STEEL ALLOYS AND ROLLING MILL ROLLS PRODUCED THEREFROM

A cast ferrous alloy which contains in addition to iron and inevitable impurities the following components wherein all percentages relate to the percentage content by weight: carbon 1.05 to 3.8 %, chromium 2.0 to less than 8.0 %, molybdenum 1.0 to 6.0 %, tungsten 1.05 to 8.0 %, niobium 1.0 to 10.0 %, and vanadium 1.0 to 10.0 % and which may further contain one or more of the following optional elements in the following percentage amounts by weight: manganese up to 1.5 %, silicon up to 1.5 %, cobalt up to 5.0 %, nickel up to 5.0 %, titanium up to 3.0 %, nitrogen up to 3.0 %, and cerium and/or other rare earth element(s) up to 0.2 % in total. Such alloys can be cast into rolling mill rolls with attractive mechanical properties and wherein unwanted carbide precipitation can be avoided.
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STEEL ALLOYS AND ROLLING MILL ROLLS PRODUCED THEREFROM

This invention is concerned with ferrous alloys, rolling mill rolls made therefrom, methods of making the alloys and the rolls and the use of the rolls in rolling mills.

High speed steel materials which are highly alloyed ferrous alloys are generally not usable or used in the cast state for traditional tooling applications as the mechanical properties of such cast materials are generally accepted as being undesirable. These materials are beginning to find use for rolling mill rolls, but it is generally accepted that rolls so made are more sensitive to fracture than traditional roll materials. This is an undesirable situation which this invention seeks to overcome.

In the literature, the paper 'cast tool steels,' the British Foundryman, July 1985, 289-296 discloses cast steel tools wherein the cast microstructure is refined and modified by using elements which are strongly carbide-forming, in particular titanium, vanadium and niobium, in making cast tool steels which are of the high speed steel type. The paper is directed at improving the mechanical properties of cast tool steels and therefore make them more useful as cast tool steels but there remain problems with such materials.

The type of metal alloys disclosed in the 'cast tool steels' paper have not found widespread acceptance in the conventional tooling applications for which they were intended. The principal problem is apparently insufficient toughness in the intended tools, despite improvements in toughness and other properties over unmodified cast material.

European patent application EP-0-430-241-A1 describes high speed steel (HSS) rolling mill rolls hardened by additional vanadium with the intention to avoid separation of primary crystals in the molten steel.

European patent application EP-0-347-512-A1 discloses bimetallic rolls containing vanadium, titanium or
niobium between 0.2-4% only to cause hardening by fine precipitation during heat-treatment. Further the alloy so described does not contain tungsten.

European patent application EP-0-346-293 discloses ferrous alloy rolling mill rolls of bi-metallic construction wherein the working surface has only globular carbides; the alloy including vanadium and optionally titanium and/or niobium to impart wear resistance.

Having examined the requirements for the outer working layer of rolling mill rolls we have now found that a sufficient degree of toughness, not currently attainable with cast high speed steels, can be achieved with modified materials of the high speed steel type. These materials are similar to those alloys disclosed in the 'cast tool steels' paper, but with the additional advantages of further improvements in toughness and other properties tailored for their specific use in rolls. This is achieved by control of the constituents to specifically fulfill the requirements of cast rolls for rolling mill stands and trains, either when statically cast or when centrifugally cast.

In particular we have now surprisingly found that use of niobium is essential as a primary carbide forming element and that whilst titanium and vanadium may be present as other strong carbide formers, they may be present in relatively minor amounts compared to the amount of niobium in the ferrous alloys. Therefore we prefer not to use titanium and/or vanadium as the principal carbide formers since the low density of their carbides can cause them to separate out.

The density of niobium carbide which forms in the molten steel during casting is similar to the density of the molten steel. This is of particular importance in that aspect of this invention which is concerned with methods of making rolling mill rolls by centrifugal casting. Substantial differences in density between the principal carbide former and the molten steel would cause that carbide to separate out from the molten steel. Hence the refining process disclosed in the 'cast tool steels' paper could not
be applicable to centrifugal casting of rolls and could still give separation problems in the static casting of rolls. By adding carefully controlled amounts of niobium with additional carbon to combine with it, we can modify and refine the cast structure of the base material, which is in the nature of a high speed steel.

