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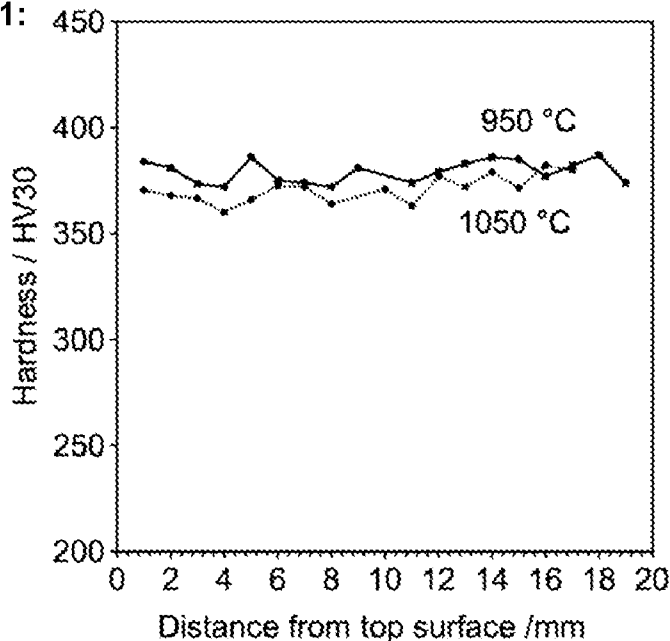
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(54) Title: MARTENSITIC STEEL ALLOY WITH RESISTANCE TO HYDROGEN EMBRITTLEMENT

Figure 1:



(57) Abstract: The present invention relates to a steel alloy and methods for the preparation thereof and its use. In particular, the steel alloy has a microstructure comprising tempered martensite, and: from 0.05 to 0.15 wt% carbon; from 1.0 to 4.0 wt% nickel; from 1.0 to 4.0 wt% chromium; from 0.1 to 0.5 wt% manganese; vanadium in an amount such that the molar ratio of V :C in the alloy is in the range: 0.7 to 1.3: 1; molybdenum and/or tungsten in an amount such that the molar ratio of (Mo + W) :C in the alloy is in the range 1.6 to 2.4:1; wherein the molar ratio of (Mo + W + V) :C in the alloy is at least 2.8 :1; optionally one or more of: from 0 to 0.01 wt% titanium; from 0 to 0.01 wt% niobium; from 0 to 0.01 wt% phosphorus; from 0 to 0.01 wt% sulphur; from 0 to 0.01 wt% nitrogen; from 0 to 0.01 wt% oxygen; from 0 to 2.0 wt% aluminium; from 0 to 0.8 wt% silicon; from 0 to 0.008 wt% boron; from 0 to 2.0 wt% copper; and the balance iron, together with unavoidable impurities.

MARTENSITIC STEEL ALLOY WITH RESISTANCE TO HYDROGEN
EMBRITTLEMENT

The present invention relates to a steel alloy, methods of manufacture and uses thereof. In particular, the invention is directed to a steel alloy having a microstructure comprising tempered martensite with mixed carbide precipitate dispersion which exhibits a unique combination of properties making it particularly useful for high stress applications, such as in the case of subsea structures. Specifically, the steel alloy of the invention exhibits high strength, good toughness and good hardness whilst at the same time also exhibiting good corrosion, hydrogen diffusion and hydrogen embrittlement resistance. Furthermore, the steel alloy is suitable for welding and may be prepared in tonnage quantities and with uniform properties, even across very thick forged sections.

Steel alloys are often utilised in constructions and installations which require the alloy to have particular properties to best suit the application and the operating conditions associated therewith. Often, high strength steel alloys are required in order to withstand severe operating conditions where there is exposure to high pressures (e.g. in excess of 200 MPa) and high temperatures (e.g. in excess of 200 °C). Steel alloys used in the preparation of subsea structures must be capable of withstanding such high stresses, as well as having sufficient resistance to corrosion and fracture.

A problem that is exacerbated by increasing the strength of steel alloys is hydrogen embrittlement resulting from exposure of the steel to diffusible (i.e. mobile) hydrogen.

For instance, martensitic steel alloys are known to have superior strength compared with austenitic alloys, yet martensitic alloys are generally more susceptible to hydrogen embrittlement. Hydrogen is able to diffuse through steel and collect in voids and cavities associated with dislocations within the microstructure creating pressure, which can ultimately lead to cracking. It can also modify the mechanical properties at the microstructure level, rendering the material more susceptible to failure / fracture.

EP 2803743 discloses a low alloy steel which contains, by mass percent, C: 0.01 to 0.15%, Si: 3% or less, Mn: 3% or less, B: 0.005 to 0.050%, and Al: 0.08% or less, and

the balance being Fe and impurities. This alloy is said to have good resistance to hydrogen embrittlement and may suitably be used in steel pipe, including for sea-bed pipelines. This document states that the presence of an amount of boron in the steel alloy can improve resistance to hydrogen embrittlement. Boron is known to facilitate formation of extended austenitic grains which improve hydrogen embrittlement resistance. However, there is no indication that this alloy is suitable for larger steel structures having thick forged sections.

EP1985720 discloses a high strength austenitic steel with resistance to hydrogen embrittlement comprising, by weight, C: 0.3 to 0.7%, Cr: 0.95 to 5.0%, Mn: 0.05 to 0.6%, and Si: 0.7 to 2.5%, and additionally containing at least one of Mg, Sr, Ba, Li, Na and K at no more than 0.05%. High Cr content is believed to confer good corrosion resistance, whilst Mg, Sr, Ba, Li, Na and/or K are present as hydroxide generators which suppress corrosion pitting, reduce hydrogen penetration and diffusion and therefore also increase hydrogen embrittlement resistance. The steel alloy is said to be suitable as high strength spring steel, although its high carbon content means that has low weldability.

EP 1676932 discloses a high strength martensitic thin steel sheet with resistance to hydrogen embrittlement comprising, by weight, C: 0.10 to 0.25%; Si: 1.0 to 3.0%; Mn: 1.0 to 3.5%; P: 0.15% or less; S: 0.02% or less; and Al: 1.5% or less (higher than 0%). The presence of lath-shaped residual austenite in the alloy is said to trap hydrogen and thereby improve hydrogen embrittlement resistance. However, this disclosure relates specifically to thin steel sheets of less than 5 mm thickness and not to thick forged sections that are of use in installations located in high stress environments.

EP 2492361 discloses a high strength steel pipe with high toughness at low temperature and good sulfide stress corrosion cracking resistance comprising, by weight, C: 0.05%-0.16%; Mn: 0.20%-0.90%; Si: 0.10%-0.50%; Cr: 1.20%-2.60%; Ni: 0.05%-0.50%; Mo: 0.80%-1.20%; Nb: <0.03%; Ti <0.02%; V: 0.005%-0.12%; Al 0.008%-0.040%; N: 0.0030-0.012%; Cu <0.3%; S <0.01% max, P: <0.02%, Ca: 0.001-0.005%; B <0.0020%; As <0.020%; Sb <0.0050%; Sn <0.020%; Zr <0.030%; Ta <0.030%; Bi <0.0050%; O <0.0030%; H <0.00030%, with the balance being iron

and inevitable impurities. The steel alloy may comprise tempered martensite as a major portion of the microstructure and exhibit no ferrite, no upper bainite, and no granular bainite.

- 5 Molybdenum is added to the steel composition of EP 2492361 to improve hardenability and assist in retarding softening during tempering, promoting the formation of very fine MC and M₂C precipitates which are uniformly distributed in the matrix. These carbides are thought to act as beneficial hydrogen traps, slowing down the atomic hydrogen diffusion towards dislocations, usually at grain boundaries, which
10 behave as crack nucleation sites. The presence of vanadium in the steel composition is also said to increase strength by precipitation of fine, round carbonitride particles during tempering which may also be substantially uniformly distributed within the matrix and act as beneficial hydrogen traps to reduce hydrogen embrittlement. However, EP 2492361 relates to steel pipes having a relatively thin wall thickness of
15 approximately between 8 to 35 mm. There is no indication that this steel alloy is suitable for use in thick sections that may be of use in installations located in high stress environments.

In order to be most effective, steel alloys used in high stress applications, such as for
20 subsea-structures, require a combination of properties such as high strength, toughness, hardenability and elongation. Whilst means are known for improving hydrogen embrittlement resistance in steel alloys as described hereinbefore, a steel alloy has not hitherto been proposed which exhibits properties useful for high stress applications, whilst at the same time exhibiting high hydrogen embrittlement
25 resistance; good weldability; uniformity across a thick section (e.g. on the order of 100 to 600 mm thickness); and be preparable in tonnage quantities. The present invention is based on the discovery of a steel alloy which exhibits all of the above advantageous properties together in combination for the first time.

- 30 In a first aspect, the present invention provides a steel alloy having a microstructure comprising tempered martensite, and:

from 0.05 to 0.15 wt% carbon;

from 1.0 to 4.0 wt% nickel;
from 1.0 to 4.0 wt% chromium;
from 0.1 to 0.5 wt% manganese;
vanadium in an amount such that the molar ratio of V : C in the alloy is in the
5 range: 0.7 to 1.3 : 1;
molybdenum and/or tungsten in an amount such that the molar ratio of (Mo +
W) : C in the alloy is in the range 1.6 to 2.4 : 1;
wherein the molar ratio of (Mo + W + V) : C in the alloy is at least 2.8 : 1;

10 optionally one or more of:

from 0 to 0.01 wt% titanium;
from 0 to 0.01 wt% niobium;
from 0 to 0.01 wt% phosphorus;
15 from 0 to 0.01 wt% sulphur;
from 0 to 0.01 wt% nitrogen;
from 0 to 0.01 wt% oxygen;
from 0 to 2.0 wt% aluminium;
from 0 to 0.8 wt% silicon;
20 from 0 to 0.008 wt% boron;
from 0 to 2.0 wt% copper;

and the balance iron, together with unavoidable impurities.

25 The combination of elements in the alloy, in the specified ranges, has been found to
give rise to a particular combination of advantageous properties once the tempered
martensite microstructure has been formed. In particular, tempered martensitic alloys
according to the present invention have been found to exhibit the following properties
in combination:

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- uniform through-thickness properties with forged sections of up to 150 mm thickness;
- Yield strength of from 650 to 1100 MPa;

- Ultimate Tensile strength of from 700 to 1200 MPa;
- Elongation (25 mm gauge length) of from above 10 % up to 25 % as measured according to BS EN 10002-1:2001;
- Charpy toughness of above 40 and even up to 280 J at -40 °C as measured according to ASTM E23-12c;
- Hydrogen trapping capacity of up to 8 ppmw as measured by thermal desorption analysis;
- Low apparent diffusivity of hydrogen of from 0.1 to $0.5 \times 10^{-11} \text{ m}^2\text{s}^{-1}$ as measured according to G 148 – 97 (Reapproved 2003);
- Vickers Hardness of from 230 to 370 (HV30);
- Weldable and retaining parent properties in the heat affected zone (HAZ), even in the absence of post-weld heat treatment (PWHT); and
- Microstructural and strength stability at a maximum service temperature of up to 250 °C.

