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(54) Title: STEEL ALLOY

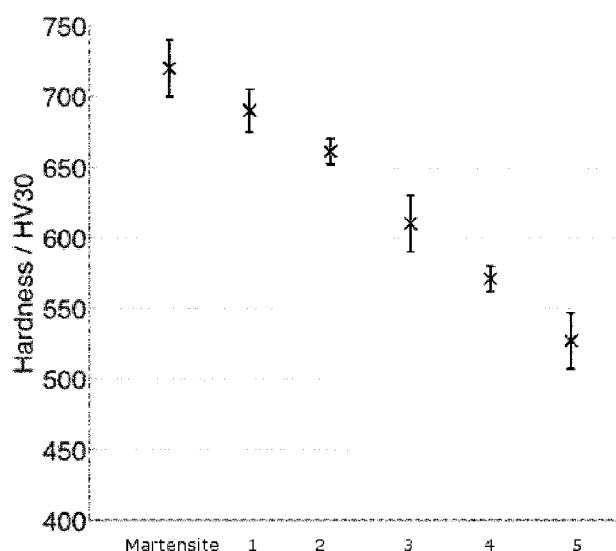


Figure 2

(57) Abstract: The present invention relates to a steel alloy having a composition comprising: from 0.6 to 1.0 wt% carbon from 0.5 to 2.0 wt% silicon from 1.0 to 4.0 wt% chromium optionally one or more of from 0 to 0.25 wt% manganese from 0 to 0.3 wt% molybdenum from 0 to 2.0 wt% aluminium from 0 to 3.0 wt% cobalt from 0 to 0.25 wt% vanadium and the balance iron, together with unavoidable impurities. The microstructure of the steel alloy comprises bainite and, more preferably, superbainite.



GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ,
UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD,
RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ,
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Steel Alloy

Technical Field

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The present invention relates generally to the field of metallurgy and to an improved steel alloy and a method for producing the same. The steel has high tensile strength and toughness and may be used in a number of applications, including, for example, bearings.

Background

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Bainitic steel alloys are produced by the transformation of austenite to ferrite at intermediate temperatures of typically from 200 to 550°C. The cooling of the austenite leads to a microstructure comprising ferrite, carbides and retained austenite. Bainite itself comprises a structure of supersaturated ferrite containing particles of carbide, the dispersion of the latter depending on the formation temperature. The hardness of bainite is usually somewhere intermediate between that of pearlite and martensite.

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Superbainite alloys have been produced without the presence of carbides (or at least with a very small volume fraction of carbides). That is, the structure is formed of a fine mixture of bainitic ferrite and carbon-enriched retained austenite. This produces a combination of high toughness (typically up to 40MPam^{1/2}) and high tensile strength (typically around 2500MPa).

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Superbainite alloys are produced by austenisation followed by prolonged isothermal transformation at a temperature slightly above the martensite start (Ms) temperature. Lower transformation temperatures are desirable because they allow for the formation of a finer structure having improved mechanical properties. However, lower temperatures result in longer processing times.

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Accordingly, there is a desire for a steel alloy that can be produced faster with a fine structure. It is an object of the present invention to provide such an alloy and to address the problems associated with the prior art, or at least to provide a commercially useful alternative thereto. The steel may be used in the manufacture of a bearing component, for example a raceway or rolling element.

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Summary

The present invention provides a steel alloy having a composition comprising:

from 0.6 to 1.0 wt% carbon

from 0.5 to 2.0 wt% silicon

5 from 1.0 to 4.0 wt% chromium

optionally one or more of

from 0 to 0.25 wt% manganese

10 from 0 to 0.3 wt% molybdenum

from 0 to 2.0 wt% aluminium

from 0 to 3.0 wt% cobalt

from 0 to 0.25 wt% vanadium

15 and the balance iron, together with unavoidable impurities.

The structure of the steel comprises bainite and more preferably superbainite. Thus, the present invention advantageously provides a superbainitic steel alloy. A typical superbainitic structure comprises untransformed retained austenite and bainitic ferrite. Typically, the main structural feature is the fineness of the bainitic ferrite platelets, which are typically tens of nanometres thick.

The present invention will now be further described. In the following passages different aspects of the invention are defined in more detail. Each aspect so defined may be combined with any other aspect or aspects unless clearly indicated to the contrary. In particular, any feature indicated as being preferred or advantageous may be combined with any other feature or features indicated as being preferred or advantageous.

