(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) **World Intellectual Property Organization**
International Bureau

(43) International Publication Date
11 August 2011 (11.08.2011)

PCT

(10) International Publication Number
WO 2011/094800 A1

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

(21) International Application Number:
PCT/AU2011/000092

(22) International Filing Date:
1 February 2011 (01.02.2011)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2010900457 5 February 2010 (05.02.2010) AU
2010904416 1 October 2010 (01.10.2010) AU

(71) Applicant *(for all designated States except US):* **WEIR MINERALS AUSTRALIA LTD** [AU/AU]; 1 Marden Street, Artarmon, New South Wales 2064 (AU).

(72) Inventor; and
(75) Inventor/Applicant *(for US only):* **DOLMAN, Kevin** [AU/AU]; 29 Chester Street, Epping, New South Wales 2121 (AU).

(74) Agent: GRIFFITH HACK; Level 3, 509 St Kilda Road, Melbourne, Victoria 3004 (AU).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available):* AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available):* ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

(54) Title: HARD METAL MATERIALS

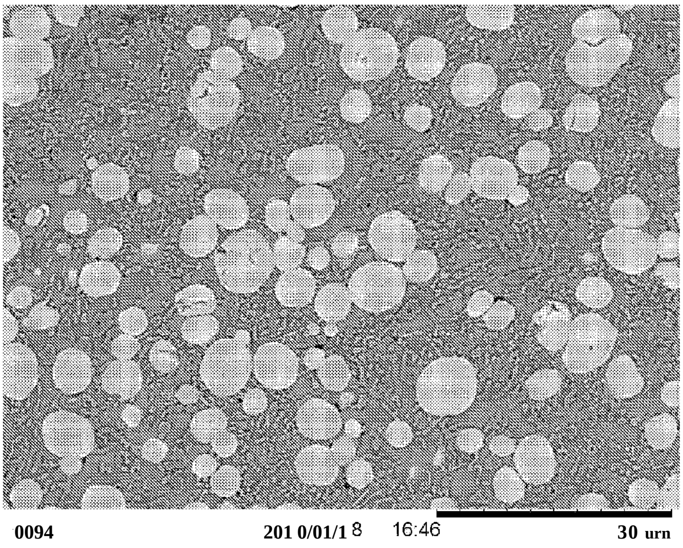

Figure 1

(57) Abstract: A hard metal material and a method of manufacturing a component of the hard metal material are disclosed. The hard metal material comprises 5-50 volume % particles of a refractory material dispersed in a host metal. The method comprises forming a slurry of 5-50 volume % particles of the refractory material dispersed in a liquid host metal in an inert atmosphere and pouring the slurry into a mould and forming a casting of the component.

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HARD METAL MATERIALS

Field of the invention

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.

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.

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.

The present invention also provides a method of manufacturing the components from the hard metal materials.

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.

Background

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).

Powder metallurgy processes involve sintering mechanically mixed refractory powders at elevated temperatures under pressure, usually in an inert atmosphere.

"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 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.

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 more than lOOkgs 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.

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 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.

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 resistance can be achieved through controlling the alloy composition, but there is a trade-off against other properties.

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 .

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 are interchangable .

Summary of the disclosure

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 5-50 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 .

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.

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 .

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 .

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.

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.

In broad terms , the present invention provides a hard metal material comprising 5-50 volume % particles of a refractory material dispersed in a host metal.

In the context of the present invention, the term "hard metal material" is understood to comprise particles of high melting point carbides and/or nitrides and/or borides of any one or more than one of the nine transition metals titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten 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 and/or borides and/or nitrides of one transition metal, such as NbC .

The particles of the refractory material may be carbides and/or borides and/or nitrides of more than one transition metal where the particles are a chemical mixture (as opposed to a physical mixture) of the carbides and/or borides and/or nitrides 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.

The hard metal material may comprise 5-40 volume % particles of the refractory material dispersed in the host metal.

