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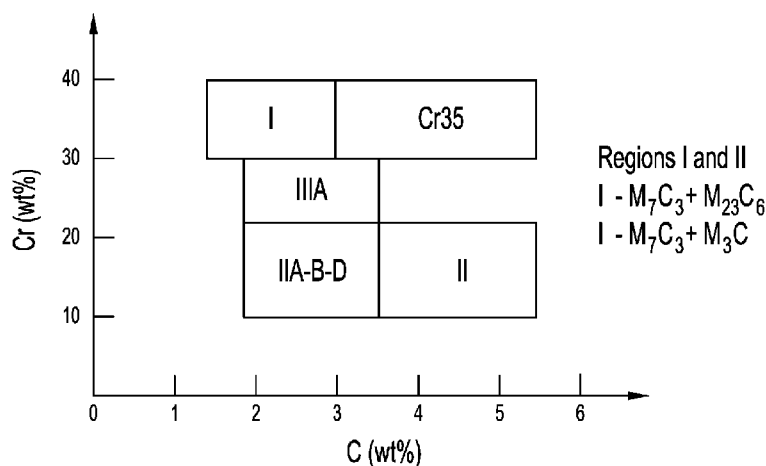


Figure 1

(57) Abstract: An end-use casting of a high chromium white iron, i.e. a casting that has been heat-treated, includes a ferrous matrix and at least two different chromium carbides dispersed in the matrix, with at least one of the chromium carbides including a transformation product of an as-cast chromium carbide.



TOUGH AND CORROSION RESISTANT WHITE CAST IRONSTechnical Field

5 The present invention relates to tough and corrosion resistant high chromium white irons (also referred to herein as high chromium white cast irons) comprising hard material particles dispersed in a host metal (which term includes metal alloy).

10 The present invention also relates to equipment used in the mining and mineral processing industries, such as pump components (including components for slurry pumps), that include castings or facings of high chromium white irons where the equipment is
15 exposed to any one or more than one of severe abrasion, impact, erosion and corrosion wear.

 The present invention also relates to a method of forming high chromium white irons.

 The present invention also relates to a method
20 of forming castings or facings of high chromium white irons as at least a part of equipment used in the mining and mineral processing industries.

Background

25 Equipment used in the mining and mineral processing industries often is subject to any one or more than one of severe abrasion, impact, erosion and corrosion wear.

30 The equipment includes, for example, slurry pumps and pipelines, mill liners, crushers, transfer chutes and ground-engaging tools.

 By way of particular example, metal "wet-end" components in slurry pumps are subject to abrasion,
35 impact, erosion and corrosion wear in service due to the passage of high tonnages of hard, sharp mineral

particles through the pumps. The pump components include frame plate liners, impellers, volutes and throat bushes. Typically, the components range in size from 2 kilograms up to approximately 20 or more tonnes in mass. The components include castings of wear resistant materials or facings of wear resistant materials where the equipment is subject to any one or more than one of severe abrasion, impact, erosion and corrosion wear and require replacement at periodic intervals to maintain pump performance in service.

Material loss in the slurry pump metal wet-end components in service can be attributed to one or more of the following mechanisms:

- Erosive wear by mineral particles (nominally 0.1 – 100 mm in diameter) flowing through the equipment.
- Corrosion as a consequence of contact with liquids (which term includes slurries) flowing through the pumps, where the pH of the liquids can vary from very acidic to very basic.
- Spalling or cracking due to impact loading in service.

A family of high chromium white irons known as high chromium white cast irons (HCWCIs) described in International Standards Association ISO 21988, Sections 1 c) and 3.3 provides a range of alloys that optimise the three major properties of (a) wear resistance, (b) corrosion resistance and (c) fracture toughness that are required for slurry pump wet-end components in a wide range of operating conditions.

The first HCWCI was developed 100 years ago and patented in 1917 (US patent 1245552).

The nominal bulk chemistry of the first HCWCI alloy, as defined in claim 1 of the US patent, is:

- Chromium: 20–35 wt.%.
- Carbon: 1.5–3.0 wt.%.

- Silicon: 0.0–3.0 wt.%.
- Iron: balance.

The first HCWCI alloy, designated as "Cr27" in Table 3 of International Standards Association ISO 21988 and referred to hereinafter as "Cr27", complies with the US patent 1245552 claims and is essentially the "workhorse" material used today in many slurry pump applications that are subject to abrasion, erosion and corrosion wear.

The ISO composition of Cr27 is as follows, in wt.%:

C	Si max.	Mn	P max.	S max.	Cr	Ni max.	Mo max.	Cu max.
1.8–3.6	1.0	0.5–2.0	0.08	0.08	23–30	2.0	3.0	1.2

The microstructure of castings of Cr27 consists of two distinct phases, namely:

- 25 volume % of chromium carbides.
- 75 volume% ferrous matrix.

There have been further developments in the field of high chromium white cast irons since the above-described first HCWCI was developed about 100 years ago. These developments have resulted in improvements in performance in a number of areas.

By way of example, a family of HCWCI, designated Cr35, was developed by the applicant to produce slurry pump parts to satisfy a number of high wear applications.

Cr35 was adopted by the Australian Standards Association and the International Standards Association as a designated wear resistant material and was incorporated in AS/NZS 2027 and ISO 21988, respectively, about 10 years ago.

The ISO composition of Cr35 is as follows, in wt.%:

C	Si max.	Mn	P max.	S max.	Cr	Ni max.	Mo max.	Cu max.
3.0-5.5	1.0	1.0-3.0	0.06	0.06	30-40	1.0	1.5	1.2

The wear resistance of the Cr35 family is recognised as superior to that of Cr27 alloy in many slurry pump applications where erosive wear is the dominant mode of material loss.

The applicant has realised that there is still a need for further improvements in some applications, including slurry pump applications (and for other equipment in a range of other applications), especially where impact wear is significant.

The above description should not be taken to be an admission of the common general knowledge in Australia or elsewhere.

15 Summary of the disclosure

The applicant has identified a combination of composition and microstructure of castings of high chromium white irons that exhibit toughness and corrosion resistance that are very useful in a number of end-use applications of the castings.

The combination identified by the applicant is high chromium white irons that have compositions that are characterised by (a) ranges (which can be described as "regions" when the Cr concentration range is plotted against the C concentration range - such as shown in Figure 1) of Cr and C and (b) Cr:C ratios within these ranges that are cast and then heat-treated so that at least part of the chromium carbides in as-cast forms of the castings transform to another chromium carbide, whereby the end-use forms of the castings have mixtures of chromium carbides with at least one of the chromium carbides

being a transformation product of an as-cast chromium carbide.

The term "transformation product" is understood herein to mean a product that forms as a result of
5 heat treatment and has a different phase to the original un-heat-treated phase of the product.

The microstructures of these end-use forms of the castings are quite different to the microstructures of other end-use forms of castings of
10 HCWCIs such as Cr27 and Cr35.

The microstructure of the invention is defined in this specification in two states. One state is the microstructure in the as-cast form of the casting. The other state is the microstructure in
15 the end-use form of the casting.

Typically, the end-use form of a casting is a heat-treated as-cast casting.

Typically, the heat treatment increases the amount of chromium carbides and decreases the amount
20 of elemental chromium in solution in the matrix of the casting.

In general terms, the invention provides a casting of a high chromium white iron that, in an end-use form of the casting after heat treatment,
25 includes a ferrous matrix and at least two different chromium carbides dispersed in the matrix, with at least one of the chromium carbides including a transformation product of an as-cast chromium carbide.

30 In any given situation, the amount of the transformation product may be selected based on a range of factors, including but not limited to the requirements for the end-use form of the casting and the composition of the casting.