The present inventors have discovered an advantageous blend of alloying elements that allows for the formation of a superbainitic steel composition at lower temperatures. As a result, when transformed at low temperatures, the mechanical properties of the product are substantially improved. Alternatively, products of equivalent properties to known superbainite materials may be produced with significantly reduced processing times.

35 The steel composition comprises from 0.6 to 1.0 wt% carbon. When the carbon content is higher than 1wt% there is a reduction in the maximum volume fraction of the bainitic ferrite

portion of the microstructure. When the carbon content is lower than 0.6 wt% the alloys have a higher martensite start temperature (Ms). The martensite start temperature acts as a lower limit for conducting the superbainite isothermal transformation and thus constrains the low temperature superbainite formation. Preferably the steel composition comprises
5 from 0.7 – 0.9 wt% carbon. Most preferably the steel composition comprises about 0.8 wt% carbon.

The steel composition comprises from 0.5 to 2.0 wt% silicon. The addition of silicon is advantageous because it suppresses the formation of carbides (cementite). If the silicon
10 content is lower than 0.5 wt%, then cementite may be formed at low temperatures preventing the formation of superbainite. However, too high a silicon content (for example above 2 wt%) may result in undesirable surface oxides and a poor surface finish. Preferably the steel composition comprises 1.5 to 2.0 wt% silicon.

The steel composition comprises from 0 to 0.25 wt% manganese. In one embodiment, the steel composition comprises from 0.1 to 0.25 wt% manganese, preferably from 0.1 to 0.20 wt%, more preferably from 0.1 to 0.15 wt%. Conventional superbainite compositions comprise large amounts of manganese as a cost-effective means to increase the hardenability of the alloy. However, the present inventors have discovered that reducing the
15 manganese content actually serves to accelerate the formation of superbainite at low temperatures. It has been found that if the manganese content is greater than 0.25 wt%, then the formation rate of superbainite is retarded. As a consequence, the steel composition preferably comprises 0.20 wt% manganese or less, more preferably 0.15 wt% or less. In one embodiment, the steel composition comprises substantially no manganese.
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The steel composition comprises from 1.0 to 4.0 wt% chromium. Preferably the steel composition comprises from 1.5 to 2.5 wt% chromium. Chromium is advantageous because it increases the hardenability of the alloy. This is important in the claimed composition because the reduction in the manganese content over known alloys leads to a reduction in
25 the temperature at which superbainite can be formed. Therefore, an increase in chromium to compensate is desirable. Chromium in excess of 4.0 wt% is known to have a corrosion resistant effect, but there is no further increase in the hardenability of the composition.
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The steel composition comprises from 0 to 0.3 wt% molybdenum. In one embodiment, the steel composition comprises from 0.1 to 0.3 wt% molybdenum. Molybdenum is added to avoid grain boundary embrittlement. The molybdenum content in the alloy is preferably no
35 more than about 0.3 wt% otherwise the austenite transformation into bainitic ferrite may

cease too early, which can result in significant amounts of austenite being retained in the structure.

The steel composition comprises from 0 to 2.0 wt% aluminium. In one embodiment, the steel composition comprises from 0.1 to 2.0 wt% aluminium. Aluminium is advantageous because it suppresses the formation of carbides (cementite). However, the use of aluminium requires stringent steel production controls to ensure cleanliness and this increases the processing costs. In one embodiment, the steel composition comprises substantially no aluminium.

Silicon and aluminium additions both act to suppress carbide formation. The superbainite formation is encouraged by the suppression of cementite. Accordingly, in one embodiment, the total amount of aluminium and silicon is from 1 to 2.5 wt%, more preferably from 1.5 to 2 wt%.

The steel composition comprises from 0 to 3.0 wt% cobalt. In one embodiment, the steel composition comprises from 0.1 to 1.5 wt% cobalt. The addition of cobalt further increases the rate of superbainite formation. However, cobalt is an expensive alloying element and it is therefore economically desirable to avoid the inclusion of this element where possible.

The steel composition comprises from 0 to 0.25 wt% vanadium. In one embodiment, the steel composition comprises from 0.1 to 0.2 wt% vanadium. Vanadium can be useful during austenisation because it helps to control the austenite grain size. In another embodiment, the steel composition comprises substantially no vanadium.