The hard metal material may comprise greater than 10 volume % particles of the refractory material dispersed in the host metal.

The hard metal material may comprise greater than 15 volume % particles of the refractory material dispersed in the host metal.

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

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

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.

The present invention also provides a method of forming a hard metal material comprising:

(a) forming a slurry of a hard metal material comprising 5-50 volume % particles of a refractory material dispersed in a liquid host metal, for example in an inert atmosphere, and

(b) allowing the slurry to solidify to form a solid hard metal material.

The present invention also provides a method of manufacturing a component of a hard metal material comprising:

(a) forming a slurry of a hard metal material comprising 5-50 volume % particles of a refractory material dispersed in a liquid host metal in an inert atmosphere, and

(b) pouring the slurry into a mould and forming a casting of the component in an inert atmosphere.

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.

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.

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

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.

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

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

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

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.

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

Most of the transition metal refractory materials described above are classed as "reactive elements", i.e. the individual metal elements and/or their carbide, nitride or boride 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 CO_2 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.

Selection of refractory material particles having lower thermal expansion or contraction than the host metal

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

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

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.

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.

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.

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.

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.

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.

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.

Accordingly, there is provided a method of forming a wear resistant hard metal material, the method comprising adding (a) niobium or (b) niobium and titanium to a melt containing a host metal in a form that produces particles of niobium carbide and/or particles of a chemical mixture of niobium carbide and titanium carbide in a range of 10 to 40 wt% of the total weight of the hard metal material, and allowing the melt to solidify to form the solid hard metal material.

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.

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.

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.

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

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 .

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.

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

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

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.

The particles of niobium/ titanium carbides may be any suitable chemical mixture of a general formula $(Nb_x,Ti_y)C$. 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 $(Nb_{0.75},Ti_{0.25})C$.

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.

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.

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.

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.

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

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.

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.

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.

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.

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.

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

There is also provided a hard metal material formed according to the method described above.

There is also provided a method of casting the above-described hard metal material with a dispersion of particles of a chemical mixture of niobium carbides and titanium carbides in a host metal, which forms a matrix of the casting that comprises selecting the density of the niobium/ titanium particles in relation to the density of the matrix material and therefore selectively controlling the dispersion of the niobium/ titanium particles in the matrix ranging from a uniform dispersion to a non-uniform dispersion.

There is also provided a casting of the above-described hard metal material made by the above-described method.

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.

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.

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

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

The applicant carried out an extensive series of laboratory melting trials on the addition of 10 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

The applicant has carried out further extensive work reviewing data compiled by the applicant directly and in other sources in relation to carbides , borides , and nitrides of transition metals , and chemical combinations of carbides , borides , and nitrides of these metals, and has established that the findings of the laboratory work reported herein are equally applicable to these carbides, borides, and nitrides of transition metals and combinations of elements in ferrous host metals.

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.

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.

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.

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.

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.

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.

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.

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.

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.

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

(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.

(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.

(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.

(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.

(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.

(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.

(i) By observing the resultant microstructures is it 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.

(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.

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.

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.

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.

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.

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.

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 isomorphorous, 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).

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 $(Nb_x,Tiy)C$. By way of example, the niobium/ titanium carbides may be $(Nbo.5,Ti_{0.5})C$ 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.

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.

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 spectrograghic analysis technique) do not clearly convey the simple difference between these two hard metal materials.

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-l .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% NbC

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

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

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

Microstructure = 90 volume% Hadfield Steel + 10 volume % NbC

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

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

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

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.

It is noted that the bulk chemistry is even more complicated when carbides and/or nitrides and/or borides of two or more transition metals are included in the hard metal materials .

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.

Many modifications may be made to the embodiments of the present invention as described above without departing from the spirit and scope of the present invention.

It will be understood that the term "comprises" or its grammatical variants as used in this specification and claims is equivalent to the term "includes" and is not to be taken as excluding the presence of other features or elements .