The transformation product may be at least 5%, typically at least 10%, typically less than 60% of the as-cast chromium carbides.

Typically, the high chromium white iron consists of two different chromium carbides dispersed in the matrix of the end-use form of the casting, i.e. after heat treatment.

In one embodiment, the chromium carbides dispersed in the matrix of the end-use form of the casting, i.e. after heat treatment, are M_7C_3 and $M_{23}C_6$, where "M" comprises Cr, Fe, and Mn.

In this embodiment, at least a part of the $M_{23}C_6$ is a transformation product of M_7C_3 with the $M_{23}C_6$ forming during heat treatment of the as-cast form of the casting. It is noted that there may be some $M_{23}C_6$ in an as-cast form of the casting and, therefore, in this situation the heat treatment increases the amount of $M_{23}C_6$ as a consequence of transforming some of the M_7C_3 .

The chromium carbides in the heat-treated end-use form of the casting may include particles that have a hard core of M_7C_3 surrounded by a softer shell of $M_{23}C_6$ which acts as a transition zone between the softer metal matrix and the extremely hard M_7C_3 carbide core.

The composition of the casting may comprise the following composition ranges, described herein as Region I and with the Cr and C concentration ranges shown in Figure 1 as Region I:

- Cr: 30-40 wt.%
- C: 1.5-3 wt.%
- Cr/C ratio (wt.%): 9:1 - 15:1
- Up to 3 wt.% each of any one or more than one of Mn, Si, Ni, Mo, and Cu,
- Incidental impurities
- Balance: Fe

The composition ranges described in the preceding paragraph, including the Cr/C ratio, are based on direct experimental work and casting and metallurgy experience of the applicant and computer
5 modelling work carried out by the applicant.

The impurities may include sulphur, phosphorus, and aluminum.

The chromium carbides dispersed in the matrix may be 30-60 vol.% of the casting.

10 The chromium carbides dispersed in the matrix may be 40-50 vol.% of the casting.

The M_7C_3 chromium carbides may be 10-20 vol.% of the casting.

15 The M_7C_3 chromium carbides may be 15-20 vol.% of the casting.

The $M_{23}C_6$ chromium carbides may be 20-35 vol.% of the casting.

The $M_{23}C_6$ chromium carbides may be 25-30 vol.% of the casting.

20 The matrix may be 40-70 vol.% of the casting.

The Cr/C ratio (wt.%) may be 10:1 - 15:1.

The Cr/C ratio (wt.%) may be 10:1 - 14:1.

In this embodiment, a proportion of the chromium carbides are in the form of primary M_7C_3 due to the
25 relative chromium and carbon contents of the alloys. The presence of primary carbides in high chromium white irons is associated with improved wear resistance but poor impact toughness. The invention seeks to overcome this limitation due to the binary
30 nature of the primary carbides. Typically, at least some of the particles of chromium carbides have a hard core of M_7C_3 that is surrounded by a softer shell of $M_{23}C_6$ which acts as a transition zone between the much softer metal matrix and the extremely hard
35 M_7C_3 carbide core, allowing dissipation of impact energy leading to a reduced propensity for the

primary carbides to crack during large particle
impingement and impact. Furthermore, the
comparatively elevated chromium in these compositions
leads to a desirable increase in the corrosion
5 resistance of a casting. This combination of high
carbide volume fraction, impact resistant primary
carbides and increased corrosion resistance makes
this alloy particularly suitable for slurry pumping
duties in minerals processing circuits, oil sands
10 hydro-transport, and coarse mine tailings duties.

In another embodiment, the chromium carbides
dispersed in the matrix of the end-use form of the
casting, i.e. after heat treatment, are M_7C_3 and M_3C ,
where "M" comprises Cr, Fe, and Mn.

15 The chromium carbides in the heat-treated end-
use form of the casting may include particles that
have a hard core of M_7C_3 surrounded by a softer shell
of M_3C which acts as a transition zone between the
softer metal matrix and the extremely hard M_7C_3
20 carbide core.

In this embodiment the at least a part of the
 M_3C is a transformation product of M_7C_3 with the M_3C
forming during heat treatment of the as-cast form of
the casting. It is noted that there may be some M_3C
25 in an as-cast form of the casting and, therefore, in
this situation the heat treatment increases the
amount of M_3C as a consequence of transforming some
of the M_7C_3 .

The composition of the casting may comprise the
30 following composition ranges, described herein as
Region II and with the Cr and C concentration ranges
shown in Figure 1 as Region II:

- Cr: 10-23 wt.%
- C: 3.3-5.5 wt.%
- 35 • Cr/C ratios (wt.%): 2:1 - 4:1
- Up to 3 wt.% each of any one or more than one of

Mn, Si, Ni, Mo, and Cu

- Incidental impurities
- Balance: Fe

The composition ranges described in the
5 preceding paragraph, including the Cr/C ratio, are
based on direct experimental work and casting and
metallurgy experience of the applicant and computer
modelling work carried out by the applicant.

The chromium carbides dispersed in the matrix
10 may be 30-70 vol.% of the casting.

The chromium carbides dispersed in the matrix
may be 30-60 vol.% of the casting.

The matrix may be 30-70 vol.% of the casting.

The Cr/C ratio (wt.%) may be 2.5:1 - 3.5:1.

15 In this embodiment, at least some of the
particles of chromium carbides have a hard core of
 M_7C_3 that is surrounded by a softer shell of M_3C which
acts as a transition zone between the much softer
metal matrix and the extremely hard M_7C_3 carbide
20 core, allowing dissipation of impact energy leading
to a reduced propensity for the primary carbides to
crack during large particle impingement and impact.

The invention also provides a casting of a high
chromium white cast iron that, in the as-cast form of
25 the casting, includes a ferrous matrix with chromium
in solution in the matrix and chromium carbides
dispersed in the matrix, with the casting
characterised by:

- Cr: 30-40 wt.%
- 30 • C: 1.5-3 wt.%
- Cr/C ratios (wt.%): 9:1 - 15:1
- Total carbides in the casting: 30-60 vol.%
- Up to 3 wt.% each of any one or more than one of
Mn, Si, Ni, Mo, and Cu
- 35 • Incidental impurities
- Balance: Fe.

The invention also provides a casting of a high chromium white cast iron that, in the as-cast form of the casting, includes a ferrous matrix with chromium in solution in the matrix and chromium carbides dispersed in the matrix, with the casting characterised by:

- Cr: 10-23 wt.%
- C: 3.3-5.5 wt.%
- Cr/C ratios (wt.%): 2:1 - 4:1
- Total carbides in the casting: 30-70 vol.%
- Up to 3 wt.% each of any one or more than one of Mn, Si, Ni, Mo, and Cu,
- Incidental impurities
- Balance: Fe

The purpose of Mn, Si, Ni, Mo, and Cu, when part of the composition, is to contribute to forming required martensitic, austenitic, ferritic, or mixed ferrous matrices.

The microstructure of the as-cast form of the casting typically includes a ferrous matrix with chromium in solution in the matrix, eutectic chromium carbides dispersed in the matrix, primary chromium carbides dispersed in the matrix, and optionally secondary carbides dispersed in the matrix.

Typically, the eutectic carbides, the primary carbides, and the secondary carbides in the as-cast casting are M_7C_3 carbides where "M" comprises Cr, Fe, and Mn.

The term "primary carbides" is understood to mean carbides that precipitate from a melt between the liquidus and solidus temperatures.

The term "eutectic carbides" is understood to mean carbides that precipitate from a melt at the solidus temperature.