It will be appreciated that the steel according to the present invention may contain unavoidable impurities, although, in total, these are unlikely to exceed 0.5 wt% of the composition. Preferably, the alloys contain unavoidable impurities in an amount of not more than 0.3 wt% of the composition, more preferably not more than 0.1 wt.% of the composition.

Phosphorous and sulphur are preferably kept to a minimum.

The steel alloys according to the present invention may consist essentially of the recited elements. It will therefore be appreciated that in addition to those elements that are mandatory other non-specified elements may be present in the composition provided that the essential characteristics of the composition are not materially affected by their presence.

The steel composition of the present invention enables the formation of superbainite. This structure typically has a fine-scale bainitic-ferrite with excellent mechanical properties. It is achieved by transforming austenite to bainite at a relatively low temperature, typically from 150 to 300°C.

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Preferably at least 50 vol% of the microstructure comprises bainitic ferrite, more preferably at least 70 vol%, still more preferably at least 90 vol%. In one embodiment, essentially all of the structure is bainitic ferrite. That is at least 95 vol%, more preferably at least 98 vol%, more preferably at least 99 vol% of the structure comprises bainitic ferrite. The bainitic ferrite typically has a very fine structure.

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The steel composition of the present invention preferably has a structure comprising at most 10 vol% carbides, more preferably at most 5 vol%, still more preferably at most 2 vol%. In a preferred embodiment, the structure is substantially carbide-free.

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The superbainite structure is well known and easily characterised using high-resolution techniques. It typically comprises a fine mixture of bainitic ferrite and carbon-enriched retained austenite. In one aspect, the average size of the sandwiched platelets of ferrite/austenite is typically less than 50 nm, for example 20 to 40 nm, more typically 25 to 35 nm.

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In one embodiment, up to 50 vol% of the microstructure comprises retained austenite. More particularly, 1 to 50 vol% of the structure comprises retained austenite, more preferably 5 to 45 vol%, still more preferably 5 to 40 vol%, still more preferably 5 to 30 vol%. The retained austenite is typically carbon-enriched.

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In one embodiment, the structure advantageously comprises 5 to 20 vol% retained austenite, optionally up to 5 vol% carbides, and the balance comprising bainitic ferrite. More preferably, the structure comprises 10 to 20 vol% retained austenite, optionally up to 2 vol% carbides, and the balance comprising bainitic ferrite.

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Bearings are devices that permit constrained relative motion between two parts. Rolling element bearings comprise inner and outer raceways and a plurality of rolling elements (balls or rollers) disposed there-between. For long-term reliability and performance it is important that the various elements have resistance to rolling fatigue, wear and creep.

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According to a second aspect of the present invention, there is provided a bearing component, comprising a steel alloy as herein described. Examples of bearing components where the steel can be used include a rolling element (ball or cylinder), an inner ring, and an outer ring. The present invention also provides a bearing comprising a bearing component as herein described.

According to a third aspect of the present invention, there is provided an engine component, an armour component or a railway track component comprising a steel alloy as herein described. The material may also be used in marine and aerospace applications, applications, for example gears and shafts.

According to a further aspect, there is provided a method for preparing a steel alloy as herein described, the method comprising:

(i) providing a steel composition comprising:

from 0.6 to 1.0 wt% carbon

from 0.5 to 2.0 wt% silicon

from 1.0 to 4.0 wt% chromium

optionally one or more of

from 0 to 0.25 wt% manganese

from 0 to 0.3 wt% molybdenum

from 0 to 2.0 wt% aluminium

from 0 to 3.0 wt% cobalt

from 0 to 0.25 wt% vanadium

and the balance iron, together with unavoidable impurities;

(ii) heating the steel composition to at least partially austenitise the composition; and

(iii) maintaining the composition at a superbainite formation temperature until a superbainite structure is formed.

The step of heating the composition to at least partially austenitise the composition will typically involve raising the temperature of the composition to at least about 900°C, preferably at least 930°C.

- 5 The step of maintaining the composition at a superbainite formation temperature until a superbainite structure is formed will typically comprise adjusting the temperature of the hot austenitised composition to a temperature in the range of from 150 to 300°C. The preferred heat-treatment is from 200 to 250°C. The treatment is preferably, but not necessarily, isothermal. This leads to the most consistent structure. The processing time is typically
10 from 6 to 72 hours, although longer times are possible. The greater the temperature, the shorter the treatment time that will be required, but the less refined the final structure.