The steel alloy according to the present invention comprises from 0.05 to 0.15 wt% carbon. Preferably, the steel alloy composition comprises from 0.05 to 0.12 wt% carbon, more preferably from 0.08 to 0.12 wt% carbon; even more preferably from 0.09 to 0.11 wt% carbon, for example 0.10 wt% carbon. In some embodiments, the steel alloy comprises from about 0.05 to 0.09 wt% carbon. The presence of carbon in the specified amount may serve to increase the strength and hardness of the steel alloy, primarily as a result of the formation of carbide precipitates. The formation of particular mixed carbide precipitates comprising carbon, chromium, vanadium, and tungsten/molybdenum also gives rise to the steel alloy's resistance to hydrogen embrittlement, as discussed below. However, the level of carbon in the steel alloy must be low enough such that the steel alloy remains weldable. Steel alloys used in high strength structural installations typically require welding in order to be secured.

The steel alloy according to the present invention comprises from 1.0 to 4.0 wt% nickel. Preferably, the steel alloy composition comprises from 2.0 to 4.0 wt% nickel; more preferably from 2.5 to 3.5 wt% nickel, even more preferably from 2.7 to 3.3 wt% nickel, for example 3.0 wt% nickel. The presence of nickel in the specified amount may serve to increase the low temperature toughness and hardenability and improve

impact strength. Nickel may also have a beneficial effect on lowering the martensitic transformation temperature.

5 The steel alloy according to the present invention comprises from 1.0 to 4.0 wt% chromium. Preferably, the steel alloy composition comprises from 1.5 to 3.5 wt% chromium; more preferably 2.0 to 3.0 wt% chromium; even more preferably from 2.3 to 2.7 wt% chromium, for example 2.5 wt% chromium. The presence of chromium in the specified amount may provide improved corrosion resistance. However, the upper limit of chromium used in the alloy of the invention is not sufficient to create a passive
10 film on the steel alloy, for instance through the formation of a hard oxide on the metal surface which acts to inhibit corrosion. Chromium may also have a beneficial effect on hardenability and lowering the martensitic transformation temperature. The presence of chromium in the specified amount can also provide the steel alloy with increased resistance to hydrogen embrittlement. As discussed in greater detail below, this
15 results from the formation of chromium containing mixed carbides, such as, for example, (V,Mo/W,Cr)(C), which are preferably nanometer-scaled (i.e. having a diameter of less than or equal to 100 nm).

The steel alloy according to the present invention comprises from 0.1 to 0.5 wt%
20 manganese. Preferably, the steel alloy composition comprises from 0.10 to 0.35 wt% manganese; more preferably from 0.15 to 0.25 wt% manganese, even more preferably from 0.17 to 0.23 wt% manganese, for example 0.20 wt% manganese. The presence of manganese in the specified amount, together with other alloying elements, may increase hardness and strength of the alloy and may also have a
25 beneficial effect on lowering the martensitic transformation temperature. Presence of manganese in the specified amount may also have a beneficial effect on weldability and reducing hot cracking on forging, as well as for fixing sulphur, which otherwise may have a detrimental effect on the alloy.

30 The steel alloy according to the present invention comprises vanadium in an amount such that the molar ratio of vanadium to carbon is in the range of 0.7 to 1.3 : 1, and such that the molar ratio of (Mo + W + V) : C in the alloy is at least 2.8 : 1, preferably the molar ratio of (Mo + W + V) : C in the alloy is at least 2.9 : 1. Preferably, vanadium

is present in an amount such that the molar ratio of vanadium to carbon in the steel alloy is in the range 0.8 to 1.2 : 1, more preferably wherein the molar ratio is in the range of 0.9 to 1.2 : 1, even more preferably wherein the molar ratio is in the range of 1.0 to 1.1 : 1. The presence of vanadium in the specified amount can provide the steel alloy with increased resistance to hydrogen embrittlement. As discussed in greater detail below, this results from the formation of vanadium containing mixed carbides, such as, for example, (V,Mo/W,Cr)(C), which are preferably nanometer-scaled (i.e. having a diameter of less than or equal to 100 nm). Vanadium may also act to increase the hardness of the alloy and the yield strength and/or tensile strength and may also have a beneficial effect on lowering the martensitic transformation temperature.

The steel alloy according to the present invention comprises molybdenum and/or tungsten in an amount such that the molar ratio of (Mo + W) : C is in the range of 1.6 to 2.4 : 1, and such that the molar ratio of (Mo + W + V) : C in the alloy is at least 2.8 : 1, wherein preferably the molar ratio of (Mo + W + V) : C in the alloy is at least 2.9 : 1. Preferably, molybdenum and/or tungsten are present in an amount such that the molar ratio of (Mo + W) : C is in the range of 1.8 to 2.4 : 1, more preferably wherein the molar ratio is in the range of 2.0 to 2.4 : 1, even more preferably in the range of 2.2 to 2.4 : 1. The presence of molybdenum and/or tungsten in the specified amount can provide the steel alloy with increased resistance to hydrogen embrittlement. As discussed in greater detail below, this results from the formation of certain mixed carbides such as, for example, (V,Mo/W,Cr)(C), which are preferably nanometer-scaled (i.e. having a diameter of less than or equal to 100 nm). Molybdenum and tungsten may also act to increase the hardenability of the alloy and may also have a beneficial effect on lowering the martensitic transformation temperature.

Thus, in some embodiments, the steel alloy of the present invention comprises molybdenum and tungsten or one of these elements may be present in the substantial absence of the other. It will therefore be appreciated that where reference is made herein to a molar ratio incorporating the sum of the molar amounts of molybdenum and tungsten (i.e. "(Mo + W) : C" or "(Mo + W + V) : C"), if either of molybdenum or

tungsten are absent from the alloy then the molar sum of those components will correspond to the molar amount of either one of those elements that is present alone.

5 Tungsten containing carbides have a weaker hydrogen-trapping effect than molybdenum containing carbides. Tungsten is also significantly more expensive than molybdenum as a raw material. Therefore, in preferred embodiments, the steel alloy of the invention comprises molybdenum but tungsten is not present or present only as an unavoidable impurity. Where molybdenum is present in the alloy in the substantial absence of tungsten, the molar ratio of molybdenum to carbon in the alloy is suitably
10 in the range of 1.6 to 2.4 : 1. Preferably, the molar ratio of molybdenum to carbon in the alloy is in the range of 1.8 to 2.2 : 1, more preferably wherein the molar ratio is in the range of 1.85 to 2.1 : 1.

15 In other embodiments, the steel alloy of the invention comprises tungsten but molybdenum is not present or present only as an unavoidable impurity. Where tungsten is present in the alloy in the substantial absence of molybdenum, the molar ratio of tungsten to carbon in the alloy may be in the range of 1.6 to 2.4 : 1. Preferably, the molar ratio of tungsten to carbon in the alloy is in the range of 1.8 to 2.2 : 1, preferably wherein the molar ratio is in the range 1.85 to 2.1 : 1.

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The steel alloy according to the invention may optionally comprise up to 0.01 wt% titanium, for example from 0.001 to 0.005 wt% titanium. Preferably, the content of titanium in the steel alloy of the invention is kept to a minimum.

25 The steel alloy according to the invention may optionally comprise up to 0.01 wt% niobium, for example from 0.001 to 0.005 wt% niobium. Preferably, the content of niobium in the steel alloy of the invention is kept to a minimum.

30 The steel alloy according to the invention may optionally comprise up to 2.0 wt% aluminium, for example from 0.01 to 0.05 wt% aluminium. Aluminium may be used as a deoxidiser in the alloy or aluminium may also act to control grain size in the alloy. The presence of nickel in the alloy of the invention may also result in the formation of NiAl, which can further enhance the strength of the steel alloy.

The steel alloy according to the invention may optionally comprise up to 0.8 wt.% silicon, for example from 0.01 to 0.1 wt% silicon. Silicon may also be used as a deoxidizer and may also contribute the steel's strength and hardness.

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The steel alloy according to the invention may optionally comprise up to 0.008 wt.% boron, for example from 0.001 to 0.005 wt% boron.

10 The steel alloy according to the invention may optionally comprise up to 2.0 wt.% copper, for example from 0.1 to 0.5 wt% copper. Copper may act to provide improved corrosion resistance and copper precipitates may form which can strengthen the steel.

15 Other elements that may be present in the alloy according to the invention include oxygen, nitrogen, phosphorus and sulphur at a maximum individual content of 0.01 wt%. Preferably, the presence of these elements is kept to a minimum. If phosphorus is present, it is preferably less than 0.005 wt%. If sulphur is present, it is preferably less than 0.005 wt%. If oxygen is present, it is preferably less than 0.01 wt%. If nitrogen is present, it is preferably less than 0.005 wt%.

20 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, sulphur, oxygen and nitrogen contents are preferably kept to
25 a minimum.

The steel alloy 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
30 provided that the essential characteristics of the composition are not materially affected by their presence.

With regard to the above described aspect and embodiments of the invention, it will be appreciated that any embodiment may be combined together with other compatible embodiments of the invention. A particularly preferred embodiment of the present invention is where the steel alloy comprises or consists essentially of:

- 5
- from 0.09 to 0.11 wt% carbon;
 - from 2.7 to 3.3 wt% nickel;
 - from 2.3 to 2.7 wt% chromium;
 - from 0.17 to 0.23 wt% manganese;
 - 10 vanadium in an amount such that the molar ratio of V : C in the alloy is in the range of 1.0 to 1.1 : 1;
 - molybdenum in an amount such that the molar ratio of Mo: C in the alloy is in the range of 1.8 to 2.0 : 1;
 - wherein the molar ratio of (Mo + V) : C in the alloy is at least 2.9 : 1;
 - 15
 - less than 0.005 wt% phosphorus;
 - less than 0.005 wt% sulphur;
 - less than 0.005 wt% oxygen;
 - less than 0.005 wt% nitrogen;
 - 20
 - and optionally one or more of:
 - from 0.001 to 0.005 wt% titanium;
 - from 0.001 to 0.005 wt% niobium;
 - 25 from 0.01 to 0.05 wt% aluminium;
 - from 0.01 to 0.1 wt% silicon;
 - from 0.001 to 0.005 wt% boron;
 - from 0.1 to 0.5 wt% copper;
 - 30
 - and the balance iron, together with unavoidable impurities.