The term "secondary carbides" is understood to mean carbides that form via solid-state reactions in castings.

The reference to "as-cast form of the casting" in the preceding paragraph (and as used in the earlier part of the specification) is understood to mean the casting at the point the casting is formed and cooled continuously in a mould to ambient temperature. The cooling time could be minutes for smaller castings and several weeks for larger castings. Typically, the castings could be 1 or 2 kilograms and up to approximately 20 tonnes in mass.

The term "as-cast form of the casting" does not extend to castings that have been subjected to after-casting heat treatments, for example that result in precipitation of secondary chromium carbides from solution in the matrix and therefore changes the concentration of elements in solution in the matrix.

The ferrous matrix of the as-cast casting may be any suitable matrix.

By way of example, the ferrous matrix may be substantially austenite.

The ferrous matrix of the end-use casting, i.e. after heat treatment of the as-cast form of the casting, may be any suitable matrix. By way of example, the ferrous matrix may be substantially martensite.

The casting may be at least 100 kg.

The casting may be at least 200 kg.

The casting may be at least 400 kg.

The casting may be at least 1 tonne.

The casting may be at least 2 tonnes.

The casting may be at least 3 tonnes.

The fracture toughness of the casting may be selected as required having regard to the end-use application of the casting.

The corrosion resistance of the casting may be selected as required having regard to the applications for the end-use form of the casting. Corrosion resistance is not a material property and, as is the case with wear resistance, depends on a number of operating factors.

The wear resistance of the casting may be selected as required having regard to the end-use application of the casting. Wear resistance is not a material property. Wear resistance is a system property and depends on a number of operating factors, e.g. in the case of pumps conveying slurries, the hardness of slurry particles, the size and angularity of slurry particles, slurry velocity, and slurry pH, etc.

The invention also comprises equipment used in the mining and mineral processing industries, such as pump components, that includes the above-described end-use form of the casting where the equipment is exposed to any one or more than one of severe abrasion, erosion and corrosion wear.

As noted above, equipment of particular interest to the applicant is "wet-end" components in mill circuit slurry pumps.

The equipment may also include, for example, pipelines, mill liners, crushers, transfer chutes and ground-engaging tools.

The invention also provides a method of producing the above-described as-cast form of the casting that includes the steps of:

(a) forming a melt of a high chromium white cast iron, such as the above-described high chromium white cast irons;

(b) pouring the melt into a mould and forming a casting of the high chromium white cast iron having a microstructure that includes a ferrous matrix that

contains chromium in solution, eutectic chromium carbides dispersed in the matrix, and primary chromium carbides dispersed in the matrix, and optionally secondary carbides dispersed in the matrix.

The invention also provides a method of producing the above-described end-use form of the casting that includes a heat treatment step of heating the as-cast form of the casting and transforming at least part of the as-cast chromium carbides to a mixture of chromium carbides.

The transformation product may be at least 5%, typically at least 10%, typically less than 60% of the as-cast chromium carbides.

The heat treatment step may include heating the as-cast form of the casting to 800-1000°C, typically 850-950°C and holding the casting at temperature for up to 1 day and air cooling the casting to ambient temperature.

The treatment step may further include tempering the heat-treated casting at 200-400°C, typically 250-350°C, for up to 12 hours to further improve toughness and/or stress relief.

Where the as-cast form of the casting includes M_7C_3 and $M_{23}C_6$, the heat treatment step may be selected to transform at least part of the M_7C_3 and forming $M_{23}C_6$ as a transformation product.

The chromium carbides in the heat-treated end-use form of the casting may include particles that have a hard core of M_7C_3 surrounded by a softer shell of $M_{23}C_6$ which acts as a transition zone between the softer metal matrix and the extremely hard M_7C_3 carbide core.

Where the as-cast form of the casting includes M_7C_3 and M_3C , the heat treatment step may be selected

to transform at least part of the M_7C_3 and forming M_3C as a transformation product.

The chromium carbides in the heat-treated end-use form of the casting may include particles that
5 have a hard core of M_7C_3 surrounded by a softer shell of M_3C which acts as a transition zone between the softer metal matrix and the extremely hard M_7C_3 carbide core.

10 Brief Description of the Drawings

Embodiments of the invention are now described, by way of example only, with reference to the following Figures, of which:

15 Figure 1 is a Cr/C diagram that shows two embodiments of ranges (i.e. regions) of Cr and C concentrations in high chromium white cast irons in accordance with the invention;

Figure 2A is a representative SEM image of a
20 sample end-use casting, i.e. as-cast and heat-treated casting, in accordance with an embodiment of the invention;

Figure 2B is a pie chart of the constituents of the microstructure of the end-use casting shown in
25 Figure 2A;

Figure 3 is a graph of relative corrosion resistance versus C concentration of compositions of samples of end-use castings, i.e. as-cast and heat-treated casting, in accordance with an embodiment of
30 the invention and samples of embodiments of end-use castings of known HCWCIs exposed to solutions having different pHs;

Figures 4A, 4B, and 4C are graphs of relative mass loss versus C concentration of compositions of
35 samples of embodiments of end-use castings, i.e. as-cast and heat-treated casting, in accordance with the

invention and samples of embodiments of end-use castings of known HCWCIs exposed to solutions having different pHs;

Figure 5 is graph of relative erosion resistance and relative impact resistance of a sample embodiment of an end-use casting, i.e. as-cast and heat-treated casting, in accordance with the invention and end-use castings of Cr27 and Cr35 HCWCIs; and

Figure 6 is a representative SEM image of a sample end-use casting, i.e. as-cast and heat-treated casting, in accordance with an embodiment of the invention.

Detailed Description of Embodiments

As noted above, the applicant has identified a combination of composition and microstructure of castings of high chromium white irons that exhibit corrosion resistance and toughness that are very useful in a number of end-use applications of the castings.

The combination identified by the applicant is high chromium white irons that have compositions that are characterised by (a) ranges of Cr and C concentrations and (b) Cr:C ratios within these ranges that can be cast and then heat-treated so that at least part of the chromium carbides in as-cast forms of the castings transform to another chromium carbide, whereby the end-use forms of the castings have mixtures of chromium carbides with at least one of the chromium carbides including a transformation product of an as-cast chromium carbide.

The amount of the transformation product may be selected based on a range of factors, including the requirements for the end-use form of the casting and the composition of the casting.

The microstructures of the end-use forms of the castings are quite different to the microstructures of other end-use forms of castings of HCWCIs such as Cr27 and Cr35.

5 It is evident from the above that (a) selected Cr and C concentrations, (b) selected Cr:C ratios and (c) heat-treated microstructures of end-use castings of these Cr and C concentrations and Cr:C ratios are important to produce end-use castings of the
10 invention.

Figure 1 is a Cr/C diagram that shows two embodiments of Cr and C concentration ranges in high chromium white cast irons in accordance with the invention. The two embodiments are identified as
15 Regions I and II in the Figure.

Figure 1 also shows the Cr and C concentration regions of the known Cr27 and Cr35 high chromium white cast irons. The Cr27 regions are described as ASTM A532 IIIA and IIA, IIB and IID in the Figure.

20 With reference to Figure 1, the composition ranges of Region I are:

- Cr: 30-40 wt.%
- C: 1.5-3 wt.%

As a result of direct experimental work and
25 casting and metallurgy experience of the applicant and computer modelling work carried out by the applicant, the applicant has also identified that the Cr/C ratios (wt.%) in Region I should be in a range of 9:1 - 15:1, typically, 10:1 - 15:1. The applicant
30 has also identified in this work that it is preferable that the total carbides in an end-use form of the casting be 30-60 vol.%, and the composition have up to 3 wt.% each of any one or more than one of Mn, Si, Ni, Mo, and Cu, with incidental impurities,
35 and the balance Fe.