The structure of the steel alloy described herein can be determined by conventional microstructural characterisation techniques such as, for example, optical microscopy, TEM,
15 SEM, AP-FIM, and X-ray diffraction, including combinations of two or more of these techniques.

Figures

- 20 The invention will now be described in relation to the figures annexed hereto by way of non-limiting examples.

Figure 1 shows an exemplary schematic of a processing route and heat-treatment for the steel.

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Figure 2 shows test result data demonstrating the improved hardness of the steel.

Figures 3(a) and 3(b) show TEM images of the structure of an exemplary steel alloy transformed isothermally into a superbainitic structure at 200 °C and 250°C respectively.

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According to the schematic shown in Figure 1, in a first step 1 an alloy composition is prepared and cast. The alloy composition is then subjected to a conventional high temperature soaking step 2, which is followed by a hot-rolling step 3.

- 35 The hot rolling step 3 is typically carried out at a starting temperature of 1150°C. Several hot-rolling passes may be applied as necessary. The hot-rolled steel, which can be in a bar or plate form, is then allowed to cool slowly to room temperature to avoid the formation of

high-carbon martensite. A typical preferred structure in the as hot-rolled condition, at room temperature, is pearlite.

The hot-rolled material may then optionally be homogenised in a homogenisation step 4, such as a 1200°C treatment for 24 to 48 hours in a vacuum. Optionally, the bars may then be furnace cooled in a cooling step 5, to allow them to cool down slowly to room temperature, also under vacuum.

If desired, the material can then be machined in a machining step to near-net-shape components, for example bearing components (this optional step is not shown). The material or machined shapes are subsequently fully or partially austenitised. For example, a 900°C austenitising heat-treatment for 30 minutes (step 6). The austenitisation may be full or partial, depending on the desired carbon content in the austenite phase.

Immediately after austenitisation, the material (or component) is cooled down to the bainite transformation regime and allowed to transform isothermally (step 7). Superbainite transformation can be carried out at a fixed transformation temperature, for example at 200°C for 24 to 72 hours. A multi-step transformation temperature schedule may also be adopted to tailor the phase fractions in the structure.

After the isothermal treatment step 7, the material (or component) is air-cooled (step 8) and then finished by machining and/or grinding to the required final dimensions (step 9). Finally, an optional step of honing, lapping or polishing can be performed (step 10).

Examples

The invention will now be explained with reference to the following non-limiting examples.

A composition according to the present invention (Steel Alloy G) and a comparative composition (Steel Alloy SP10) were prepared as described in Table 1 below (all wt%):

Table 1 (all wt%)

	C	Si	Mo	Cr	Mn	Al	Co	Fe
Steel Alloy G	0.8	1.9	0.25	1.9	0	0	0	Balance
Steel Alloy SP10	0.79	1.56	0.24	1.01	1.98	1.01	1.51	Balance

For both steel alloys: $P \leq 0.002$; and $S \leq 0.002$.

The steel samples were vacuum arc melted and subsequently homogenised at 1200°C for 24 hours, cooled down to room temperature, and further heat treated following the sequences prescribed in Table 2 below, before quenching in air to room temperature. Samples 1, 2 and 4 correspond to Steel Alloy G, while Comparative Samples 3 and 5 correspond to Steel Alloy SP10.

Table 2

	Austenitisation	Isothermal Transformation	Hardness /HV30*
Sample 1	900°C 30minutes	200°C 72 Hours	690
Sample 2	900°C 30minutes	250°C 16 Hours	660
Sample 3 (comparative)	920°C 30minutes	200°C 72 Hours	610
Sample 4	900°C 30minutes	300°C 6 Hours	570
Sample 5 (comparative)	920°C 30minutes	300°C 6 Hours	530

* Tempered martensite has a Vickers hardness of approximately 720.

Optical microscopy and scanning electron microscopy (SEM) were used to examine the obtained microstructures. The specimens were hot-mounted in Bakelite and then ground and polished using standard techniques. This is followed by etching in 2 vol.% nital solution.

The specimens were then examined using a JEOL 5800LV SEM operated at 10-15 kV.

