

## 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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| Y         | JP 62001836 A (KOMATSU MFG CO LTD) 07 January 1987 (07.01.1987), 07 January 1991, English abstract                           | 1-3                   |
| Y         | JP 1052001 A (KOBE STEEL LTD) 28 February 1989 (28.02.1989), 28 February 1989, English Abstract                              | 1-3                   |
| Y         | RU 2079392 C1 (INST POROSHKOVOJ METALLURG) 20 May 1997 (20.05.1997), 20 May 1997, English abstract and the whole publication | 1-3                   |
| X         | US 3650729 A (KINDLIMANN LYNN E et al.) 21 March 1972 (21.03.1972), 21 March 1972, column 3 lines 24-26, table 1, claims     | 1-3                   |
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☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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| Y         | US 4894090 A (EKEMAR CARL S G et al.) 16 January 1990 (16.01.1990),<br>16 January 1990, column 5 | 1-3                   |

**INTERNATIONAL SEARCH REPORT**  
**Information on patent family members**

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| Patent document<br>cited in search report | Publication<br>date | Patent family<br>members(s)                                                                                                                                                    | Publication<br>date                                                                                                                                    |
|-------------------------------------------|---------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------|
| JP 3090543 A                              | 16/04/1991          | None                                                                                                                                                                           |                                                                                                                                                        |
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