

(19)



(11)

EP 2 531 630 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention of the grant of the patent:
24.05.2023 Bulletin 2023/21

(51) International Patent Classification (IPC):
C22C 29/02 ^(2006.01) **C22C 29/14** ^(2006.01)
C22C 29/16 ^(2006.01)

(21) Application number: **11739260.5**

(52) Cooperative Patent Classification (CPC):
C22C 1/1068; C22C 29/02; C22C 29/14;
C22C 29/16; C22C 37/00; C22C 37/06; C22C 37/10

(22) Date of filing: **01.02.2011**

(86) International application number:
PCT/AU2011/000092

(87) International publication number:
WO 2011/094800 (11.08.2011 Gazette 2011/32)

(54) **HARD METAL MATERIALS**

HARTMETALLMATERIALIEN

MATÉRIAUX À BASE DE MÉTAL DUR

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR

(74) Representative: **MacLeod, Roderick William et al**
The Weir Group PLC
1 West Regent Street
Glasgow G2 1RW (GB)

(30) Priority: **01.10.2010 AU 2010904416**
05.02.2010 AU 2010900457

(56) References cited:
WO-A1-01/88213 **WO-A1-94/11541**
WO-A1-2004/104253 **WO-A1-2011/091479**
DE-A1- 2 063 181 **JP-A- 60 169 515**
RU-C1- 2 017 578 **US-A- 3 528 808**
US-A- 6 013 141 **US-A- 6 013 141**
US-A1- 2009 025 834

(43) Date of publication of application:
12.12.2012 Bulletin 2012/50

(73) Proprietor: **Weir Minerals Australia Ltd**
Artarmon, New South Wales 2064 (AU)

(72) Inventor: **DOLMAN, Kevin**
Epping
New South Wales 2121 (AU)

EP 2 531 630 B1

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

DescriptionField of the invention

- 5 **[0001]** The present invention relates in general terms to hard metal materials comprising refractory material particles, as described herein, dispersed in a host metal or metal alloy.
- [0002]** The ASM Materials Engineering Dictionary defines the term "hard metal" as a collective term for a sintered material with high hardness, strength and wear resistance.
- 10 **[0003]** The present invention also provides components manufactured from the hard metal materials. The present invention relates particularly, although by no means exclusively, to large components weighing more than 100kgs and typically more than 1 tonne.
- [0004]** The present invention also provides a method of manufacturing the components from the hard metal materials.
- [0005]** In more particular terms, although by no means exclusive terms, the present invention relates to hard metal materials that are useful for applications requiring wear resistance.

15

Background

- [0006]** It is known to use powder metallurgy to manufacture small components from hard metal materials comprising refractory particles dispersed in a host metal (which term is understood herein to include metal alloy).
- 20 **[0007]** Powder metallurgy processes involve sintering mechanically mixed refractory powders at elevated temperatures under pressure, usually in an inert atmosphere.
- [0008]** "Sintering" comprises bonding powdered materials, usually under pressure, by solid-state reactions at temperatures lower than that required for the formation of a liquid phase. During a sintering process, at temperatures below the melting point of the metallic binders, powders of metallic binder phase and refractory particles are welded together
- 25 by pressure and heat. Sintering is traditionally used for manufacturing ceramic components and has also found uses in such fields as powder metallurgy for the manufacture of products containing very high melting point materials.
- [0009]** Powder metallurgy is a useful process for manufacturing relatively small, simple-shaped, wear resistant components such as tungsten carbide tool bits. However, powder metallurgy is not a practical process for manufacturing larger, complex-shaped, hard metal, wear resistant components such as pump impellers and crusher wear parts weighing
- 30 more than 100kgs and typically more than 1 tonne from hard metal materials. This is an issue, particularly in applications in the mining and minerals processing industries where large high wear resistant components are often required.
- [0010]** It is known to use wear resistant metal alloys, such as high chromium white cast irons, in the manufacture of components used in applications in the mining and minerals processing industries, such as applications involving transporting solid materials. For example, hard-facing alloys are formed on the trays of dump trucks that transport mined ore
- 35 from a mine site to a minerals processing plant. In another example, castings of wear resistant alloys are used to form pumps for transporting slurries of ore particles suspended in water through processing stages in flotation circuits in a minerals processing plant.
- [0011]** The fracture toughness and corrosion resistance requirements for the wear resistant alloy in each of the above examples are different and, accordingly, the wear resistant alloy compositions are different. The common factor between both, however, is a need to provide wear resistance in addition to other properties. Generally speaking, higher wear
- 40 resistance can be achieved through controlling the alloy composition, but there is a trade-off against other properties.
- [0012]** For any given circumstance where wear resistance is an important property, it is desirable to provide materials with desirable properties and improved wear resistance by compromising less on the balance of these properties.
- [0013]** It is noted that the specification includes references to weight percent (wt.%) and volume percent (vol.%). In the context of the references to NbC in the specification, where NbC has a density similar to a host metal, these terms
- 45 are interchangeable.
- [0014]** In WO 94/11541 A1, there is described a method of making an engineering ferrous metal comprising the steps of adding to liquid engineering ferrous metal solid alloy carbide particles and thereafter permitting the ferrous metal to solidify. The alloy carbide particles are coated with iron or an iron alloy to allow wetting to occur between the powder
- 50 and the liquid ferrous metal and the particles have a density which matches that of the ferrous metal to provide a uniform distribution of the carbide particles in the ferrous metal.
- [0015]** DE 2063181 A1 relates to casting processes wherein a TiC-containing carbide component is incorporated into a Fe, Co or Ni based alloy. The alloy may also contain other carbides of metals which belong to groups IVa, Va and VIa of the periodic table, primarily tungsten carbide, and, for example, carbides of zirconium, vanadium, niobium and tantalum.
- 55 **[0016]** In WO 2004/104253 A1, there is disclosed a casting of a white cast iron alloy. The casting comprises the following alloy composition, in weight%: chromium: 12 - 25%; carbon: 1.5 - 6%; manganese: 2 - 7%; silicon: up to 1.5%; molybdenum: up to 2; nickel: up to 4%; microalloying elements selected from the group consisting of titanium, zirconium, niobium, boron, vanadium, and tungsten: up to 2% of each of one or more of the elements; and iron: balance. The

microstructure of the casting comprises 15-60 vol% eutectic carbides and primary carbides dispersed in a ferrous matrix that comprises martensite and is at least substantially free of pearlite.

[0017] In JP H07 30429 there is disclosed sintered products having excellent thermal shock resistance and thermal fatigue resistance. The sintered products comprise carbides dispersed in a matrix of a high-alloy steel. The dispersed carbides are selected from 2-20% vanadium carbides, 2-20% of carbides (except vanadium carbide) of the metals of groups VIa, Va, and VIa of the periodic table, and one or more nitrides and carbonitrides of the metals of groups VIa and Va, and one or more solid solutions of two or more thereof.

[0018] US 5,030,519 discloses a matrix-bonded carbide-containing material of high hardness prepared using a mixture containing a matrix alloy having a composition in weight percent of from about 15 - 45 percent chromium, from 0 - 3 percent silicon, from about 2 - 6 percent boron, from about 3 - 11 percent titanium (either as metal or as a compound), balance iron and impurities, and a mass of tungsten carbide particles, the tungsten carbide particles preferably being present in an amount of from about 15-60 percent by weight of the total mixture and the matrix alloy preferably being present in an amount of from about 85 - 40 percent by weight of the total mixture.

[0019] US 3,528,808 discloses a casting of a nickel-base, cobalt-base or chromium-base alloy and a reinforcing phase consisting essentially of a refractory carbide, present predominantly in the form of high strength fibers integrally embedded in the base metal matrix.

