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(54) **Title**: Steel Alloy

(57) **Abstract**: A steel alloy comprising: from 0.8 to 1.2 wt% carbon from 0.1 to 0.8 wt% manganese from 0.5 to 2.5 wt% chromium from 0.3 to 0.8 wt% vanadium optionally one or more of from 0 to 1.0 wt% silicon from 0 to 0.3 wt% molybdenum from 0 to 0.5 wt % copper from 0 to 3..5 wt% nickel from 0 to 0.1 wt% aluminium from 0 to 0.05 wt% phosphorus from 0 to 0..05 wt% sulphur from 0 to 0..1 wt% titanium from 0 to 0..1 wt% niobium from 0 to 0..1 wt% tantalum from 0 to 0..1 wt% tungsten from 0 to 0..1 wt% boron from 0 to 0..1 wt% nitrogen from 0 to 0.1 wt% oxygen from 0 to 0.1 wt% calcium from 0 to 0.1 wt% cobalt and the balance iron, together with unavoidable impurities.

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Steel Alloy

Technical Field

The present invention relates generally to the field of metallurgy and to an improved steel alloy and a method of heat-treating an alloy. The steel alloy exhibits resistance to hydrogen embrittlement and high hardness. The steel alloy may be used in a number of applications, including, for example, bearings.

Background

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 therebetween. For long-term reliability and performance it is important that the various elements have a high resistance to rolling contact fatigue, wear and creep.

Steelmaking companies have been active in lowering the hydrogen content during casting, since this element can have an adverse effect on the rolling contact fatigue life. The hydrogen concentration should typically not exceed 1 ppm. Even if the hydrogen content is very low in the as-produced steel, its amount is likely to increase during service, for example due to oil decomposition or electric current breaking through the layer of oil, resulting in the decomposition of oil molecules into products including free hydrogen, making its ingress into the bulk possible.

Hydrogen embrittlement is likely to occur when the steel contains mobile hydrogen. For this reason it has been proposed to immobilise hydrogen in the alloy microstructure.

The steel known as 100Cr6 has the following composition: 0.974 wt% carbon, 0.282 wt% silicon, 0.276 wt% manganese, 0.056 wt% molybdenum, 1.384 wt% chromium, 0.184 wt% nickel, 0.042 wt% aluminium, 0.21 wt% copper, 0.01 wt% phosphorus and 0.017 wt% sulphur, the balance being iron (and any unavoidable impurities). This steel exhibits high hardness and is suitable for use in a bearing component. However, 100Cr6 exhibits moderate-to-low resistance to hydrogen embrittlement.

It is an object of the present invention to address or at least mitigate some of the problems associated with prior art, or at least to provide a commercially useful alternative thereto.

Summary

In a first aspect the present invention provides a steel alloy having a composition comprising:

from 0.8 to 1.2 wt% carbon
from 0.1 to 0.8 wt% manganese
from 0.5 to 2.5 wt% chromium
from 0.3 to 0.8 wt% vanadium

optionally one or more of

from 0 to 1.0 wt% silicon
from 0 to 0.3 wt% molybdenum
from 0 to 0.5 wt% copper
from 0 to 3.5 wt% nickel
from 0 to 0.1 wt% aluminium
from 0 to 0.05 wt% phosphorus
from 0 to 0.05 wt% sulphur
from 0 to 0.1 wt% titanium
from 0 to 0.1 wt% niobium
from 0 to 0.1 wt% tantalum
from 0 to 0.1 wt% tungsten
from 0 to 0.1 wt% boron
from 0 to 0.1 wt% nitrogen
from 0 to 0.1 wt% oxygen
from 0 to 0.1 wt% calcium
from 0 to 0.1 wt% cobalt

and the balance iron, together with unavoidable impurities.

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 steel alloy according to the present invention comprises from 0.8 to 1.2 wt% carbon. Preferably, the steel alloy composition comprises from 0.9 to 1.1 wt% carbon, more preferably from 0.95 to 1.05 wt% carbon. In one example, the alloy comprises about 0.99 wt% carbon. The presence of carbon in the specified amount serves to increase the hardness of the steel alloy. In addition, the presence of carbon together with vanadium enables the formation of carbides comprising carbon and vanadium. As discussed below, the presence of such carbides increases the alloy's resistance to hydrogen embrittlement.

The steel alloy comprises from 0.1 to 0.8 wt% manganese, more typically from 0.1 to 0.6 wt% manganese. Preferably, the alloy comprises from 0.2 to 0.5 wt% manganese, more preferably from 0.2 to 0.4 wt% manganese. In one example, the alloy comprises about 0.28 wt% manganese. The manganese, in combination with the other alloying elements, increases hardness and contributes to the steel's strength. Manganese may also have a beneficial effect on surface quality.

The steel alloy comprises from 0.5 to 2.5 wt% chromium. Preferably, the alloy comprises from 1.0 to 2.0 wt% chromium, more preferably from 1.2 to 1.6 wt% chromium. In one example, the alloy comprises about 1.42 wt% chromium. The presence of chromium in the specified amount provides an improved corrosion resistance property to the steel alloy. The chromium leads to a hard oxide on the metal surface to inhibit corrosion. Chromium may also have a beneficial effect on hardenability.

The steel alloy comprises from 0.3 to 0.8 wt% vanadium. Preferably, the alloy comprises from 0.4 to 0.7 wt% vanadium, more preferably from 0.5 to 0.6 wt% vanadium. In one example, the alloy comprises about 0.55 wt% vanadium. In combination with the other alloying elements, vanadium in the specified amounts has been found to form carbides, such as, for example, V_4C_3. Such carbides, which are preferably nanometre-scaled, may act as hydrogen traps. The presence of such carbides is believed to provide the steel alloy with increased resistance to hydrogen embrittlement. The presence of vanadium in the range of about 0.3 to about 0.8 wt% makes carbide formation (for example V_4C_3) thermodynamically possible at about 600°C, and is also beneficial for delaying grain growth during austenitisation. Vanadium may also act to increase yield strength and tensile strength of the alloy.