Claims:

1. A hard metal material comprising 5-50 volume % particles of a refractory material dispersed in a host metal.

2. The hard metal material defined in claim 1 wherein the refractory material comprises particles of carbides and/or nitrides and/or borides of any one or more than one of the nine transition metals titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten.

3. The hard metal material defined in claim 1 or claim 2 comprises 5-40 volume % particles of the refractory material dispersed in the host metal.

4. The hard metal material defined in any one of the preceding claims comprises greater than 10 volume % particles of the refractory material dispersed in the host metal.

5. The hard metal material defined in any one of the preceding claims comprises greater than 15 volume % particles of the refractory material dispersed in the host metal.

6. The hard metal material defined in any one of the preceding claims comprises less than 30 volume % particles of the refractory material dispersed in the host metal.

7. The hard metal material defined in any one of the preceding claims comprises less than 25 volume % particles of the refractory material dispersed in the host metal.

8. The hard metal material defined in any one of the preceding claims wherein the host metal comprises a ferrous alloy (such as a steel or a cast iron), a stainless steel, an austenitic-manganese steel, or a iron-based or nickel-based or cobalt-based superalloy.

9. A method of manufacturing a component of a hard metal material comprising:

(a) forming a slurry of a hard metal material comprising 5-50 volume % particles of a refractory material dispersed in a liquid host metal in an inert atmosphere, and

(b) pouring the slurry into a mould and forming a casting of the component, such as in an inert atmosphere .

10. The method defined in claim 9 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 .

11. The method defined in claim 9 or claim 10 comprises selecting the production parameters to form the slurry in step (a) with a required fluidity for processing in step (b) .

12. The method defined in claim 11 wherein the production parameters comprise any one or more of the particle size, shape, reactivity, density, and solubility of the refractory materials.

13 . The method defined in any one of claims 9 to 12 wherein the refractory material is less than 400 microns particle size.

14 . The method defined in any one of claims 9 to 13 wherein the refractory material is less than 150 microns particle size.

15. The method defined in any one of claims 9 to 14 comprises selecting the refractory material to have a smaller thermal contraction than the host metal.

16. The method defined in any one of claims 9 to 15 comprises selecting 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.

17. The method defined in any one of claims 9 to 16 comprises selecting the refractory material to have minimal solid solubility in the liquid host metal.

18. A method of forming a wear resistant hard metal material, the method comprising adding (a) niobium or (b) niobium and titanium to a melt containing a host metal in a form that produces particles of niobium carbide and/or particles of a chemical mixture of niobium carbide and titanium carbide in a range of 10 to 40 wt% of the total weight of the hard metal material in a microstructure of a solidified metal alloy, and allowing the melt to solidify to form the solid hard metal material.

19. The method as defined in claim 18 comprising adding the niobium and/or the titanium 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.

20. The method as defined in claim 18 or claim 19 wherein the particles of niobium/titanium carbides have a general formula $(Nb_x,Ti_y)C$.

21. The method as defined in any one of claims 18 to 20 comprising adding niobium and/or titanium to the melt in the form of particles of niobium carbide and/or niobium/titanium carbides.

22. The method as defined in claim 21 comprising forming a slurry of particles of niobium carbide and/or niobium/titanium

carbides suspended in the melt and allowing the melt to solidify to form the solidified hard metal material .

23. A method of casting a hard metal material having a dispersion of a chemical mixture of niobium carbides and titanium carbides in a host metal which forms a matrix of the hard metal material, the method comprising selecting the density of the niobium/ titanium particles in relation to the density of the host metal and therefore selectively controlling the dispersion of the niobium/ titanium particles in the matrix ranging from a uniform dispersion to a non-uniform dispersion.

24 . A casting of the metal alloy made by the method defined in claim 23 .