[0020] US 2009/025834 discloses an amorphous steel alloy with up to 10 wt% of NbC.

Summary of the disclosure

[0021] The applicant has found in the course of extensive research and development work that a liquid host metal, containing a dispersion, typically a dispersion, of 10-50 volume % fine particles of a refractory material that is insoluble in the host metal, and is described herein as a liquid metal slurry, has very good fluidity during pouring in a foundry and the slurry readily flows to fill sand moulds to produce sound castings of the hard metal material.

[0022] The term "insoluble" is understood herein to mean that for all intents and purposes the refractory material is not soluble in the host metal. There may be limited solubility. However, the refractory particles are essentially distinct from the host metal in that there is negligible partitioning of the transition metals in the refractory material particles to the host metal.

[0023] The present invention is defined with more precision in the appended claims to which reference should now be made.

[0024] The applicant has also found that mixing and dispersing the insoluble refractory particles in the host metal may be carried out in an effective way in the liquid state in an inert atmosphere, such as in a vacuum furnace, to minimise oxidation of the reactive elements in the refractory material particles.

[0025] The present invention is a departure from standard foundry practice known to the applicant that involves the complete melting of all alloying additions contained in a casting to form a single phase liquid to ensure maximum fluidity during pouring into a mould.

[0026] The applicant has also found that the fluidity of liquid metal slurries, when cast within certain production parameters in accordance with the present invention, is sufficient to produce a family of sound hard metal material castings ranging from small to large casings with specific wear resistance, fracture toughness and corrosion resistance that suit a wide range of operating conditions in service.

[0027] The production parameters may comprise any one or more of the particle size, reactivity, thermal expansion or contraction, density, and solubility of the refractory material, as discussed further below.

[0028] The present invention provides a hard metal material as set forth in claim 1.

[0029] In the context of the present invention, the term "hard metal material" is understood to comprise particles of high melting point carbides of any of titanium and niobium dispersed in a tough host metal, which acts as a binder phase. Typically the host metal is a ferrous metal alloy. Each of these particles is a particle of a refractory material and is referred to herein as a "refractory material". The particles of the refractory material may be carbides of one transition metal, such as NbC.

[0030] The particles of the refractory material may be carbides of more than one transition metal where the particles are a chemical mixture (as opposed to a physical mixture) of the carbides of the transition metals. In other words, in the case of carbides, the particles of the refractory material may be of the type described as $(M_1, M_2)C$, where "M" is a transition metal. One example that is discussed further herein in $(Nb, Ti)C$.

[0031] The hard metal material may comprise 10-40 volume % particles of the refractory material dispersed in the host metal.

[0032] The hard metal material may comprise less than 30 volume % particles of the refractory material dispersed in the host metal.

[0033] The hard metal material may comprise less than 25 volume % particles of the refractory material dispersed in the host metal.

[0034] The host metal may be a ferrous alloy (such as a steel or a cast iron), a stainless steel, an austenitic-manganese steel such as a Hadfield steel, or a iron-based or nickel-based or cobalt-based superalloy.

[0035] The present invention also provides a method of forming a hard metal material as set forth in claim 8.

[0036] The present invention also provides a method of manufacturing a component of a hard metal material as set forth in claim 4.

[0037] The method may comprise forming the slurry and thereafter forming the casting of the component in a chamber under vacuum conditions which remove air from the chamber and supplying an inert gas, such as argon, into the chamber. By way of example, the method may be carried out in a vacuum melting furnace.

[0038] The method may comprise selecting the production parameters to form the slurry in step (a) that has a required fluidity for processing in step (b). In any given situation, a skilled person will be able to determine a required fluidity for processing step (b) having regard to standard foundry practice considerations such as the size and shape of the component to be formed and the required dispersion (uniform or segregated) to provide the required microstructure for the component.

[0039] The production parameters may comprise any one or more of the particle size, reactivity, density, and solubility of the refractory materials, as discussed further below.

Refractory material particle size

[0040] The refractory material may be a fine particle size. A fine refractory material particle size may be required to ensure a homogeneous dispersion in the host metal. The melting points of the majority of the transition metal refractory materials are in excess of 1800°C and the refractory materials are generally insoluble in host liquid metals. The applicant has found that refractory powders with particle sizes less than 500 microns, typically less than 150 microns, in diameter provide optimum flow characteristics in liquid metal slurries and yield a desirable uniform dispersion of the refractory particulates in the microstructures of the Hard Metal castings.

[0041] The refractory material may be less than 400 microns particle size.

[0042] The refractory material may be less than 200 microns particle size.

[0043] The refractory material may be less than 150 microns particle size.

[0044] The refractory material may be added to the host liquid metal as follows.

(a) As a fine powder with a selected particle size distribution.

For example, 15 wt.% of particles of a refractory material in the form of niobium carbide (NbC) (minus 50 microns in diameter) added to a liquid host metal in the form of a high chromium white cast iron host metal. NbC exhibits a Vickers Hardness of 24 GPa, a melting point of 3600°C, and a very low solubility in the host liquid metal at a casting temperature of about 1500°C. The liquid metal slurry comprises a suspension of insoluble NbC particles (minus 50 microns in diameter) in the host liquid metal. On solidification, the microstructure exhibits a dispersion of 15 volume% fine NbC particles (minus 50 microns in diameter) in a high chromium white cast iron matrix containing a negligible amount (less than 0.3 wt.%) of niobium in solution in the matrix.

(b) The transition metals mentioned above or ferro-alloys of the same transition metals can be added to a wide range of host metals containing all the combinations and permutations of the elements carbon, boron and nitrogen.

[0045] For example, as is described in more detail below, the applicant has found that Fe-Nb readily dissolves in the host liquid metal at 1500°C and niobium immediately combines with carbon in the host liquid metal to form niobium carbides in situ with particle sizes less than 50 microns in diameter.

Reactive refractory materials

[0046] Most of the transition metal refractory materials described above are classed as "reactive elements", i.e. the individual metal elements and/or their carbide compound forms react readily with air at metal casting temperatures about 1500°C to form undesirable metal oxides and/or copious quantities of gases such as CO₂ which can result in severe porosity in the castings. The problems of oxidation and porosity in hard metal castings, produced by a liquid metal slurry, and associated with chemical reactions of the reactive refractory materials in air at elevated temperatures are overcome by melting and pouring the liquid metal slurry in an inert atmosphere.

[0047] Selection of refractory material particles having lower thermal expansion or contraction than the host metal.

[0048] Poor bonding between refractory particles and the host metal in hard metal materials have been variously reported in the literature. The applicant found no evidence of poor bonding between the refractory particles and a wide range of the host metals evaluated by the applicant. Whilst not wishing to be bound by the following comment, the observed excellent bonding is attributed by the applicant in large part to the use of an inert atmosphere during casting of the hard metal materials and the thermal contraction of the transition metal refractory particles being much less,

typically about 50% lower, than the thermal contraction of the host metals during cooling from the solidus to ambient temperature generating compressive forces on the refractory material particles that firmly held the particles in the host metals on solidification. All refractory particles in hard metal material castings produced by the applicant in an inert atmosphere were found to be under compressive loading ensuring intimate contact and good bonding with the host metals.