With further reference to Figure 1, the composition ranges of Region II are:

- Cr: 10-23 wt.%
- C: 3.3-5.5 wt.%

5 As a result of direct experimental work and casting and metallurgy experience of the applicant and computer modelling work carried out by the applicant, the applicant has also identified that the Cr/C ratios (wt.%) in Region II should be in a range
10 of 2:1 - 4:1. The applicant has also identified in this work that it is preferable that the total carbides in an end-use form of the casting 30-70 vol.%, and the composition have up to 3 wt.% each of any one or more than one of Mn, Si, Ni, Mo, and Cu,
15 incidental impurities, and balance Fe.

Figure 2A is a representative SEM image of a sample end-use casting, i.e. an as-cast and heat-treated casting, in Region I of Figure 1.

Figure 2B is a pie chart of the constituents of the microstructure of the casting shown in Figure 2A.
20

The sample comprised 35 wt.% Cr.

With reference to Figure 2A, the microstructure of the end-use casting comprises a ferrous matrix (shown by way of example as points 3 and 6 in Figure
25 2A) and chromium carbides dispersed in the matrix. The chromium carbides comprise M_7C_3 carbides (see points 1 and 4 in Figure 2A) and $M_{23}C_6$ carbides (see points 2 and 5 in Figure 2A), where "M" comprises Cr, Fe, and Mn. At least a part of the $M_{23}C_6$ carbides form
30 as a transformation product of M_7C_3 carbides in the as-cast form of the casting. At least some of the chromium carbides have a hard core of M_7C_3 that is surrounded by a softer shell of $M_{23}C_6$. This feature is discussed further below in relation to Figure 6.

35 Figure 2B shows that the matrix in the end-use casting in Figure 2A is 56 vol.% and the chromium

carbides in the end-use casting in Figure 2A are 44 vol.% of the total volume of the end-use casting, with the matrix comprising 14 wt.% Cr and 0.25 wt.% C, and the chromium carbides comprising 16 vol.% M_7C_3 carbides and 28 vol.% $M_{23}C_6$ carbides of the total volume of the casting.

The as-cast form of the casting comprised an austenite matrix with M_7C_3 carbides dispersed in the matrix. Heat treatment of the as-cast form of the casting to produce the sample shown in Figure 2A transformed the austenite matrix to martensite and transformed part of the M_7C_3 carbides to $M_{23}C_6$ carbides.

It can readily be appreciated that the relative proportions of the matrix and the chromium carbides in the casting, the Cr and C concentrations in the matrix, and the relative proportions of the M_7C_3 carbides and the $M_{23}C_6$ carbides in the chromium carbides may be varied as required having regard to the requirements of end-use applications of the castings. In this regard, as noted above, the important variables include the Cr and C concentrations within Region I, the selection of the Cr:C ratios within Region I to be within the range of 9:1 - 15:1, and the heat treatment conditions to achieve a required transformation of as-cast M_7C_3 carbides to $M_{23}C_6$ carbides.

Figure 6 is a representative SEM image of another sample end-use casting, i.e. as-cast and heat-treated casting, in Region I of Figure 1.

The purpose of Figure 6 is to provide more detail on the chromium carbides that have a hard core of M_7C_3 that is surrounded by a softer shell of $M_{23}C_6$ that is described above in relation to Figure 2A. With reference to Figure 6, a representative chromium carbide particle generally identified by the numeral

11 comprises a core 13 of M_7C_3 and an outer shell 15 of $M_{23}C_6$ in a matrix 17. The $M_{23}C_6$ in the particle forms as a transformation product of as-cast M_7C_3 . The $M_{23}C_6$ acts as a transition zone between the much
5 softer metal matrix 17 and the extremely hard M_7C_3 carbide core 15, allowing dissipation of impact energy leading to a reduced propensity for the primary carbides to crack during large particle impingement and impact.

10 Figure 3 is a graph of relative corrosion resistance versus C concentration of compositions of samples of end-use castings, i.e. as-cast and heat-treated castings, in accordance with the invention and samples of end-use castings of known HCWCIs
15 exposed to solutions having different pHs.

Figure 3 shows relative corrosion resistance results for (a) samples of end-use castings having a nominal C concentration of 3 wt.% in Region I of Figure 1 in accordance with the invention and (b)
20 samples of end-use castings of known HCWCIs have respective nominal C concentrations of 1 wt.%, 2 wt.%, 4 wt.%, 5 wt.% and 6 wt.%. The samples were exposed to solutions of pH3, pH5, and pH7.

It is clear from Figure 3 that, in relative
25 terms, the corrosion resistance of the sample in accordance with the invention performed considerably better than the samples of known HCWCIs.

Figures 4A, 4B, and 4C are graphs of relative mass loss versus C concentration of compositions of
30 samples of end-use castings, i.e. as-cast and heat-treated casting, in accordance with the invention and samples of end-use castings of known HCWCIs exposed to solutions having different pHs.

The experimental work reported in Figures 4A,
35 4B, and 4C was carried out in accordance with ASTM

1095. The experimental work assessed slurry pot erosion at impingement angles of 45° and 90°.

Figures 4A, 4B, and 4C show the results for (a) samples of end-use castings having a nominal C concentration of 3 wt.% in Region I of Figure 1 in accordance with the invention and (b) samples of end-use castings of known HCWCIs have respective nominal C concentrations of 1 wt.%, 2 wt.%, 4 wt.%, 5 wt.% and 6 wt.%. The samples were exposed to solutions of pH3, pH5, and pH7.

It is clear from Figures 4A, 4B, and 4C that, the erosion resistance of the sample in accordance with the invention performed considerably better than the samples of known HCWCIs.

Figure 5 is graph of relative erosion resistance and relative impact resistance of a sample end-use casting, i.e. as-cast and heat-treated casting, in accordance with the invention and end-use castings of Cr27 and Cr35 HCWCIs.

The relative erosion resistance tests were carried out in accordance with a standard Coriolis Scouring Erosion Testing procedure of the National Research Council of Canada. The relative impact resistance tests were carried out in accordance with a procedure and on a test rig developed by the applicant. In accordance with the procedure, impact particles were allowed to free-fall and hit a sample casting at a velocity of 9m/s.

Figure 5 shows that the erosion resistance of the sample end-use casting in accordance with the invention was better than that of the Cr27 sample.

Figure 5 also shows that the impact resistance of the sample end-use casting in accordance with the invention was better than that of the Cr35 sample.

The applicant has found in a series of field trials that the combination of corrosion resistance,

erosion resistance, and impact resistance, i.e. toughness, of the end-use casting in accordance with the invention is well-suited to a range of applications.

5 One field trial was carried out to evaluate the performance of castings of 150MCU impellers of pumps on SAG duty at a gold mining operation. The current 150MCU impellers are made from Cr35 HCWCI and these were found to shatter at about 2500 hours in service.
10 The impellers all wore thin and shattered. In a field trial with an impeller comprising an end-use casting in accordance with the invention, the impeller remained intact for 3000 hours and was changed on the basis of a scheduled maintenance at
15 this service life.

Many modifications may be made to the embodiments of the invention described in relation to the Figures without departing from the spirit and scope of the invention.

20 In the claims which follow and in the preceding description of the invention, except where the context requires otherwise due to express language or necessary implication, the word "comprise" or variations such as "comprises" or "comprising" is
25 used in an inclusive sense, i.e. to specify the presence of the stated features but not to preclude the presence or addition of further features in various embodiments of the invention.