The steel alloy may optionally comprise up to 0.5 wt% copper, for example from 0.1 to 0.5 wt% copper. Preferably, the alloy comprises from 0.2 to 0.5 wt% copper, still more preferably from 0.2 to 0.4 wt% copper. In one example, the alloy comprises about 0.25 wt% copper. The copper may act to provide improved corrosion resistance.

The steel alloy may optionally comprise up to 1.0 wt.% silicon, more typically up to 0.5 wt% silicon, for example from 0.1 to 0.5 wt% silicon. Preferably, the alloy comprises from 0.1 to 0.4 wt% silicon, more preferably from 0.2 to 0.3 wt% silicon. Silicon may be added during the steel making process as a deoxidizer. Silicon may also act to increase strength and hardness.

The steel alloy may optionally comprise up to 0.3 wt% molybdenum, for example from 0.01 to 0.3 wt% molybdenum. Preferably, the alloy comprises from 0.01 to 0.2 wt% molybdenum, more preferably from 0.05 to 0.1 wt% molybdenum. In one example, the alloy comprises about 0.093 wt% molybdenum. In combination with the other alloying elements (particularly the vanadium and the carbon), molybdenum in the specified amounts is thought to improve hydrogen-trapping capacity of the steel alloy, possibly owing to more favourable coherency strains. This provides the steel alloy with increased resistance to hydrogen embrittlement. Molybdenum may also act to increase the hardenability of the alloy.

The steel alloy may optionally comprise up to 3.5 wt% nickel, more typically up to 1 wt% nickel, more typically up to 0.1 wt% nickel. Preferably, the alloy comprises from 0.005 to 0.05 wt% nickel, more preferably from 0.007 to 0.02 wt% nickel. In one example, the alloy comprises about 0.01 wt% nickel. Nickel may act to increase hardenability and impact strength.

The steel alloy may optionally comprise up to 0.1 wt% aluminium. Preferably, the steel alloy comprises from 0.001 to 0.01 wt% aluminium, more preferably from 0.002 to 0.005 wt% aluminium. In one example, the steel alloy comprises about 0.003 wt% aluminium. Aluminium may be used as a deoxidizer. Aluminium may also act to control grain size in the alloy.

The steel alloy may optionally comprise up to 0.1 wt% of one or more of titanium, niobium, tantalum, tungsten, boron, nitrogen, calcium and cobalt.

Other elements that may be present include oxygen, phosphorus and sulphur. Preferably, the presence of these elements is kept to a minimum. If phosphorus is present, the content thereof should generally not exceed 0.05 wt%. Typically the phosphorus content will be about 0.004 wt%. If sulphur is present, the content should generally not exceed 0.05 wt%. Typically the sulphur content will be about 0.003 wt%. If oxygen is present, the content should generally not exceed 0.1 wt%. Preferably, the oxygen content does not exceed 15 ppm.

It will be appreciated that the steel alloy may contain unavoidable impurities, although, in total, these are unlikely to exceed 0.5 wt.% of the composition. Preferably, the alloy contains 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. As noted above, the phosphorus and sulphur contents are preferably kept to a minimum.

A most preferred steel alloy according to the present invention comprises:

about 0.0994 wt% carbon
about 0.282 wt% manganese
about 1.42 wt% chromium
about 0.247 wt% copper
about 0.549 wt% vanadium
about 0.272 wt % silicon
about 0.093 wt % molybdenum
about 0.01 wt% nickel
about 0.003 wt% aluminium
about 0.004 wt% phosphorus
about 0.003 wt% sulphur

and the balance iron, together with unavoidable impurities.

The alloys according to the present invention may consist essentially of the recited elements. It will therefore be appreciated that in addition to those elements which 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 alloy typically has a microstructure comprising martensite, optionally cementite, and carbides comprising vanadium and carbon. If the alloy undergoes a tempering heat-treatment, then cementite is present in the final microstructure.

The carbides may consist of vanadium and carbon, for example V_4C_3, or may include one or more additional alloying elements. Thus, the term carbide as used herein is meant to encompass also, for example, carbo-nitrides and carbo-oxy-nitrides and also mixed metal carbides, carbo-nitrides and carbo-oxy-nitrides.

The microstructure typically comprises at least 70 vol. % martensite, more typically at least 75 vol. %. Preferably, the microstructure comprises from 1 to 5 vol. % carbides (comprising vanadium and carbon) and from 5 to 20 vol. % cementite, the remainder being martensite. Most preferably, the microstructure comprises about 2 vol. % carbides (comprising vanadium and carbon), about 10 vol. % cementite, and the remainder being martensite.

Within the martensite matrix the carbide precipitates comprising vanadium and carbon are though to act as hydrogen traps. The presence of cementite precipitates impart strength.

The carbide precipitates comprising vanadium and carbon are advantageously nanometre-sized and, preferably, have a mean diameter of from 1 to 50 nm, more preferably from 1 to 30 nm, even more preferably from 5 to 25 nm. Most preferably, the carbides have a mean diameter of about 10 nm. Carbides having such sizes are particularly effective as hydrogen traps.

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

In a second aspect, the present invention provides an engine component or an armour component comprising a steel alloy as defined herein. The material may also be used in marine and aerospace applications, for example gears and shafts.

In a third aspect, the present invention provides a bearing component comprising a steel alloy as defined herein. The bearing component may be at least one of a rolling element (for example ball or cylinder), an inner ring, and/or an outer ring.

In a fourth aspect, the present invention provides a bearing comprising a bearing component as described herein.

In a fifth aspect, the present invention provides a method of heat-treating a steel alloy comprising:

(i) providing a steel alloy composition as herein described;

(ii) heating the composition at a temperature of from 780 to 950°C to at least partially austenitise the composition;

(iii) further heating the at least partially austenitised composition to a temperature of from 1050 to1350°C;

(iv) ageing the alloy at a temperature of from 540 to 660°C; and

(v) optionally carrying out a tempering heat-treatment following the ageing step (iv).

In step (ii), the composition is at least partially austenitised, preferably completely austenitised. This is achieved by heating the alloy composition to a temperature of from 780 to 950°C, preferably from 820 to 900°C, more preferably from 840 to 880°C, and most preferably about 860°C. The composition may be maintained in this temperature regime for up to 30 minutes, preferably from 5 to 20 minutes, even more preferably for about 15 minutes. However, longer heating times are also possible.