Density of refractory materials

[0049] The density of the refractory material of the particles, compared to the density of the host metal in the liquid state, is a parameter to consider during the method of the present invention to control the dispersion of refractory particles in the hot host metal. In some situations it may be important to avoid segregation of refractory material particles in the liquid host metal. In other situations, segregation may be desirable. For example, the nominal density of a host ferrous liquid metal at 1400 °C is 6.9 grams/cc. When tungsten carbide particles, with a density of 15.7 grams/cc, are added to a host ferrous metal, the WC particles will sink to the bottom of the mould prior to solidification of the host metal. When titanium carbide particles, with a density of 4.8 grams/cc, are added to the same host ferrous metal, the TiC particles will float to the top of the ladle or mould. Niobium carbide, with a density of 7.7 grams/cc at 1400 C, is fairly close to the density of the host liquid metal at 6.9 grams/cc and is less prone to segregation in the liquid host metal than TiC or WC. However, the applicant has observed that NbC particles will segregate to the bottom of large section white iron castings during the process of the present invention when solidification times are in the order of 30 minutes or more. As described in more detail below, niobium carbide and titanium carbide have similar crystal structures and are isomorphous. Selecting the required Nb/Ti ratio in a (Nb,Ti)C chemical compound yields a refractory material with any required density in the range 4.8 - 7.7 grams/cc at the casting temperature. Matching the density of the solid refractory particles and the liquid host metal at the casting temperature eliminates segregation of the particulates in the melt during the process of the present invention.

Solubility of refractory materials

[0050] The addition of refractory material particles that are for all intents and purposes insoluble, i.e. having minimal solid solubility in the host liquid metal, to produce a casting in accordance with the method of the present invention, produces a hard metal material that displays physical and chemical properties that are very similar to the host metal with substantially improved wear resistance due to the presence of a controlled dispersion of a high volume % of hard refractory material particles in the microstructure.

[0051] For example, the solubility of a refractory material in the form of (Nb,Ti)C in liquid host metals in the form of (a) liquid Hadfield steel and (b) liquid 316 stainless steel and (c) liquid high chromium white cast iron at elevated temperatures is negligible (<0.3 weight%). The addition of 15 weight% (Nb,Ti)C with the required densities to these three metal alloys, followed by standard heat treatment procedure for each host metal produces microstructures consisting of a uniform dispersion of 15 volume% primary niobium-titanium carbides in the host metals which are substantially free of niobium and titanium, i.e. there is negligible partitioning of the transition metals in the refractory material slurry particles to the liquid host metal.

[0052] Consequently, there is a negligible influence of the refractory materials of the particles on the chemistry and response to heat treatment of the host metal.

[0053] The three hard metal materials produced by the method of the present invention display the known physical and chemical properties of (a) Hadfield steel, (b) 316 stainless steel and (c) high chromium white cast iron respectively with an increased wear resistance due to the presence of a dispersion of 15 volume% of primary niobium-titanium carbides in the microstructures.

[0054] In addition to the above, in particular the applicant has found that providing a hard metal material with a microstructure that includes particles of niobium carbide and/or particles of a chemical (as opposed to a physical) mixture of niobium carbide and titanium carbide dispersed in a matrix of a host metal considerably improves wear resistance of the hard metal material without detrimentally affecting the contribution that other alloying elements have on other properties of the hard metal material.

[0055] In addition, in particular the applicant has found that it is possible to adjust the density of particles of a chemical mixture of niobium carbide and titanium carbide to a sufficient extent in relation to the density of a host metal, which forms a matrix of the hard metal material, to make it possible to selectively control the dispersion of the particles in the matrix from a uniform dispersion to a non-uniform dispersion of the particles. This opportunity for density control is an important finding in relation to castings of the hard metal material. In particular, by virtue of this finding it is now possible to produce castings of the hard metal material with controlled segregation of the particles in parts of the castings. This is important for some end-use applications for castings, such as where it is desirable to have a concentration of high wear resistant particles near a surface of a casting of a hard metal material. Equally, in other end-use applications for castings it is desirable to have a uniform dispersion of the particles in the matrix of the casting.

[0056] In addition, the applicant has found that forming a hard metal material and castings of the material to include particles of niobium carbide and/or particles of a chemical mixture of niobium carbide and titanium carbide in a range of 10 to 25 wt%, or even up to 33 wt% or higher, dispersed in a host metal, which forms a matrix of the hard metal material, does not have a significant negative impact on corrosion resistance and toughness of ferrous material in the host metal. Hence, the present invention makes it possible to achieve high wear resistance of a hard metal material without a loss of other desirable material properties.

[0057] Accordingly, there is provided a method of forming a wear resistant hard metal material as set forth in claim 9.

[0058] The terms "a chemical mixture of niobium carbide and titanium carbide" and "niobium/titanium carbides" are hereinafter understood to be synonyms. In addition, the term "chemical mixture" is understood in this context to mean that the niobium carbides and the titanium carbides are not present as separate particles in the mixture but are present as particles of niobium/titanium carbides.

[0059] Niobium carbides and titanium carbides each have a Vickers hardness (HV) around 2500, which is about 1000 HV above the hardness of chromium carbides. Accordingly, hard metal materials having a microstructure containing 10 to 40 wt% particles of niobium carbide and/or niobium/titanium carbides have excellent wear resistance properties. However, a significant aspect of the applicant's work has recognised that niobium carbides and titanium carbides and niobium/titanium carbides are substantially inert chemically with respect to other constituents in the hard metal material so those constituents provide the hard metal material with the properties for which they were selected. For example, chromium added to cast iron alloys still produces chromium carbides and provides corrosion resistance.

[0060] The melt may be in the form of a weld pool in a hard-facing process. In these circumstances, the niobium and/or the titanium may be added to the weld pool in a wire alloy in order to meter the addition of niobium and/or titanium.

[0061] The melt may be in the form of a melt for forming a casting.

[0062] The niobium and the titanium may be added to the melt in any suitable form, bearing in mind the requirement of forming particles of niobium carbides and/or niobium/titanium carbides in the solid hard metal material.

[0063] For example, the method may comprise adding the niobium to the melt in the form of ferro-niobium, for example particles of ferro-niobium. In this situation, the ferro-niobium dissolves in the melt and the resultant free niobium and carbon in the melt form niobium carbides in the melt.

[0064] The method may also comprise adding the niobium to the melt as elemental niobium.

[0065] The method may also comprise adding the niobium and the titanium to the melt as ferro-niobium-titanium.

[0066] The method may also comprise adding the niobium to the melt in the form of particles of niobium carbide. The method may also comprise adding the niobium and the titanium to the melt in the form of particles of niobium/titanium carbides. In both cases, the solidified metal alloy may be formed from a slurry of particles of niobium carbide and/or niobium/titanium carbides suspended in the melt. It is anticipated that if the weight fraction of these carbides in the melt slurry is too high, the flow properties of the slurry may be adversely affected with the result that unsound castings of the melt may be produced. Nevertheless, casting a slurry contrasts with the standard operating procedure in foundries which involves casting clear (single phase) liquid melts, i.e. where the melt is above the liquidus temperature of the highest melting point constituent of the melt.

[0067] The particles of niobium/titanium carbides may be any suitable chemical mixture of a general formula $(\text{Nb}_x, \text{Ti}_y)\text{C}$. By way of example, the niobium/titanium carbides may be $(\text{Nb}_{0.5}, \text{Ti}_{0.5})\text{C}$ or $(\text{Nb}_{0.25}, \text{Ti}_{0.75})\text{C}$ or $(\text{Nb}_{0.75}, \text{Ti}_{0.25})\text{C}$.

[0068] The niobium and/or the titanium may be added to the melt to produce particles of niobium carbide and/or niobium/titanium carbides in a range of 12 wt% to 33 wt% niobium carbides and niobium/titanium carbides of the total weight of the solidified hard metal material.

[0069] The niobium and/or the titanium may be added to the melt to produce particles of niobium carbide and/or niobium/titanium carbides in a range of 12 wt% to 25 wt% niobium carbides and niobium/titanium carbides of the total weight of the solidified hard metal material.

[0070] The quantity of particles of niobium carbide and/or niobium/titanium carbides in the microstructure of the solidified hard metal material may depend on the system.

