Abstract: A centrifugally cast composite metal product having an axis of rotational symmetry and a mass of at least 5kg, comprises a host metal and insoluble solid refractory particles of refractory material in a non-uniform distribution throughout the host metal. The particles have a density that is within 30% of the density of the host metal at its casting temperature.
COMPOSITE METAL PRODUCT

TECHNICAL FIELD

The present disclosure relates to a method of centrifugal casting of a composite metal product, the finished product typically ranging in mass from 20-5,000 kg, having a host metal matrix, typically a ferrous metal matrix, and comprising outer surface layer, nominally 1-20 mm thick, of hard, insoluble refractory particles for enhanced wear resistance.

The present disclosure also relates to centrifugally cast composite metal products,

In the context of the present disclosure, the term "refractory particles" is understood to include 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. Each of these refractory particles is a particle of a refractory material and is referred to herein as a "refractory material". Typically, the host metal is a ferrous metal alloy. The host metal may also be nickel-based and cobalt-based superalloys.

In the context of the present disclosure, the term "insoluble" is understood to mean that, for all intents and purposes, the refractory material is not soluble in the host metal at the casting temperatures, typically in a range 1200 -1600°C for ferrous host metals. There may be limited solubility. However, the refractory particles are essentially distinct from the host metal to the extent that there is negligible partitioning of the elements in
the refractory material particles to the host metal during the casting method and in the solidified product.

SUMMARY OF THE DISCLOSURE

In a first aspect, embodiments are disclosed of a centrifugally cast composite metal product having an axis of rotational symmetry and a mass of at least 5 kg, typically at least 10 kg, and more typically at least 20 kg, and comprising a metal host and XnsoXubXe soXid particles of a refractory material in a non-uniform distribution throughout the host metal, wherein the particles have a density that is within 30%, typically within 20%, of the density of the metal host at its casting temperature.

The composite metal product comprises two distinct zones throughout the solidified material, namely a zone of insoluble solid particles of the refractory material and an at least substantially refractory particle-free region of the host metal, with the refractory particles being essentially distinct from the host metal to the extent that there is negligible partitioning of elements in the refractory material particles to the host metal at the casting temperature and in the solidified product.

The feature of the invention of solid particles of the refractory material that are insoluble in the host metal at the casting temperature and after solidification distinguishes the invention from proposals in the prior art, such as JPS632864, for the addition of ferroalloys (a) Fe-W, (b) Fe-Mo and (c) Fe-Cr to a host ferrous alloy that forms respectively (a) tungsten carbide, (b) molybdenum carbide and (c) chromium carbide which are soluble to varying degrees in the host metal at the usual casting temperatures. As a consequence, in these systems, the volume % of hard, insoluble refractory carbides in the
microstructure is substantially reduced and the dissolved tungsten and/or molybdenum and/or chromium may adversely influence the physical and chemical properties of the host metal at room temperature by an unknown amount, (e.g. reduced toughness and a different response to heat treatment).

In some embodiments, the refractory particles may have a density that is higher than that of the host metal, in which case there will be a higher concentration of the refractory particles towards an exterior surface of the composite centrifugally cast metal product.

In some embodiments, the refractory particles may have a density that is lower than that of the host metal, in which case there will be a higher concentration of the refractory particles towards an interior surface of the product.

In some embodiments, the non-uniform distribution of refractory particles may comprise a first concentration of refractory particles in an exterior or interior surface layer of the product that is higher than a second concentration of refractory particles in another layer in the product.

In some embodiments, the first concentration of refractory particles in the exterior surface layer of the product may be at least 50 vol%, typically at least 60 vol%, typically at least 70 vol%, and more typically 50-120 vol% higher than the nominal volume percentage of the refractory material in the product.

In some embodiments, the first concentration of refractory particles in the exterior surface layer of the product may be at least 10%, typically at least 20%, typically less than 40%, and more typically in a range of
10-40 vol%, of the total volume of the exterior surface layer.

In some embodiments, the second concentration of refractory particles in the other layer of the product may be in a range of 2-4.5 vol%, typically 2-3.5 vol%, of the total volume of the other layer.

In some embodiments, the exterior or interior surface layer of the product may extend at least 5%, typically at least 20%, more typically at least 25% of the radial thickness of the product from the exterior or interior surface.

In some embodiments, the exterior or interior surface layer of the product may extend less than 50%, typically less than 40%, more typically less than 30%, and more typically less than 20% of the radial thickness of the radial thickness of the product from the exterior or interior surface.

In some embodiments, the exterior or interior surface layer of the product may extend at least 10 mm, typically at least 20 mm, typically less than 50 mm, typically 1-50 mm, and more typically 5-20 mm from the exterior or interior surface.

In some embodiments, the first concentration of refractory particles in the exterior surface layer of the product may be in a range of at least 5 vol%, typically at least 10 vol%, typically 5-90 vol%, and more typically 10-40 vol%, of the total volume of the particles.

In some embodiments, the overall concentration of the refractory particles in the product may be at least 5 vol%, typically at least 10 vol%, and more typically in a range of 5-80 vol% of the total volume of the product.
In some embodiments, the overall concentration of the refractory particles in the product may be in a range of 5-40 vol% of the total volume of the product.

In some embodiments, the overall concentration of the refractory particles in the product may be in a range of 5-20 vol% of the total volume of the product.

In some embodiments, the refractory particles may be carbides and/or borides and/or nitrides of one or 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 refractory particles may be of the type described as \((M_1, M_2)C\) or \((M_1, M_2, M_3)C\), where "M" is a transition metal. One example that is discussed further herein is \((\text{Nb}, \text{Ti}, \text{W})C\).

The host metal may be any suitable host metal. The host metal may be a ferrous alloy, such as a stainless steel or an austenitic manganese steel or a cast iron. The host metal may be a non-ferrous host metal, such as titanium or a titanium alloy.

In some embodiments, the host metal may be an alloy comprising any one of the following alloys:

(a) Hadfield steel for use for example in gyratory crusher mantles;

(b) 420C stainless steel for use for example in shaft sleeves in slurry pumps; and

(c) high chromium white cast iron.

As used in some embodiments, the Hadfield steel may comprise:

1.0 - 1.4 wt% C
0.0 - 1.0 wt% Si,
As used in some embodiments, the 420C stainless steel may comprise:

- 0.3 - 0.5 wt% C,
- 0.5 - 1.5 wt% Si,
- 0.5 - 3.0 wt% Mn,
- 0.0 - 0.5 wt% Mo,
- 0.0 - 1.0 wt% Cr,
- 0.0 - 1.0 wt% Ni,

with the remainder being Fe and incidental impurities.

As used in some embodiments, the high chromium white cast iron may comprise:

- 1.5 - 4.0 wt% C,
- 0.0 - 1.5 wt% Si,
- 0.5 - 7.0 wt% Mn,
- 0.0 - 1.0 wt% Mo,
- 15 - 35 wt% Cr,
- 0.0 - 1.0 wt% Ni,

with the remainder being Fe and incidental impurities.

The composite metal product may be any product that is adapted to be centrifugally cast and requires high wear and high toughness properties. Examples of such products include a gyratory crusher mantle for a primary, secondary or tertiary crusher, a slurry pump shaft sleeve, rollers for use in crushers (including large diameter rollers that are of the order of 1 m in diameter with radial wall thicknesses in a range of 300-400 mm), and other components of crushers and pumps.
In a second aspect, embodiments are disclosed in which the composite metal product of the first aspect may be a gyratory crusher mantle for a primary, secondary or tertiary crusher.

In a third aspect, embodiments are disclosed in which the composite metal product of the first aspect may be a slurry pump shaft sleeve.

In a fourth aspect, embodiments are disclosed of a method of centrifugally casting a composite metal product having an axis of rotational symmetry and a mass of at least 5kg, typically at least 10 kg, and more typically at least 20kg and comprising a host metal and a non-uniform dispersion of insoluble solid refractory particles of a refractory material, with the method comprising:

(a) forming a slurry comprising solid particles of the refractory material dispersed in a liquid host metal, with the refractory particles comprising 5-50 vol%, typically 5-40 vol%, of the total volume of the slurry, with the refractory particles being insoluble at a casting temperature, and with the refractory particles having a density that is within 30%, typically within 20%, of the density of the metal host at the casting temperature; and

(b) pouring the slurry into a mould for the composite metal product and centrifugally casting the product in the mould and obtaining a non-uniform distribution of insoluble solid refractory particles throughout the host metal.