CLAIMS

1. A casting of a high chromium white iron that, in an end-use form of the casting after heat treatment,
5 includes a ferrous matrix and at least two different chromium carbides dispersed in the matrix, with at least one of the chromium carbides including a transformation product of an as-cast chromium carbide.
- 10 2. The end-use casting defined in claim 1 wherein the chromium carbides dispersed in the matrix are M_7C_3 and $M_{23}C_6$, where "M" comprises Cr, Fe, and Mn.
3. The end-use casting defined in claim 2 wherein the $M_{23}C_6$ is a transformation product of M_7C_3 with the
15 $M_{23}C_6$ forming during heat treatment of the as-cast form of the casting.
4. The end-use casting defined in claim 2 or claim 3 wherein the composition of the casting comprises the following composition:
20
 - Cr: 30-40 wt.%
 - C: 1.5-3 wt.%
 - Cr/C ratios (wt.%): 9:1 - 15:1
 - Up to 3 wt.% each of any one or more than one of Mn, Si, Ni, Mo, and Cu,
 - 25 • Incidental impurities
 - Balance: Fe
5. The end-use casting defined in any one of claims 2 to 4 wherein the chromium carbides dispersed in the matrix are 30-60 vol.% of the casting.
- 30 6. The end-use casting defined in claim 5 wherein the M_7C_3 chromium carbides are 40-50 vol.% of the casting.
7. The end-use casting defined in claim 6 wherein the M_7C_3 chromium carbides are 10-20 vol.% of the
35 casting.

8. The end-use casting defined in claim 7 wherein the M_7C_3 chromium carbides are 15-20 vol.% of the casting.
9. The end-use casting defined in any one of claims 5 to 8 wherein the $M_{23}C_6$ chromium carbides are 20-35 vol.% of the casting.
10. The end-use casting defined in claim 9 wherein the $M_{23}C_6$ chromium carbides are 25-30 vol.% of the casting.
11. The end-use casting defined in any one of claims 2 to 10 wherein the matrix is 40-70 vol.% of the casting.
12. The end-use casting defined in claim 1 wherein the chromium carbides dispersed in the matrix are M_7C_3 and M_3C , where "M" comprises Cr, Fe, and Mn.
13. The end-use casting defined in claim 12 wherein the M_3C is a transformation product of M_7C_3 with the M_3C forming during heat treatment of the as-cast form of the casting.
14. The end-use casting defined in claim 12 or claim 13 wherein the composition of the casting comprises the following composition:
- Cr: 10-23 wt.%
 - C: 3.3-5.5 wt.%
 - Cr/C ratios (wt.%): 2:1 - 4:1
 - Up to 3 wt.% each of any one or more than one of Mn, Si, Ni, Mo, and Cu,
 - Incidental impurities
 - Balance: Fe
15. The end-use casting defined in any one of claims 12 to 14 wherein the chromium carbides dispersed in the matrix are 30-70 vol.% of the casting.
16. The end-use casting defined in any one of claims 12 to 15 wherein the matrix is 30-70 vol.% of the casting.

17. A casting of a high chromium white cast iron that, in an as-cast form of the casting, includes a ferrous matrix with chromium in solution in the matrix and chromium carbides dispersed in the matrix,
5 with the casting characterised by:
- Cr: 30-40 wt.%
 - C: 1.5-3 wt.%
 - Cr/C ratios (wt.%): 9:1 - 15:1
 - Total carbides in the casting: 30-60 vol.%
 - 10 • Up to 3wt% each of any one or more than one of Mn, Si, Ni, Mo, and Cu,
 - Incidental impurities
 - Balance: Fe
18. A casting of a high chromium white cast iron
15 that, in an as-cast form of the casting, includes a ferrous matrix with chromium in solution in the matrix and chromium carbides dispersed in the matrix, with the casting characterised by:
- Cr: 10-23 wt.%
 - 20 • C: 3.3-5.5 wt.%
 - Cr/C ratios (wt.%): 2:1 - 4:1
 - Total carbides in the casting: 30-70 vol.%
 - Up to 3wt% each of any one or more than one of Mn, Si, Ni, Mo, and Cu,
 - 25 • Incidental impurities
 - Balance: Fe
19. The as-cast form of the casting defined in claim 17 or claim 18 includes a ferrous matrix with chromium in solution in the matrix, eutectic chromium
30 carbides dispersed in the matrix, primary chromium carbides dispersed in the matrix, and optionally secondary carbides dispersed in the matrix.
20. The as-cast form of the casting defined in claim 19 wherein the eutectic carbides, the primary
35 carbides, and the secondary carbides in the as-cast

casting are M_7C_3 carbides where "M" comprises Cr, Fe, and Mn.

21. Equipment used in the mining and mineral processing industries, such as pump components, that
5 includes the end-use form of the casting defined in any one of claims 1 to 16.

22. A method of producing the as-cast form of the casting defined in any one of claims 17 to 20 includes the steps of:

10 (a) forming a melt of a high chromium white cast iron;

(b) pouring the melt into a mould and forming a casting of the high chromium white cast iron having a microstructure that includes a ferrous matrix that
15 contains chromium in solution, eutectic chromium carbides dispersed in the matrix, and primary chromium carbides dispersed in the matrix, and optionally secondary carbides dispersed in the matrix.

20 23. A method of producing the end-use form of the casting defined in any one of claims 1 to 16 includes a heat treatment step of heating the as-cast form of the casting defined in any one of claims 17 to 20 and transforming at least part of the as-cast chromium
25 carbides to a mixture of chromium carbides.

24. The method defined in claim 23 wherein the heat treatment step includes heating the as-cast form of the casting to 800-1000°C and holding the casting at temperature for up to 1 day and air cooling the
30 casting to ambient temperature.

25. The method defined in claim 24 wherein the heat treatment step further includes tempering the heat-treated casting at 200-400°C for up to 12 hours to further improve toughness and/or stress relief.

35 26. The method defined in any one of claims 23 to 25 wherein, when the as-cast form of the casting

includes M_7C_3 and $M_{23}C_6$, the method includes transforming at least part of the M_7C_3 and forming $M_{23}C_6$ as a transformation product.

27. The method defined in any one of claims 23 to 25
- 5 wherein, when the as-cast form of the casting includes M_7C_3 and M_3C , the method includes transforming at least part of the M_7C_3 and forming M_3C as a transformation product.