[0071] The applicant is concerned particularly with solid hard metal materials that include host metals in the form of ferrous alloys, such as ferrous alloys described as high chromium white cast irons, stainless steels, and austenitic manganese steels (such as Hadfield steels). For ferrous alloys the quantity of particles of niobium carbide and/or niobium/titanium carbides in the final microstructure may be in a range of 10 to 33 wt% or in a range of 12 to 25 wt% of the total weight of the solidified hard metal material.

[0072] The particle size of niobium carbide and/or niobium/titanium carbide may be in a range of 1 to 150 μm in diameter.

[0073] The method may comprise stirring the melt with an inert gas or magnetic induction or any other suitable means in order to disperse particles of niobium carbide and/or niobium/titanium carbides in the melt.

[0074] The method may comprise adding particles of niobium carbide and/or particles of niobium/titanium carbides to the melt under inert conditions, such as an argon blanket, to reduce the extent to which niobium carbide and/or titanium carbide oxidize while being added to the melt.

[0075] The method may comprise adding particles of ferro-niobium and/or ferro-titanium and/or ferro-niobium-titanium

to the melt under inert conditions, such as an argon blanket, to reduce the extent to which niobium and/or titanium oxidize while being added to the melt.

[0076] In a situation where particles of niobium/titanium carbides are required in the solidified hard metal material, the method may comprise pre-melting ferro-niobium and ferro-titanium and/or ferro-niobium-titanium under inert conditions and forming a liquid phase that is a homogeneous chemical mixture of iron, niobium and titanium and solidifying this chemical mixture. The chemical mixture can then be processed as required, for example by crushing to a required particle size, and then added to the melt (containing carbon) under inert conditions. The iron, niobium and titanium dissolve in the melt and the niobium and titanium and carbon in the melt form niobium/titanium carbides in the melt.

[0077] The method may comprise forming the solidified hard metal material by casting the melt into a cast product, such as a pump impeller or a pump throatbush.

[0078] The cast product may be subject to subsequent thermal treatment for adjusting the microstructure to achieve desired alloy properties.

[0079] There is also provided a method of casting the above-described hard metal material as set forth in claim 10.

[0080] The casting may comprise a uniform dispersion of the niobium/titanium carbide particles in the matrix. For example, the casting may be a pump impeller.

[0081] The casting may comprise a non-uniform dispersion of the niobium/titanium carbide particles in the matrix. For example, the casting may be a pump throatbush.

[0082] The host metal may be a ferrous alloy, such as a high chromium white cast iron, a stainless steel, or an austenite manganese steel (such as a Hadfield steel).

Brief description of the drawings

[0083] Embodiments of the invention will now be described, by way of example only, with reference to the accompanying drawings, in which:

Figure 1 is a micrograph of a high chromium white cast iron alloy including 27 wt% chromium and 15 wt% niobium carbides.

Figure 2 is a micrograph of martensitic stainless steel (grade 420C) including 15 wt% niobium carbides.

Detailed description

[0084] The applicant carried out an extensive series of laboratory melting trials on the addition of 10 (comparative) to 30 wt% NbC and Nb/TiC particles to a wide selection of ferrous alloys including high chromium white irons, austenitic-manganese steels (including Hadfield steels), superalloys, stainless steels (including duplex, ferritic, austenitic and martensitic) and hard-facing weld deposits.

[0085] An example of a microstructure of a high chromium white cast iron alloy including 15 wt% NbC is shown in Figure 1. The alloy was produced by casting a 50g ingot from a melt produced in an electric arc melting furnace under a partial pressure of argon in a water cooled copper hearth, i.e. the ingot was chill cast. The NbC was added to the furnace melt as discrete particles which had a particle size range of 2 to 20 μm in diameter.

[0086] In further embodiments the applicant has examined the use of various other particle size ranges of NbC, including <45 μm in diameter, 45 to 75 μm in diameter, 75 to 150 μm in diameter and <100 μm in diameter.

[0087] High chromium white cast iron alloys conventionally rely on the high chromium content to produce a significant volume of hard chromium carbides that provide castings with high wear resistance. In addition, high chromium white cast iron alloys conventionally rely on some chromium remaining in the ferrous matrix and provides alloys with corrosion resistance.

[0088] The microstructure in Figure 1 exhibits a ferrous matrix containing a fine dispersion of eutectic M_7C_3 carbides (approximating 30 volume%) and a dispersion of 15 wt% NbC particles which appear as a phase of white coloured spheroids in the Figure.

[0089] The microstructure shown in Figure 2 is a form of 420C grade martensitic stainless steel that was produced by the same process described above for the high chromium white cast iron shown in Figure 1.

[0090] In contrast, NbC particles (white coloured in Figure 2) are not regular spheroids as in the high chromium white cast iron, but rather an irregular NbC carbide shape that appears to be typical for various stainless steel grades that have been alloyed with NbC.

[0091] The experimental work reported above and other experimental work carried out by the applicant indicates that alloys produced with niobium carbide particles in the range of 10-30 wt% NbC in a ferrous host metal show very promising microstructures, welding characteristics and foundry casting characteristics. The indications are that the addition of high NbC contents to these materials substantially increases wear resistance without adversely affecting castability, weldability, response to heat treatment and the mechanical properties of the original ferrous materials.

EP 2 531 630 B1

5 [0092] The microstructures of the test castings in Figure 1 and other test castings produced by the applicant show that all the NbC particles added to the ferrous alloys are primary carbides in suspension in the liquid metal. The analogy is that all conventional castings above the liquidus temperature (approximately 1300-1400°C) are "clear liquids", i.e. single phase liquids. However, when niobium carbide particles were added, for example 20 wt%, the particles remained in suspension so the liquid metal and NbC particles approximate a "slurry" (2 phases) with good fluidity, which is a mandatory requirement for producing sound castings. The experimental work found a similar outcome when niobium/titanium carbide particles were added to a liquid melt.

10 [0093] It will be appreciated, however, that niobium carbides can form as solid particles in a melt, rather than added to the melt, by adding ferro-niobium to the melt. In such cases, the melt contains carbon, and the weight% carbon is greater than one eighth of the weight% of niobium. In the case of ferro-niobium additions, the iron and niobium separate in the melt. The niobium, which has a high affinity for carbon, chemically combines with carbon from the liquid melt to form solid niobium carbide particles dispersed in the liquid melt. Upon casting, the melt is cast as a "slurry" consisting of solid niobium carbide particles suspended in the liquid melt. Upon solidification, the casting will have a microstructure that includes niobium carbides dispersed in a ferrous matrix. A similar microstructure is achieved with niobium/titanium carbide particles.

15 [0094] The advantages of adding 10-30 wt% NbC particles to ferrous materials are summarised below.

20 (a) Hardness of NbC is approx 2500 HV which compares to a hardness of 1500 HV for M_7C_3 carbides present in high chromium white cast iron alloys.

(b) Niobium is a very strong carbide former and can be added as ferro niobium or NbC powder to the ferrous melt.

25 (c) The melting point of NbC is 3600°C, i.e. about 2000°C above the temperature of the ferrous melt of steels, cast irons and hard-facing weld deposits. Additionally, fine NbC particles (e.g. 2 to 20 μm in diameter) do not grow in size or coalesce in the melt during the casting process. This is important in terms of the castability of the melt and the resultant wear resistance of the cast product. The wear resistance of the cast product is optimised when a dispersion of fine NbC particles is evenly distributed throughout the microstructure.

30 (d) Other elements, e.g. Cr, Mn and Fe, do not dissolve in the high melting point NbC particles. Accordingly, the chemical composition of the NbC particles is not altered and they will retain their physical properties during preparation of the melt and after casting.

35 (e) The solubility of NbC in the ferrous matrix is negligible (<0.3 wt%) which suggests that the addition of NbC to ferrous materials will result in no observable effect on the response to heat treatment or change in material properties of the ferrous matrix.