Further heating of the at least partially austenitised composition in step (iii) is carried out at a temperature of from 1050 to1350°C, preferably from 1100 to 1300°C, more preferably from 1150 to 1250°C, and most preferably about 1200°C. Step (iii) results in the dissolution of any coarse vanadium carbides formed on austenitisation. The composition may be maintained in this elevated temperature regime for up to 10 minutes, preferably from 30 seconds to 5 minutes, even more preferably for about 1 minute.

Between steps (iii) and (iv), the compositions may optionally be quenched, preferably to a temperature lower than 200°C, more preferably to a temperature lower than 150 °C. The quenching may occur using helium quenching gas, and may occur at a cooling rate of 10 °C/minute or more, preferably 25 °C/minute or more.

In step (iv), the alloy is aged at a temperature of from 540 to 660°C, preferably from 560 to 640°C, more preferably from 580 to 620°C, and most preferably about 600°C. The alloy may be aged for up to 120 minutes, preferably from 30 to 90 minutes, even more preferably for about 60 minutes.

The heat-treatment method according to the present invention preferably further comprises further heating the composition following the ageing step (iv) and prior to the optional tempering step (v). Such further heating may be carried out at a temperature of from 780 to 950°C, preferably from 820 to 900°C, more preferably from 840 to 880°C, and most preferably about 860°C. This further heating facilitates dissolution of cementite and the formation of martensite on quenching.

Following step (iv) (or the optional further heating step thereafter), the composition may optionally undergo a quench, preferably to a temperature lower than 200°C, more preferably to a temperature lower than 150 °C. The quenching may occur using helium quenching gas, and may occur at a cooling rate of 10 °C/minute or more, preferably 25 °C/minute or more.

The heat-treatment method according to the present invention may further comprise carrying out an optional spheroidising treatment prior to the austenetising step (ii). This may increase the machinability of the alloy composition.

Figures

The present invention will now be described further, by way of example, with reference to the following figures:

Figure 1 shows heat treatment schedules of: (a) 100Cr6 (comparative example); and (b) 100Cr6+V (present invention).

Figure 2 shows optical micrographs of: (a) 100Cr6 (comparative example); and (b) 100Cr6+V (present invention).

Figure 3 shows transmission electron micrographs of 100Cr6+V (present invention): (a) bright field TEM image after spheroidisation and a diffraction pattern of spheroidised cementite indicated by the arrow (the zone axis is [-101]); (b) bright field TEM image after the first temperature spike and a diffraction pattern taken from the ferritic lath visible on the image (the zone axis is [-1-11]); (c) bright field TEM image after the first temperature spike followed by tempering at 600°C for 1 hour, the diffraction pattern is taken from the elongated cementite particle indicated by the arrow (the zone axis of cementite is [111] and of ferrite is [3-11]).

Figure 4 shows transmission electron micrographs of 100Cr6+V (present invention): (a) bright field and dark field images after the second temperature spike, the diffraction pattern is taken from the V_4C_3 particle indicated by the arrow (the zone axis of V_4C_3 is [0-11]); (b) diffraction pattern and bright filed image after completed heat-treatment (diffraction pattern taken from [1-32] cementite spot).

Figure 5 shows thermal desorption analysis results of 100Cr6 (comparative example) and 1000Cr6+V (present invention): (a) just after H-charging; and (b) 24 hours after H-charging.

Examples

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

Production of steel alloys

100Cr6 was employed as a baseline and a modified version of it with an intended addition of 0.5 wt% V was cast. The latter will be referred to hereafter as 100Cr6+V. The compositions of both grades were determined using a glow discharge atomic emission spectrometer, LECO GDS850A, and the results are set out in Table 1 below.

Grade	C	Si	Mn	Mo	Cr	Ni	Al	Cu	P	S	V
100Cr6	0.974	0.282	0.276	0.056	1.384	0.184	0.042	0.21	0.01	0.017	0.00
100Cr6+V	0.994	0.272	0.282	0.093	1.42	0.01	0.003	0.247	0.004	0.003	0.549

Table 1 – Chemical compositions of 100Cr6 steel (comparative example) and 100Cr6+V steel (present invention) (wt%).

Both grades were spheroidised according to conventional methods and were then heat-treated according to the schedules shown in Figure 1. The samples were cut into rods of 4 and 8 mm diameter and 12 mm length, and heat-treated in vacuum on a Thermecmaster dilatometer with helium quenching gas at a cooling rate of 25 $°Cs^{-1}$.

As shown in Figure 1, the heating schedules were as follows. The 100Cr6 alloy was heated to about 860 °C and maintained at that temperature for about 15 minutes. Following quenching, the alloy was then heated to a temperature of about 215 °C and maintained at that temperature for about 210 minutes.

The 100Cr6+V alloy was heated to about 860 °C and maintained at that temperature for about 15 minutes. The temperature was then raised to about 1200 °C and held for about 1 minute before quenching. The temperature was then raised to about 600 °C and held for about 60 minutes before being raised to about 860 °C. After about 3 minutes, the alloy was quenched. The alloy was then heated to a temperature of about 215 °C and maintained at that temperature for about 210 minutes

Optical microscopy

Heat-treated 8 mm diameter samples were cut in half, hot-mounted in conductive bakelite, ground using 1200 grit SiC paper and polished with 6 μm and 1 μm diamond paste. The samples were etched in 2% nital (2% Nitric acid and 98% Methanol). Optical micrographs were obtained using a Zeiss Axioplan2. The micrographs for 100Cr6 and 100Cr6+V after the heat-treatments shown in Figure 1 are shown in Figures 2a and 2b, respectively. From the micrographs it can be seen that 100Cr6+V does not contain the coarse cementite particles visible in 100Cr6 steel.

Hardness measurements

Hardness tests were carried out by using a Vickers hardness testing machine with a 30 kg load. A mean value of hardness for each alloy was calculated from the lowest and highest single values from 10 readings. The mean hardness of 100Cr6+V (804 HV30) was found to be higher than that exhibited by 100Cr6 (785 HV30).