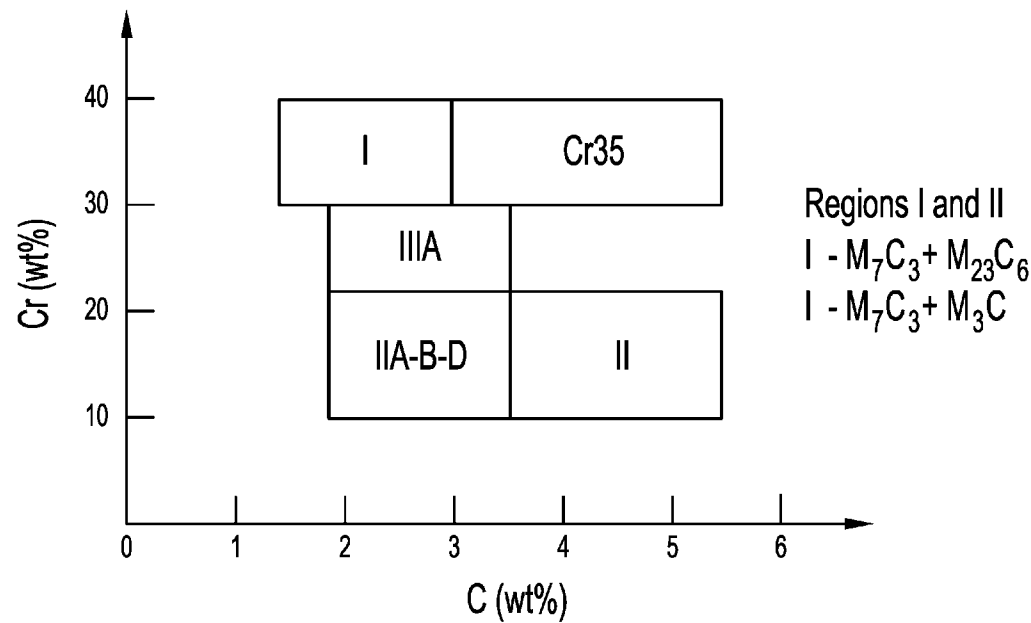


Figure 1

Corrosion Resistance - pH (Fe-35Cr-xC) - as cast and heat treated samples

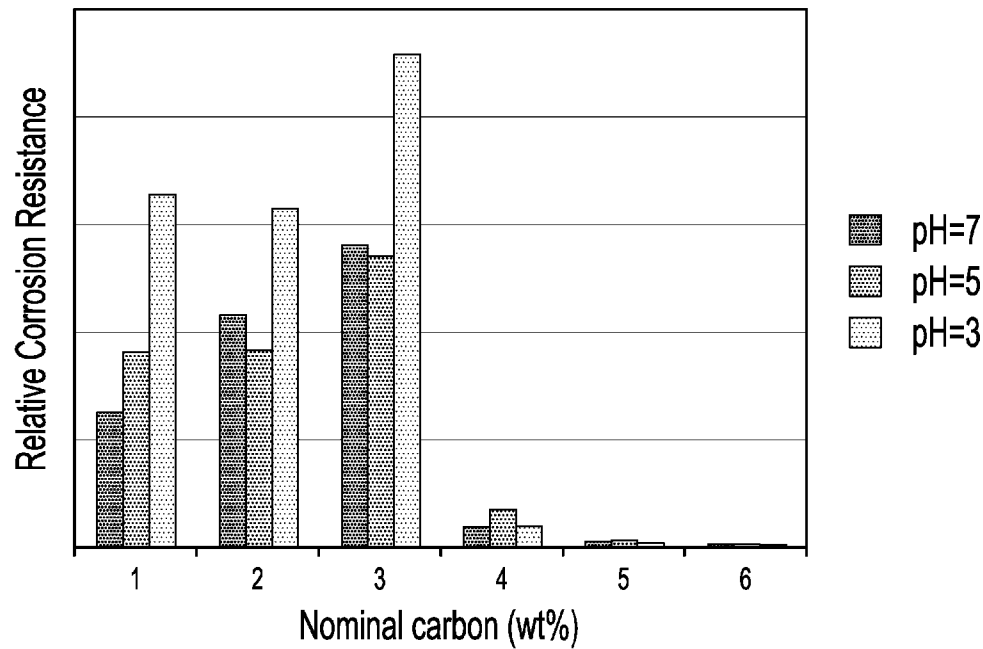
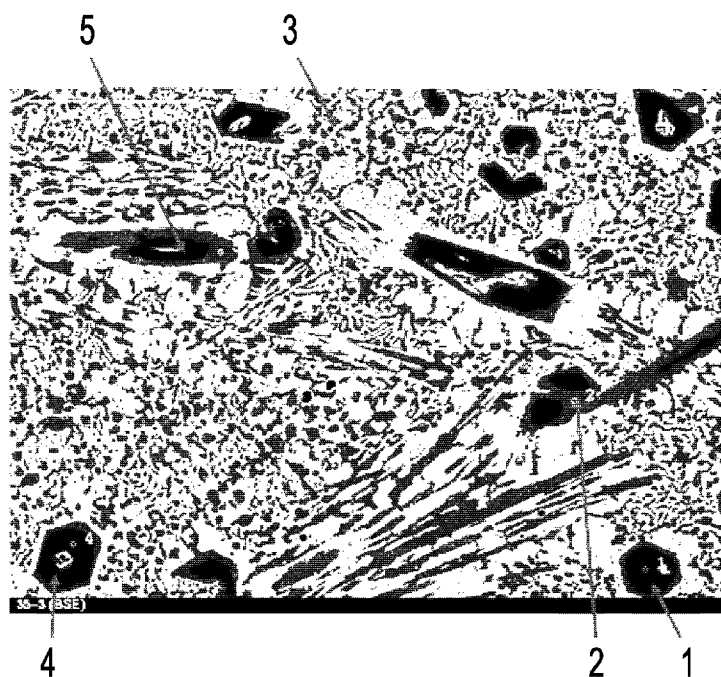


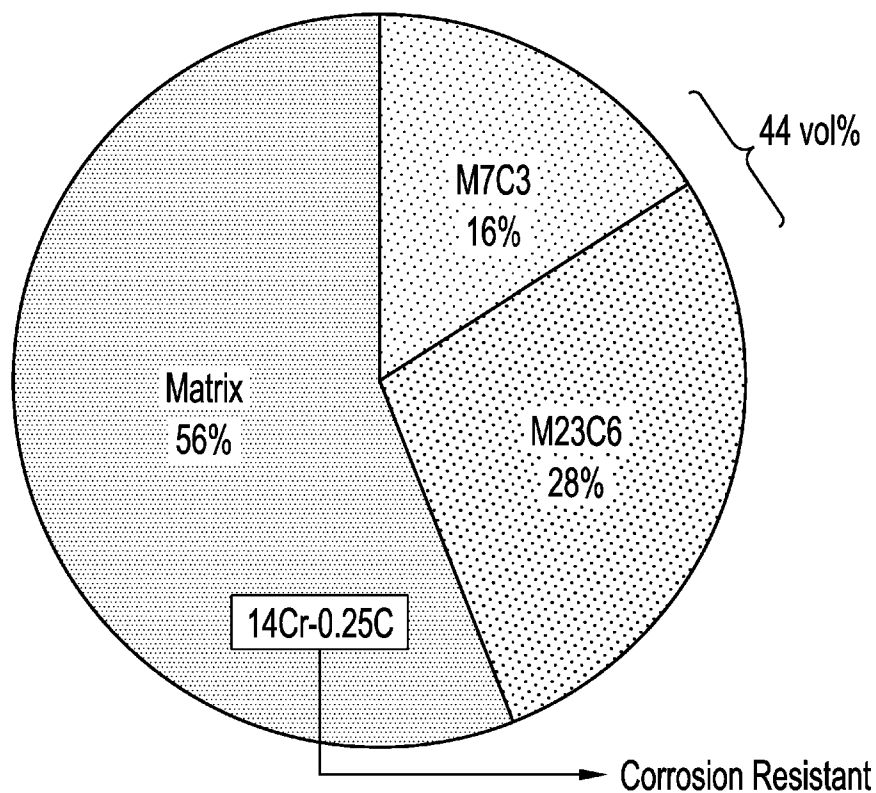
Figure 3

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One Example in Region I - as cast and then heat treated sample