Transmission electron microscopy (TEM) specimens were machined to 3 mm diameter rods and sliced to 100 µm thick discs and subsequently ground down to 50 µm thickness foils on wet 800 grit silicon carbide paper. These foils were finally electropolished with a Struers TenuPol-5 twin-jet electropolisher at an operating voltage of 20 V at 16°C in a mixture of 15% perchloric acid and 85% ethanol. The samples were examined in a JEOL 2000FX TEM at an operating voltage of 200 kV. The TEM analysis was useful in proving the carbide-free nature of selected grades, and in quantifying the size of their bainitic sub-units.

Figures 3(a) and 3(b) show TEM images of the microstructure of Samples 1 and 2 respectively. A superbainite structure is present.

Quantitative X-ray analysis was used to determine the volume fraction of retained austenite. After grinding and final polishing using 1 µm diamond paste, the specimens were step-

scanned in a Philips PW1820 diffractometer using unfiltered Cu K radiation. The machine was operated at 40 kV and 40 mA. The step size was 0.025° and a dwell time of 18 s. The Highscore Plus software suite was used to analyse the diffraction peaks. The volume fraction of retained austenite was determined by Rietveld refinement.

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Vickers hardness tests (30 kg load) were carried out on SP10 transformed at 200°C (Comparative Sample 3) and 300°C (Comparative Sample 5) in order to investigate the effect of the transformation temperature.

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Isothermal transformation of the inventive steel (Steel Alloy G) at 200°C, 250°C and 300°C led to the formation of superbainite as determined by the optical and SEM micrographic techniques applied. The inventive steel transformed at 200°C displays a higher hardness than that transformed at 300°C. This is because at the lower transformation temperature a finer structure can be achieved.

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TEM images of the inventive and the comparative SP10 steels isothermally transformed at a low temperature (200°C) for a long time show an essentially carbide-free microstructure.

After the transformation into bainite has ceased, during the subsequent air cooling, the inventive steel structure shows the presence of some martensite. Nevertheless, with the

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proper content of carbon in the alloy, the formation of martensite is reduced or avoided.

The foregoing detailed description has been provided by way of explanation and illustration, and is not intended to limit the scope of the appended claims. Many variations in the presently preferred embodiments illustrated herein will be apparent to one of ordinary skill in the art, and

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remain within the scope of the appended claims and their equivalents.

Claims:

1. A steel alloy comprising:

5 from 0.6 to 1.0 wt% carbon
 from 0.5 to 2.0 wt% silicon
 from 1.0 to 4.0 wt% chromium

optionally one or more of

10 from 0 to 0.25 wt% manganese
 from 0 to 0.3 wt% molybdenum
 from 0 to 2.0 wt% aluminium
 from 0 to 3.0 wt% cobalt
15 from 0 to 0.25 wt% vanadium

and the balance iron, together with unavoidable impurities, the steel alloy having a superbainitic structure.

20 2. A steel alloy as claimed in claim 1 comprising from 0.7 – 0.9 wt.% carbon.

3. A steel alloy as claimed in claim 1 or claim 2 comprising from 1.5 – 2.0 wt.% silicon.

25 4. A steel alloy as claimed in any one of the preceding claims comprising from 1.5 to 2.5 wt% chromium.

5. A steel alloy as claimed in any one of the preceding claims comprising from 0 to 0.20 wt% manganese.

30 6. A steel alloy as claimed in any one of the preceding claims comprising substantially no manganese.

7. A steel alloy as claimed in any one of the preceding claims comprising substantially no cobalt and/or vanadium and/or aluminium.

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8. A steel alloy as claimed in any one of the preceding claims comprising at least one of:

from 0.1 to 0.25 wt% manganese; and/or
from 0.1 to 0.3 wt% molybdenum; and/or
from 0.1 to 2.0 wt% aluminium.