Transmission electron microscopy

After each heat-treatment step shown in Figure 1b, discs of 3 mm diameter and 0.5 mm thickness were cut in order to produce thin foils. These were then mechanically polished to ~50 µm by using 1200 grit SiC paper and cleaned in acetone, and then further electropolished in 15% perchloric acid and 85% ethanol solution using a Struers Tenupol 5 electropolisher. A current of ~130mA and 20.5 V resulted in samples of sufficient thickness for transmission electron microscopy (TEM). TEM micrographs were obtained using JEOL 2000FX (200kV) and Philips CM30 (300 kV) transmission electron microscopes. The two spikes heat-treatment was interrupted after selected heat-treatment stages to verify the presence and size of vanadium carbides (e.g. V_4C_3) and cementite.

100Cr6 is spheroidised before the hardening heat-treatment to enhance machinability. Figure 3a shows a TEM micrograph of 100Cr6+V after spheroidisation. Large and evenly distributed cementite particles with a radius around 200-500 nm are observed. The microphotographs taken after the first temperature spike (Figure 3b) show ferritic laths without cementite and vanadium carbide particles (e.g. V_4C_3). The diffraction pattern shows additional spots believed to be epsilon carbides, which can form at room temperature, presumably since the TEM investigations were carried out approximately two weeks after heat treatment. The tempering stage at 600 °C shows the undesired large cementite particles and confirms the preference of a second temperature spike for its dissolution (Figure 3c). The growth of vanadium carbides, which is expected to appear at this stage, is difficult to confirm because of the small amount and size of the vanadium carbides in contrast with the large amount of comparably coarse cementite, which makes the diffraction patterns difficult to analyse. Nevertheless, Figure 4a confirms the presence of vanadium carbides following cementite dissolution. Following cementite dissolution, the diffraction patterns are easier to analyse because the amount of diffraction spots decreases, meaning that they become more easily identifiable. The TEM microphotographs after the full heat-treatment (Figure 4b) show fine cementite and vanadium carbide particles (e.g. V_4C_3). Their presence was confirmed by electron diffraction. The phases confirmed by the TEM micrographs are consistent with those predicted via thermodynamic and kinetic modelling.

Thermal desorption

For thermal desorption, heat-treated samples were cut into cylinders of 4 mm diameter and 6 mm length. Hydrogen was introduced into the specimens with cathodic electrolysis using an electrolyte solution of 1 dm^3 distilled H_2O, 4 g NaOH and 4 g Thiourea. The samples were put into the charging cells and surrounded by platinum wires (counter electrode). The polarity of the samples was negative. Subsequently, the cell was connected to a current source of 8 mA. The charging process took 24 hours and the electrolyte was stirred and kept at a stable temperature of 80 °C during the whole process. After charging, the samples were gently polished and ultrasonically cleaned with petroleum ether and acetone, respectively. The hydrogen content was measured by means of thermal desorption analysis with pulsed discharge detector with helium carrier gas and the samples were heated up by a Pyroprobe 5000 unit at a rate of 2.6 °C/min. The samples were analysed in subsequent 3 minute intervals, which allows for the separation of peaks due to hydrogen, oxygen and nitrogen. Hydrogen desorption peak positions were analysed to identify the types of trapping site, and the peak areas were analysed for estimating the amount of trapped hydrogen. 100Cr6 and 100Cr6+V were tested in two conditions: just after H-charging; and 24 hours after H-charging.

Because the hydrogen traps become activated at certain temperatures, thermal desorption analysis was conducted at a constant heating rate to investigate the type of traps present in the microstructure. As shown in Figure 5, the thermal desorption charts of the 100Cr6+V alloy display a very high trapping capacity compared to the baseline steel, 100Cr6. The temperature peaks for 100Cr6+V (which contain vanadium carbide traps – e.g. V_4C_3) show a maximum desorption rate at 219 °C. The temperature peaks of 100Cr6 occur at a lower temperature of 188 °C, suggesting that these peaks correspond to dislocations.

The amount of hydrogen trapped in the alloy steels can be calculated by integrating the area under the curves. For 100Cr6+V, the amount of trapped hydrogen was calculated to be ~6 ppmw in samples just after hydrogen charging, and ~4.5 ppmw 24 hours after hydrogen charging. As expected, the hydrogen levels decreased after 24 hours. The hydrogen desorbed after 24 hours indicates the trapped hydrogen, whereas the hydrogen desorbed just after charging comprises a mixture of both diffusible and trapped hydrogen. Referring to the baseline steel (100Cr6), the hydrogen trapped by dislocations decreased strongly from ~1 ppmw (immediately after charging) to ~0.12 ppmw (24 hours after charging). This shows that 100Cr6 does not intrinsically posses good hydrogen trapping capacity, and that modification in accordance with the present invention results in an increase in its trapping capacity of approximately 300 times.

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

Claims:

1. A steel alloy comprising:

from 0.8 to 1.2 wt% carbon
from 0.1 to 0.8 wt% manganese
from 0.5 to 2.5 wt% chromium
from 0.3 to 0.8 wt% vanadium

optionally one or more of

from 0 to 1.0 wt% silicon
from 0 to 0.3 wt% molybdenum
from 0 to 0.5 wt% copper
from 0 to 3.5 wt% nickel
from 0 to 0.1 wt% aluminium
from 0 to 0.05 wt% phosphorus
from 0 to 0.05 wt% sulphur
from 0 to 0.1 wt% titanium
from 0 to 0.1 wt% niobium
from 0 to 0.1 wt% tantalum
from 0 to 0.1 wt% tungsten
from 0 to 0.1 wt% boron
from 0 to 0.1 wt% nitrogen
from 0 to 0.1 wt% oxygen
from 0 to 0.1 wt% calcium
from 0 to 0.1 wt% cobalt

and the balance iron, together with unavoidable impurities.

2. A steel alloy as claimed in claim 1 comprising from 0.9 to 1.1 wt.% carbon, preferably from 0.95 to 1.05 wt.% carbon.

3. A steel alloy as claimed in claim 1 or claim 2 comprising from 0.1 to 0.4 wt.% silicon, preferably from 0.2 to 0.3 wt.% silicon.