The particular molar ratio of vanadium to carbon and molybdenum/tungsten to carbon specified herein, namely that vanadium is present in an amount such that the molar

ratio of V : C in the alloy is in the range: 0.7 to 1.3 : 1; molybdenum and/or tungsten is/are present in an amount such that the molar ratio of (Mo + W) : C in the alloy is in the range 1.6 to 2.4 : 1; and wherein the molar ratio of (Mo + W + V) : C in the alloy is at least 2.8 : 1, has been found to be particularly advantageous in the present invention. In that regard, the ratio of these elements, together with the amount of chromium specified, has been found to give particularly favorable mixed carbide precipitation in the alloy such that good strength, toughness and hardenability can be obtained in combination with the other essential elements of the steel composition whilst at the same time obtaining increased hydrogen embrittlement resistance. The mixed carbides formed in the steel alloy of the invention, (V,Mo/W,Cr)(C), differ from M_2C (where M = W or Mo) and V_4C_3 carbide precipitates which have been identified in other steel alloys not of the invention.

As described in more detail below, mixed carbide precipitates contained in the steel alloys of the present invention include carbon together with at least vanadium, molybdenum (as well as tungsten, if present) and chromium, and may also include one or more additional alloying elements. The term carbide as used herein is intended to encompass a compound composed of carbon and one or more elements contained in the steel alloy. The term preferably does not cover oxygen and nitrogen containing precipitants, such as carbo-nitrides and carbo-oxy-nitrides.

Carbon is required in the steel alloy of the invention in order to provide a source for carbide precipitation and also to increase hardenability and lower the martensitic phase transformation temperature (M_s). However, the level of carbon cannot be so high that weldability of the alloy is negatively impacted. Therefore, the present invention also balances the amount of carbon required for carbide formation in order to achieve hydrogen embrittlement resistance and the other properties mentioned above with the need to ensure that the alloy is weldable.

Chromium, vanadium and molybdenum/tungsten elements of the alloy of the present invention lead to the formation of stable mixed carbides comprising those elements. These stable carbides have been found to be beneficial for conferring hardenability to the steel alloy, whilst also acting to increase resistance to hydrogen embrittlement.

Carbides based on chromium, vanadium, molybdenum and/or tungsten can act as hydrogen traps, where hydrogen is held in an innocuous form and prevented from accumulating in cavities and voids associated with dislocations in the microstructure. Hydrogen trapping thus mitigates hydrogen embrittlement.

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The carbides based on carbon, chromium, vanadium and molybdenum/tungsten elements have been found to form a fine, uniform dispersion of (V,Mo/W,Cr)(C) carbides in the matrix of the steel alloy according to the present invention. The carbides based on chromium, vanadium and molybdenum/tungsten elements have been found to be nanometer-scaled (i.e. having a diameter of less than 100 nm). In that regard, the presence of molybdenum and/or tungsten generally retards the growth of the carbide precipitates, for instance during tempering, which would otherwise have an increased softening effect on the alloy. Moreover, coarsening of the carbide precipitates negatively impacts upon coherency strain fields around the carbides; lowering the capacity for hydrogen trapping and thereby reducing resistance to hydrogen embrittlement.

Thus, in preferred embodiments, mixed carbide precipitates based on carbon, chromium, vanadium and molybdenum/tungsten in the steel alloys of the present invention 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. Mixed carbide precipitates based on carbon, vanadium or molybdenum/tungsten formed in the alloy of the invention have been found to have a fine disk/plate shaped morphology, which is considered to be particularly advantageous in terms of hydrogen trapping ability.

The ratio of V, Mo/W and C in the alloy of the invention also ensures there are adequate amounts of vanadium and molybdenum/tungsten, together with chromium, to eliminate substantially all of the cementite which forms during tempering of martensite, which would otherwise negatively impact upon the properties of the alloy. Carbide precipitation resulting from the particular ratio of V, Mo/W and C, in addition to the specified amount of chromium, in the alloy of the invention thus confers desirable

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strength and hardenability, in combination with the other essential elements of the compositions, whilst also providing hydrogen embrittlement resistance. This combination of properties is particularly unexpected for a steel alloy comprising a martensitic microstructure. Surprisingly, it has also been found that the steel alloy composition of the present invention has a greater resistance to hydrogen diffusion through the alloy compared with conventional steel alloys used in high stress applications (e.g. ASTM A182 Grade F22 steel). This is believed to enhance the hydrogen embrittlement resistance of the steel alloy of the invention even further.

The alloy of the present invention has a microstructure comprising martensite. Preferably, the microstructure comprises at least 70 vol.% martensite, more preferably at least 80 vol.% martensite, most preferably at least 90 vol.% martensite.

More particularly, the martensitic alloy of the present invention is a tempered martensite. Tempering martensite typically reduces the hardness and brittleness of the alloy and improves toughness. As explained in more detail below, the initial stages of tempering step lead to the formation of cementite precipitates which can have a detrimental effect on the properties of the alloy. However, adequate further tempering can provide an alloy in which the cementite is substantially eliminated as a result of the presence of vanadium and molybdenum/tungsten elements in the specified ratio. Thus, preferably the steel alloy according to the invention comprises less than 2.5 vol.% cementite, more preferably less than 1 vol.% cementite, most preferably less than 0.05 vol.% cementite. Tempering also substantially eliminates the presence of any retained austenite phase in the steel alloy of the present invention. Preferably, the microstructure comprises less than 0.5 vol.% retained austenite phase, more preferably the microstructure comprises less than 0.01 vol.% retained austenite phase, and most preferably the microstructure comprises substantially no retained austenite phase. The volume fraction of martensite, retained austenite and cementite in the alloy may suitably be measured according to ASTM E562-08 or ASTM E1245.

The tempered martensite formed in the steel alloy microstructure in accordance with the present invention typically consists of laths (strips) or plates. Meanwhile, as mentioned above, it has been found that the carbide precipitates based on carbon,

chromium, vanadium and molybdenum/tungsten have a fine disk/plate shaped morphology which is considered to be particularly advantageous in terms of hydrogen trapping ability.

- 5 The structure of the steel alloy described herein can be determined by conventional microstructural characterization techniques such as, for example, optical microscopy, TEM, SEM, AP-FIM, TDA and X-ray diffraction, including combinations of two or more of these techniques.
- 10 The steel alloy of the present invention is preparable in tonnage quantities and in the form of large forged sections which advantageously have uniform properties across their thicknesses. In some embodiments, the thickness of the installation component can be 25 to 200 mm, preferably a thickness of 100 to 150 mm.
- 15 The steel alloy of the present invention is of use in all applications where the advantageous properties of the alloy, such as high strength in combination with high hydrogen embrittlement resistance, may be desirable. For example, the steel alloy of the present invention may be deployed in numerous applications relevant to oil and/or gas exploration and recovery. The steel alloy of the invention may thus be utilized in
- 20 wells, completions or subsea equipment/facilities, and including, for instance, in tubulars and downhole equipment.

In another aspect, the present invention provides a subsea structure component comprising a steel alloy according to the invention as described hereinbefore.

- 25 Reference herein to a subsea structure is intended to mean any subsea structure which is suitable for use in offshore oil and/or gas field applications and includes fixed and mobile subsea structures. Examples of subsea structures include manifolds, pipeline end terminations, well bore heads, pipeline end manifolds, subsea trees, submersible structures, semi-submersible structures and the like. A component of a
- 30 subsea structure may, for instance, correspond to a steel pipe section intended for use as sea-bed conduit, a riser or a connector component.

In yet another aspect, the present invention provides a use of an alloy as described hereinbefore in oil and/or gas field applications, preferably subsea applications, for example in subsea structures described hereinbefore..

- 5 The steel alloy of the present invention may suitably be prepared by solution heat treatment, cooling and tempering steps, of which the person of skill in the art is aware, in order to obtain an alloy having a microstructure comprising tempered martensite.

Thus, in a further aspect, the present invention provides a method for preparing a
10 steel alloy as described hereinbefore, comprising:

- (i) providing a steel alloy composition comprising, and:

from 0.05 to 0.15 wt% carbon;
15 from 1.0 to 4.0 wt% nickel;
from 1.0 to 4.0 wt% chromium;
from 0.1 to 0.5 wt% manganese;
vanadium in an amount such that the molar ratio of V : C in the alloy is in the range: 0.7 to 1.3 : 1; molybdenum and/or tungsten in an amount such that the
20 molar ratio of (Mo + W) : C in the alloy is in the range 1.6 to 2.4 : 1; wherein the molar ratio of (Mo + W + V) : C in the alloy is at least 2.8 : 1;

optionally one or more of:

25 from 0 to 0.01 wt% titanium;
from 0 to 0.01 wt% niobium;
from 0 to 0.01 wt% phosphorus;
from 0 to 0.01 wt% sulphur;
from 0 to 0.01 wt% nitrogen;
30 from 0 to 0.01 wt% oxygen;
from 0 to 2.0 wt% aluminium
from 0 to 0.8 wt% silicon;
from 0 to 0.008 wt% boron;

from 0 to 2.0 wt% copper;

and the balance iron, together with unavoidable impurities;

- 5 (ii) heating the composition at a temperature of from 750 °C to 1200 °C to at least partially austenitise the composition;
- (iii) cooling the austenitised composition from step (ii) to form a martensite phase;
- (iv) further heating the product of step (iii) at a temperature of from 400 °C to 700 °C.

10

It will be appreciated that the elements and weight ranges thereof in the steel alloy described hereinbefore may suitably be used for providing a steel composition for undergoing the above heat treatment for conversion to a tempered martensite. Therefore, where preferred steel alloys are described hereinbefore, the elemental composition and weight ratios are also preferably used in providing a steel composition for heat treatment in accordance with the above further aspect of the invention.

15

In step (i), the composition of elements in addition to iron is provided, for instance, by melting, followed by casting and forging, as is well understood by a person of skill in the art. Between casting and forging the composition may be held at a specific temperature after being taken out from the mould. Cutting of the melt, as well as hot rolling at a suitable forging reduction ratio (e.g. 3:1 to 5:1, preferably 4:1), and optionally finish rolling may also be undertaken after forging.