In some embodiments, step (a) may comprise forming the refractory particles in situ in the molten host metal and dispersing the particles within a molten form of the host metal.

In some embodiments, step (a) may comprise adding refractory particles to a molten form of the host metal.
In some embodiments, steps (a) and (fa) may be carried out under an inert environment, such as in an inert gas atmosphere.

In some embodiments, step (b) may comprise preparing the mould by forming an inert environment within the mould.

In some embodiments, step (b) may comprise rotating the mould about the axis subsequent to and/or during pouring the slurry into the mould to cause a concentration of refractory particles at or near an exterior surface or at or near an interior surface of the composite metal product that is higher than the concentration of particles elsewhere in the product.

In some embodiments, step (b) may comprise rotating the mould at a 10-120 G-Factor, where G-Factor is the centrifugal force acting on a rotating body divided by the gravitational force.

In some embodiments, step (b) may comprise rotating the mould at a peripheral speed of 2,5-25 m/s.

In some embodiments, step (b) may comprise rotating the mould for sufficient time to obtain the non-uniform distribution of solid particles throughout the host metal.

In some embodiments, step (b) may comprise rotating the mould until the host metal has solidified.

In some embodiments, step (b) may comprise pouring the slurry into the mould at a casting temperature in a range of 1200-2000°C typically in a range of 1350-1650°C.
In some embodiments, 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).

The production parameters may comprise any one or more of the particle size, reactivity, density, and solubility of the refractory materials, as described in International patent application PCT/AU2011/000092 (WO2011/09480G) in the name of the present applicant. The disclosure in the International application is incorporated herein by cross-reference. Density and solubility of the refractory materials are discussed below.

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 disclosure to control the dispersion of refractory particles in the hot host metal.

The nominal density of a host ferrous liquid metal at 1400°C is 6.9 grams/cc. When refractory particles in the form of tungsten carbide (WC) particles, with a density of 15.7 grams/cc at 25°C, are added to a host ferrous metal to form the slurry, the WC particles will sink to the bottom of the slurry. When refractory particles in the form of titanium carbide (TiC) particles, with a density of 4.8 grams/cc at 1400°C, are added to the same host ferrous metal, the TiC particles will float to the top of the slurry. Refractory particles in the form of niobium carbide (NbC), with a density of 7.7 grams/cc at 1400°C, are fairly close to the density of the host ferrous liquid metal at 6.9 grams/cc and are less prone to the above-described segregation in the liquid host ferrous metal than TiC or WC.
TiC, with a density of 4.9 grams/cc at 25°C, is completely soluble in NbC, which has a density of 7.8 grams/cc at 25°C. Therefore, refractory particles with densities in the range 4.9-7.8 grams/cc at 25°C can be obtained by selecting (Nb,Ti)C particles with the required niobium and titanium contents.

Tungsten carbide (WC), with a density of 15.7 grams/cc at 25°C, is mostly soluble in NbC, TiC and (Nb,Ti)C. Therefore, refractory particles with densities in the range 4.8-15.7 grams/cc at 25°C can be obtained by selecting (Nb,Ti,W)C particles with the required niobium, titanium and tungsten contents.

All refractory particles, described by the formula (Nb,Ti,W)C, are insoluble in liquid ferrous host metals at casting temperatures in the range 1200-1600°C.

Hiobium carbide and titanium carbide have similar crystal structures and are isomorphous.

It is evident from the above that selecting the required Nb:Ti ratio in a (Nb,Ti)C chemical compound or the required Nb:Ti:W ratio in a (Nb,Ti,W)C chemical compound can yield a refractory material with a required density within 20% of the density of the ferrous host metal.

The addition of refractory particles that are, for all intents and purposes, insoluble, (that is, having minimal solid solubility in a host liquid metal), to produce a centrifugally cast casting of a composite metal product in accordance with the method of the present disclosure, produces a product 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 of the host metal.

For example, the solubility of a refractory material in the form of (Nb,Ti,W)C in liquid host metals in the form of (a) liquid Hadfield steel and (b) liquid 420C stainless steel and (c) liquid high chromium white cast iron at elevated temperatures is negligible (<0.3 wt%). The addition of (Nb,Ti,W)C with the required densities to these three host metal alloys, followed by centrifugally casting a composite metal product and standard heat treatment procedure for each host metal produces microstructures in the product comprising a dispersion of primary niobium-titanium-tungsten carbides in the host metals which are substantially free of niobium, titanium and tungsten, that is, 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 particulate refractory materials on the physical properties (for example, melting point) and chemical properties (for example, response to heat treatment) of the host metal.

In addition to the above, in particular the applicant has found that providing a composite metal product with a microstructure that includes particles of niobium carbide and/or particles of a chemical (as opposed to a physical) mixture of two or more than two of niobium carbide, titanium carbide, and tungsten 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 composite metal product,
In addition, and as described above, in particular the applicant has found that it is possible to adjust the density of particles of a chemical mixture of two or more than two of niobium carbide, titanium carbide and tungsten carbide to a sufficient extent in relation to the density of a host metal, which forms a matrix of the composite metal product. This opportunity for density control is an important finding in relation to centrifugally cast castings of the hard metal material.

In particular, by virtue of this finding, it is possible to produce centrifugally cast castings of the composite metal product with controlled non-uniform distribution, that is, segregation, of the particles in parts of the castings. This is important for end-use applications for castings where it is desirable to have a concentration of high wear resistant particles near a surface of a casting of a hard metal material.

In addition, the applicant has found that forming castings of the composite metal product to include particles of niobium carbide and/or particles of a chemical mixture of two or more than two of niobium carbide, titanium carbide and tungsten carbide in a range of 5-50 vol%, typically 5-40 vol%, more typically 5-20 vol% of the total volume of the composite metal product, dispersed in a host metal, which forms a matrix of the composite metal product, does not have a significant negative impact on corrosion resistance and toughness of ferrous material in the host metal. Hence, the present disclosure makes it possible to achieve high wear resistance of a composite metal product without a loss of other desirable material properties.

Accordingly, in a fifth aspect there is provided a method of centrifugally casting a composite metal product having an axis of rotational symmetry and a mass of at
least Skg and comprising a host metal and a non-uniform
distribution of insoluble solid refractory particles of a
refractory material, the method comprising adding (a)
niobium or (b) two or more than two of niobium and
titanium and tungsten to a melt containing a host metal in
a form that produces solid refractory particles of niobium
carbide that are insoluble at a casting temperature and/or
solid refractory particles of a chemical mixture of two or
more than two of niobium carbide and titanium carbide and
tungsten carbide that are insoluble at the casting
temperature, with the solid refractory particles being in
a range of 5-50 vol%, typically 5-40 vol%, more typically
5-20 vol%, of the total volume of the product, and
centrifugally casting the product in a mould and obtaining
a non-uniform distribution of insoluble solid particles
throughout the host metal.

The terms "a chemical mixture of niobium carbide and
titanium carbide" and "niobium/titanium carbide" 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 particles of single metal carbides in
the mixture but are present as particles of
niobium/titanium carbides, (Nb,Ti)C,

The terms "a chemical mixture of niobium carbide and
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"chemical mixture" is understood in this context to mean
that the niobium carbides and the titanium carbides and
the tungsten carbides are not present as particles of
single metal carbides in the mixture but are present as
particles of niobium/titanium/tungsten carbides,
(Nb,Ti,W)C.
Niobium carbide and titanium carbide and tungsten carbide each have a Vickers hardness around 25 GPa, which is about 10 GPa above the hardness of chromium carbides (nominally 15 GPa). Accordingly, composite metal products having a microstructure containing 5-50 vol%, typically 5-40 vol%, of niobium carbide and/or niobium/titanium carbide and/or niobium/titanium/tungsten carbide have excellent wear resistance properties. The applicant has recognised that niobium carbides and titanium carbides and tungsten carbides and niobium/titanium carbides and niobium/titanium/tungsten carbides are substantially inert chemically with respect to other constituents in the composite metal product so those constituents provide the product 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 niobium and the titanium and the tungsten may be added to a melt of the host metal to form the slurry in any suitable form, bearing in mind the requirement of forming insoluble solid particles of niobium carbides and/or niobium/titanium carbides and/or niobium/titanium/tungsten carbides in the composite metal product.