4. A steel alloy as claimed in any one of the preceding claims comprising from 0.2 to 0.5 wt% manganese, preferably from 0.2 to 0.4 wt% manganese.

5. A steel alloy as claimed in any one of the preceding claims comprising from 0.01 to 0.2 wt% molybdenum, preferably from 0.05 to 0.1 wt% molybdenum.

6. A steel alloy as claimed in any one of the preceding claims comprising from 1.0 to 2.0 wt% chromium, preferably from 1.2 to 1.6 wt% chromium.

7. A steel alloy as claimed in any one of the preceding claims comprising from 0.005 to 0.05 wt% nickel, preferably from 0.007 to 0.02 wt% nickel.

8. A steel alloy as claimed in any one of the preceding claims comprising from 0.001 to 0.01 wt% aluminium, preferably from 0.002 to 0.005 wt% aluminium.

9. A steel alloy as claimed in any one of the preceding claims comprising from 0.1 to 0.5 wt% copper, preferably from 0.2 to 0.5 wt% copper.

10. A steel alloy as claimed in any one of the preceding claims comprising from 0.4 to 0.7 wt% vanadium, preferably from 0.5 to 0.6 wt% vanadium.

11. A steel alloy as claimed in any one of the preceding claims having a microstructure comprising martensite, optionally cementite, and carbide precipitates comprising vanadium and carbon.

12. A steel alloy as claimed in claim 11, wherein the microstructure comprises at least 70 vol. % martensite.

13. A steel alloy as claimed in claim 11 or claim 12, wherein the carbide precipitates have a mean diameter of from 1 to 50 nm, preferably from 1 to 30 nm, more preferably from 5 to 25 nm.

14. An engine component or an armour component comprising a steel alloy as defined in any one of the preceding claims.

15. A bearing component comprising a steel alloy as defined in any of claims 1 to 13.

16. A bearing component as claimed in claim 15, which is at least one of a rolling element, an inner ring, and/or an outer ring.

17. A bearing comprising a bearing component as claimed in claim 15 or claim 16.

18. A method of heat-treating a steel alloy comprising:

(i) providing a steel alloy composition as defined in any one of claims 1 to 13;

(ii) heating the composition at a temperature of from 780 to 950°C to at least partially austenitise the composition;

(iii) further heating the at least partially austenitised composition to a temperature of from 1050 to1350°C;

(iv) ageing the alloy at a temperature of from 540 to 660°C; and

(v) optionally carrying out a tempering heat-treatment following the ageing step (iv).

19. A method as claimed in claim 18, further comprising further heating the composition to a temperature of from 780 to 950°C following the ageing step (iv) and prior to the optional tempering step (v).

20. A method as claimed in claim 18 or claim 19, further comprising carrying out a spheroidising treatment prior to the austenetising step (ii).

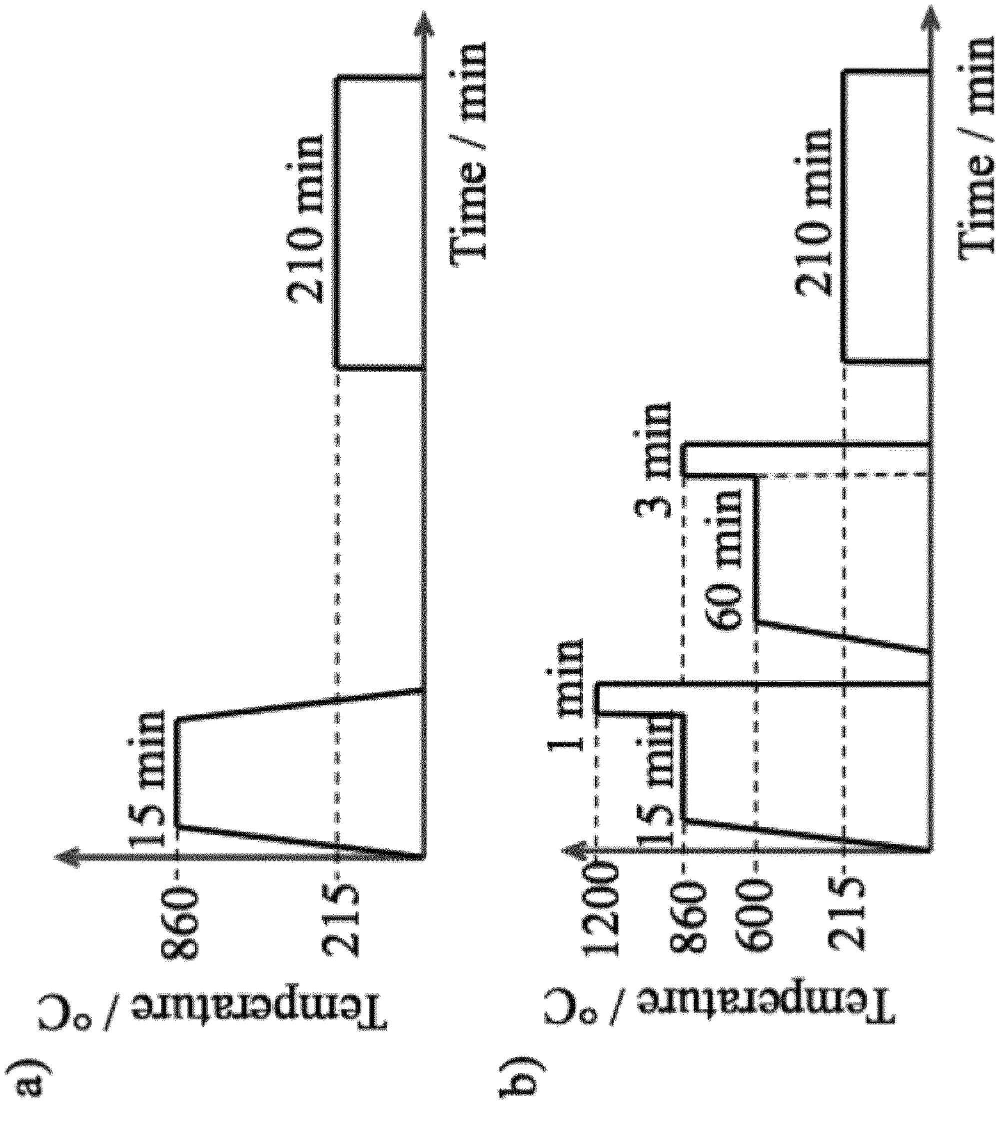
a)
Temperature / °C
860
215
15 min
210 min
Time / min
b)
Temperature / °C
1200
860
600
215
15 min
1 min
60 min
3 min
210 min
Time / min