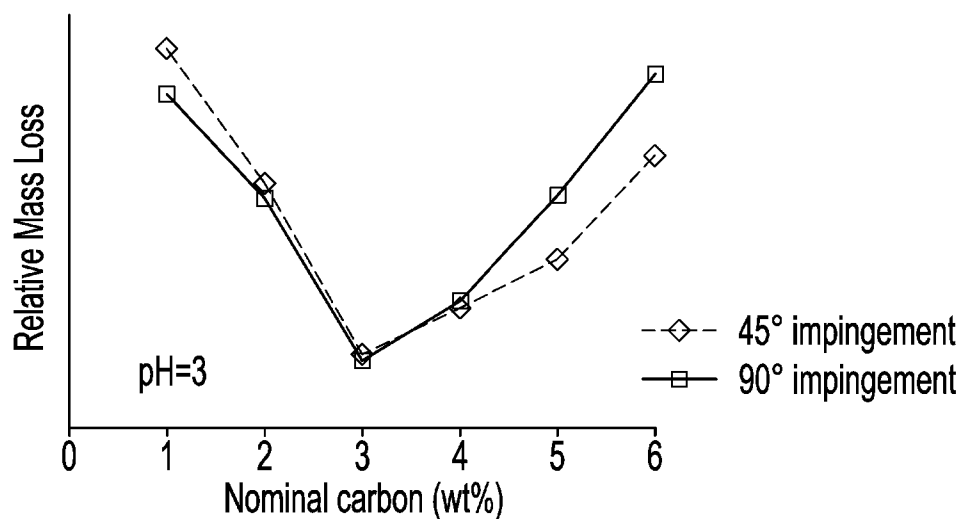
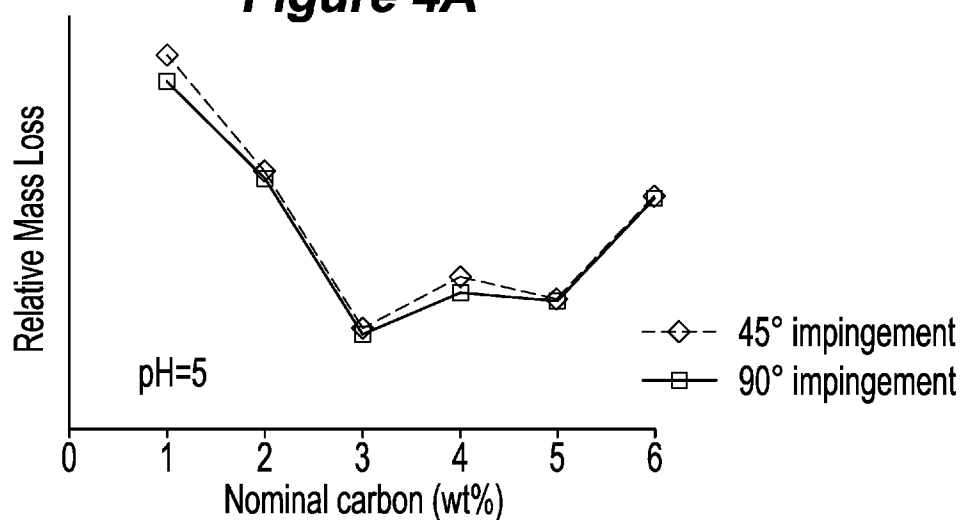
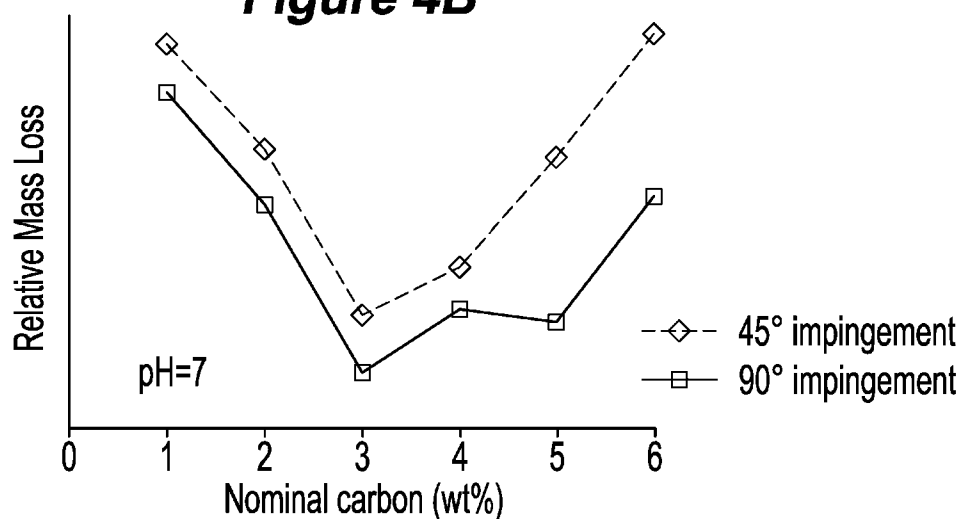


Points 1 & 4 - M_7C_3
Points 2 & 5 - $M_{23}C_6$
Points 3 & 6 Ferrous matrix

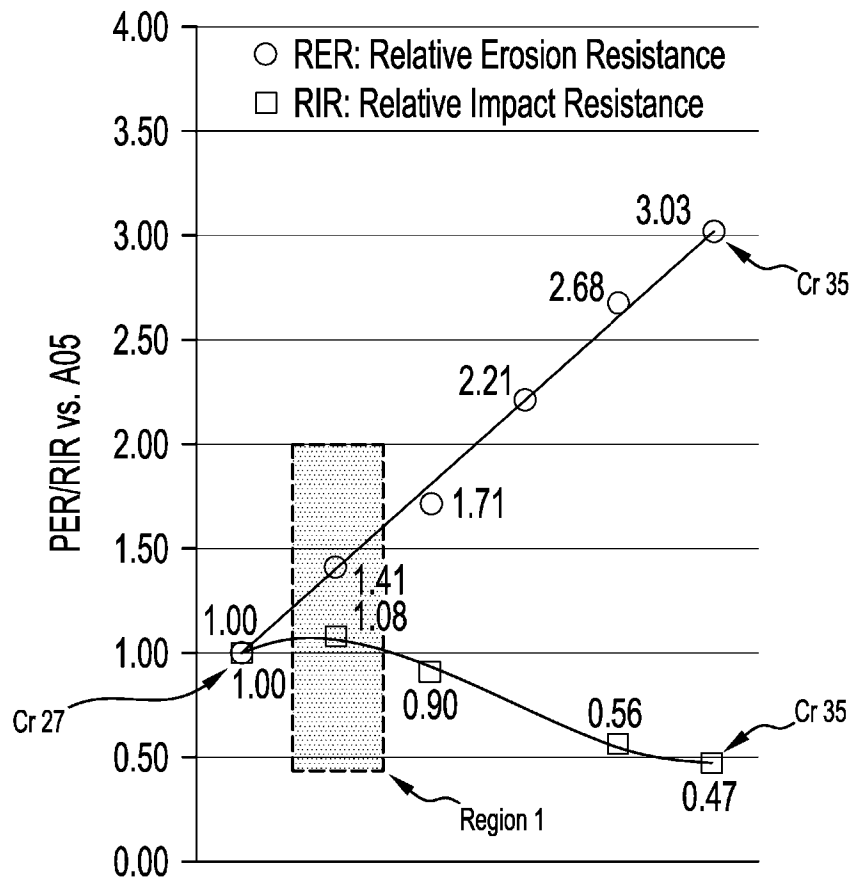
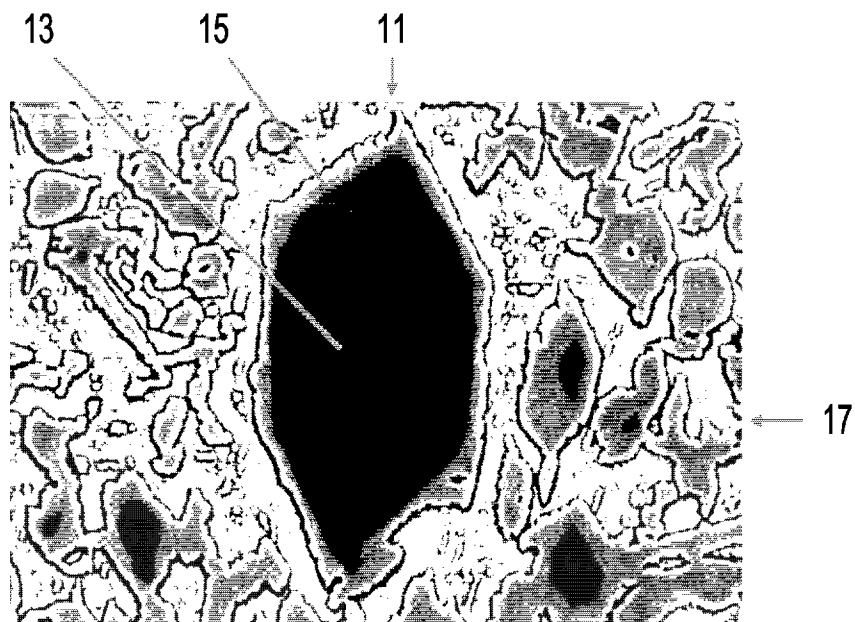
Figure 2A**Figure 2B**