40 (f) The density of NbC is 7.82 grams/cc at room temperature. This is very close to the densities of ferrous materials which are approximately 7.5 grams/cc. This means that NbC particles will not segregate in the liquid melt by sinking (compared with tungsten carbide, for example, which has a density of 15.8 grams/cc) or by floating (compared with titanium carbide, for example, which has a density of 4.93 grams/cc).

(g) The presence of a high volume fraction of NbC particles in the microstructure will result in a finer ferrous matrix grain size during casting and heat treatment. This improves mechanical properties of the castings.

45 (h) It is estimated that 20 wt% addition of NbC to the existing family of wear resistant high chromium white cast iron alloys, will improve the wear resistance of these materials, in some cases possibly by an order of magnitude.

50 (i) By observing the resultant microstructures it is considered that the addition of 10-25 weight% NbC to various stainless steels, for example martensitic, austenitic, ferritic and duplex, will substantially increase wear life with negligible reduction in toughness, corrosion resistance and mechanical properties for the various grades.

55 (j) The addition of 20 wt% NbC to Hadfield steel (which is normally used in liners of primary rock crushers, such as jaw and gyratory crushers, where high impact toughness is required) will produce a material with a much greater wear life than the original Hadfield steel without diminishing the exceptional toughness and work hardening capacity which is inherent in this steel.

(k) The addition of 20 wt% NbC to tool steels will greatly improve tool wear life while maintaining the original material properties.

EP 2 531 630 B1

[0095] Niobium carbide can be added to ferrous alloys, such as high chromium white cast irons in two distinct ways, as follows.

1. As fine niobium carbide particles (2-100 microns in diameter) to a melt, as per the above-mentioned laboratory work.
2. As fine ferro-niobium powder (minus 1 mm diameter) in the presence of the required stoichiometric amount of carbon previously dissolved in the melt.

[0096] The density of NbC is 7.8 grams/cc at room temperature and this is close to the density of high chromium white cast iron (7.5 grams/cc). The presence of phases with similar densities assists in achieving a uniform dispersion of NbC particles in the liquid metal during a casting process.

[0097] However, a laboratory test carried out by the applicant showed that segregation of NbC occurred in a high chromium white cast iron + 5wt% NbC alloy by settling of the fine NbC particles to the bottom of the ingot when the melt was allowed to stand for 15 minutes at about 150°C below the liquidus temperature of the host metal.

[0098] The density difference between high chromium white cast iron and NbC increases with temperature. The coefficient of thermal expansion of high chromium white cast iron is double that of NbC. In addition, high chromium white cast iron undergoes a step increase in volume at the solid to liquid phase change at approximately 1260°C.

[0099] As a consequence, the density of high chromium white cast iron in the liquid state at 1400°C is 6.9 grams/cc whereas the density of NbC at 1400°C is about 7.7 grams/cc. The applicant has found that this density difference is sufficient to cause segregation of NbC particles in liquid high chromium white cast iron at foundry casting temperatures of 1300°C or greater.

[0100] Titanium carbide is similar in many characteristics to NbC. The crystal structures are the same, with group number 225. The lattice parameter of NbC is 4.47 Angstroms and the lattice parameter of TiC is 4.32 Angstroms. TiC and NbC are isomorphous, i.e. Ti atoms will readily substitute for Nb atoms in NbC. The hardness of TiC is similar to NbC. The melting point of TiC is 3160°C, which is similar to the melting point of NbC (3600°C).

[0101] However, the density of TiC is 4.9 grams/cc at room temperature, and this is much less than the density of NbC. Since TiC and NbC are isomorphous, it is possible to achieve any density value for the mixed carbide in a range 4.9-7.8 grams/cc by selecting the corresponding chemical composition with the general formula (Nb_xTi_y)C. By way of example, the niobium/titanium carbides may be (Nb_{0.5}Ti_{0.5})C or (Nb_{0.25}Ti_{0.75})C or (Nb_{0.75}Ti_{0.25})C. This density difference is the basis of a cost effective method of reducing the segregation of hard, solid carbides in liquid metal at usual foundry casting temperatures. Specially, it is possible to selectively adjust the density of the niobium/titanium carbides within the range of 4.9-7.8 grams/cc and control whether the particles will form a uniform dispersion in or segregate in a casting of a metal alloy, such as a high chromium white iron, which includes the particles. This selection may be desirable for some castings where uniform wear resistance through the castings is desirable and for other castings where it is desirable to have a concentration of wear resistant particles in one section, such as a surface, of the castings.

[0102] The specification refers to the microstructures of hard metal materials of the present invention by volume % rather than the usual bulk chemical weight %. The table set out below is provided to explain the reason for this selection of nomenclature.

[0103] In the first 2 cases in the table, the chemistry of the host metal is identical and is essentially a high chrome white chromium cast iron, with a chemistry = Fe-27Cr-2.7C-2Mn-0.5Si. It is intuitively simple to visualize the microstructures of the two hard metal materials (namely 10 and 20 volume % NbC) in the same host metal. However, the bulk chemistries of the two hard metal materials (as determined by the usual foundry spectrographic analysis technique) do not clearly convey the simple difference between these two hard metal materials.

[0104] The third and fourth cases in the table, the exercise is repeated for 10 and 20 volume % NbC in Hadfield steel. The chemistry of the host metal is identical and is essentially Fe-12Mn-1.2C-2 Mn-0.5Si. Again, the bulk chemistries of these two hard metal materials are widely different and are not descriptive of the microstructures.

Microstructure = 90 volume% white cast iron + 10 volume% (comparative)

NbC

Furnace Charge	Volume	Composition (Wt%)					
Desc	(%)	Cr	C	Mn	Si	Nb	Fe
NbC	10		11.4			88.6	0.00

EP 2 531 630 B1

(continued)

5

Furnace Charge	Volume	Composition (Wt%)					
Desc	(%)	Cr	C	Mn	Si	Nb	Fe
Host metal	90	27.0	2.7	2.0	0.5		67.80
Bulk Chemistry	100	24.3	3.57	1.80	0.45	8.86	61.02

10

Microstructure = 80 volume% white cast iron + 20 volume% NbC

15

Furnace Charge	Volume	Composition (Wt%)					
Desc	(%)	Cr	C	Mn	Si	Nb	Fe
NbC	20		11.4			88.6	0.00
Host metal	80	27.0	2.7	2.0	0.5		67.80
Bulk Chemistry	100	21.6	4.44	1.60	0.40	17.72	54.24

20

Microstructure = 90 volume% Hadfield Steel+ 10 volume% NbC (comparative)

25

30

Furnace Charge	Volume	Composition (Wt%)					
Desc	(%)	Cr	C	Mn	Si	Nb	Fe
NbC	10		11.4			88.6	0.00
Host metal	90		1.2	12.0	0.5		86.30
Bulk Chemistry	100		2.22	10.80	0.45	8.86	77.67

35

Microstructure = 80 volume% Hadfield Steel+ 20 volume% NbC

40

Furnace Charge	Volume	Composition (Wt%)					
Desc	(%)	Cr	C	Mn	Si	Nb	Fe
NbC	20		11.4			88.6	0.00
Host metal	80		1.2	12.0	0.5		86.30
Bulk Chemistry	100		3.24	9.60	0.40	17.72	69.04

45

50

[0105] In all of the work carried out by the applicant in relation to the present invention the applicant has found that the final bulk chemistry of each of the hard metal materials is a complex function of the selected microstructure and the actual bulk chemistry is not a useful means of describing the required features of the hard metal materials. The required features of the hard metal material of the present invention are (a) host metal chemistry and (b) volume% of the selected refractory particles.