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 chemically combine to form insoluble solid 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 and the titanium and tungsten to the melt as ferro-niobium-titanium-tungsten,

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 insoluble solid particles of niobium/titanium carbides.

In each of these cases, the solidified metal alloy may be formed from a slurry of particles of niobium carbide and/or niobium/titanium/tungsten carbides suspended in the melt. 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.

The insoluble solid particles of niobium/titanium carbides may be any suitable chemical mixture of a general formula (Nbₓ,TiₙC).

The insoluble solid particles of niobium/titanium/tungsten carbides may be any suitable chemical mixture of a general formula (Nbₓ,Tiₙ,Wₙ)C. By way of example, the niobium/titanium/tungsten carbides may be (Nb₀.₂₅,Ti₀.₃₅,W₀.₂₅)C.
The niobium and/or the titanium and/or the tungsten may be added to the melt to produce insoluble solid particles of niobium carbide and/or niobium/titanium carbides and/or niobium/titanium/tungsten carbides in a range of 12-33 wt% niobium carbides or niobium/titanium carbides or niobium/titanium/tungsten carbides of the total weight of the cast product.

The niobium and/or the titanium and/or the tungsten may be added to the melt to produce insoluble solid particles of niobium carbide and/or niobium/titanium carbides and/or niobium/titanium/tungsten carbides in a range of 12-25 wt% niobium carbides and niobium/titanium carbides and niobium/titanium/tungsten carbides of the total weight of the cast composite metal product.

The quantity of particles of niobium carbide and/or niobium/titanium carbides and/or niobium/titanium/tungsten carbide in the micro-structure of the solidified hard metal material may depend on the system.

The applicant is concerned particularly with solid hard composite metal products 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 insoluble solid particles of refractory material in the form of niobium carbide and/or niobium/titanium carbides and/or niobium/titanium/tungsten carbides in the final composite metal product may be in a range of 5-50 vol%, typically 5-40 vol%, more typically 5-20 vol%- , of the total volume of the cast composite metal product.
The particle size of niobium carbide and/or niobium/titanium carbide and/or niobium/titanium/tungsten carbide may be in a range of 1-150 μm in diameter.

The method may comprise stirring the slurry 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 and/or niobium/titanium/tungsten carbides in the slurry.

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

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

In a situation where particles of niobium/titanium/tungsten carbides are required in the cast composite metal product, the method may comprise pre-melting ferro-niobium and ferro-titanium and ferro-tungsten and ferro-niofoium-titanium-tungsten under inert conditions and forming a liquid phase that is a homogeneous chemical mixture of iron, niobium and titanium and tungsten 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 and tungsten dissolve in the melt and
chemically combine with carbon to form niobium/titanium/tungsten carbides in the melt.

Other aspects, features, and advantages will become apparent from the following detailed description when taken in conjunction with the accompanying drawings, which are a part of this disclosure and which illustrate, by way of example, principles of inventions disclosed.

**BRIEF DESCRIPTION OF THE DRAWINGS**

Notwithstanding any other forms which may fall within the scope of the method and resultant composite metal product as set forth in the Summary, specific embodiments of the method and resultant composite metal product will now be described by way of example and with reference to the accompanying Figures, of which:

Figure 1 is a diagram that illustrates a typical centrifugal casting method;

Figure 2 is a SEM image of a section of one of the samples from centrifugally cast test cylinder "37863" (AOS host metal + 5 vol% Nb particles) produced during experimental work in relation to the invention;

Figure 3 comprises cross-sections of optical images of samples from centrifugally cast test cylinders "37628", "37629", "3763G"% and "37655" (AGS host metal + S vol% Nb particles) produced during experimental work in relation to the invention;

Figure 4 is a graph of hardness versus distance from outer surfaces to inner surfaces of the samples described in relation to Figure 3;
Figure 5 comprises optical images of cross-sections of samples from centrifugally cast test cylinders "37632", "37633", and "37636" (AOS host metal + 12 vol% NbC particles) produced during experimental work in relation to the invention;

Figure 6 is a graph of hardness versus distance from outer surfaces to inner surfaces of the samples described in relation to Figure 5;

Figure 7 comprises optical images of cross-sections of samples from centrifugally cast test cylinders "37634" and "37635" (AOS host metal + 17 vol% NbC particles) produced during experimental work in relation to the invention;

Figure 8 is a graph of hardness versus distance from outer surfaces to inner surfaces of the samples described in relation to Figure 7;

Figure 9 is an optical image of a cross-section of a sample of a centrifugally cast test cylinder A352 (C21 host metal + 10 vol% NbC particles) produced during experimental work in relation to the invention;

Figure 10 is an optical image of a cross-section of the outer layer of the cross-section of the sample shown in Figure 9 after etching the sample;

Figure 11 is an optical image of a cross-section of a sample of a centrifugally cast test cylinder A323 cylinder (A49 host metal + 1S vol% HbC particles); and

Figure 12 is a graph of hardness versus distance from outer surfaces to inner surfaces of sections of the sample described in relation to Figure 11.
Figure 13 is a graph of the thickness of the NbC particle-rich outer layer versus the nominal vol% of NbC in the total composition of centrifugally cast cylinders of AOS host metal + NbC particles; and

Figure 14 is a graph of the vol% NbC in the NbC particle-rich outer layer versus the nominal vol% of NbC in the total composition of centrifugally cast cylinders of AOS host metal + NbC particles.

**DETAILED DESCRIPTION OF SPECIFIC EMBODIMENTS**

Figure 1 was sourced from the internet and illustrates in diagrammatic form the basic steps in a centrifugal casting method.

These centrifugal casting steps include forming a molten melt and pouring the melt into a suitable mould and rotating the mould about a vertical axis (in the case of the arrangement shown in the Figure) at a required rate of rotation to form a cast product.

In alternative arrangements, such as the arrangement used to carry out the experimental work described below, the casting mould is positioned horizontally and the mould is rotated about a horizontal axis.

In the context of the present disclosure, typically the molten melt comprises a slurry of hard, insoluble solid refractory particles in a host metal and the cast product is a composite metal product, typically ranging in mass from 5 kg to 5,000 kg, having a ferrous metal matrix (the host metal) and comprises a non-uniform distribution of hard, insoluble refractory particles in the ferrous metal matrix, specifically an outer surface layer, nominally 10-20 mm thick, of hard, insoluble refractory
particles that provide enhanced wear resistance in the surface layer.

The actual centrifugal casting conditions may be selected in any given situation based on the required characteristics of an actual product to be cast. The casting conditions include, by way of example, the rate of rotation of the mould and the rotation time and the cooling conditions and the conditions in which the casting is conducted, for example in an inert atmosphere.

Refractory particle property requirements may include:

- Density greater than or less than the host ferrous metal.
- Hardness in excess of 15 GPa.
- Diameter less than 500 microns, preferably less than 50 microns.
- 10-80 vol% refractory particles present in the hard surface layer,
  - 5-50 vol%, typically 5-40 vol%, more typically 5-40 vol%, refractory particles in the composite metal product.

The composite metal products produced by the centrifugal casting process of the indention include by way of example only the following products:

1. Slurry pump shaft sleeves
   - Stainless steel cylinders
   - Size: ranging from 25-400 mm diameter, 10 - 50 mm wall thickness and 2000 mm long.
   - Outer surface layer, 1-10 mm thick, containing a high concentration of hard, insoluble refractory particles.
The prior art comprises hard faced welding a stainless steel cylinder to obtain approximately 1 mm thick tungsten carbide surface layer. Hard-faced layers then require grinding/machining to achieve a smooth finish.

Centrifugally casting a slurry pump shaft sleeve in accordance with the invention permits the manufacture of a cylinder approximately 2000 mm long with a required smooth, hard surface layer in one casting operation. In addition, the long cylinder can be sectioned to yield a number of shaft sleeves which range in length from 60 to 300 mm.

2. Outer surface of gyratory crusher mantles

The standard composition of gyratory crusher mantles is austenitic manganese steel (Hadfield steel). The initial hardness of Hadfield steel is approximately 200 Brinell (HB) and the surface layer of the steel work hardens to approximately 550 HB in service while the interior maintains a lower hardness and extremely high toughness. The yield strength for Hadfield steel with a hardness of 200 HB is about 1/3 the tensile strength. Severe plastic deformation can occur in service before work hardening to 550 HB occurs. As a result, crusher mantles wear rapidly and undergo excessive plastic deformation in the early stages of operation. All previous attempts to improve the initial hardness and yield strength of Hadfield steel have invariably resulted in unacceptable loss in toughness and a high risk of catastrophic cracking in service.