An additional benefit of using niobium carbide as the principal carbide former is that since niobium carbide is one of the hardest carbides, this also contributes significantly to increasing the wear resistance of the present alloys and rolls made therefrom. Moreover use of niobium enables production of the alloy and rolls wherein most of the carbides are physically precipitated by the casting process and only incidental precipitated by subsequent heat treatments.

According to this invention we provide in a first aspect a cast ferrous alloy which contains in addition to iron and inevitable impurities, the following essential additional components in the given percentages by weight:

C 1.05-3.8%, more preferably 1.3-3.8%
Cr 2 less than 8%, preferably 2 less than 8%, more preferably 4.0-7.8%
Mo 1-8%, preferably 2-7%, more preferably 2.2-5%
W 1.05-8%, preferably 1.2 to 8%, more preferably 2-6%
Nb 1-10%, preferably 2-8%, more preferably 4-8%
V 1-10%, preferably 1.8 to 6%, more preferably 1.8 to 3.8%

and possibly one or more of the following optional components:

Mn 0.2-1.5%, preferably 0.5-1.5%, more preferably more than 1.2%
Si 0.2-1.5%, preferably 0.5-0.9%
Co up to 5%, although it may be absent or no higher than 0.1%.
Ni up to 5%, for example 2 to 4%
Ti up to 3.0%, such as 0.1 to 3.0%, preferably 0.1 to 1.0% especially in centrifugally cast rolls.
N up to 3.0%, and
Ce and/or other rare earth element(s) up to 0.2% in total.

The total of V and Nb is preferably more than 3% by weight. The total of niobium and optional elements present may also be more than 3% by weight. The amount of niobium preferably matches or more preferably exceeds the amount of vanadium.
In a second aspect we provide compound (bi-metallic) rolling mill rolls wherein the outer working surface is constructed from a ferrous alloy as specified in the first aspect.

In a third aspect we provide methods of statically casting a rolling mill roll from a ferrous alloy according to the first aspect. Herein, the lack of flotation and/or sinkage of carbides is advantageous.

In a fourth aspect we provide methods of centrifugally casting a rolling mill roll from a ferrous alloy as specified in the first aspect. Herein there is minimal centrifugal separation of the formed carbides from the molten steel. Centrifugally cast rolls are preferred wherein centrifugal separation of the niobium carbides from the molten steel is avoided.

In a fifth aspect we also provide a rolling mill stand or a rolling mill train which comprises at least one roll as specified in the second aspect.

The principle of the invention and in particular of the third and fourth aspects thereof is to form solid particles in the liquid steel that will nucleate the growth of solid crystals or grains in the steel and thus refine its structure. This may be enhanced by the use of small additions of the following

(i) Titanium (0.01 - 3.0%) combined with nitrogen (0.01 - 3.0%) which react to form Titanium nitride or titanium carbo-nitride particles in the molten steel which may then act as centres to promote the formation of niobium carbide particles.

(ii) Cerium (0.01 - 0.1%) or other Rare Earth metals that react with sulphur, which is present as an impurity in the liquid steel, and form cerium sulphide particles which may act as centres to promote the formation of niobium carbide particles.

(iii) The alloy may advantageously contain up to 5% Cobalt. This improves the hot hardness of the alloy which is beneficial in a hot rolling mill.
Cobalt also improves the heat-treatment characteristics in the manufacture of the roll.

(iv) The alloy may advantageously contain up to 5% Nickel. This stabilises the austenite phase during heat-treatment and may allow the use of a slower cooling rate as required in the manufacture of rolls to achieve optimum properties.

The rolls produced will be composite with an intermediate zone of the same composition as the core, or alternatively a cast steel core may be used. The cores used may have a strength of the order 450 N/mm². The alloy rolls preferably have a fully martensitic structure, and excess carbon and retained austenite may be present.

Advantages over the 'cast tool steels' paper include an optimised composition and the optional use of cobalt and nickel to give the best combination of mechanical properties to make the material suitable for the working layer of rolling mill rolls. This includes achieving optimum hardness through control of carbide content and heat-treatment response.

Our invention seeks to create in the ferrous alloy and hence in the outer working surface of rolls primary crystals based on niobium since these can be controlled to avoid separation. This results in a refined microstructure with improved properties, a more uniform carbide distribution and facilitates the use of much higher carbide contents for increased wear resistance. The manufacturing procedure for producing the cast rolls will be known to those skilled in the art, although the Nb and Ti (if present) should be added as late as possible to the molten steel before casting. The Ti may be added to the furnace or the ladle. The required elemental additions may be by way of ferro-alloys.