55

[0106] It is noted that the bulk chemistry is even more complicated when carbides of two transition metals are included in the hard metal materials.

[0107] It is noted that the hard metal material of the present invention may be cast as a final product shape and may be formed as a solid material that is subsequently hot worked in a downstream processing operation to form a final

product shape. For example, the hard metal material of the present invention may be formed as an ingot and subsequently hot worked by rolling or forging as required into a final product such as a bar or a plate.

5 **Claims**

1. A hard metal material in the form of a casting comprising greater than 15 and up to 50 volume % particles of a refractory material dispersed in a host metal, wherein the particles of the refractory material are selected from : (a) particles of niobium carbide containing refractory particles; and (b) particles of a chemical mixture of niobium carbide and titanium carbide, and wherein the particles are insoluble in the host metal at its casting temperature and the host metal comprises a ferrous alloy (such as a steel, a cast iron, a stainless steel, an austenitic-manganese steel).
2. The hard metal material defined in claim 1 comprising less than 30 volume % particles of the refractory material dispersed in the host metal, and preferably less than 25 volume % particles of the refractory material dispersed in the host metal.
3. The hard metal material defined in any one of the preceding claims wherein the particles of the refractory material have a particle size of less than 500 micron.
4. A method of manufacturing a component of a hard metal material comprising:
 - (a) forming a slurry of a hard metal material comprising greater than 15 and up to 50 volume % particles of a refractory material dispersed in a liquid host metal in an inert atmosphere, with the particles of the refractory material selected from: particles of niobium carbide; and particles of a chemical mixture of niobium carbide and titanium carbide, and with the host metal comprising a ferrous alloy (such as a steel, a cast iron, a stainless steel, an austenitic-manganese steel), wherein the particles are insoluble in the host metal at its casting temperature, and
 - (b) pouring the slurry into a mould and forming a casting of the component, such as in an inert atmosphere.
5. The method defined in claim 4 comprises forming the slurry and thereafter forming the casting of the component in a chamber under vacuum conditions which remove air from the chamber and supplying an inert gas, such as argon, into the chamber.
6. The method defined in claim 4 or claim 5 wherein the refractory material is less than 400 microns particle size, and preferably less than 150 microns particle size.
7. The method defined in any one of claims 4 to 6 comprises selecting one or more than one of (a) the refractory material to have a smaller thermal contraction than the host metal, (b) the density of the refractory material, compared to the density of the host metal in the liquid state, to control the dispersion of the particles of the refractory material in the host metal, and (c) the refractory material to have minimal solid solubility in the liquid host metal.
8. A method of forming a hard metal material defined in any one of claims 1 to 3 comprising:
 - (a) forming a slurry of a hard metal material comprising greater than 15 and up to 50 volume % particles of a refractory material dispersed in a liquid host metal, with the particles of the refractory material selected from: (a) particles of niobium carbide containing refractory particles; and (b) particles of a chemical mixture of niobium carbide and titanium carbide, and with the host metal comprising a ferrous alloy (such as a steel, a cast iron, a stainless steel, an austenitic-manganese steel), wherein the particles are insoluble in the host metal at its casting temperature, and
 - (b) allowing the slurry to solidify to form a solid hard metal material.
9. A method of forming a wear resistant hard metal material defined in any one of claims 1 to 3, the method comprising adding titanium, and niobium to a melt of a host metal in a form that produces: (a) particles of niobium carbide containing refractory particles; and (b) particles of a chemical mixture of niobium carbide and titanium carbide, in a range of greater than 15 and up to 50 volume % of the total volume of the hard metal material, with the host metal comprising a ferrous alloy (such as a steel, a cast iron, a stainless steel, an austenitic-manganese steel), wherein the particles are insoluble in the host metal at its casting temperature, and allowing the melt to solidify to form the solid hard metal material.

10. A method of casting a hard metal material having a dispersion of refractory material of: (a) particles of niobium carbide containing refractory particles; and/or (b) particles of a chemical mixture of niobium carbide and titanium carbide, in a host metal comprising a ferrous alloy (such as a steel, a cast iron, a stainless steel, an austenitic-manganese steel) which forms a matrix of the hard metal material in a solid casting, wherein the particles comprise greater than 15 and up to 50 volume % and are insoluble in the host metal at its casting temperature, the method comprising selecting the density of the refractory material particles in relation to the density of the host metal and therefore selectively controlling the dispersion of the refractory material particles in the matrix of a solid casting ranging from a uniform dispersion to a non-uniform dispersion.

Patentansprüche

1. Hartmetallmaterial in Form eines Gussstücks, umfassend mehr als 15 und bis zu 50 Vol.-% Partikel eines feuerfesten Materials, das in einem Wirtsmetall dispergiert ist, wobei die Partikel des feuerfesten Materials ausgewählt sind aus: (a) Partikeln aus Niobcarbid, die feuerfeste Partikel enthalten; und (b) Partikeln aus einer chemischen Mischung aus Niobcarbid und Titancarbid, und wobei die Partikel bei ihrer Gießtemperatur im Wirtsmetall unlöslich sind und das Wirtsmetall eine Eisenlegierung (wie z. B. Stahl, Gusseisen, rostfreien Stahl, austenitischen Manganstahl) umfasst.
2. Hartmetallmaterial nach Anspruch 1, umfassend weniger als 30 Vol.-% Partikel des feuerfesten Materials, das in dem Wirtsmetall dispergiert ist, und bevorzugt weniger als 25 Vol.-% Partikel des feuerfesten Materials, das in dem Wirtsmetall dispergiert ist.
3. Hartmetallmaterial nach einem der vorhergehenden Ansprüche, wobei die Partikel des feuerfesten Materials eine Partikelgröße von weniger als 500 Mikrometer aufweisen.
4. Verfahren zur Herstellung einer Komponente aus einem Hartmetallmaterial, umfassend:
 - (a) Ausbilden einer Aufschlämmung eines Hartmetallmaterials in einer inerten Atmosphäre, umfassend mehr als 15 und bis zu 50 Vol.-% Partikel eines feuerfesten Materials, das in einem flüssigen Wirtsmetall dispergiert ist, wobei die Partikel des feuerfesten Materials ausgewählt sind aus: Partikeln aus Niobcarbid und Partikeln aus einer chemischen Mischung aus Niobcarbid und Titancarbid, und wobei das Wirtsmetall eine Eisenlegierung (wie z. B. Stahl, Gusseisen, rostfreien Stahl, austenitischen Manganstahl) umfasst, wobei die Partikel bei ihrer Gießtemperatur im Wirtsmetall unlöslich sind, und
 - (b) Gießen der Aufschlämmung in eine Form und Ausbilden eines Gussstücks der Komponente, beispielsweise in einer inerten Atmosphäre.
5. Das Verfahren nach Anspruch 4 umfasst das Ausbilden der Aufschlämmung und danach das Ausbilden des Gussstücks der Komponente in einer Kammer unter Vakuumbedingungen, die Luft aus der Kammer entfernen, und das Zuführen eines Schutzgases, wie z. B. Argon, in die Kammer.
6. Verfahren nach Anspruch 4 oder Anspruch 5, wobei das feuerfeste Material eine Partikelgröße von weniger als 400 Mikrometer und bevorzugt eine Partikelgröße von weniger als 150 Mikrometer aufweist.
7. Das Verfahren nach einem der Ansprüche 4 bis 6 umfasst das Auswählen eines oder mehrerer von Folgendem: (a) des feuerfesten Materials, auf eine Weise, dass es eine geringere thermische Kontraktion aufweist als das Wirtsmetall, (b) der Dichte des feuerfesten Materials im Vergleich zu der Dichte des Wirtsmetalls in dem flüssigen Zustand auf eine Weise, dass die Dispersion der Partikel des feuerfesten Materials in dem Wirtsmetall gesteuert wird und (c) des feuerfesten Materials auf eine Weise, dass es eine minimale Feststofflöslichkeit in dem flüssigen Wirtsmetall aufweist.
8. Verfahren zum Ausbilden eines Hartmetallmaterials nach einem der Ansprüche 1 bis 3, umfassend:
 - (a) Ausbilden einer Aufschlämmung eines Hartmetallmaterials, umfassend mehr als 15 und bis zu 50 Vol.-% Partikel eines feuerfesten Materials, das in einem flüssigen Wirtsmetall dispergiert ist, wobei die Partikel des feuerfesten Materials ausgewählt sind aus: (a) Partikeln aus Niobcarbid, die feuerfeste Partikel enthalten; und (b) Partikeln aus einer chemischen Mischung aus Niobcarbid und Titancarbid, und wobei das Wirtsmetall eine Eisenlegierung (wie z. B. Stahl, Gusseisen, rostfreien Stahl, austenitischen Manganstahl) umfasst, wobei die