Centrifugally casting a Hadfield steel crusher mantle in accordance with the present disclosure and forming an outer surface layer of insoluble solid refractory carbides in the casting, while maintaining the original Hadfield...
steel composition in the body of the casting, provides a more wear-resistant material with minimal loss of toughness.

3. White cast irons

Centrifugally casting high chromium white cast irons with refractory particles produces composite metal products having surface layers containing a high concentration of refractory particles for improved wear resistance.

4. Breaker bars, hammer tips, ground engaging tools

Centrifugally casting breaker bars, hammer tips and ground engaging tools from high chromium white cast irons with refractory particles produces a surface layer containing a high concentration of refractory particles for improved wear resistance.

EXPERIMENTAL WORK

In order to investigate the invention the applicant has carried out extensive experimental work in relation to particles of a particular refractory material, namely NbC particles, in different ferrous host metals.

Specifically, the experimental work investigated the effects of vol% of NbC particles and wall thickness and centrifugal forces on the NbC-rich zones in centrifugally cast products.

Xn the experimental work fourteen cylinders were centrifugally cast in a horizontally arranged centrifugal casting arrangement.
The fourteen cylindrical shaft sleeves with different concentrations of NbC particles and a ferrous-based host metal, as summarised below, were centrifugally cast and machined and then tested.

- Four A3G1 cylinders (AOS host metal + 5 vol% NbC particles of the total volume).
- Four A3G3 cylinders (AOS host metal + 12 vol% NbC particles of the total volume).
- Four A304 cylinders (AOS host metal + 17 vol% NbC particles of the total volume).
- One A352 cylinder (C21 host metal + 10 vol% NbC particles of the total volume).
- One A323 cylinder (A49 host metal + 15 vol% NbC particles of the total volume).

AOS is a eutectic high Cr cast iron, C21 is a 420C stainless steel, and A43 is a hypoeutectic high Cr cast iron. The nominal compositions of the AOS, C21, and A49 ferrous alloys are as follows, with the amounts of each element in wt%:

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cr</th>
<th>Mn</th>
<th>C</th>
<th>Ni</th>
<th>Si</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>A05</td>
<td>27</td>
<td>2.0</td>
<td>3.0</td>
<td>0.5</td>
<td>0.5</td>
<td>balance</td>
</tr>
<tr>
<td>C21</td>
<td>14</td>
<td>2.0</td>
<td>0.5</td>
<td>1.0</td>
<td>1.0</td>
<td>Balance</td>
</tr>
<tr>
<td>A49</td>
<td>28</td>
<td>1.5</td>
<td>1.5</td>
<td>2.0</td>
<td>1.5</td>
<td>Balance</td>
</tr>
</tbody>
</table>

1. RESULTS AND DISCUSSION

Twelve A05 steel-based cylinders with different nominal chemical compositions were centrifugally cast at various rotational speeds (RPM).

1.1. Centrifugal casting of four A301 cylinders (AOS host metal + 5 vol% NbC particles)

Four cylinders containing 5 vol% NbC particles in A05 eutectic high Cr cast iron host metal were centrifugally
cast at various rotational speeds or centrifugal forces. The casting temperature was in a range of 1400-1500°C. The density difference between the HbC particles and the host metal at the casting temperature was approximately 12%. The cylinder dimensions and casting conditions are in Table 1.

<table>
<thead>
<tr>
<th>Job No.</th>
<th>ID (mm)</th>
<th>OD (mm)</th>
<th>Length (mm)</th>
<th>RPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>37628</td>
<td>91</td>
<td>130</td>
<td>400</td>
<td>924</td>
</tr>
<tr>
<td>37629</td>
<td>90.5</td>
<td>130</td>
<td>400</td>
<td>1100</td>
</tr>
<tr>
<td>37630</td>
<td>91</td>
<td>130</td>
<td>400</td>
<td>1285</td>
</tr>
<tr>
<td>37655</td>
<td>82.3</td>
<td>130</td>
<td>400</td>
<td>924</td>
</tr>
</tbody>
</table>

Each 400mm cylinder was sectioned into three rings of roughly 280mm, 20mm and 100mm in length. The 20mm-thick rings were used for inspection and metallurgical analysis.

1.1.1. Metallurgical Examination

Samples were prepared from each 20mm-thick ring by cutting through the thickness at two locations roughly 15mm apart and forming cross-sections of the rings. Each cut was made perpendicular to the outer and inner circumference of the ring. Hence the width of the sample decreased from outer surface to the inner surface. The samples were mounted, ground and polished following standard metallographic procedures, and were then etched with Acidified Ferric Chloride (AFC) for raetallographic examination. The microstructures of the samples were examined with a scanning electron microscope. Also, an optical stereomicroscope was used for macroscopic examination of the samples.

Analysis of the samples from the cylinders established that the casting microstructure in each instance comprised the AOS eutectic high Cr cast iron host.
metal and a non-uniform distribution of solid NbC particles throughout the host metal. Figure 2 is a SEM image of a section of one of the samples, Figure 2 shows the non-uniform distribution of HbC particles in the host metal. The Figure indicates that NbC was undetectable in the host metal. More particularly, the NbC particles were found to be insoluble in the host metal at the easting temperature and in the cast cylinders.

Figure 3 comprises optical images of cross-sections of samples from cylinders "3?628", "37629", "37630", and "376SS".

Figure 3a shows that the sample from cylinder "37628" had a HbC particle-rich outer layer of about 2mm thickness. Internally of the outer layer there are three layers numbered 2-4 in the Figure. There are boundaries between the layers. Each layer is about 3-5mm thick. The layers 2-4 form an inner region having a lower concentration of HbC particles than the outer layer.

Figure 3b shows that the sample from cylinder "37629" had a similar layered (i.e. banded) structure, but with more layers than shown in Figure 3a. The high concentration NbC particle outer layer (identified by the numeral 1 in the Figure) is about 2mm thick with HbC particles spread uniformly throughout the sample. The outer layer 1 and the innermost layer (identified by the numeral 6 in the Figure) are the most distinct, and the layers in between (i.e. layers 2-5 in the Figure) are very similar to one another in terms of appearance but are nevertheless distinct layers separated by boundaries. The microstructures of layers 1 and 6 were found to be very different from each other as well as from the microstructures of layers 2-5. The microstructures of layers 2-5 were found to be quite similar to each other. Each layer 1-6 is about 3-4mm thick.
Cylinder "37630'" was cast at the highest rotation speed. Figure 3c shows that the sample had three layers. Compared to the samples of the other three cylinders, this casting had the lowest NbC particle concentration in the inner layers. The high rotation speed forced more NbC particles to the outer layer, resulting in the thickest high concentration NbC particle layer of all the castings.

Cylinder "37655" was cast at the same rotation speed as cylinder "37628", but was cast with a 5mm thicker wall thickness. Figure 3d shows that the NbC particle-rich layer in the sample from cylinder "37655" was about 3.5mm thick, greater than that in the sample from cylinder "37628". This shows that even if rotation speeds are the same, a thicker wall results in a thicker MbC particle-rich zone.

The NbC particle vol fractions of (a) the MbC particle-rich outer layer and (b) the low concentration MbC particle inner layer were calculated from SEM images of various areas of the layers at 1G0x magnification. The values shown in Table 2 are the averages of multiple measurements.

Table 2, NbC particles in outer and inner layers

<table>
<thead>
<tr>
<th>ID</th>
<th>NbC-rich layer</th>
<th>Inner layer vol%NbC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>thickness mm</td>
<td>vol%NbC</td>
</tr>
<tr>
<td>37628</td>
<td>2</td>
<td>12.9</td>
</tr>
<tr>
<td>37629</td>
<td>2</td>
<td>13.6</td>
</tr>
<tr>
<td>37630</td>
<td>3-5</td>
<td>14.2</td>
</tr>
<tr>
<td>37655</td>
<td>3.5</td>
<td>13.5</td>
</tr>
</tbody>
</table>

From Table 2, it is evident that the rotation speed during the casting had an effect on the MbC particle-rich
layer of the cast cylinders. The sample for cylinder "3763G", which was cast at the highest speed, had the highest layer thickness and the highest volume fraction of the MbC particles. The sample for cylinder "37629", which was cast with the second highest speed, came close in terms of MbC volume fraction, but the thickness of the layer was almost half that of the layer in sample "37630". Comparing the samples for cylinders "37628" and "37655" shows that even with the same rotation speed, if the casting wall thickness is greater (i.e. more material), then the MbC particle-rich outer layer and its volume fraction of MbC particles are greater as well.