The required amount of carbon that combines with the niobium, and Titanium if present, to form the NbC and (Nb,Ti) C carbides may be added at any stage during the melting of the alloy with no special precautions necessary.

The invention is further illustrated by the following, non-limiting examples wherein the core portion is cast in two stages using techniques known in the art, both parts of the
core being of the same composition and bonded through use of an appropriate flux material.

Example 1
A batch of sample alloy materials were cast statically and centrifugally using a ferrous alloy according to the first aspect and of the following composition:

1.2% C, 5% Cr, 5% Mo, 7% W, 3% Nb, 2% V, 4% Co.

Example 2
A batch of sample alloy materials were cast statically and centrifugally using a ferrous alloy according to the first aspect and of the following composition:

2% C, 5% Cr, 5% Mo, 7% W, 7% Nb, 2% V.
Example 3

We have cast an outer layer of a roll using ferrous alloy according to the first aspect, of the following composition:

1.9% C, 5.0% Cr, 3.0% Mo, 3.0% W, 4.0% Nb, 4.0% V.

The roll materials obtained in Examples 1-3 had attractive mechanical properties and wear resistance. In all cases the ferrous alloy was multi-phase with a martensitic matrix. Subsequent heat treatment can be applied for example tempering. It may only be necessary to use one tempering step and the majority of the carbides were found to have formed during the casting procedures and not in the subsequent heat treatments. However some secondary carbides (e.g. vanadium carbides) may form exclusively and intentionally during heat treatments.
Not only may titanium be added to the molten steel to promote the formation of NbC particles but we have found that its use is essential when the said alloys are centrifugally cast. When cast by this method the smallest difference in density between the primary carbide particles and the molten steel can cause separation of the carbide particles to a greater or lesser extent. Without the use of titanium the carbide particles are slightly denser than the molten steel and tend to centrifugally separate towards the outside of the mould. In order to avoid this a tungsten content in excess of 7% would be required to sufficiently increase the density of the molten steel. However, this results in unacceptable quantities of brittle tungsten carbides in the solid alloy which reduces toughness of that alloy.

We have found that by adding carefully controlled amounts of titanium (e.g. 0.01 to 3.0% by weight preferably 0.1 to 1.0% by weight of Ti) to the liquid steel then it is incorporated into the carbide particles to form composite particles of the type (Ti, Nb) C whose density is strongly controlled by the titanium content. Since titanium carbide is less dense than niobium carbide, the composite particles become less dense as their titanium content increases and hence their density may be tailored to that of the liquid steel. Further increases in the titanium content facilitate reductions in the tungsten content of the liquid steel which is advantageous in increasing the toughness of the alloy.

**Example 4**

A roll was centrifugally cast with an outer layer of the following composition:

2.2% C, 5.0% Cr, 5.0% Mo, 6% W, 5.5% Nb, 4% V, 0.3% Ti.

The carbide separation when compared to an alloy without the titanium addition was reversed and largely eliminated.

In all cases the alloy formed can be regarded as multi-phase, containing several carbides which are not precipitated by heat treatment together with vanadium and secondary carbides which are precipitated by heat treatment. As far as heat treatments after formation of the alloy are concerned, the present process for producing rolls may only require one
tempering step.

Heat-Treatments

Heat-treatments preferably comprises a high temperature hardening treatment at 1000-1100°C followed by at least one tempering step at 450-580°C. However, depending upon the as-cast hardness of the roll the heat-treatment may comprise only at least one tempering step.

The major advantage in using niobium as the principal carbide former in centrifugally cast rolls according to the invention is the minimal centrifugal separation of the niobium carbide from the molten steel.

This invention seeks to form primary carbides in the molten steel when centrifugally cast in contrast to inventions by others that seek to avoid primary carbide formation.

The major advantage of using niobium carbide as the principal carbide former in rolls cast statically according to the invention is the lack of flotation or sinkage of the niobium carbide formed.
1. A cast ferrous alloy which contains in addition to iron and inevitable impurities the following components wherein all percentages relate to the percentage content by weight:

- Carbon 1.05 to 3.8 %,
- Chromium 2.0 to less than 8.0 %,
- Molybdenum 1.0 to 8.0 %,
- Tungsten 1.05 to 8.0 %,
- Niobium 1.0 to 10.0 %, and
- Vanadium 1.0 to 10.0 %

and which may further contain one or more of the following optional elements in the following percentage amounts by weight:

- Manganese up to 1.5 %
- Silicon up to 1.5 %
- Cobalt up to 5.0 %
- Nickel up to 5.0 %
- Titanium up to 3.0 %
- Nitrogen up to 3.0 %, and
- Cerium and/or other rare earth element(s) up to 0.2% in total.