- 5 9. A steel alloy as claimed in any one of the preceding claims wherein the total amount of aluminium and silicon is from 1 to 2.5 wt%.
- 10 10. A steel alloy as claimed in any one of the preceding claims wherein bainitic ferrite makes up at least 50 vol% of the structure, preferably at least 70 vol% of the structure, more preferably at least 90 vol% of the structure.
11. A steel alloy as claimed in any one of the preceding claims having a structure that comprises at most 10 vol% carbides and preferably is substantially carbide free.
- 15 12. An engine component, an armour component or a track component comprising a steel alloy as defined in any one of the preceding claims.
13. A bearing component comprising a steel alloy as defined in any of claims 1 to 11.
- 20 14. A bearing component as claimed in claim 13, which is at least one of a rolling element, an inner ring, and/or an outer ring.
15. A bearing comprising a bearing component as claimed in claim 13 or claim 14.
- 25 16. A method for preparing a steel alloy according to any of claims 1 to 11, the method comprising:
- (i) providing a steel composition comprising:
- 30 from 0.6 to 1.0 wt% carbon
from 0.5 to 2.0 wt% silicon
from 1.0 to 4.0 wt% chromium
- optionally one or more of
- 35 from 0 to 0.25 wt% manganese
from 0 to 0.3 wt% molybdenum
from 0 to 2.0 wt% aluminium

from 0 to 3.0 wt% cobalt
from 0 to 0.25 wt% vanadium

and the balance iron, together with unavoidable impurities;

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(ii) heating the steel composition to at least partially austenitise the composition; and

(iii) maintaining the composition at a superbainite formation temperature until a superbainite structure is formed.

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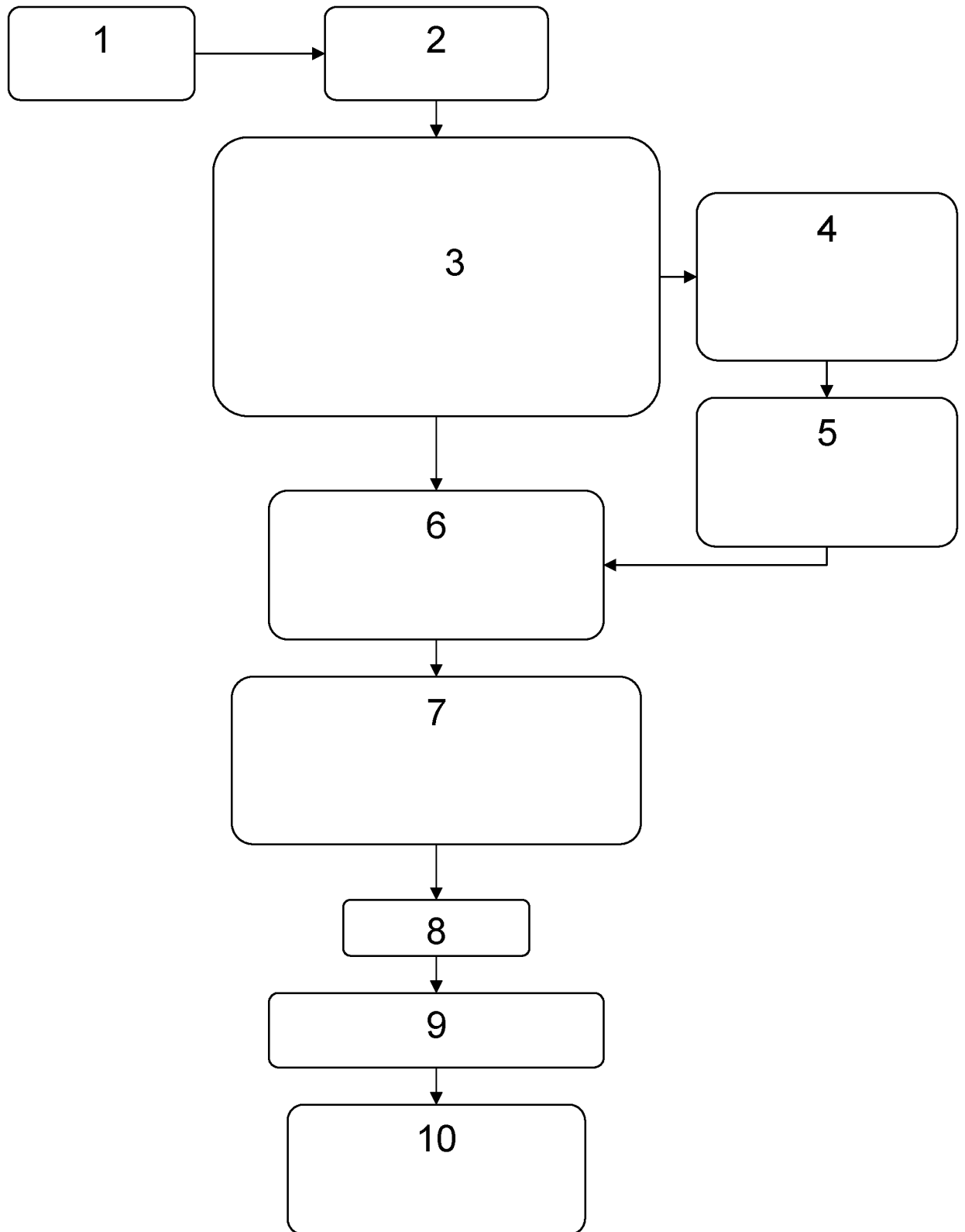