In addition, all four castings had similar levels of MbC particles present in the non-concentrated MbC particle inner layers, collectively described as an inner region for each sample. Most of the MbC particles observed in the inner regions were typical "Chinese script" morphology. A small amount of spherical and dendritic MbC particles were also observed.

1,1.2, Hardness and ferrite measurements

Vickers hardness traverse tests with a load of 10kg were carried out on the polished surfaces of each sample. The measurements started at the outside diameter (OD) of each sample and then traversed through the thickness of the sample at 1mm intervals to finish at the inside diameter (ID) of the sample.

Table 3 shows the average hardness and ferrite readings for each of the two regions. Traverse hardness profiles are shown in Figure 4.
Table 3. Hardness and ferrite measurements

<table>
<thead>
<tr>
<th>Sample</th>
<th>Region</th>
<th>HV10</th>
<th>Ferrite Reading (% magnetic)</th>
</tr>
</thead>
<tbody>
<tr>
<td>37628</td>
<td>Outer</td>
<td>640</td>
<td>13.4</td>
</tr>
<tr>
<td></td>
<td>Inner</td>
<td>536</td>
<td>9.4</td>
</tr>
<tr>
<td>37629</td>
<td>Outer</td>
<td>676</td>
<td>16.2</td>
</tr>
<tr>
<td></td>
<td>Inner</td>
<td>557</td>
<td>10.4</td>
</tr>
<tr>
<td>37630</td>
<td>Outer</td>
<td>660</td>
<td>12.6</td>
</tr>
<tr>
<td></td>
<td>Inner</td>
<td>551</td>
<td>8.9</td>
</tr>
<tr>
<td>37655</td>
<td>Outer</td>
<td>608</td>
<td>14.2</td>
</tr>
<tr>
<td></td>
<td>Inner</td>
<td>531</td>
<td>9.7</td>
</tr>
</tbody>
</table>

Xt is evident from Table 3 and Figure 4 that the NbC particle-rich outer layer of each of the samples was considerably harder than the inner region of the sample and that the highest hardness values were typically at the outer surface of each sample and decreased uniformly to around 8 mm from the outer surface and remained generally constant through the remainder of the sample. XN addition, the ferrite measurement results for the four castings showed a general trend of the NbC particle-rich outer layer having higher ferrite measurements than the layers forming the inner regions. The differences in ferrite content were minor, with the NbC particle-rich outer layers ranging from 13 to 16% while the inner regions ranged between 9 and 10%.

1.1.3, Summary

* All four of A301 centrifugal castings (A05 host metal + 5 vol% NbC particles) exhibited NbC segregation, resulting in outer layers of each sample having high concentrations of NbC particles.
* All four castings exhibited layers below the NbC particle-rich outer layer which were marginally different.
from each other. Each casting had a different number of layers.

The thickness and hardness of the NbC particle-rich layers and the volume fractions of HbC particles in the outer layers of the centrifugally cast cylinders depended on the different casting parameters, including casting rotation rate and wall thickness.

Samples for cylinders "37628" and "37655" were cast at the same rotation speeds but with different material mass, resulting in different dimensions. The "37655" sample had a slightly thicker HbC particle-rich outer layer and it also contained a larger number of different banded layers through the thickness of the samples.

The sample for cylinder "37629" was similar to the sample for cylinder "37628", despite being cast at a higher rotation speed. The faster rotation speed did not affect the thickness of the NbC particle-rich outer layer, but it did affect the volume fraction of NbC particles in the outer layer slightly.

The sample for cylinder "37630" sample was cast at the fastest rotation speed, and this was reflected directly on several features. The sample had the thickest NbC particle-rich outer layer and the highest volume fraction of NbC particles in the outer layer. Consequently, the hardness of the outer layer was the highest recorded for this group of cylinders.

The ferrite measurement results for the four castings showed a general trend of the MbC particle-rich outer layer having higher ferrite measurements than the layers forming the inner regions. The differences in ferrite content were minor, with the HbC particle-rich outer layers ranging from 13 to 16% while the inner regions ranged between 9 and 10%.
1.2. Centrifugal casting of four Ά303 cylinders (A05 host metal + 12 vol% MbC particles)

Four cylinders were cast under the same conditions as the four cylinders described in section 1.1 above, with the same host metal (A05), but with a higher overall MbC volume fraction of 12%. The cylinder dimensions and rotational speeds are in Table 4.

Table 4, Job codes and dimension of cylinders containing 12vol% of NbC

<table>
<thead>
<tr>
<th>Job No.</th>
<th>ID (mm)</th>
<th>OD (mm)</th>
<th>Length (mm)</th>
<th>RPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>37631</td>
<td>89</td>
<td>130</td>
<td>400</td>
<td>922</td>
</tr>
<tr>
<td>37632</td>
<td>95</td>
<td>130</td>
<td>400</td>
<td>1104</td>
</tr>
<tr>
<td>37633</td>
<td>90</td>
<td>130</td>
<td>400</td>
<td>1280</td>
</tr>
<tr>
<td>37863</td>
<td>81</td>
<td>130</td>
<td>400</td>
<td>925</td>
</tr>
</tbody>
</table>

Each 400mm cylinder was sectioned into three rings of roughly 280mm, 20mm and 100mm in length. The 20mm-thick rings were used for inspection and metallurgical analysis. Samples were prepared and tested using the same methodology described in section 1.1 above.

Figure 5 comprises optical images of samples from cylinders "37631", "37632", "37633" and "37636".

It is evident from Figure 5 that, as was the case with the lower MbC particle volume fraction cylinders described in section 1.1 above, the NbC particles formed a non-uniform distribution in the host metal through the thickness of the castings, with the outer layers of the samples having higher concentrations of MbC particles.

Similarly, as was the case with the lower MbC particle volume fraction cylinders described in section 1.1 above, SEM analysis established that NbC was
undetectable in the host metal. More particularly, the HbC particles were found to be insoluble in the host metal at the casting temperature and in the cast cylinders.

The HbC particle volume fractions of the NbC particle-rich outer layers and the thicknesses of the outer layers were calculated from SEM images of various areas of the layers at 100x magnification. The values shown in Table 5 are the averages of multiple measurements.

Table 5 Thickness of outer layer and average vol%NbC particles

<table>
<thead>
<tr>
<th>Sample</th>
<th>OD (mm)</th>
<th>ID (mm)</th>
<th>NbC layer thickness (mm)</th>
<th>NbC layer volume fraction (%)</th>
<th>RPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>37631</td>
<td>130</td>
<td>89</td>
<td>6</td>
<td>25.098</td>
<td>922</td>
</tr>
<tr>
<td>37632</td>
<td>130</td>
<td>95</td>
<td>7</td>
<td>26.027</td>
<td>1104</td>
</tr>
<tr>
<td>37633</td>
<td>130</td>
<td>90</td>
<td>Min. 5, Max. 7</td>
<td>28.989</td>
<td>1280</td>
</tr>
<tr>
<td>37863</td>
<td>130</td>
<td>81</td>
<td>5</td>
<td>28.45</td>
<td>925</td>
</tr>
</tbody>
</table>

Vickers hardness traverse tests with a load of 10kg were carried out on the polished surfaces of each sample. The measurements started at the outside diameter (OD) of each sample and then traversed through the thickness of the sample at 1mm intervals to finish at the inside diameter (ID) of the sample.

Table 6 shows the average hardness and ferrite readings for each of the two regions. Traverse hardness profiles are shown in Figure 6.
Table 6. Hardness and Ferrite measurements

<table>
<thead>
<tr>
<th>Sample</th>
<th>Region</th>
<th>HV10</th>
<th>Ferrite Reading (% magnetic)</th>
</tr>
</thead>
<tbody>
<tr>
<td>37631</td>
<td>Outer</td>
<td>671</td>
<td>12.8</td>
</tr>
<tr>
<td></td>
<td>Inner</td>
<td>515</td>
<td>10.4</td>
</tr>
<tr>
<td>37632</td>
<td>Outer</td>
<td>772</td>
<td>11.5</td>
</tr>
<tr>
<td></td>
<td>Inner</td>
<td>584</td>
<td>9.8</td>
</tr>
<tr>
<td>37633</td>
<td>Outer</td>
<td>821</td>
<td>14.6</td>
</tr>
<tr>
<td></td>
<td>Inner</td>
<td>587</td>
<td>10.4</td>
</tr>
<tr>
<td>37863</td>
<td>Outer</td>
<td>771</td>
<td>15.2</td>
</tr>
<tr>
<td></td>
<td>Inner</td>
<td>593</td>
<td>11.5</td>
</tr>
</tbody>
</table>

It is evident from Tables 5 and 6 and Figures 5 and 6 that the same basic results were obtained with the higher volume percentage of the A303 cylinders as with the A301 cylinders described in section 1.1 above.