25

In step (ii), the composition is at least partially austenitised, preferably completely austenitised. This may be achieved by heating the alloy composition to a temperature of from 700 to 1200 °C, preferably from 750 to 1000 °C, more preferably from 800 to 900 °C. The steel or forged composition may be maintained in this temperature regime for any suitable time period to achieve the desired level of austenisation, which is dependent on heating rate, as well as the dimension and shape of the material. For example, the temperature may be maintained for up to 6 hours, preferably up to 2 hours, more preferably from 30 minutes to 90 minutes, or even more preferably for

30

about 1 hour. However, longer heating times are also possible. Step (ii) may result in the formation of (V,Mo/W,Cr)(C) mixed carbides. Step (ii) is not expected to give rise to any formation of cementite.

5 The heat treatment of step (ii) has an effect on the prior austenite grain size that is produced. In particular, higher treatment temperatures tend to produce larger prior austenite grain sizes. The average prior austenite grain size can, for instance, be measured in accordance with ASTM E112. Nevertheless, austenite grain size has not been found to materially affect the hardness evolution following conversion to
10 martensite and tempering according to steps (iii) and (iv). Although, the amount of carbide precipitates that form versus the amount of carbide forming elements that are retained in the matrix is affected by the austenisation temperature, this has not been observed to significantly affect the hardness of the tempered martensite ultimately obtained.

15 In step (iii), the at least partially austenitised composition is cooled in order to effect a phase change to martensite. Thus, the microstructure converts from a face-centred cubic (FCC) austenitic phase to a body-centered tetragonal (BCT) or body-centred cubic (BCC) martensitic phase as the martensite start temperature (M_s) is reached.
20 Cooling may suitably be undertaken such that the temperature of the alloy composition is, for example, below 150 °C, preferably below 100 °C, more preferably below 50 °C.

Normally, in order to form a martensite phase it is necessary to implement rapid
25 quench cooling, for instance in an oil or water bath. Typically, as the cooling rate increases, the risk of forming other non-martensitic products is reduced, but the distortion in the component potentially increases, and the section thickness of a part that can be processed thus decreases. Quench cooling is logistically difficult for larger forged sections, particularly those which are preparable in tonnage quantities, and it is
30 difficult to achieve a fast, uniform rate of cooling throughout the thickness of the section. It is therefore normally difficult to prepare a martensitic phase with uniform properties in a forged section over certain thicknesses (e.g. above 30 mm).

With the steel alloy composition of the present invention, both very fast cooling (e.g. at a rate of over $3000\text{ }^{\circ}\text{C h}^{-1}$) and even very slow controlled cooling (e.g. at a rate of about $60\text{ }^{\circ}\text{C h}^{-1}$) have been found to form the desired martensite microstructure. This is particularly advantageous because it means that very thick sections can be readily
5 formed by simply slow cooling, rather than rapid quenching. Thus, it is possible to prepare very thick sections with uniform properties which are suitable for use in larger installations located in high stress environments, such as in the case of subsea applications.

10 The rate of cooling which may be used in step (iii) may therefore vary considerably without impacting significantly on the formation of the martensite phase. For example, the cooling rate may range from $50\text{ }^{\circ}\text{C h}^{-1}$ to $5000\text{ }^{\circ}\text{C h}^{-1}$. In some embodiments, a slow, controlled cooling rate may be implemented in the range of $50\text{ }^{\circ}\text{C h}^{-1}$ to $150\text{ }^{\circ}\text{C h}^{-1}$, for example $60\text{ }^{\circ}\text{C h}^{-1}$, or $120\text{ }^{\circ}\text{C h}^{-1}$. In preferred embodiments, a fast cooling rate
15 may be implemented in the range of $2000\text{ }^{\circ}\text{C h}^{-1}$ to $4000\text{ }^{\circ}\text{C h}^{-1}$, for example $3400\text{ }^{\circ}\text{C h}^{-1}$. Cooling may be achieved by quenching with a suitable medium such as oil, water or an inert gas. Air-cooling or controlled furnace cooling may also be used.

The hardening and softening behaviour of the martensite during tempering in step (iv)
20 is affected by the rate of cooling. In general, where very fast cooling is adopted (e.g. at a rate of over $2000\text{ }^{\circ}\text{C h}^{-1}$), higher resistance to softening during the subsequent tempering step (iv) is observed compared with controlled slow rate cooling (e.g. at a rate of 50 to $150\text{ }^{\circ}\text{C h}^{-1}$). Furthermore, the peak hardness achieved during the subsequent tempering step (iv) is also observed to be higher in the case of samples
25 cooled at a very fast rate compared with those cooled at a slow rate. This is believed to relate to the increased formation and coarsening of carbide precipitates during slow cooling. Coarsening of the carbide precipitates has a deleterious effect on hardness, whilst the presence of coarse carbide precipitates formed during cooling also reduces the level of 'fresh' precipitation of fine carbides during the tempering stage which
30 would otherwise contribute to hardness.

In step (iv) of the process, the martensitic product of cooling step (iii) is tempered by heating, typically with the object of reducing hardness (softening) and increasing

toughness. Although heating may initially increase levels of hardness by inducing further carbide precipitation, further tempering leads to coarsening of the fresh and existing carbide precipitates leading to a reduction in hardness. Tempering is suitably undertaken at a temperature of from 400 °C to 700 °C, preferably 550 °C to 650 °C, for example 600 °C and may suitably be carried out over a time period of 30 minutes to 100 hours, preferably 6 hours to 24 hours, more preferably 8 to 12 hours.

Carbon is an interstitial solute in iron and has a high mobility. Consequently, iron carbides are the first to form on tempering virgin martensite and, as such, cementite precipitates first in the tempering process. Cementite precipitates contribute towards hardness, but negatively impact upon toughness and they have little or no hydrogen trapping qualities that make them useful for hydrogen embrittlement resistance. The presence of cementite in the tempered martensite is therefore desirably minimised. Cementite is less stable than other alloy carbides and, over the course of tempering, chromium, vanadium and molybdenum/tungsten mixed carbide precipitates form and grow at the expense of cementite, which eventually leads to its complete dissolution. The tempering step is therefore preferably conducted for a time period such that a desired amount of precipitation and coarsening of chromium, vanadium and molybdenum/tungsten based mixed carbides is achieved together with dissolution of cementite precipitates.

The skilled person is able to select a suitable time period over which tempering is performed depending on the tempering temperature and the desired degree of softening and/or toughening required based on carbide precipitation and coarsening and cementite dissolution. For instance, it is known that the time period for tempering may be reduced when tempering temperature is increased. Furthermore, the skilled person is able to modify the degree of tempering based on the nature of the cooling step implemented to form the martensite phase. For example, if slow cooling has been adopted, less tempering will be required since the peak hardness of the alloy will be lower. Alternatively, more tempering will be required to achieve an adequate reduction in hardness when fast cooling has been implemented since the peak hardness will be higher, as explained above.

The transformation from austensite to martensite during cooling results from shear-stresses created in the crystal lattices which give rise to the formation of dislocations between the crystals. During tempering, diffusible carbon can precipitate in these dislocation sites in the microstructure and form cementite (Fe_3C), to the detriment of alloy toughness, which increases as the cementite grains coarsen during tempering. However, vanadium and molybdenum/tungsten elements of the alloy of the present invention replace the iron component of the carbide precipitates and therefore convert cementite into alternative stable carbides. These stable carbides have been found to be beneficial for conferring hardness to the steel alloy, whilst also acting to increase resistance to hydrogen embrittlement.

Mixed carbides based on chromium vanadium, and molybdenum/tungsten act as “hydrogen traps”, where hydrogen is held in an innocuous form and does not accumulate as hydrogen molecules, as it would otherwise do, in cavities and voids associated with dislocations in the microstructure. Hydrogen trapping thus mitigates hydrogen embrittlement. The mixed carbides formed in the tempered martensite in the presence of chromium, vanadium and molybdenum/tungsten elements in accordance with the invention generally correspond to a fine dispersion of mixed carbides in the matrix. In that regard, molybdenum and tungsten retard the growth of the mixed carbide precipitates during the tempering process which otherwise can have an overly softening effect on the alloy and reduce the hydrogen trapping properties of the carbides.

The invention will now be described by reference to the following Examples and Figures, wherein:

Figure 1: shows the hardness across the thickness of the hot rolled steel used in the examples prior to heat treatment to convert to tempered martensite;

Figure 2a: shows the hardness of the alloy during tempering at 600 °C as a function of the prior cooling condition;

Figure 2b: shows the effect of tempering temperature on hardness evolution after solution heat treatment at 1050 °C and air-cooling;

5 Figure 2c: shows the effect of solution heat treatment on hardness evolution during tempering at 600 °C for air-cooled samples;

Figure 2d: shows a comparison of the effect of solution heat treatment on hardness evolution during tempering at 600 °C for control cooled ($120\text{ }^{\circ}\text{C h}^{-1}$) samples;

10 Figure 3a: shows the effect of tempering time and temperature after solution heat treatment at 950 °C on yield strength and proof strength of the alloy;

Figure 3b: shows the effect of solution heat treatment temperature (not austenisation time) after tempering at 600 and 650 °C for 10 h on yield strength and proof strength
15 of the alloy;

Figure 4: shows a plot of 0.2 % proof strength (YS) and ultimate tensile strength (UTS) versus elongation for alloy samples of the invention;

20 Figure 5: shows the relationship between impact toughness and tensile strength for the alloy of the invention, as well as comparison of the Charpy toughness against industry standard steel alloy, F22 (ASTM A182 Grade);

Figure 6: is a light microscopy image showing a tempered martensite microstructure
25 for an alloy of the invention obtained by solution treatment at 1050°C for 0.5 h, air cooling, followed by tempering at 600°C for 10 h;

Figure 7: shows the transmission electron micrograph of an alloy of the invention obtained after tempering at 600 °C for 10 h;

30

Figure 8: shows the thermal desorption system used in the thermal desorption analysis; and

Figure 9: shows the hydrogen thermal desorption spectra of alloys of the invention obtained after: (i) austenitization at 850 °C for 3.5 h before tempering temperature at 600 °C for 10 h; or (ii) austenitization at 850 °C for 5.85 h before tempering at 625 °C for 10 h, as well as the hydrogen thermal desorption spectra for industry standard steel alloy, F22 (ASTM A182 Grade).

Examples

Test alloy

A steel alloy melt was prepared and a 100 kg cast ingot formed, which was subsequently cut into 125×125×90 mm sample blocks and hot rolled to 20 mm thick plates (corresponding to a forging reduction ratio of 4.5 to 1). The reheating condition before seven passes of hot rolling was 1250 °C for 1 h. Two different finish rolling temperatures (1050 °C and 950 °C) were chosen to investigate the consequences of potential temperature non-uniformity during industrial forging on alloy behaviour. The measured chemical composition of the alloy is shown in Table 1 below (elements in wt % and the balance being iron).