Figure 1

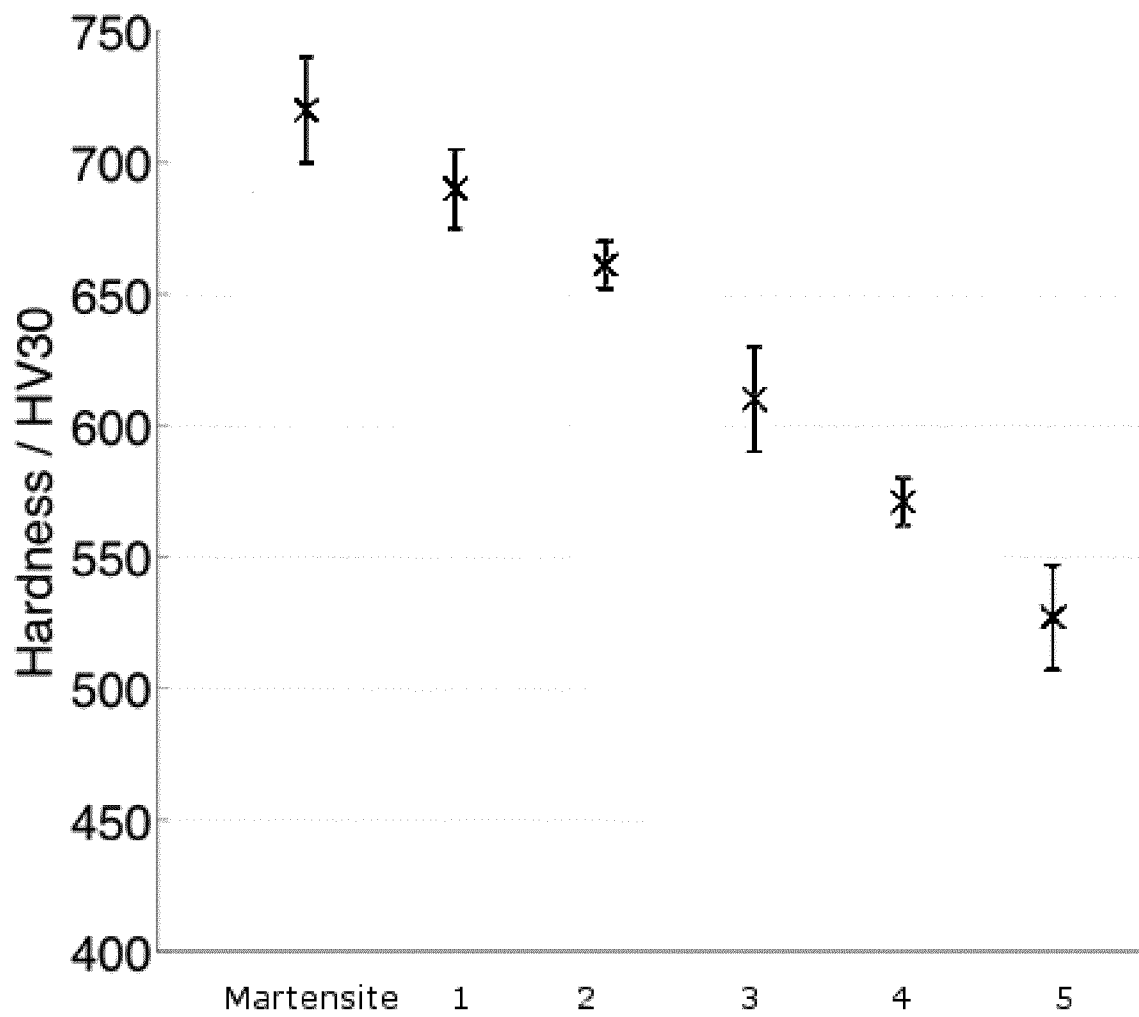
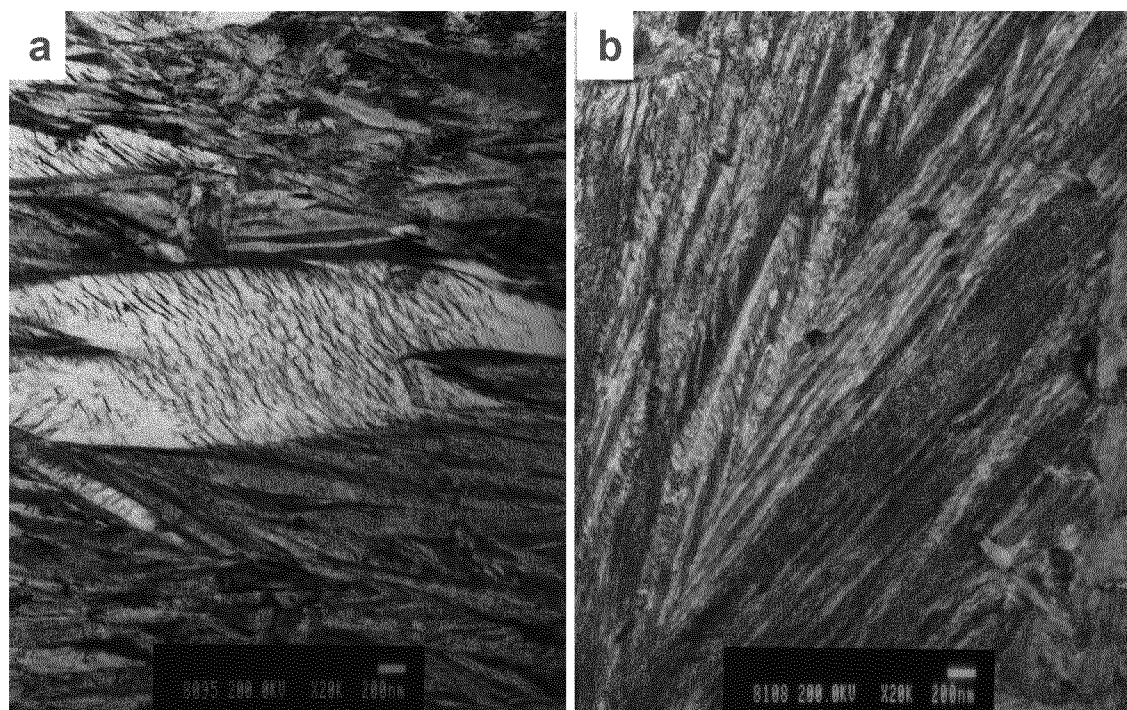