Figure 1

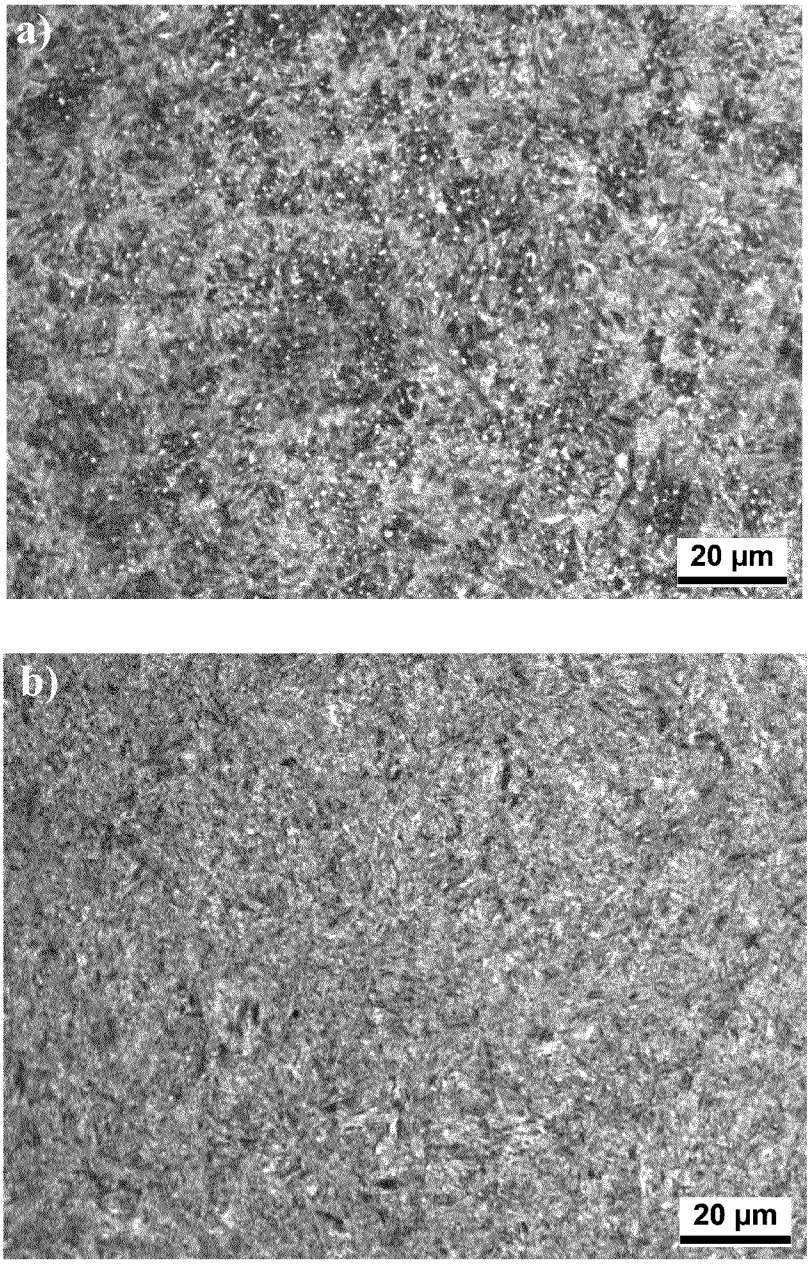

Figure 2

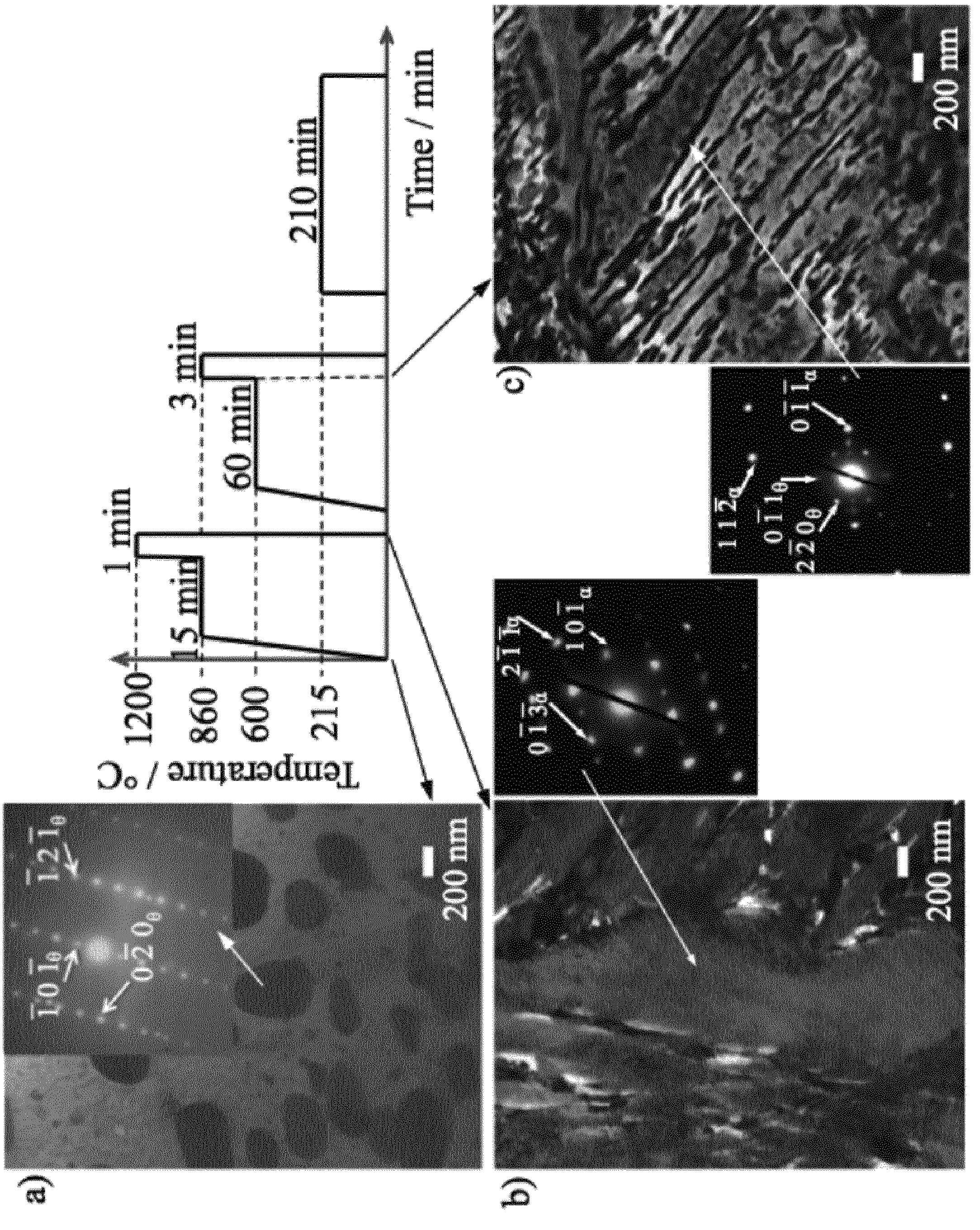
a)
b)
c)
Temperature / °C
1200
860
600
215
15 min
1 min
60 min
3 min
210 min
Time / min
200 nm
200 nm
200 nm
$\bar{1}0\bar{1}_\theta$
$0\bar{2}0_\theta$
$\bar{1}2\bar{1}_\theta$
$0\bar{1}\bar{3}_\alpha$
$2\bar{1}\bar{1}_\theta$
$10\bar{1}_\alpha$
$11\bar{2}_\alpha$
$0\bar{1}1_\theta$
$\bar{2}\bar{2}0_\theta$
$0\bar{1}\bar{1}_\alpha$