Table 1

Element	C	Mn	Cr	V	Mo	Ni	Si	P	S	O	N
Wt%	0.10	0.21	2.4	0.44	1.5	2.8	0.054	0.0044	0.0026	0.0033	0.0029

Molar ratio of V to C in test alloy = 1.06 : 1

Molar ratio of Mo to C in test alloy = 1.88 : 1

Molar ratio of (V + Mo) to C in test alloy = 2.94 : 1

Analysis

Metallographic techniques were used to characterize the steel alloy before and after heat treatment. Prior austenite grain sizes were measured using linear intercept method according to ASTM E112. The hardness was measured using a Vickers hardness machine. Samples for tensile and standard Charpy impact tests were cut from plates in longitudinal and transverse directions. Impact tests were carried out at -

40 °C using standard Charpy V-notched specimens and measured according to ASTM E23-12c. The tensile tests were performed using cylindrical specimens of 4 mm diameter and 20 mm gauge length using a strain rate of 0.002 s^{-1} at room temperature and measured according to BS EN 10002-1:2001. Light microscopy was used to visualise the microstructure of the tempered martensite and transmission electron microscopy (TEM) was used to undertake a preliminary identification of the carbides generated by tempering.

Figure 1 illustrates the Vickers hardness across the thickness of the hot rolled steel prior to heat treatment to convert to tempered martensite. Figure 1 shows that uniform hardness is achieved across the thickness for both processing conditions, within expected experimental variation. The hardness obtained in the processed steel with a low finish rolling temperature is slightly higher than steel prior to processing or following processing with a higher finish rolling temperature.

Heat Treatment

As part of the heat treatment investigation, the steel was solution heat treated under various conditions, cooled with different cooling rates and tempered at different temperatures over varying time periods. Vickers hardness evolution results are provided in Figures 2a to 2d, wherein **ST** = Solution temperature; **TT** = Tempering temperature, **CR** = Cooling rate; Dashed line = Finish rolling temperature of 950 °C; Solid line = Finish rolling temperature of 1050°C.

Example 1

Three sample plates of each of the test alloys obtained with the two finish rolling temperatures (1050 °C and 950 °C) were austenitised at 1050 °C for 30 min in a furnace before being i) air-cooled at a rate of approximately 3400 °C h^{-1} to room temperature (approximately 20 to 25 °C); ii) furnace cooled at a controlled rate of 120 °C h^{-1} ; and iii) furnace cooled at a controlled rate of 60 °C h^{-1} . The cooled samples were subsequently tempered at 600 °C, during which the Vickers hardness of the samples was measured to monitor hardness evolution over the course of tempering.

Results for the hardness evolution are provided in Figure 2a, which shows that the cooling rate has an effect on the hardening and softening behaviour of the different samples during tempering. Higher resistance to softening is observed in the air-cooled sample with the highest rate of cooling, irrespective of the difference in finish rolling temperature. Higher peak hardness is also observed in the air-cooled sample with high finish rolling temperature. Formation of carbides during slow cooling as described hereinbefore is thought to be a likely reason for differences observed for the different cooling rates.

Figure 2a demonstrates that similar hardenability may be obtained during tempering despite differences in cooling rates; indicating that martensite formation is not affected by the rate of cooling. As discussed hereinbefore, this is particularly advantageous in terms of preparation of tonnage quantities of the heat treated alloy and also preparation of very thick sections, for instance, those which are suitable for large forged parts of subsea structures. Fast cooling, which is typically required for the formation of the martensite microstructure, can be physically difficult to achieve in such large samples.

Example 2

Two sample plates of each of the test alloys obtained with the two finish rolling temperatures (1050 °C and 950 °C) were austenitised at 1050 °C for 30 min in a furnace before being air-cooled at a rate of approximately 3400 °C h⁻¹ to room temperature (approximately 20 to 25 °C). The cooled samples were subsequently tempered at either 600 °C or 650 °C, during which the Vickers hardness of the samples was measured to monitor hardness evolution over the course of tempering.

Results for the hardness evolution are provided in Figure 2b, which shows that tempering temperature has an effect on hardness evolution. Peak hardness is observed after a shorter period of time when tempering at the higher tempering temperature (650 °C), following which hardness decreases monotonically with time. Rate of hardness decrease for the higher tempering temperature (650 °C) is also

greater than at the lower tempering temperature (600 °C). Little difference in hardness evolution is observed as a result of the different finish rolling temperatures prior to heat treatment. As discussed hereinbefore, the reason for the difference in hardness evolution based on tempering temperature is believed to be related to coarsening of the precipitates, which is thought to occur at a faster rate at higher temperatures.

Example 3

Three sample plates of each of the test alloys obtained with the two finish rolling temperatures (1050 °C and 950 °C) were austenitised in a furnace at i) 1050 °C for 30 min; ii) 950 °C for 4 h; and iii) 850 °C for 2 h, before being air-cooled at a rate of approximately 3400 °C h⁻¹ to room temperature (approximately 20 to 25 °C). The cooled samples were subsequently tempered at 600 °C, during which the Vickers hardness of the samples was measured to monitor hardness evolution over the course of tempering.

Results for the hardness evolution are provided in Figure 2c, which shows that there is no significant variation in hardness as a result of the different solution heating temperatures adopted. The microstructural differences noted after heat treatment at different solution temperatures, include variations in prior austenite grain size, amount of carbide precipitates that form during solution treatment and the carbide forming elements that are left in the solution. The austenite grain size does not influence the hardness evolution, but the carbide forming elements left in the solution will. Based on these results, variation in solution treatment conditions over the range studied is not expected to significantly influence the evolution of hardness during tempering.

Example 4

Two sample plates of each of the test alloys obtained with the two finish rolling temperatures (1050 °C and 950 °C) austenitised in a furnace at i) 1050 °C for 30 min; and ii) 850 °C for 2 h, before being furnace cooled at a controlled rate of 120 °C h⁻¹ to room temperature (approximately 20 to 25 °C). The cooled samples were

subsequently tempered at either 600 °C, during which the Vickers hardness of the samples was measured to monitor hardness evolution over the course of tempering.

Results for the hardness evolution are provided in Figure 2d, which shows that there is no significant effect in the long term tempering behaviour resulting from the different solution heat treatments used. However, there is a difference in terms of the peak hardness obtained, with a greater peak hardness associated with the lower solution treatment temperature. As discussed hereinbefore, the carbide precipitate present after the solution treatment will continue to coarsen during slow cooling, which affects the amount of 'fresh' carbide available for precipitation during tempering. Fine carbide precipitates that are formed initially contribute to hardness whereas coarsening of the precipitates reduces hardness.

A solution treatment at a higher temperature means that, where cooling rate is constant, a longer cooling time period is applied to cool the sample to a certain temperature compared to the case for a solution treatment at a lower temperature. As a result, less 'fresh' carbide precipitation is thought to be available for formation during tempering and therefore peak hardness is reduced compared to the sample cooled from a lower solution temperature.

Examples 1 to 4 generally demonstrate that no significant difference is observed in terms of hardness evolution behaviour between samples that undergo different finish rolling temperatures.

Effect of heat treatment on mechanical properties

Example 5

Samples of the test alloy prepared using a finish rolling temperature of 1050 °C were subjected to different heat treatments for conversion to the martensite phase. Table 2 below provides details of solution treatment temperature and time as well as the tempering temperature and time, following a fast rate water quench (corresponding to a cooling rate of approximately 1000 °C/h to 3000 °C/h), for each experiment (Nos. 1

to 7), together with the measured mechanical properties of the heat treated alloy obtained in each case.

Figure 3a illustrates graphically the effect of tempering time and temperature on 0.2 % yield strength and proof strength following the different heat treatments according to Table 2. Figure 3b illustrates graphically the effect of solution treatment temperature on 0.2 % yield strength and proof strength following the different heat treatments according to Table 2. The results show that solution treatment at low temperatures and tempering at high temperatures, or for a long time, leads to a pronounced decrease in the strength. The skilled person is able to modify solution treatment temperature and tempering temperatures and time in order to modify the strength of the resulting alloy, as desired.

Figure 4 illustrates graphically the relationship between ultimate tensile strength (UTS) / 0.2% proof strength (YS) and elongation. These results show that it is possible to achieve a balance of good strength and good elongation (i.e. above 10 % and up to 25 % elongation).

Figure 5 illustrates graphically the results in Table 2 which show a linear relationship between tensile strength and toughness. These results also demonstrate that the alloy can be heat treated to satisfy desired properties in the alloy that is obtained. It is evident from a comparison with literature data included in the plot for industry standard steel alloy, ASTM A182 Grade F22, that a similar level of toughness can be achieved with heat treated alloys of the invention yet in combination with higher strength than the ASTM A182 Grade F22 steel. This combination of strength and toughness in the heat treated alloys of the present invention is particularly advantageous in high stress applications.

Table 2

Exp. No.	Solution Treatment		Tempering		Transverse				Longitudinal			
	°C	h	°C	h	YS	UTS	EI	CVN	YS	UTS	EI	CVN
1	950	1	600	10	1050	1162	17	30	1061	1163	16	18
2	950	1	600	10	762	869	19	169	774	864	18	190
3	950	1	600	24	983	1087	17	64	976	1076	17	82
4	850	5.5	600	10	899	1000	18	146	879	978	18	145
5	850	5.5	600	10	656	748	21	255	690	780	22	278
6	1050	0.5	600	10	1053	1179	16	21	1066	1162	16	22
7	1050	0.5	600	10	804	917	18	126	852	967	19	129

YS = 0.2% proof strength (MPa), UTS = Tensile strength (MPa), EI = Total Elongation (%), CVN = Charpy impact toughness energy measured at -40 °C (J).

Microstructure analysis

Optical microstructure analysis of the differently heat-treated specimens indicated that each of the specimens were very similar in nature, all being tempered martensite. A typical light microscopy image for a tempered sample according to the present invention, prepared with a solution heat treatment at 1050 °C for 30 min, air-cooling at a rate of approximately 3400 °C h⁻¹ and tempering at 600 °C for 10 h, is shown in Figure 6.

One observable difference between the different specimens tested is the prior austenite grain size. The measured prior austenite grain size after different solution treatment is shown below in Table 3. As expected, heat treatment at high temperature produces larger grain sizes, even compared to a sample held at low solution temperature for a significantly longer period of time.