25. The casting defined in claim 24 comprising a uniform dispersion of niobium/ titanium particles in the matrix.

26. The casting defined in claim 24 comprising a non-uniform dispersion of niobium/ titanium particles in the matrix.

27 . The casting defined in any one of claims 23 to 26 wherein the metal alloy is a ferrous alloy (such as a steel or a cast iron, such as a high chromium white cast iron) , a stainless steel or an austenitic manganese steel (such as a Hadfield steel) .

28. A method of forming a hard metal material comprising:

(a) forming a slurry of a hard metal material comprising 5-50 volume % particles of a refractory material dispersed in a liquid host metal, and

(b) allowing the slurry to solidify to form a solid hard metal material .

29. A method of forming a wear resistant hard metal material, the method comprising adding any one or more of the nine

transition metals titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten to a melt of a host metal in a form that produces particles of carbides and/or nitrides and/or borides of any one or more of the nine transition metals in a range of 5 to 50 volume % of the total volume of the hard metal material, and allowing the melt to solidify to form the solid hard metal material .

30 A method of casting a hard metal material having a dispersion of refractory material particles of carbides and/or nitrides and/or borides of any one or more of the nine transition metals titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten in a host metal which forms a matrix of the hard metal material in a solid casting, 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.

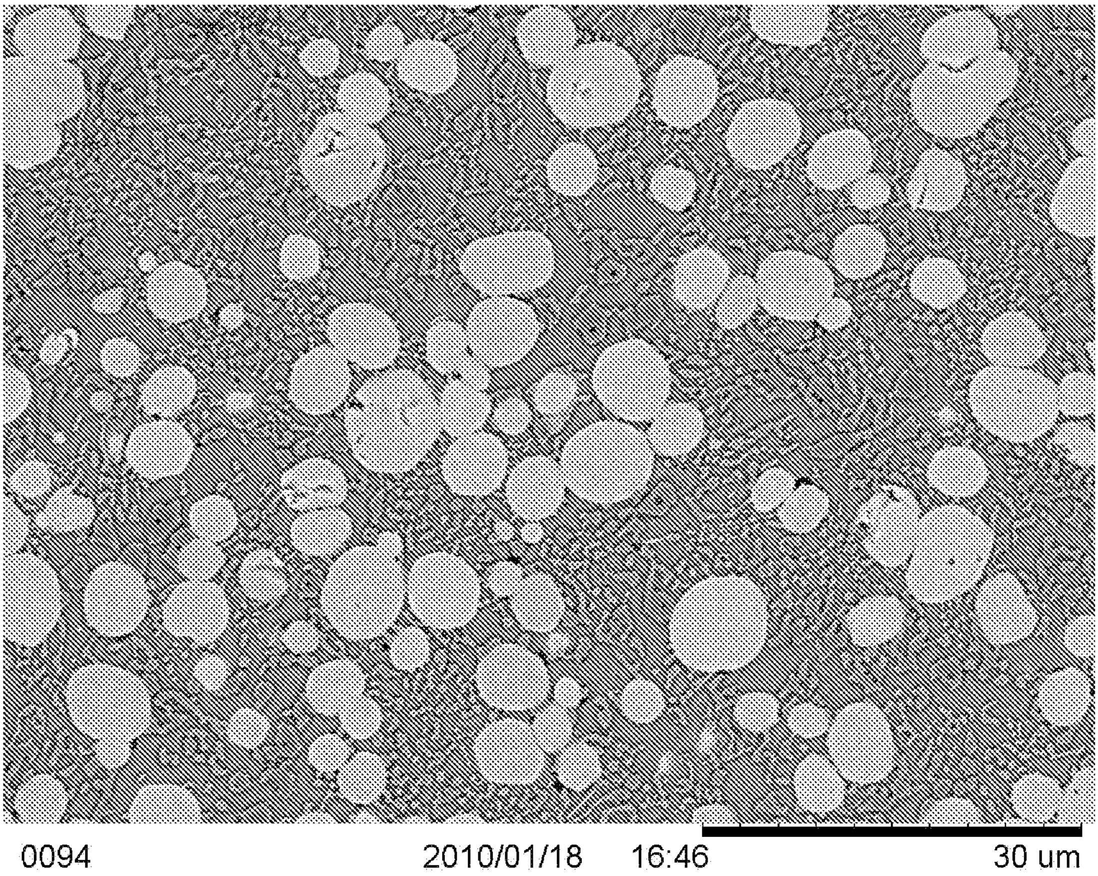

Figure 1

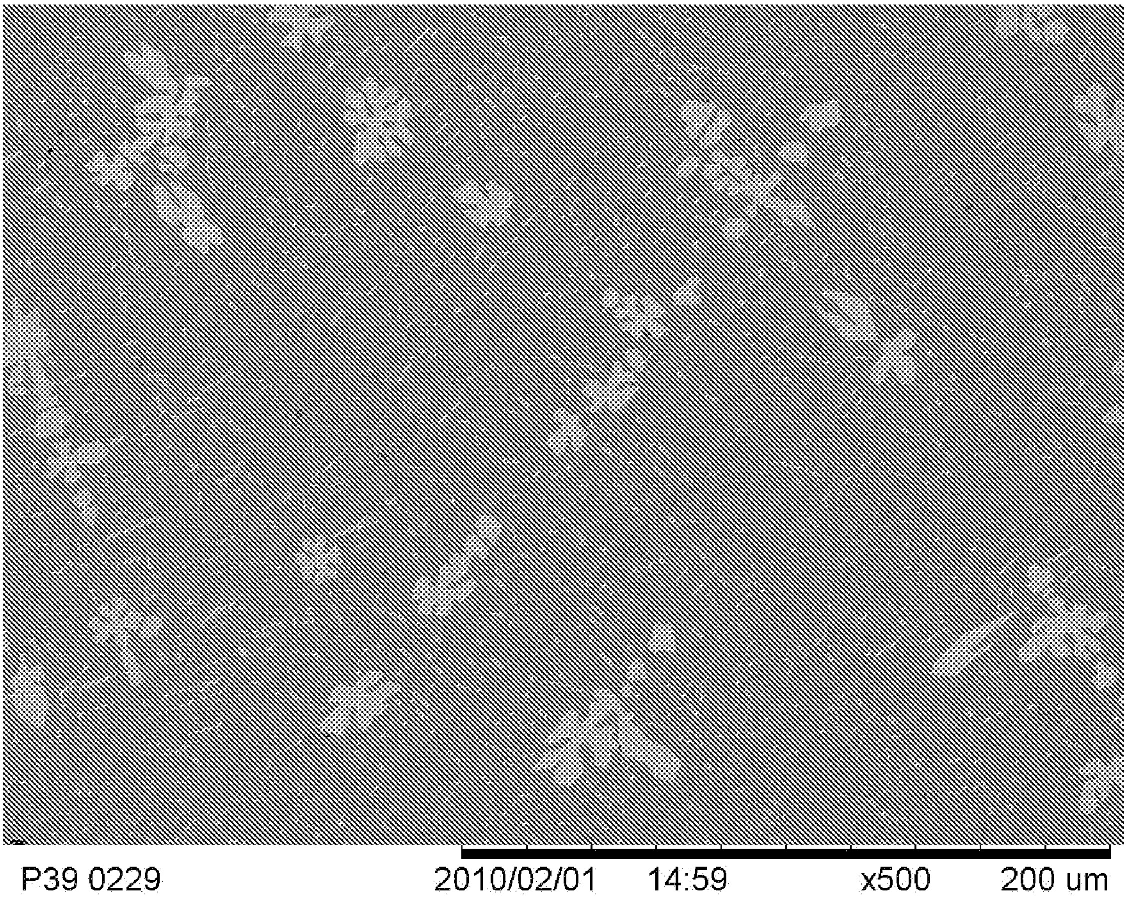

Figure 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2011/000092

A. CLASSIFICATION OF SUBJECT MATTER

Int. CI.