Figure 3

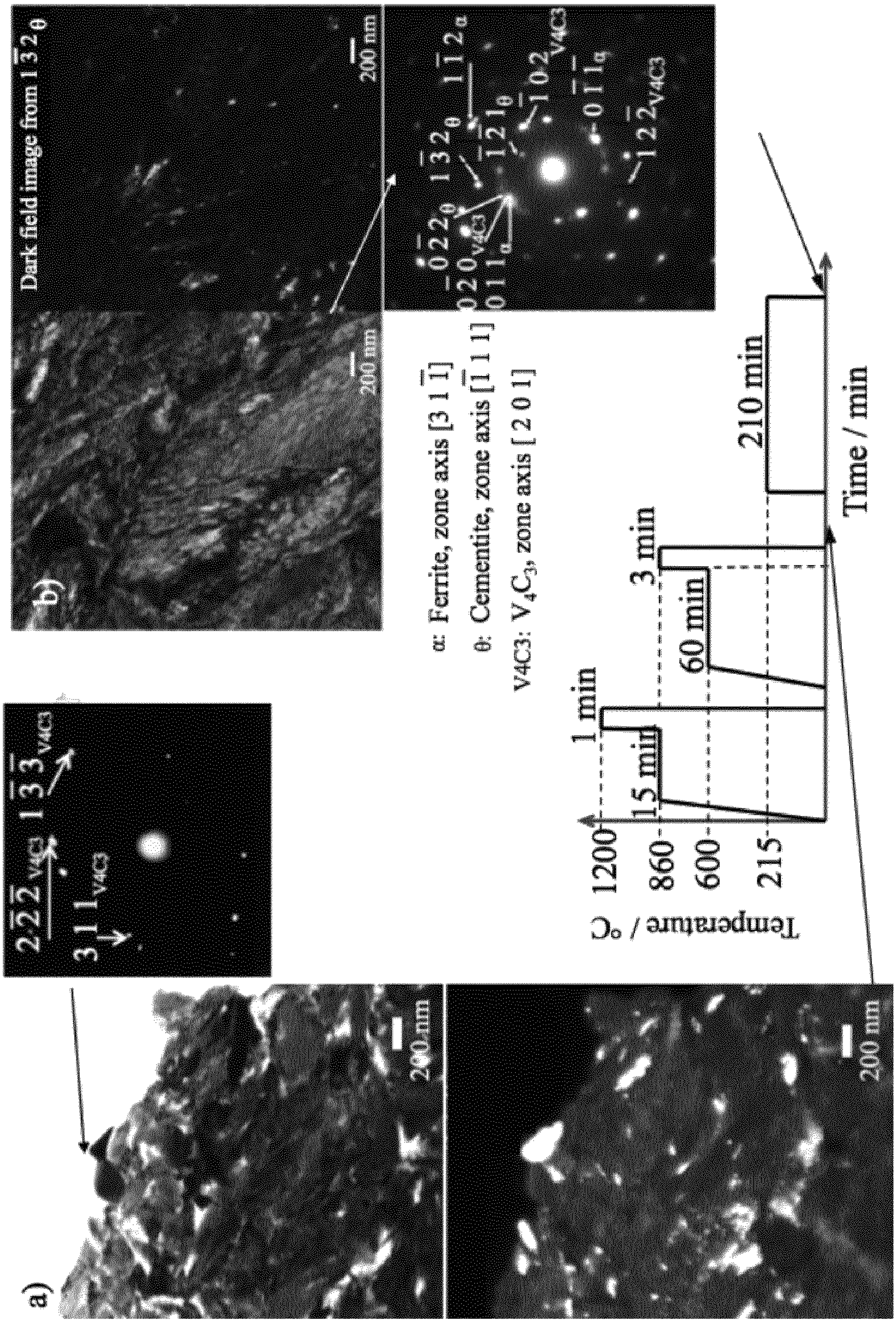
a)
200 nm
200 nm
2 2̄ 2̄ V4C3
3 1 1 V4C3
1 3̄ 3̄ V4C3
b)
200 nm
Dark field image from 1 3̄ 2 θ
200 nm
0 2̄ 2 θ
0 2 0 V4C3
0 1 1 α
1 3 2 θ
1̄ 2̄ 1 θ
1 1̄ 2 α
1̄ 0 2 V4C3
0 1̄ 1̄ α
1 2 2̄ V4C3
α: Ferrite, zone axis [3 1 1̄]
θ: Cementite, zone axis [1̄ 1 1]
V4C3: V4C3, zone axis [2 0 1]
Temperature / °C
1200
860
600
215
15 min
1 min
60 min
3 min
210 min
Time / min