Table 3

Solution treatment		Prior Austenite grain size (μm)
Temperature (°C)	Time (h)	
850	5.5	31
950	1	53
1050	0.5	65

Figure 7 shows the transmission electron micrograph of an alloy tempered at 600 °C for 10 h. Significant amount of fine disk-shaped mixed carbide precipitates are observed within a martensite lath. These disk-shaped mixed carbide precipitates, confirmed as containing V, Mo and Cr, are particularly beneficial as hydrogen trapping sites for increasing the hydrogen embrittlement resistance.

Hydrogen Embrittlement Resistance Analysis

Example 6

Hydrogen Charging

Test coupons (18 × 65 × 1 mm) of the tempered martensitic steel alloy according to the invention were prepared as described above by either employing (i) an

austenitization temperature of 850 °C for 3.5 h and a tempering temperature of 600 °C for 10 h; or (ii) an austenitization temperature of 850 °C for 5.85 h and a tempering temperature of 625 °C for 10 h. Each of the samples prepared was subsequently ground using 400 SiC grit papers. The coupons were electrochemically charged with hydrogen for 48 h in an aqueous solution of 3.5 wt.% NaCl at 0.5 mA cm⁻². No discolouration of the surface was observed during this process. The samples were cleaned with acetone or isopropanol and stored in liquid nitrogen at 22 °C until all the diffusible hydrogen had been desorbed, leaving only that which is trapped before the thermal desorption analysis commenced. The time taken for all diffusible hydrogen to be desorbed is both sample and heat treatment dependent and ranges from 1 to 14 days. The diffusible hydrogen detection was performed on the thermal desorption system described below, without turning on the furnace.

Thermal desorption analysis

The thermal desorption system employed for the thermal desorption analysis is illustrated in Figure 8. A resistance tube furnace capable of heating a specimen at a constant rate was used. A thermocouple was placed in proximity to the specimen for temperature measurement. Prior to measurement, the gas chromatograph was calibrated with helium gas containing hydrogen (60.7 ppmv). While the helium carrier gas was flowing at a constant rate (10 ml min⁻¹), the specimen was heated from room temperature to a pre-set temperature profile. Typically, a peak temperature of 400 °C at a constant heating rate of 100 °C/h was used.

Hydrogen desorbed from the specimen, as well as the mixtures of gases in the air, is carried by the helium gas into the gas chromatograph. The gas mixtures were injected into the gas chromatograph column at 3 min intervals. Mixtures of gases were separated out in the chromatograph column and detected by the installed pulsed discharge ionization detector at the back end of the gas chromatograph column. The hydrogen desorption rate was defined as the amount of hydrogen evolved in 1 min per g of the specimen. Total trapped hydrogen in the different samples corresponds to the area under the hydrogen desorption curve plotted against temperature.

Figure 9 corresponds to the hydrogen thermal desorption spectra for the tested samples of steel alloy according to the invention in comparison with the industry standard steel alloy, ASTM A182 Grade F22 (which was re-austenitised at 920 °C for 1 h before being tempered at 580 °C for 4.4 h to a high tensile strength of 878 MPa, prior to hydrogen thermal desorption analysis). As can clearly be seen from Figure 9, the area under the spectra indicate a substantially improved hydrogen trapping capability associated with the steel alloy samples of the invention compared to industry standard alloy, ASTM A182 Grade F22. Figure 9 also demonstrates that tempering at 600 °C compared to 625 °C traps more hydrogen. This is believed to be due to increased carbide coarsening at the higher tempering temperature; affecting coherency strain fields around the carbides and reducing the hydrogen trapping capability.

Hydrogen Permeation Analysis

Example 7

Permeation tests were carried out according to the ASTM G148 standard using a Devanathan-Stachurski hydrogen permeation cell. Hydrogen apparent diffusion coefficient (D_{app}) was determined for samples of steel alloy according to the invention and for samples of ASTM A182 grade F22 steel treated at 850°C for 5.8 h and tempered for different time periods. This determination was based on the breakthrough time method with the following expression:

$$D_{app} = \frac{L^2}{6 \cdot t_b}$$

where L represents the thickness of the steel membrane and t_b is the breakthrough time at which the current density has reached 63% i_{max} . Results are provided in Table 4 below.

Table 4

Tempering time (h)	$D_{app1} (10^{-11} \text{m}^2 \cdot \text{s}^{-1})$	$t_{b1}(\text{h})$	$D_{app2} (10^{-11} \text{m}^2 \cdot \text{s}^{-1})$	$t_{b2}(\text{h})$
0	1.90	2.15	-	-
10	0.10	35.35	0.27	13.72
24	0.13	25.10	0.47	7.06
F22 Baseline material	5.27	0.50	3.36	1.02

From the results in Table 4, it is clear that the hydrogen apparent diffusion coefficients of the steel alloy samples of the present invention, for all the heat treatment conditions, are more than one order of magnitude lower than that for the baseline ASTM A182 Grade F22 material. This reduced hydrogen diffusivity within the steel alloy of the invention is also reflected in the breakthrough times, being longer in all cases compared to the ASTM A182 Grade F22. The reduced hydrogen permeation that is exhibited by the steel alloy of the invention is also believed to further enhance desirable hydrogen embrittlement resistance properties.

Claims

1. A steel alloy having a microstructure comprising tempered martensite, and:

5 from 0.05 to 0.15 wt% carbon;

from 1.0 to 4.0 wt% nickel;

from 1.0 to 4.0 wt% chromium;

from 0.1 to 0.5 wt% manganese;

vanadium in an amount such that the molar ratio of V : C in the alloy is in the

10 range: 0.7 to 1.3 : 1; molybdenum and/or tungsten in an amount such that the

molar ratio of (Mo + W) : C in the alloy is in the range 1.6 to 2.4 : 1; wherein

the molar ratio of (Mo + W + V) : C in the alloy is at least 2.8 : 1;

optionally one or more of:

15 from 0 to 0.01 wt% titanium;

from 0 to 0.01 wt% niobium;

from 0 to 0.01 wt% phosphorus;

from 0 to 0.01 wt% sulphur;

20 from 0 to 0.01 wt% nitrogen;

from 0 to 0.01 wt% oxygen;

from 0 to 2.0 wt% aluminium

from 0 to 0.8 wt% silicon;

from 0 to 0.008 wt% boron;

25 from 0 to 2.0 wt% copper;

and the balance iron, together with unavoidable impurities.

2. A steel alloy according to Claim 1, wherein the alloy comprises from 0.05 to
30 0.12 wt% carbon; preferably from 0.08 to 0.12 wt% carbon, more preferably
from 0.09 to 0.11 wt% carbon.

3. A steel alloy according to Claim 1 or Claim 2, wherein the alloy comprises from 2.0 to 4.0 wt% nickel; preferably from 2.5 to 3.5 wt% nickel, more preferably from 2.7 to 3.3 wt% nickel.
- 5 4. A steel alloy according to any of Claims 1 to 3, wherein the alloy comprises from 1.5 to 3.5 wt% chromium; preferably from 2.0 to 3.0 wt% chromium, more preferably from 2.3 to 2.7 wt% chromium.
- 10 5. A steel alloy according to any of the preceding claims, wherein the alloy comprises from 0.10 to 0.35 wt% manganese; preferably from 0.15 to 0.25 wt% manganese, more preferably from 0.17 to 0.23 wt% manganese.
- 15 6. A steel alloy according to any of the preceding claims, wherein the alloy comprises from 0.01 to 0.10 wt% silicon; from 0.001 to 0.005 wt% titanium; from 0.001 to 0.005 wt% niobium; from 0.001 to 0.005 wt% boron; from 0.01 to 0.05 wt% aluminium; and/or from 0.1 to 0.5 wt% copper.
- 20 7. A steel alloy according to any of the preceding claims, wherein the alloy comprises less than 0.005 wt% sulphur; less than 0.005 wt% phosphorus; less than 0.01 wt% oxygen; and/or less than 0.005 wt% nitrogen.
- 25 8. An alloy according to any of the preceding claims, wherein the alloy comprises molybdenum but tungsten is not present or present only as an unavoidable impurity.
- 30 9. An alloy according to Claim 8, wherein the molar ratio of Mo : C in the alloy is in the range of 1.6 to 2.4 :1, preferably wherein the molar ratio is in the range of 1.8 to 2.2 : 1, more preferably wherein the molar ratio is in the range 1.85 to 2.1 : 1.
10. An alloy according to any of Claims 1 to 7, wherein the alloy comprises tungsten but molybdenum is not present or present only as an unavoidable impurity.

11. An alloy according to Claim 11, wherein the molar ratio of W : C in the alloy is in the range 1.6 to 2.4 : 1, preferably wherein the molar ratio is in the range 1.8 to 2.2 : 1, more preferably wherein the molar ratio is in the range 1.85 to 2.1 : 1.

12. An alloy according to any of the preceding claims, wherein the molar ratio of V : C in the alloy is in the range 0.8 to 1.2 : 1, preferably wherein the molar ratio is in the range 0.9 to 1.2 : 1, more preferably wherein the molar ratio is in the range 1.0 to 1.1 : 1.

13. An alloy according to Claim 1, wherein the alloy comprises:

from 0.09 to 0.11 wt% carbon;

from 2.7 to 3.3 wt% nickel;

from 2.3 to 2.7 wt% chromium;

from 0.17 to 0.23 wt% manganese;

vanadium in an amount such that the molar ratio of V : C in the alloy is in the range: 1.0 to 1.1 : 1;

molybdenum in an amount such that the molar ratio of Mo : C in the alloy is in the range 1.85 to 2.1 : 1;

wherein the molar ratio of (Mo + V) : C in the alloy is at least 2.9 : 1;

less than 0.005 wt% phosphorus;

less than 0.005 wt% sulphur;

less than 0.005 wt% oxygen;

less than 0.005 wt% nitrogen;

and optionally one or more of:

from 0.001 to 0.005 wt% titanium;

from 0.001 to 0.005 wt% niobium;

from 0.01 to 0.05 wt% aluminium;

from 0.01 to 0.1 wt% silicon;

from 0.001 to 0.005 wt% boron;

from 0.1 to 0.5 wt% copper;

and the balance iron, together with unavoidable impurities.