2. A cast alloy as claimed in claim 1 wherein the total amount of niobium matches or exceeds the total amount of vanadium.

3. A cast alloy as claimed in claim 1 or 2 wherein the total amount of vanadium and niobium is in excess of 3.0% by weight.

4. A cast alloy as claimed in any preceding claim wherein the total of niobium and all optional elements present is in excess of 3.0 % by weight.

5. A cast alloy as claimed in any preceding claim wherein the amount of carbon is 1.3 to 3.8%.
6. A cast alloy as claimed in any preceding claim wherein the amount of chromium is 2.0 to 7.8% preferably 4.0 to 7.8%.

7. A cast alloy as claimed in any preceding claim wherein the amount of molybdenum is 2.0 to 7.0% preferably 2.2 to 5.0%.

8. A cast alloy as claimed in any preceding claim wherein the amount of tungsten is 1.2 to 8% preferably 2.0 to 6.0%.

9. A cast alloy as claimed in any preceding claim wherein the amount of niobium is 2.0 to 8.0% preferably 4.0 to 8.0%.

10. A cast alloy as claimed in any preceding claim wherein the amount of vanadium is 1.8 to 6.0% preferably 1.8 to 3.8%.

11. A cast alloy as claimed in any preceding claim wherein the amount of manganese is 0.2 to 1.5% preferably 0.5 to 1.5% more preferably more than 1.2% to 1.5%.

12. A cast alloy as claimed in any preceding claim wherein the amount of silicon is 0.2 to 1.5% preferably 0.5 to 0.9%.

13. A cast alloy as claimed in any preceding claim wherein the amount of cobalt is less than 0.1%.

14. A cast alloy as claimed in any preceding claim wherein the amount of nickel is 2.0 to 4.0%.

15. A cast alloy as claimed in any preceding claim wherein the amount of titanium is 0.1 to 3.0% preferably 0.1 to 1.0%.

16. A cast alloy as claimed in any preceding claim wherein the amount of cerium is 0.01 to 0.1%.

17. A rolling mill roll cast from an alloy as claimed in any preceding claim such that at least the outer working surface of the cast roll is of the composition as defined therein.

18. A roll as claimed in claim 17 produced by static casting.
19. A roll as claimed in claim 17 produced by centrifugal casting.

20. A roll as claimed in any one of claims 17 to 19 which is a compound, bi-metallic roll.

21. A rolling mill stand or rolling mill train which includes at least one roll as claimed in any one of claims 17 to 20.

22. An alloy as claimed in any one of claims 1 to 16 or a roll as claimed in any one of claims 17 to 20 wherein primary carbides are formed prior to solidification.

23. A method of making an alloy as claimed in any one of claims 1 to 16 or 22 which comprises casting the alloy from a molten steel mixture containing the elements in the proportions as defined therein.

24. A method of making a roll as claimed in any one of claims 17 to 20 or 22 which comprises casting the alloy in situ in a ladle from a molten steel mixture containing the elements in the proportions as defined in any one of claims 1 to 16.

25. A method as claimed in claim 24 which is a static casting method and which is followed by only one heat treatment and/or only one tempering heat treatment.

26. A method as claimed in claim 24 which involves centrifugal casting followed by one tempering heat treatment.

27. A method as claimed in any one of claims 23 to 26 wherein the majority of carbides formed have been formed during the casting procedure and secondary carbide(s) has (have) been formed during a heat treatment.

28. A method as claimed in any one of claims 23 to 27 wherein the niobium, and titanium if present, are added to the molten steel before casting.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C22C38/22 C22C38/24 C22C38/26 B22D13/00 B21B27/00

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)
IPC 6 C22C B22D B21B

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 practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X Further documents are listed in the continuation of box C. X Patent family members are listed in annex.

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
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"O" document referring to an oral disclosure, use, exhibition or other means
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Date of the actual completion of the international search 20 June 1995

Date of mailing of the international search report 14.07.95

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INTERNATIONAL SEARCH REPORT

CATEGORIES OF DOCUMENTS CONSIDERED TO BE RELEVANT

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