Figure 4

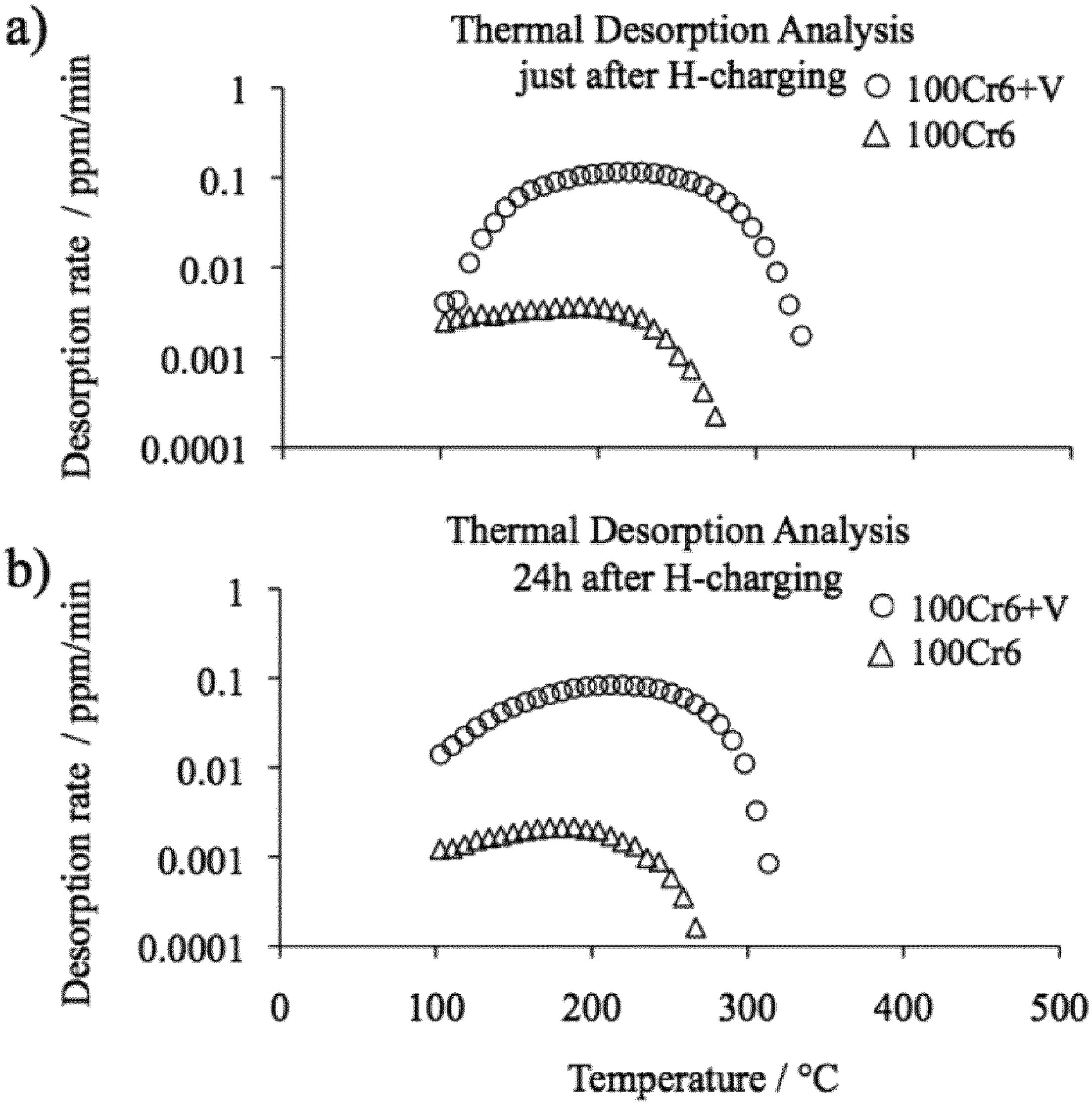
a)
Thermal Desorption Analysis
just after H-charging
○ 100Cr6+V
△ 100Cr6
Desorption rate / ppm/min
1
0.1
0.01
0.001
0.0001
b)
Thermal Desorption Analysis
24h after H-charging
○ 100Cr6+V
△ 100Cr6
Desorption rate / ppm/min
1
0.1
0.01
0.001
0.0001
0
100
200
300
400
500
Temperature / °C

Figure 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/065224

A. CLASSIFICATION OF SUBJECT MATTER
INV. C22C38/18 C21D9/40 C21D9/42
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)
C22C C21D

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, WPI Data, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2006/082673 A1 (NTN TOYO BEARING CO LTD [JP]; MAEDA KIKUO [JP]; MATSUBARA YUKIO [JP];) 10 August 2006 (2006-08-10) pages 1, 5-7; claims 1-2; figures 1-4; tables 1, ex.1, 3, 8,12 -----	1-4,6, 10,11, 13-20
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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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

"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

"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

"&" document member of the same patent family

Date of the actual completion of the international search
7 November 2012

Date of mailing of the international search report
14/11/2012

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Chebeleu, Alice

1

International application No
PCT/EP2012/065224

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	paragraphs [0029] - [0134]; claims 1-18	1-17

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1

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