Figure 2

**Figure 3**

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2012/056166

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C21D1/20 C21D6/00 C22C38/18
 ADD.

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)
 C21D C22C

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)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2012/031771 A1 (TATA STEEL UK LTD [GB]; CLARKE RICHARD [GB]; DAVIES PAUL [GB]; MADILL) 15 March 2012 (2012-03-15) p. 1-3; p. 8, Table 1 -----	1-16
A	GB 2 352 726 A (SECR DEFENCE [GB]) 7 February 2001 (2001-02-07) p. 1 -----	1-16
A	GB 2 462 197 A (SECR DEFENCE [GB]) 3 February 2010 (2010-02-03) [0009]-[0014] -----	1-16
A	JP 2003 232369 A (NSK LTD) 22 August 2003 (2003-08-22) [0012], "table 1: alloys A, 0 and P ----- -/--	1-6



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent 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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"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

16 November 2012

Date of mailing of the international search report

22/11/2012

Name and mailing address of the ISA/

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Authorized officer

Radeck, Stephanie

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2012/056166

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CABALLERO F G ET AL: "Very strong bainite", CURRENT OPINION IN SOLID STATE AND MATERIALS SCIENCE, ELSEVIER SCIENCE LTD, OXFORD, GB, vol. 8, no. 3-4, 1 June 2004 (2004-06-01), pages 251-257, XP004742050, ISSN: 1359-0286, DOI: 10.1016/J.COSSMS.2004.09.005 page 251 - page 255 -----	1-6
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2012/056166

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