1,3. Centrifugal casting of four A304 cylinders (A05 host metal + 17 vol% NbC particles)

Four A3Q4 cylinders were centrifugally cast using the same conditions as the A301 and A303 cylinders described in sections 1.1 and 1.2, respectively, above, with the same A05 host metal, but with a higher volume fraction of NbC particles. Samples were prepared and tested as described in sections 1.1 and 1.2 above. Only three cylinders were examined (cylinder "37634" cast at 920 rpm, cylinder "37635" cast at 1100 rpm and cylinder "37636" cast at 1280 rpm).

Figure 7 comprises optical images of cross-sections of samples from cylinders "37634" & "37635".

It is evident from Figure 7 that, as was the case with the lower NbC particle volume fraction cylinders described in sections 1.1 and 1.2 above, the NbC particles formed a non-uniform distribution in the host metal.
through the thickness of the castings, with the outer layers of the samples having higher concentrations of NbC particles. The cross-sections show a NbC particle-rich outer layer (or region) and a lower NbC particle concentration inner region (which may include multiple layers separated by boundaries).

In addition, as was the case with the lower NbC particle volume fraction cylinders described in sections 1.1 and 1.2 above, SEM analysis established that NbC was undetectable in the host metal. More particularly, the NbC particles were found to be insoluble in the host metal at the casting temperature and in the cast cylinders.

The test work indicated that the thicknesses of the NbC particle-rich outer layers in the samples for cylinders \(^{37634}\), \(^{37635}\) and \(^{37636}\) were 12mm, 13mm and 15mm, respectively.

The volume concentrations of the NbC particles in the outer layers of these samples were 28% for cylinder \(^{37634}\), 25% for cylinder \(^{37635}\) and 29% for cylinder \(^{37636}\).

Table 7 shows the average hardness and ferrite readings for each of the inner and outer regions of the samples from cylinders \(^{37634}\) and \(^{37635}\). Traverse hardness profiles are shown in Figure 8.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Region</th>
<th>HV1G</th>
<th>Ferrite Reading (% magnetic)</th>
</tr>
</thead>
<tbody>
<tr>
<td>37634</td>
<td>Outer</td>
<td>664</td>
<td>12.7</td>
</tr>
<tr>
<td></td>
<td>Inner</td>
<td>546</td>
<td>10.9</td>
</tr>
<tr>
<td>37635</td>
<td>Outer</td>
<td>661</td>
<td>11.7</td>
</tr>
<tr>
<td></td>
<td>Inner</td>
<td>513</td>
<td>10.1</td>
</tr>
</tbody>
</table>
It is evident from Table 7 and Figures 7 and 8 that the same basic results were obtained with the higher volume percentage of the A304 cylinders as with the H3G1 and A303 cylinders described in sections 1.1 and 1.2 above.

1.4. Centrifugal casting of an A352 cylinder (C21 host metal + 10 vol% NbC particles)

One A352 cylinder was centrifugally cast from a C21 host metal with 10 vol% NbC particles. Samples were prepared and tested as described above.

Figure 9 comprises an optical image of a cross-section of a sample of the A352 cylinder.

It is evident from Figure 9 that, as was the case with the other test cylinders described above, the NbC particles formed a non-uniform distribution through the thickness of the casting, with the outer layer of the sample having a higher concentration of NbC particles.

In addition, as was the case with the other test cylinders described above, SEM analysis established that NbC was undetectable in the host metal. More particularly, the NbC particles were found to be insoluble in the host metal at the casting temperature and in the cast cylinders.

As shown in Figure 9, the NbC-rich layer is a 20 mm thick layer, 50% of the total radial thickness of the sample. It was found that the sample contained about 25 vol% of NbC particles.

After etching, three sub-layers of the 20 mm thick NbC particle-rich outer layer were identified, and are shown in Figure 10. Figure 10 shows that there was
directional solidification across the sub-layers during centrifugal casting, it has been found that the columnar structure made a significant contribution to the wear resistance of the casting.

1.5. Centrifugal casting of an A323 cylinder (A49 host metal + 15 vol% NbC particles)

One A323 cylinder was centrifugally cast from a A49 host metal and 15 vol% NbC particles. Samples were prepared and tested as described above.

1.5.1. Metallurgical Examination

Figure 11 comprises an optical image of a cross-section of a sample of the A323 cylinder. It is evident from Figure 11 that, as was the case with the other test cylinders described above, the NbC particles formed a non-uniform distribution through the thickness of the casting, with the outer layer of the sample having a higher concentration of NbC particles.

In addition, as was the case with the other test cylinders described above, SEM analysis established that NbC was undetectable in the host metal. More particularly, the NbC particles were found to be insoluble in the host metal at the casting temperature and in the cast cylinders.

As is evident from Figure 11, the NbC particle-rich outer layer is a very distinct band along the entire outer edge of the circle. This was visible at both macroscopic and microscopic levels.

The depth of the NbC particle-rich outer layer was found to be consistent along the circumference at about 7-8 mm, i.e. approximately 25-30% of the radial thickness of
Apart from the NbC concentrations, the microstructures of the outer and the inner layers were found to have other significant differences. The NbC particles in the NbC particle-rich outer layer were mostly round without any sharp edges, while those in the inner layers had a variety of shapes, ranging from round to pointy dendritic shapes. The matrix structure of the NbC particle-rich outer layer and the other layers could be distinguished primarily by the presence/absence of "Chinese script" type NbC particles structure in the austenite dendrites of the matrix. This type of HbC structure was found extensively in the inner layers, but it was almost non-existent in the NbC particle-rich outer layer. This resulted in a difference in thermal characteristics of the NbC particle-rich outer layer and the inner layers.

A very unique microstructure was found at the boundary of the NbC particle-rich outer layer and the inner layers. The microstructure was characterised by the NbC particles being predominantly cross-shaped (dendritic). Some particles in this region resembled a shape that was a mixture of round and dendritic.

1.5.2. Hardness & Ferrite

Vickers hardness traverse tests with a load of 10kg were carried out on polished surfaces of two samples. The measurements started at the outermost edges of the samples and then traversed through the thickness of the castings at 1mm intervals to finish at the innermost edges. Table 8 shows the average hardness and ferrite reading for the NbC particle-rich outer layer and the inner layers of each sample. The NbC particle-rich outer layer of each sample
is described as the "outer region" in the Table and the inner layers of each sample are described as the "inner region" in the Table. Traverse hardness profiles are shown in Figure 12.

Table 8, Hardness and Ferrite measurements

<table>
<thead>
<tr>
<th>Sample</th>
<th>Region</th>
<th>HV10</th>
<th>Ferrite Reading (% magnetic)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4719CG-A</td>
<td>Outer</td>
<td>455</td>
<td>22.9</td>
</tr>
<tr>
<td></td>
<td>Inner</td>
<td>357</td>
<td>21.2</td>
</tr>
<tr>
<td>4719CC-B</td>
<td>Outer</td>
<td>526</td>
<td>19.1</td>
</tr>
<tr>
<td></td>
<td>Inner</td>
<td>355</td>
<td>17.6</td>
</tr>
</tbody>
</table>

The higher NbC particle concentration of the NbC particle-rich outer layer (the outer region) naturally resulted in a higher hardness than the inner region for each sample. The hardness results correlated with the volume fraction results, where a higher NbC volume fraction of the 4719CC-B sample gave a higher hardness result than the 419CC-A sample. There was no significant difference in ferrite content between the two regions of each sample.

With reference to Figure 12, the hardness traverses® tests showed that for both samples, the hardness was the highest at the very outer edge of the samples (i.e., the first test points for both tests) and the hardness at the boundary of the two regions was around 425 Vickers. The inner (bulk) region maintained consistent hardness throughout most of its thickness.
2. CONCLUSIONS

2.4. Functionally Graded Materials

In the test work summarised above, host metals (AOS, A49 and C21) with a range of volume percentages of NbC particles were centrifugally cast and examined. The results are summarized and presented in Table 9.