C22C 29/02 **(2006.01)** *C22C 29/14* **(2006.01)** *C22C 29/16* **(2006.01)**

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)

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WPI, EPODOC: IPC - C22C 29/00/-, C22C 32/00, C22C 33/04, C22C 33/08, C22.C 35/00, C22C 37/00/-, C22C 38/00/-, C22C 19/00/-, C21D 10/00, C21C 1/00/-, C21C 3/00/-, C21C 5/00/-, C21C 7/00/- & Keywords (TRANSITION, METAL, CARBIDES, NITRIDES, BORIDES, PARTICLES, SLURRY, MELT, STEEL, IRON, CAST, NICKEL, COBALT, BASED, HARD, WEAR, RESISTANT) and like terms

ESPACENET, USPTO, GOOGLE PATENTS & Keywords (HARD, WEAR, RESISTANT, MATERIAL, TRANSITION, METAL, CARBIDES, NITRIDES, BORIDES, PARTICLES, SLURRY, MELT, STEEL, IRON) and like terms

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	**Citation of document, with indication, where appropriate, of the relevant passages**	**Relevant to claim No.**
	JP 60-169515 A (KUBOTA LTD) 3 September 1985. English abstract retrieved from EPODOC database	
X	see abstract	1-8, 24
	RU 2017578 C1 (OMSKIJ POLITEKHN I [RU]) 15 August 1994. English abstract retrieved from EPODOC database	
A	see abstract	
	US 6013141 A (NYLEN et al) 11 January 2000	
A	see abstract; column 3, lines 14 - 31; claims 1, 5, 11—13	

☐ **Further documents are listed in the continuation of Box C** ☒ **See patent family annex**

*	Special categories of cited documents:			
"A"	document defining the general state of the art which is not considered to be of particular relevance		"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier application or patent but published on or after the international filing date		"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)		"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed			

Date of the actual completion of the international search 28 February 2011	Date of mailing of the international search report - 3 MAR 2011
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. +61 2 6283 7999	Authorized officer **VIJAYA MATHE** AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No : (02) 6225 6162

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2011/000092

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
   because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
   because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

- Claims 1 - 22, 28 - 29 are directed to a hard metal material comprising 5 - 50 vol% or 10 - 40 wt% of refractory material particles dispersed in a host metal; and a method of manufacturing a component of said hard metal material comprising the step of forming slurry of refractory material particles in the liquid metal. It is considered that this group of claims define a first invention.
- Claims 23 - 27, 30 are directed to a method of casting a hard metal material having a dispersion of refractory material particles in a host metal which forms a matrix of the hard metal material comprising selecting the density of the refractory material particles in relation to the density of the host metal; and selectively controlling the dispersion of the refractory material particles in the solid casting ranging from a uniform dispersion to a non-uniform dispersion. It is considered that this group of claims define a second invention.

PCT Rule 13.2, first sentence, states that unity of invention is only fulfilled when there is a technical relationship among the claimed inventions involving one or more of the same or corresponding special technical features. PCT Rule 13.2, second sentence, defines a special technical feature as a feature which makes a contribution over the prior art.

None of the abovementioned groups of claims share any special technical feature. Because there is no common special technical feature it follows that there is no technical relationship between the identified inventions. Therefore the claims do not satisfy the requirement of unity of invention *a priori*.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation,

☐ No protest accompanied the payment of additional search fees.

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
JP	60169515	NONE					
RU	2017578	NONE					
US	6013141	AU	60924/96	BR	9609266	GA	2223785
		EP	0871784	MX	9709629	NZ	310183
		WO	9639544				

Due to data integration issues this family listing may not include 10 digit Australian applicatioris filed since May 2001.

END OF ANNEX