EP 2 531 630 B1

Partikel bei ihrer Gießtemperatur im Wirtsmetall unlöslich sind, und
(b) Aushärtenlassen der Aufschlammung zum Ausbilden eines festen Hartmetallmaterials.

- 5 9. Verfahren zum Ausbilden eines verschleißbeständigen Hartmetallmaterials nach einem der Ansprüche 1 bis 3, das Verfahren das Hinzufügen von Titan und Niob zu einer Schmelze eines Wirtsmetalls umfassend, in einer Form, die Folgendes herstellt: (a) Partikel aus Niobcarbid, die feuerfeste Partikel enthalten; und (b) Partikel aus einer chemischen Mischung aus Niobcarbid und Titancarbid in einem Bereich von mehr als 15 und bis zu 50 Vol.-% des Gesamtvolumens des Hartmetallmaterials, wobei das Wirtsmetall eine Eisenlegierung (wie z. B. Stahl, Gusseisen, rostfreien Stahl, austenitischen Manganstahl) umfasst, wobei die Partikel bei ihrer Gießtemperatur im Wirtsmetall unlöslich sind, und das Aushärtenlassen der Schmelze zum Ausbilden des festen Hartmetallmaterials.
- 10 10. Verfahren zum Gießen eines Hartmetallmaterials mit einer Dispersion eines feuerfesten Materials, bestehend aus: (a) Partikeln aus Niobcarbid, die feuerfeste Partikel enthalten; und/oder (b) Partikeln aus einer chemischen Mischung aus Niobcarbid und Titancarbid, in einem Wirtsmetall, das eine Eisenlegierung (wie z. B. Stahl, Gusseisen, rostfreien Stahl, austenitischen Manganstahl) umfasst, die eine Matrix des Hartmetallmaterials in einem festen Gussstück ausbildet, wobei die Partikel mehr als 15 und bis zu 50 Vol.-% umfassen und in dem Wirtsmetall bei ihrer Gießtemperatur unlöslich sind, wobei das Verfahren das Auswählen der Dichte der Partikel aus feuerfestem Material im Verhältnis zu der Dichte des Wirtsmetalls und somit ein selektives Steuern der Dispersion der Partikel aus feuerfestem Material in der Matrix eines festen Gussstücks umfasst, in einem Bereich von einer gleichmäßigen Dispersion bis zu einer nicht gleichmäßigen Dispersion.
- 20

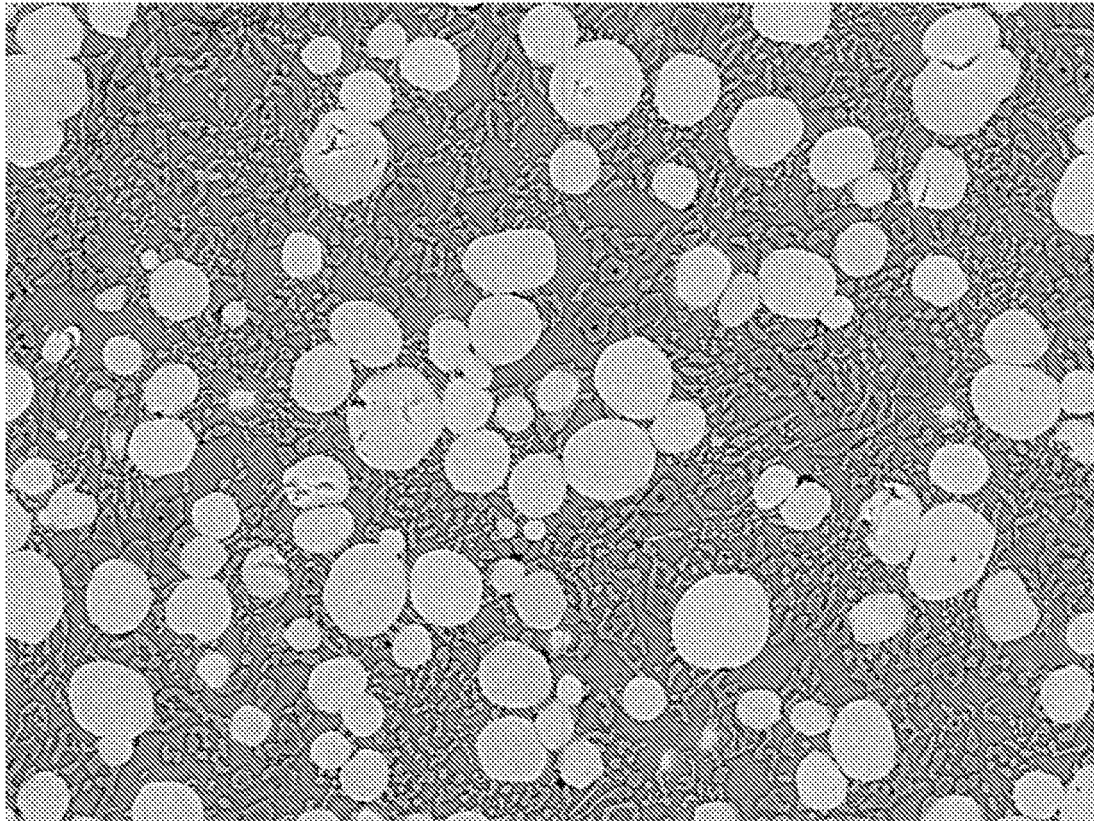
Revendications

- 25 1. Matériau de métal dur sous la forme d'une coulée comprenant plus de 15 et jusqu'à 50 % en volume de particules d'un matériau réfractaire dispersées dans un métal hôte, dans lequel les particules du matériau réfractaire sont sélectionnées parmi : (a) des particules de carbure de niobium contenant des particules réfractaires ; et (b) des particules d'un mélange chimique de carbure de niobium et de carbure de titane, et dans lequel les particules sont insolubles dans le métal hôte à sa température de coulée et le métal hôte comprend un alliage ferreux (tel qu'un acier, une fonte, un acier inoxydable, un acier austénitique au manganèse).
- 30 2. Matériau de métal dur selon la revendication 1 comprenant moins de 30 % en volume de particules du matériau réfractaire dispersées dans le métal hôte, et de préférence moins de 25 % en volume de particules du matériau réfractaire dispersées dans le métal hôte.
- 35 3. Matériau de métal dur selon l'une quelconque des revendications précédentes dans lequel les particules du matériau réfractaire ont une granulométrie inférieure à 500 microns.
- 40 4. Procédé de fabrication d'un composant d'un matériau de métal dur comprenant :
(a) la formation d'une suspension épaisse d'un matériau de métal dur comprenant plus de 15 et jusqu'à 50 % en volume de particules d'un matériau réfractaire dispersées dans un métal hôte liquide dans une atmosphère inerte, les particules du matériau réfractaire étant sélectionnées parmi : des particules de carbure de niobium ; et des particules d'un mélange chimique de carbure de niobium et de carbure de titane, et le métal hôte comprenant un alliage ferreux (tel qu'un acier, une fonte, un acier inoxydable, un acier austénitique au manganèse), dans lequel les particules sont insolubles dans le métal hôte à sa température de coulée, et
(b) le versement de la suspension épaisse dans un moule et la formation d'une coulée du composant, telle que dans une atmosphère inerte.
- 45 5. Procédé selon la revendication 4 comprenant la formation de la suspension épaisse et par la suite la formation de la coulée du composant dans une chambre dans des conditions de vide qui éliminent l'air de la chambre et l'introduction d'un gaz inerte, tel que l'argon, dans la chambre.
- 50 6. Procédé selon la revendication 4 ou la revendication 5 dans lequel le matériau réfractaire a une granulométrie inférieure à 400 microns, et de préférence inférieure à 150 microns.
- 55 7. Procédé selon l'une quelconque des revendications 4 à 6 comprenant la sélection d'un ou de plusieurs parmi (a) le fait pour le matériau réfractaire d'avoir une contraction thermique inférieure au métal hôte, (b) le fait pour la densité