Table 9. Summary of centrifugally cast 4300-family alloys

<table>
<thead>
<tr>
<th>#</th>
<th>Code</th>
<th>FMMCC</th>
<th>RPM</th>
<th>G-force (G)</th>
<th>NbC-rich Layer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Host Metal Desc.</td>
<td>Bulk NbC (vol%)</td>
<td>Thickness (mm)</td>
<td>NbC (vol%)</td>
</tr>
<tr>
<td>1</td>
<td>A323</td>
<td>A49</td>
<td>15</td>
<td>920</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>924</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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The volume fraction of refractory particles in the NbC particle-rich outer layers of the castings were up to 31% in "volume of the outer layer. In addition, high rotation speeds increased the NbC vol%, but the effects were typically very small. In the inner region of each casting, the volume percentage of NbC particles varied in the range from 2-6%. 
The relationship between thickness of the HbC particle-rich outer layer and the overall vol% of HbC in the product compositions and the relationship between the vol% of NbC in the NbC particle-rich outer layer and the overall vol% NbC in the product compositions were analysed and the results are presented in Figures 13 and 14, respectively.

As can be seen from the Figures:
(a) the thickness of the NbC-rich outer layer of each centrifugally cast cylinder was found to be directly dependent on the nominal bulk NbC content in the product composition (see Figure 13); and
(b) the final NbC content in the HbC particle-rich outer layer of each centrifugally cast cylinder was found to be dependent on the nominal bulk NbC content in the product composition, with the NbC content tending to level off at a maximum content of around 28-30% in the outer layer for the particular Al05 host metal and being 50-120 vol% higher than the nominal volume percentage of the refractory material in the whole product across the nominal NbC vol% range covered by Figure 14,

It was also found that the thickness of and the NbC particle concentration in the NbC particle-rich outer layer in each of the centrifugally cast cylinders was independent of the casting G-Factor in a range of 50-102.

In the foregoing description of preferred embodiments, specific terminology has been resorted to for the sake of clarity. However, the invention is not intended to be limited to the specific terms so selected, and it is to be understood that each specific term includes all technical equivalents which operate in a similar manner to accomplish a similar technical purpose. Terms such as "front" and "rear", "inner" and "outer",
"above", "below", "upper" and "lower" and the like are used as words of convenience to provide reference points and are not to be construed as limiting terras.

The reference in this specification to any prior publication (or information derived from it), or to any matter which is known, is not, and should not be taken as, an acknowledgement or admission or any for® of suggestion that prior publication (or information derived from it) or known matter forms part of the common general knowledge in the field of endeavour to which this specification relates.

In this specification, the word "comprising" is to be understood in its "open" sense, that is, in the sense of "including", and thus not limited to its "closed" sense, that is the sense of "consisting only of". A corresponding meaning is to be attributed to the corresponding words "comprise", "comprised" and "comprises" where they appear.

In addition, the foregoing describes only some embodiments of the invention(s), and alterations, modifications, additions and/or changes can be made thereto without departing from the scope and spirit of the disclosed embodiments, the embodiments being illustrative and not restrictive.

Furthermore, invention(s) have been described in connection with what are presently considered to be the most practical and preferred embodiments, it is to be understood that the invention is not to be limited to the disclosed embodiments, but on the contrary, is intended to cover various modifications and equivalent arrangements included within the spirit and scope of the invention(s). Also, the various embodiments described above may be implemented in conjunction with other embodiments, e.g.,
aspects of one embodiment may be combined with aspects of another embodiment to realize yet other embodiments. Further, each independent feature or component of any given assembly may constitute an additional embodiment.

By way of example, whilst the embodiments of the invention described above comprise different types of steel (such as a stainless steel or an austenitic manganese steel) as the host metal, the invention is not limited to this type of host metal and extends to any suitable host metal. By way of example, the host metal may contain wherein the host metal contain any one or more of the transition metal elements Ti, Cr, Zr, Hf, V, Nb, and Ta.

By way of further example, whilst the embodiments of the invention described above focus on NbC as the material of the insoluble solid particles of refractory material, the invention also extends to other refractory materials.

By way of further example, whilst the embodiments of the invention described above focus on NbC particles which have a density that is higher than that of the host metal, whereby there are higher concentrations of the refractory particles towards exterior surfaces of the composite metal products, the invention also extends to embodiments in which the refractory particles have a density that is lower than that of the host metal, whereby there are higher concentrations of the refractory particles towards an interior surface of the composite metal product.

By way of further example, whilst the experimental work described above was carried out on centrifugally cast cylinders, it can readily be appreciated that the invention is not limited to this particular shape casting and extends to any shape product that can be centrifugally cast.
1. A centrifugally cast composite metal product having an axis of rotational symmetry and a mass of at least 20kg and comprising a metal host and insoluble solid particles of a refractory material in a non-uniform distribution throughout the host metal, wherein the particles have a density that is within 20% of the density of the metal host at its casting temperature.

2. The composite metal product defined in claim 1, wherein the non-uniform distribution of refractory particles comprises a first concentration of particles in an exterior or interior surface layer of the product that is higher than a second concentration of particles in another layer in the product.

3. The composite metal product defined in claim 2, wherein the first concentration of refractory particles in the exterior surface layer of the product is in a range of 10-40 vol% of the total volume of the exterior surface layer.

4. The composite metal product defined in claim 2 or claim 3, wherein the second concentration of refractory particles in the other layer of the product is in a range of 2-4.5 vol% of the total volume of the other layer.

5. The composite metal product defined in any one of claims 2 to 4, wherein the first concentration of refractory particles in the exterior surface layer of the product is 50-120 vol% higher than the nominal volume percentage of the refractory material in the product.

6. The composite metal product defined in any one of claims 2 to 5, wherein the exterior or interior surface layer of the product extends less than 50% of the radial...
thickness of the product from the exterior or interior surface of the product.

7. The composite metal product defined in any one of claims 2 to 6, wherein the exterior or interior surface layer of the product extends 1-50 mm from the exterior or interior surface of the product.

8. The composite metal product defined in any one of claims 2 to 6 wherein the first concentration of refractory particles in the exterior surface layer of the product is in a range of 5-90 vol% of the total volume of the particles.

9. The composite metal product defined in any one of the preceding claims, wherein the overall concentration of refractory particles in the product is in a range of 5-50 vol%, typically 5-40 vol%, of the total volume of the product.

10. The composite metal product defined in any one of the preceding claims having a mass of at least 50kg.

11. The composite metal product defined in any one of the preceding claims having a mass of at least 75kg.

12. The composite metal product defined in any one of the preceding claims, wherein the refractory particles have a density that is within 15% of the density of the metal host at its casting temperature.

13. The composite metal product defined in any one of the preceding claims, wherein the refractory particles are carbides and/or borides and/or nitrides of one or 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.

14. The composite metal product defined in any one of the preceding claims, wherein the host metal is a ferrous alloy, such as a stainless steel or an austenitic manganese steel or a cast iron.

15. The composite metal product defined in claim 14, wherein the host metal is an alloy comprising any one of the following alloys:
   
   (a) Hadfield steel, for use for example in gyratory crusher mantles;
   
   (b) 420c stainless steel, for use for example in shaft sleeves in slurry pumps; and
   
   (c) high chromium white cast iron,

16. The composite metal product defined in claim 14, wherein the host metal is Hadfield steel comprising:

   1.0 ~ 1.4 wt% C
   0.0 - 1.0 wt% Si,
   10 - 15 wt% Mn,
   0.0 - 3.0 wt% Mo,
   0.0 - 5.0 wt% Cr,
   0.0 - 2.0 wt% Ni,

   with the remainder being Fe and incidental impurities.

17. The composite metal product defined in claim 14, wherein the host metal is a 420C stainless steel comprising:

   0.3 - 0.5 wt% C,
   0.5 - 1.5 wt% Si,
   0.5 - 3.0 wt% Mn,
   0.0 - 0.5 wt% Mo,
   10 - 14 wt% Cr,
   0.0 - 1.0 wt% Ni,

   with the remainder being Fe and incidental impurities.
18. The composite metal product defined in claim 14, wherein the host metal is a high chromium white cast iron comprising:

- 1.5 - 4.0 wt% C,
- 0.0 - 1.5 wt% Si,
- 0.5 - 7.0 wt% Mn,
- 0.0 - 1.0 wt% Mo,
- 15 - 35 wt% Cr,
- 0.0 - 1.0 wt% Ni,

with the remainder being Fe and incidental impurities.