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Slurry Pot Erosion pH (Fe-35Cr-xC) - as cast and heat treated samples

**Figure 4A****Figure 4B****Figure 4C**

Coriolis Erosion Resistance and Impact Resistance, compared to Cr35 and Cr27

**Figure 5****Figure 6**

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2018/051297

A. CLASSIFICATION OF SUBJECT MATTER

C21D 5/04 (2006.01) C22C 33/08 (2006.01) C22C 37/06 (2006.01) C22C 29/02 (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)

PATENW, ALLOYS, Google Scholar, Google Patents, Espacenet, STN (REGISTRY and CAPLUS): CPC (C21D211/004, C22C37/06/low, C22C38/18/low, C21D6/002/low, C21D6/004/low, C22C33/006, C22C33/08/low, C22C2204/00, C21D5/04/low) and Keywords (weir minerals, weir warman, warman international, carbide, white iron, ferrochrome, dolman, transform, M7C3, M23C6, M3C and like terms) and composition ranges (Cr: 10-23 or 30-40; C: 3.3-5.5 or 1.5-3)

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	



Further documents are listed in the continuation of Box C



See patent family annex

* "A"	Special categories of cited documents: 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 6 February 2019		Date of mailing of the international search report 06 February 2019	
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustalia.gov.au		Authorised officer Deborah McDonnell AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. +61262850724	

INTERNATIONAL SEARCH REPORT		International application No.
C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		PCT/AU2018/051297
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PEARCE, J.T.H. et al., "Duplex nature of eutectic carbides in heat treated 30% chromium cast iron", Journal of Materials Science Letters, 1986, Vol. 5, pages 1063-1064 pages 1063-1064	1-11, 17, 19-20, 22-26
X	KARANTZALIS, E. et al., "Microstructure and properties of high chromium cast irons: Effect of heat treatments and alloying additions", International Journal of Cast Metals Research, 2009, Vol. 22, No. 6, pages 448-456 Tables 1-2; figure 1; discussion under "As cast alloy" and "Heat Treatment B (HTB)"	1-2, 11, 21
X Y	WANG, J. et al., "Influence of secondary carbides precipitation and transformation on hardening behaviour of a 15 Cr - 1 Mo - 1.5 V white iron", Materials Characterization, 2005, vol. 55, pages 234-240 abstract; "Introduction" "Experimental procedure"	1-3, 12 14-16
X Y	EP 0371760 B1 (NIPPON PISTON RING CO LTD et al.) 06 June 1990 abstract; page 3, lines 9-29 and 33-40 abstract; page 3, lines 9-29 and 33-40	18 14-16
X Y	JP H01-162745 A (KANTO TOKUSHU SEIKO KK) 27 June 1989 abstract; figure 4 abstract; figure 4	18 14-16
A	WO 2004/104253 A1 (WEIR WARMAN LIMITED [AU]) 21 April 2004	
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Form PCT/ISA/210 (fifth sheet) (January 2015)		

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:
the subject matter listed in Rule 39 on which, under Article 17(2)(a)(i), an international search is not required to be carried out, including
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:

See Supplemental Box for Details

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.

Supplemental Box**Continuation of: Box III**

The application does not comply with the requirements of unity of invention because it does not relate to one invention or to a group of inventions so linked as to form a single general inventive concept.

While all the claims are directed to a casting of a high chromium white iron, there are different inventions based on the following features:

- Claims 1 (in part), 2-11, 17, 19-25 (in part) and 26 are characterised by an as-cast and an end-use casting of a Cr35-adjacent alloy, wherein the as-cast form comprises M7C3 carbides and the end-use form comprises M7C3 and M23C6 carbides, wherein the M23C6 carbide is a transformation product of M7C3 formed during heat treatment of the as-cast alloy.
- Claims 1 (in part), 12-16, 18, 19-25 (in part) and 27 are characterised by an as-cast and end-use casting of a Cr27-adjacent alloy, wherein the as-cast form comprises M7C3 carbides and the end-use form comprises M7C3 and MC3 carbides, wherein the MC3 carbide is a transformation product of M7C3, formed during heat treatment of the as-cast alloy.

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 one which makes a contribution over the prior art.

When there is no special technical feature common to all the claimed inventions there is no unity of invention.

In the above groups of claims, the identified features may have the potential to make a contribution over the prior art but are not common to all the claimed inventions and therefore cannot provide the required technical relationship. The only feature common to all of the claimed inventions and which provides a technical relationship among them is *a casting of a high chrome white iron that EITHER, in an as-cast form, comprises chromium in solution in a ferrous matrix and 30-60 vol% total carbides dispersed in the matrix OR that, in an end-use form, comprises at least two different chromium carbides, at least one of which is a transformation product, formed during heat treatment, of an as-cast chromium carbide.*

However, neither of these features make a contribution over the prior art because they are previously disclosed.

D1 (see passages cited in the International Search Report) discloses high chromium white cast irons that, in an end-use form, have two chromium carbides dispersed in the matrix, one of which is a transformation product, formed during heat treatment, of an as-cast chromium carbide.

D6 and D7 each disclose high chromium white cast irons that, in an as-cast form, have chromium in solution in a ferrous matrix and 15-60 vol% chromium carbides dispersed in the matrix (see abstract of each citation).

Therefore in the light of at least these documents neither of these common features can be a special technical feature. Therefore there is no special technical feature common to all the claimed inventions and the requirements for unity of invention are consequently not satisfied *a posteriori*.

INTERNATIONAL SEARCH REPORT		International application No.	
Information on patent family members		PCT/AU2018/051297	
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.			
Patent Document/s Cited in Search Report		Patent Family Member/s	
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		AU 2013203224 B2	05 Feb 2015
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		CN 102822368 A	12 Dec 2012
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.			
Form PCT/ISA/210 (Family Annex)(January 2015)			

INTERNATIONAL SEARCH REPORT Information on patent family members		International application No. PCT/AU2018/051297	
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.			
Patent Document/s Cited in Search Report		Patent Family Member/s	
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INTERNATIONAL SEARCH REPORT		International application No.	
Information on patent family members		PCT/AU2018/051297	
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.			
Patent Document/s Cited in Search Report		Patent Family Member/s	
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End of Annex			
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001. Form PCT/ISA/210 (Family Annex)(January 2015)			