EP 2 531 630 B1

du matériau réfractaire, comparée à la densité du métal hôte à l'état liquide, de réguler la dispersion des particules du matériau réfractaire dans le métal hôte, et (c) le fait pour le matériau réfractaire pour d'une solubilité à l'état solide minimale dans le métal hôte liquide.

- 5 **8.** Procédé de formation d'un matériau de métal dur selon l'une quelconque des revendications 1 à 3, comprenant :
- 10 (a) la formation d'une suspension épaisse d'un matériau de métal dur comprenant plus de 15 et jusqu'à 50 % en volume de particules d'un matériau réfractaire dispersées dans un métal hôte liquide, les particules du matériau réfractaire étant sélectionnées parmi : (a) des particules de carbure de niobium contenant des particules réfractaires ; et (b) des particules d'un mélange chimique de carbure de niobium et de carbure de titane, et le métal hôte comprenant un alliage ferreux (tel qu'un acier, une fonte, un acier inoxydable, un acier austénitique au manganèse), dans lequel les particules sont insolubles dans le métal hôte à sa température de coulée, et (b) le fait de laisser la suspension épaisse se solidifier pour former un matériau de métal dur solide.
- 15 **9.** Procédé de formation d'un matériau de métal dur résistant à l'usure défini dans l'une quelconque des revendications 1 à 3, le procédé comprenant l'ajout de titane, et de niobium à une masse fondue d'un métal hôte sous une forme qui produit : (a) des particules de carbure de niobium contenant des particules réfractaires ; et (b) des particules d'un mélange chimique de carbure de niobium et de carbure de titane, dans une plage de plus de 15 et jusqu'à 50 % en volume du volume total du matériau de métal dur, le métal hôte comprenant un alliage ferreux (tel qu'un acier, une fonte, un acier inoxydable, un acier austénitique au manganèse), dans lequel les particules sont insolubles dans le métal hôte à sa température de coulée, et le fait de laisser la masse fondue se solidifier pour former le matériau de métal dur solide.
- 20 **10.** Procédé de coulée d'un matériau de métal dur ayant une dispersion de matériau réfractaire de : (a) particules de carbure de niobium contenant des particules réfractaires ; et/ou (b) particules d'un mélange chimique de carbure de niobium et de carbure de titane, dans un métal hôte comprenant un alliage ferreux (tel qu'un acier, une fonte, un acier inoxydable, un acier austénitique au manganèse) qui forme une matrice du matériau de métal dur dans une coulée solide, dans lequel les particules représentent plus de 15 et jusqu'à 50 % en volume et sont insolubles dans le métal hôte à sa température de coulée, le procédé comprenant la sélection de la densité des particules de matériau réfractaire par rapport à la densité du métal hôte et par conséquent la régulation sélective de la dispersion des particules de matériau réfractaire dans la matrice d'une coulée solide allant d'une dispersion uniforme à une dispersion non uniforme.
- 25
- 30
- 35
- 40
- 45
- 50
- 55

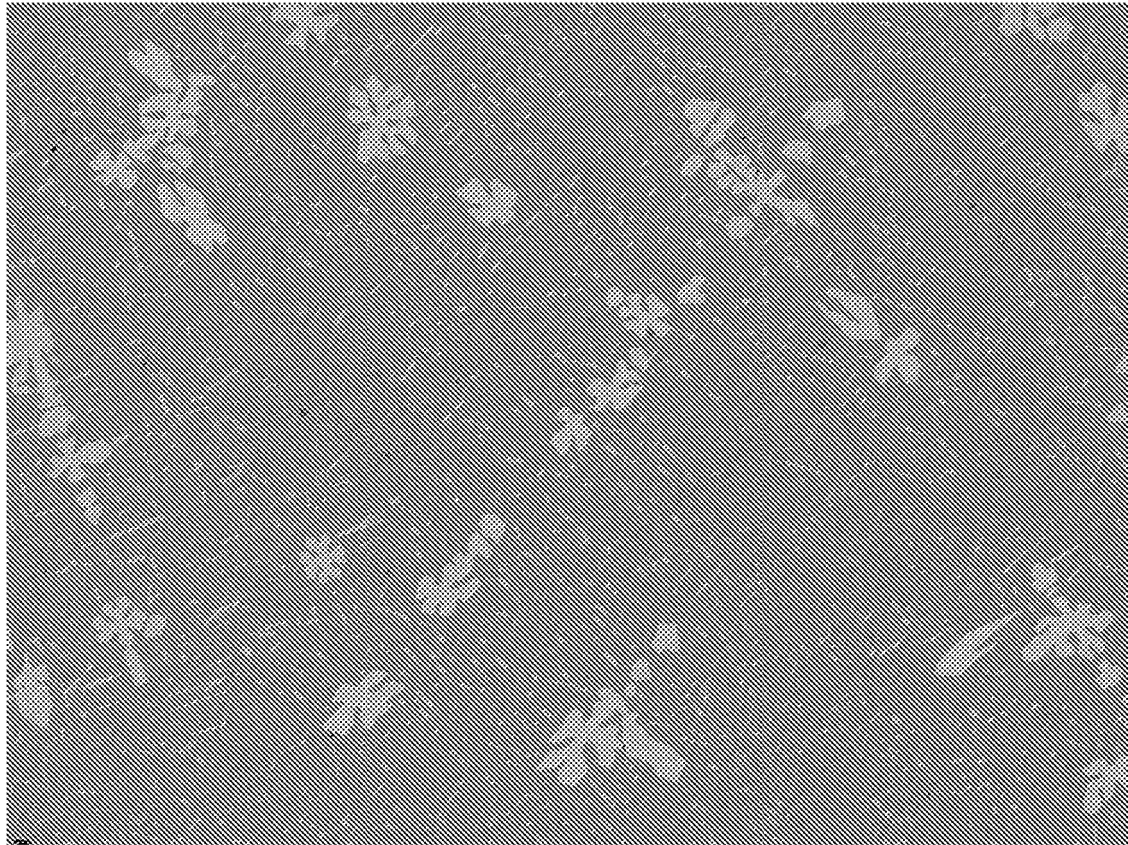


0094

2010/01/18 16:46

30 um

Figure 1



P39 0229

2010/02/01 14:59

x500

200 um

Figure 2

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- WO 9411541 A1 [0014]
- DE 2063181 A1 [0015]
- WO 2004104253 A1 [0016]
- JP H0730429 B [0017]
- US 5030519 A [0018]
- US 2009025834 A [0020]