19. The composite metal product defined in any one of claims 1-14, wherein the host metal a non-ferrous metal.

20. The composite metal product defined in any one of the preceding claims comprising a gyratory crusher mantle for a primary, secondary or tertiary crusher.

21. The composite metal product defined in any one of claims 1 to 19 comprising a slurry pump shaft sleeve.

22. A centrifugally cast composite metal product having an axis of rotational symmetry and a mass of at least 20kg and comprising a metal host and insoluble solid particles of a refractory material in a non-uniform distribution throughout the host metal, wherein the particles have a density that is within 30% of the density of the metal host at its casting temperature.

23. A centrifugally cast composite metal product having an axis of rotational symmetry and a mass of at least 5kg and comprising a metal host and insoluble solid particles of a refractory material in a non-uniform distribution throughout the host metal, wherein the particles have a density that is within 20% of the density of the metal host at its casting temperature,
24. A method of centrifugally casting a composite metal product having an axis of rotational symmetry and a mass of at least 20kg and comprising a host metal and a non-uniform dispersion of insoluble solid refractory particles of a refractory material, the method comprising:

(a) forming a slurry comprising solid refractory particles dispersed in a liquid host metal, with the refractory particles comprising 5-50 vol% of the total volume of the slurry, with the refractory particles being insoluble at a casting temperature, and with the refractory particles having a density that is within 20% of the density of the metal host at the casting temperature; and

(b) pouring the slurry into a mould for the product and centrifugally casting the product in the mould and obtaining a non-uniform distribution of insoluble solid particles throughout the host metal.

25. The method of centrifugally casting a composite metal product as defined in claim 24, wherein steps (a) and (b) are carried out under an inert environment.

26. The method of centrifugally casting a composite metal product as defined in claim 24 or claim 25, comprises preparing the mould by forming an inert environment within the mould.

27. The method of centrifugally casting a composite metal product as defined in any one of claims 24 to 26, wherein step (b) comprises rotating the mould about the axis subsequent to and/or during pouring the slurry into the mould to cause a concentration of refractory particles at or near an exterior surface or at or near an interior surface of the product that is higher than the concentration of particles elsewhere in the product.
28. The method of centrifugally casting a composite metal product as defined in any one of claims 24 to 27, wherein step (b) comprises rotating the mould at a 10-120 G-Factor.

29. The method of centrifugally casting a composite metal product as defined in any one of claims 24 to 28, wherein step (b) comprises rotating the mould at a peripheral speed of 2.5-25 meters/second.

30. The method of centrifugally casting a composite metal product as defined in any one of claims 24 to 29, wherein step (b) comprises rotating the mould until the host metal has solidified.

31. The method of centrifugally casting a composite metal product as defined in any one of claims 24 to 30, wherein step (b) comprises rotating the mould for sufficient time to obtain the non-uniform distribution of solid particles throughout the host metal.

32. The method of centrifugally casting a composite metal product as defined in any one of claims 24 to 31, wherein step (b) comprises pouring the slurry into the mould at a casting temperature in a range of 1200-1650°C, typically in a range of 1350-1550°C.

33. The method of centrifugally casting a composite metal product as defined in any one of claims 24 to 32, wherein the composite metal product has a mass of at least 50kg.

34. The method of centrifugally casting a composite metal product as defined in any one of claims 24 to 33, wherein the composite metal product has a mass of at least 75kg.

35. The method of centrifugally casting a composite metal product as defined in any one of claims 24 to 34, wherein
the refractory particles have a density that is within 15% of the density of the metal host at its casting temperature.

36. A method of centrifugally casting a composite metal product having an axis of rotational symmetry and a mass of at least 20kg and comprising a host metal and a non-uniform dispersion of insoluble solid refractory particles of a refractory material, the method comprising:

(a) forming a slurry comprising solid refractory particles dispersed in a liquid host metal, with the refractory particles comprising 5-50 vol% of the total volume of the slurry, with the refractory particles being insoluble at a casting temperature, and with the refractory particles having a density that is within 20% of the density of the metal host at the casting temperature; and

(b) pouring the slurry into a mould for the product and centrifugally casting the product in the mould and obtaining a non-uniform distribution of insoluble solid particles throughout the host metal.

37. A method of centrifugally casting a composite metal product having an axis of rotational symmetry and a mass of at least 5kg and comprising a host metal and a non-uniform dispersion of insoluble solid refractory particles of a refractory material, the method comprising:

(a) forming a slurry comprising solid refractory particles dispersed in a liquid host metal, with the refractory particles comprising 5-50 vol% of the total volume of the slurry, with the refractory particles being insoluble at a casting temperature, and with the refractory particles having a density that is within 20% of the density of the metal host at the casting temperature; and

(b) pouring the slurry into a mould for the product and centrifugally casting the product in the mould and
obtaining a non-uniform distribution of insoluble solid particles throughout the host metal,

38. A method of centrifugally casting a composite metal product having an axis of rotational symmetry and a mass of at least 5kg and comprising a host metal and a non-uniform distribution of insoluble solid particles of a refractory material, the method comprising adding (a) niobium or (b) two or more than two of niobium and titanium and tungsten to a melt containing a host metal in a form that produces solid refractory particles of niobium carbide that are insoluble at a casting temperature and/or solid refractory particles of a chemical mixture of two or more than two of niobium carbide and titanium carbide and tungsten carbide that are insoluble at a casting temperature, with the solid refractory particles being in a range of 5-50 vol% of the total volume of the product, and centrifugally casting the product in a mould and obtaining a non-uniform distribution of insoluble solid refractory particles throughout the host metal.
CENTRIFUGAL CASTING PROCESS

FIG. 1
NbC, refractory carbide, is insoluble in A05.
FIG. 4

FIG. 5a

FIG. 5b

FIG. 5c

FIG. 5d
**FIG. 6**

**FIG. 7**
Fig. 8

Fig. 9
FIG. 10
**FIG. 12**

![Graph showing hardness (HV/10) vs. distance from the outer edge (mm) for M13182 (4719CC-A) and M13183 (4719CC-B).](image)

**FIG. 13**

![Graph showing thickness (mm) vs. nominal NbC in A05 (VOL.%) with a linear relationship.(mm) = 0.6863 x VOL. %NbC](image)
FIG. 14

VOL.%NbC IN OD LAYER = - 0.1083x(VOL.%NbC) - 0.3072

SUBSTITUTE SHEET (RULE 26)
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

B22D 13/00 (2006.01)  C22C 37/00 (2006.01)  C22C 38/00 (2006.01)  C22C 29/00 (2006.01)

According to International Patent Classification (IPC) or 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, EPDOC: IPC/CPC (B22D 13/-, B22D 5/-, B22D 27/-, C22C 29/-, C22C 33/-, C22C 37/-, C22C 38/-, C21D 10/00, C21C 1/-, C21C 5/-, C21C 7/-) Using keywords (CENTRIFUGAL, REFRACTORY, CARBIDES, NITRIDES, BORIDES, PARTICLE, HOST, METAL) and like terms

WPI, EPDOC, ESPACENET, WIPO, USPTO, GOOGLE PATENTS: Using keywords (CENTRIFUGAL, REFRACTORY, CARBIDES, NITRIDES, BORIDES, PARTICLE, HOST, METAL, SLURRY) and like terms

ESPACENET: Applicant and Inventors search

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category* Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No.

Documents are listed in the continuation of Box C

X Further documents are listed in the continuation of Box C  X See patent family annex

* Special categories of cited documents:
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"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
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Date of the actual completion of the international search 27 January 2015

Date of mailing of the international search report 27 January 2015

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<td>AU 2013203 02 A1 (WEIR MINERALS AUSTRALIA LTD) 02 May 2013 abstract; page 1, lines 13 - 20; page 3, lines 33 - 37; page 7, line 29; page 11, lines 24 - 31; page 14, lines 25 - 29; claims 1 - 2, 8 - 10, 12, 16 - 30</td>
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<td>US 6805757 B1 (WINDHAGER et al.) 19 October 2004 abstract; claims 1 - 27</td>
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This Annex lists known 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.

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

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