- 5 14. An alloy according to any of the preceding claims which consists essentially of the recited elements.
- 10 15. An alloy according to any of the preceding claims, wherein the microstructure comprises at least 70 vol.% tempered martensite, preferably at least 80 vol.%, more preferably at least 90 vol.%.
- 15 16. An alloy according to any of the preceding claims which comprises less than 2.5 vol.% cementite, preferably less than 1 vol%, more preferably less than 0.05 vol%.
- 20 17. An alloy according to any of the preceding claims which comprises less than 0.5 vol.% retained austenite phase, preferably less than 0.01 vol.% retained austenite phase, more preferably wherein the alloy comprises substantially no retained austenite phase.
- 25 18. A subsea structure component comprising a steel alloy as defined in any of the preceding claims.
- 30 19. A component according to Claim 18 having a thickness of 25 to 200 mm, preferably a thickness of 100 to 150 mm.
- 35 20. A method for preparing an alloy as defined in any of Claims 1 to 17 comprising a heat solution treatment, cooling and tempering steps.
21. A method for preparing a steel alloy having a microstructure comprising a tempered martensite, said method comprising:
- (i) providing a steel alloy composition comprising:
- from 0.05 to 0.15 wt% carbon;
- from 1.0 to 4.0 wt% nickel;

from 1.0 to 4.0 wt% chromium;
from 0.1 to 0.5 wt% manganese;
vanadium in an amount such that the molar ratio of V : C in the alloy is
In the range: 0.7 to 1.3 : 1; molybdenum and/or tungsten in an amount
such that the molar ratio of (Mo + W) : C in the alloy is in the range 1.6
to 2.4 : 1; wherein the molar ratio of (Mo + W + V) : C in the alloy is at
least 2.8 : 1;

optionally one or more of:

from 0 to 0.01 wt% titanium;
from 0 to 0.01 wt% niobium;
from 0 to 0.01 wt% phosphorus;
from 0 to 0.01 wt% sulphur;
from 0 to 0.01 wt% nitrogen;
from 0 to 0.01 wt% oxygen;
from 0 to 2.0 wt% aluminium
from 0 to 0.8 wt% silicon;
from 0 to 0.008 wt% boron;
from 0 to 2.0 wt% copper;

and the balance iron, together with unavoidable impurities.

- (ii) heating the composition at a temperature of from 750 °C to 1200 °C to
at least partially austenitise the composition;
- (iii) cooling the austenitised composition from step (ii) to form a martensite
phase;
- (iv) further heating the product of step (iii) at a temperature of from 400 °C
to 700 °C.

22.A method according to Claim 21, wherein the steel alloy composition
comprises elements in the amounts defined in any of Claims 2 to 14.

23. Use of an alloy as defined in any one Claims 1 to 17 for in oil and/or gas field applications, preferably subsea applications.

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Figure 1:

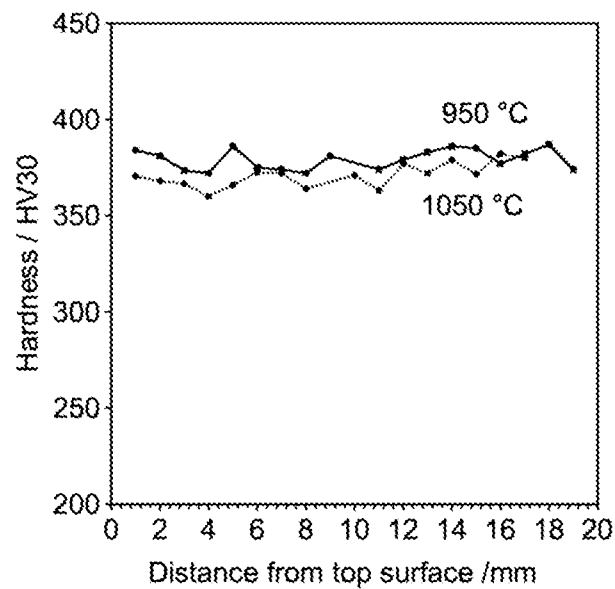


Figure 2:

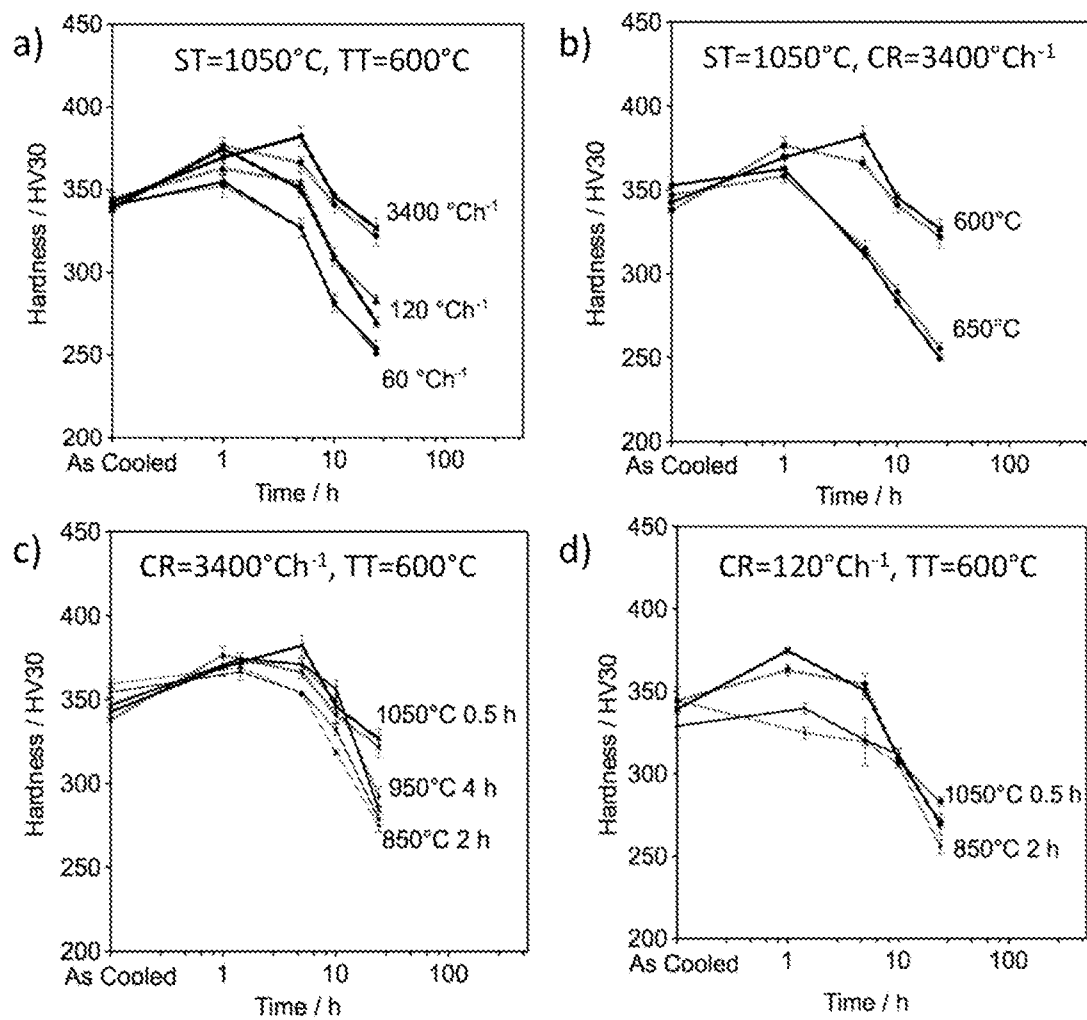


Figure 3:

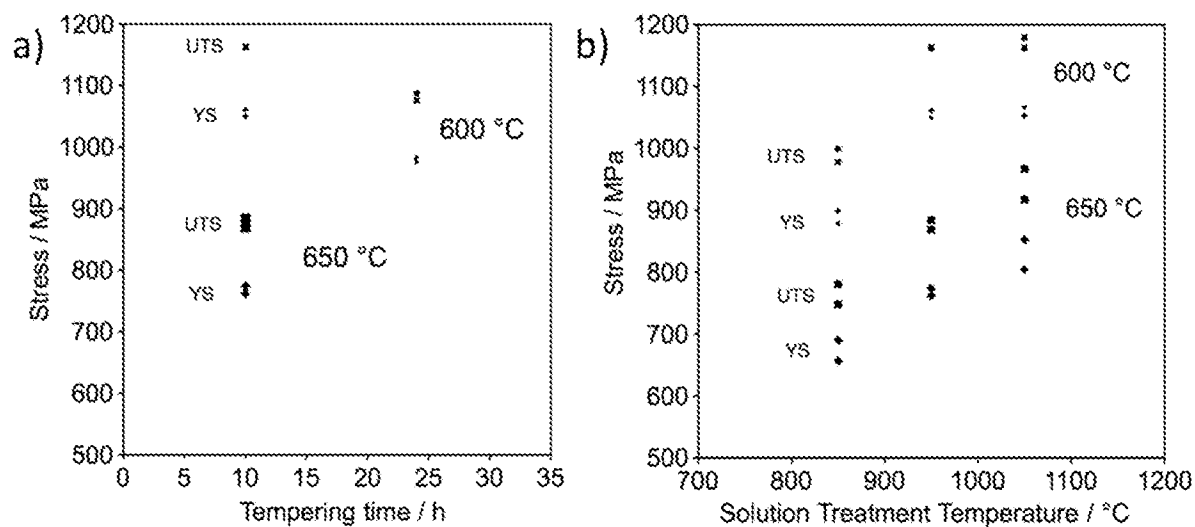


Figure 4:

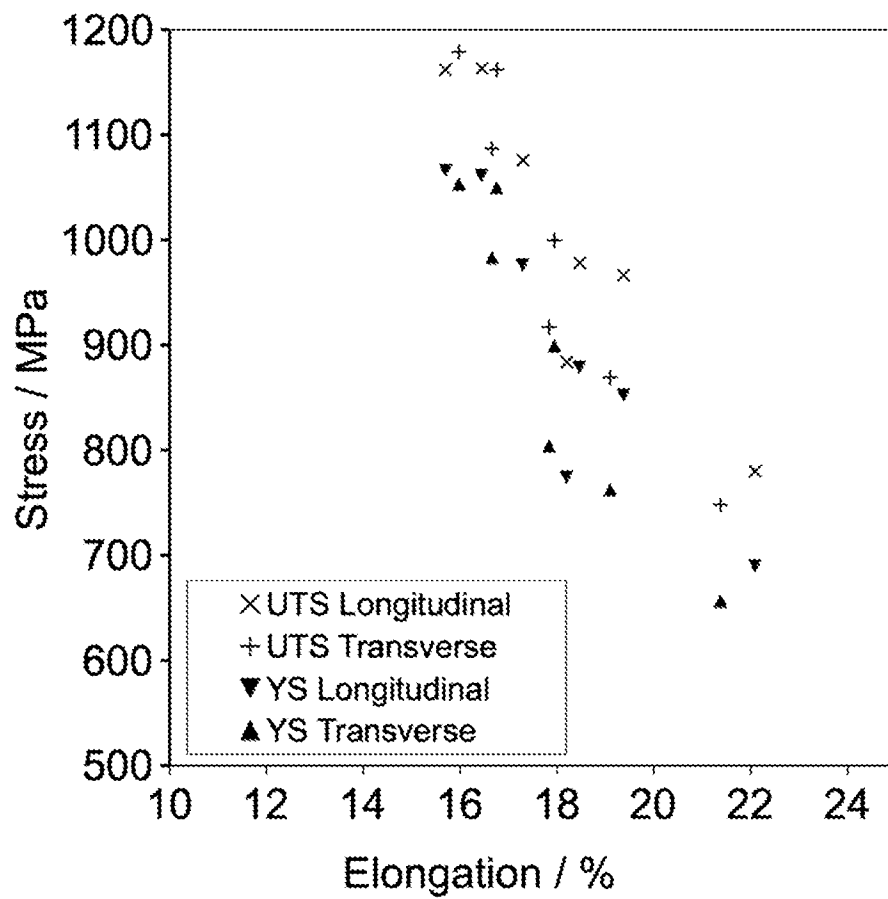


Figure 5:

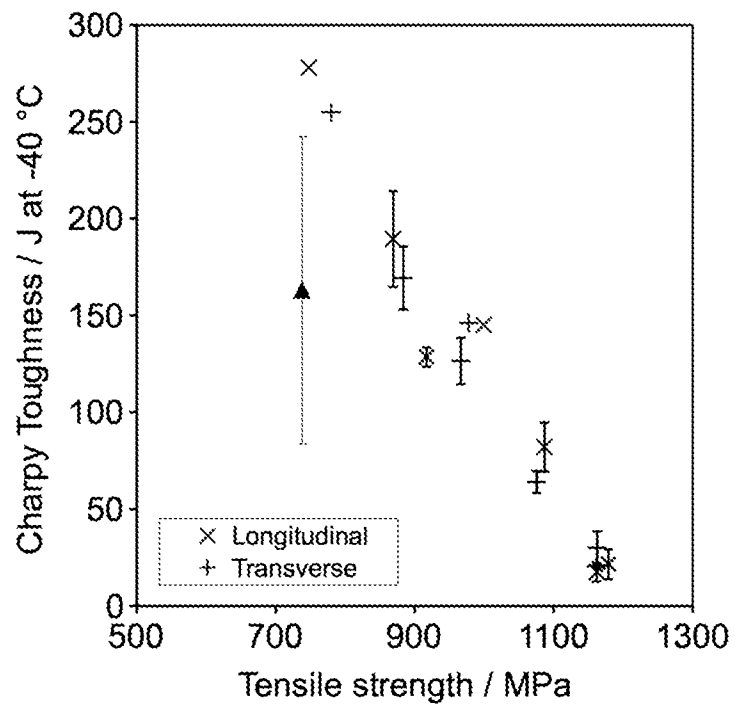


Figure 6:

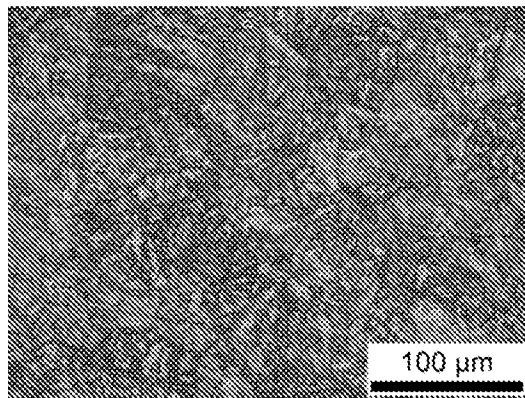


Figure 7:

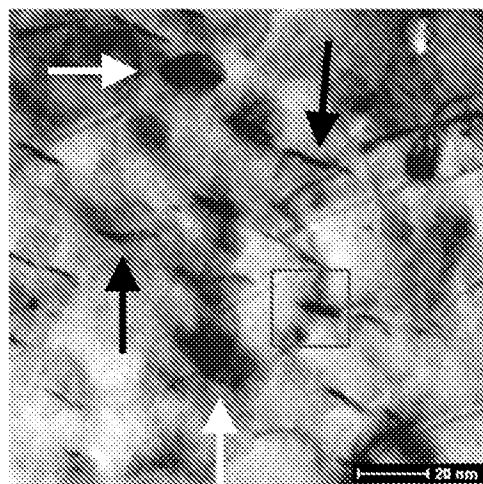


Figure 8:

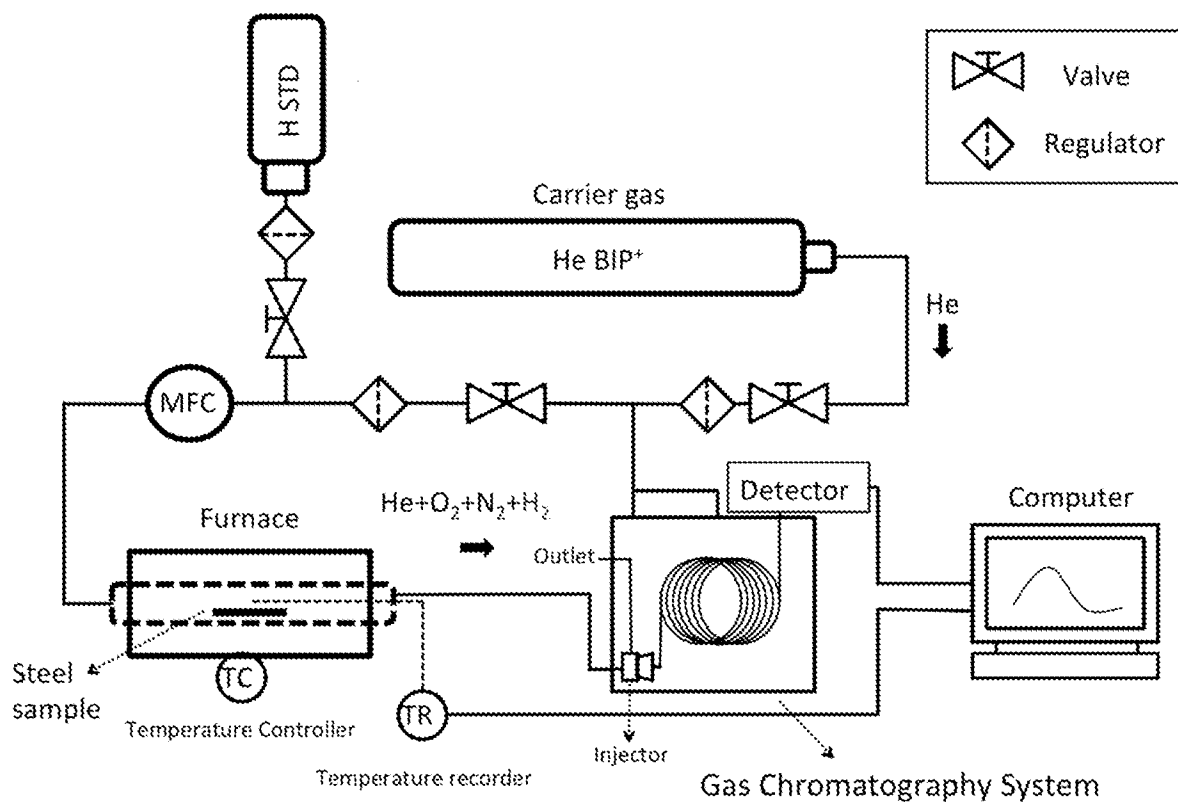
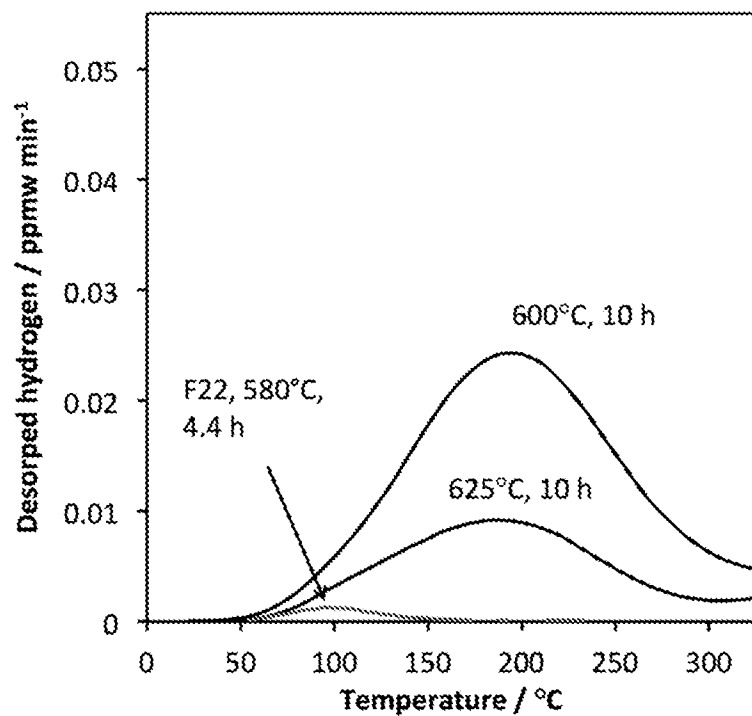


Figure 9:



INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2016/050903

A. CLASSIFICATION OF SUBJECT MATTER

INV. C22C38/44 C22C38/00 C22C38/02 C22C38/04 C22C38/06
C22C38/42 C22C38/46 C22C38/54 C21D9/00

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, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2002 363644 A (NIPPON STEEL CORP) 18 December 2002 (2002-12-18) abstract paragraphs [0010], [0013], [0018], [0026], [0031], [0032], [0052], [0061] tables 3-4 claims 2-5	1-23
X	JP 2003 253331 A (NIPPON STEEL CORP) 10 September 2003 (2003-09-10) abstract paragraphs [0001], [0005], [0008] - [0011], [0016], [0019], [0020] claims 1-4 table 2	1-23

☒ 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

"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

28 June 2016

Date of mailing of the international search report

05/07/2016

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INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2016/050903

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2003 003229 A (NIPPON STEEL CORP) 8 January 2003 (2003-01-08) abstract paragraphs [0001], [0014] - [0018], [0066] tables 2,3 claims 1-5 -----	1-23

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2016/050903

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
JP 2002363644	A	18-12-2002	NONE	

JP 2003253331	A	10-09-2003	NONE	

JP 2003003229	A	08-01-2003	JP 4445161 B2	07-04-2010
			JP 2003003229 A	08-01-2003
