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(54) **A HOT-ROLLED STEEL STRIP PRODUCT AND METHOD FOR ITS PRODUCTION**

(57) A hot-rolled steel strip product having a tensile strength (R_m) above 1400 MPa and a microstructure comprising at least 90 % by volume of martensite. The steel has a composition comprising, in percent by weight (wt.-%):

C 0.20 — 0.26

Si 0.05 — 0.5,

Mn 0.2 — 0.8,

Cr 0.2 — 0.6,

Ni 0.2 — 0.5,

Al 0.015 — 0.065,

Ti 0.005 — 0.02,

B 0.001 — 0.005,

optionally Cu <0.30,

optionally Mo <0.10,

optionally Nb <0.01,

optionally V <0.04,

balance Fe and unavoidable impurities.

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(52) Cooperative Patent Classification (CPC): (Cont.)
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Description

TECHNICAL FIELD

[0001] The present disclosure relates in general to a hot-rolled steel strip product, in particular to a hot-rolled steel strip product having a tensile strength of above 1400 MPa and having a microstructure comprising at least 90 % by volume of martensite. The present disclosure further relates in general to a method for producing such a hot-rolled steel strip product. The present disclosure also relates in general to an automotive component produced from the hot-rolled steel strip product.

BACKGROUND

[0002] For a great variety of applications, increased strength levels of steels are a pre-requisite for lightweight constructions. This is particularly important in the automotive industry. Enabling a reduction of weight *inter alia* reduces the energy needed for the propulsion of a vehicle. At the same time, there is a desire to further increase the safety of vehicles. Moreover, the continuous strive towards reducing emissions within the automotive industry for environmental reasons has led to the development of partly or fully electrically driven vehicles, such as hybrid vehicles, fully electrical vehicles and fuel cell vehicles. This often requires modifying the vehicles to, for example, accommodate battery packs. For the reasons specified above, there is a desire for an ultra-high strength steel which may be used within the automotive industry. More specifically, there is a desire for an ultra-high strength steel that may be used for example in reinforcement beams for battery packs, for chassis parts providing structural integrity and/or for roll formed bumpers for crash safety purposes.

[0003] Another property of concern within the automotive industry is resistance to hydrogen embrittlement. Hydrogen embrittlement is a possible phenomenon occurring when a steel is exposed to hydrogen dissolving and diffusing into the steel in combination with stresses, which in turn may result in loss of ductility and/or toughness and reduction in load bearing capability, even at stress levels less than the yield strength. This degradation could be potentially dangerous since the fracture is often unpredictable and preceded without any clear warnings except possibly optically visible cracks, which in turn could be hard to notice once the part is mounted in a larger unit and/or during service/usage. In general, the phenomenon is more common or prone to develop in high-strength steel grades having a tensile strength of above 1200 MPa, and becomes more pronounced as the tensile strength increases.

SUMMARY

[0004] The object of the present invention is to provide a steel strip product, suitable for automotive applications, with a good balance between the properties strength, formability, toughness and hydrogen embrittlement resistance.

[0005] The object is achieved by the subject-matter of the appended independent claim(s). Various embodiments are defined by the subject-matter of the dependent claims.

[0006] In accordance with the present disclosure, a hot-rolled steel strip product is provided. The hot-rolled steel strip product has a tensile strength (R_m) above 1400 MPa and a microstructure comprising at least 90 % by volume of martensite. The steel has a composition comprising, in percent by weight (wt.-%):

C	0.20 - 0.26,
Si	0.05 - 0.5,
Mn	0.2 - 0.8,
Cr	0.2 - 0.6,
Ni	0.2 - 0.5,
Al	0.015 - 0.065,
Ti	0.005 - 0.02,
B	0.001- 0.005,

optionally Cu <0.30,
optionally Mo <0.10,
optionally Nb <0.01,
optionally V <0.04,

balance Fe and unavoidable impurities;

wherein the unavoidable impurities P, S and N are limited to:

P	≤0.02,
S	≤0.005, and
N	≤0.0055.

[0007] By means of the hot-rolled steel strip product of the present disclosure, it is possible to obtain an excellent combination of, *inter alia*, high tensile strength, formability, toughness as well as resistance to hydrogen embrittlement. This makes the hot-rolled steel strip product particularly useful for producing various components in the automotive industry.

[0008] The hot-rolled steel strip product may have a microstructure comprising at least 95 % by volume of martensite, preferably at least 98 % by volume of martensite.

[0009] Moreover, the hot-rolled steel strip product may have a thickness of from 1.5 mm to 6 mm. Thereby, the hot-rolled steel strip product has a thickness suitable for producing components within the automotive industry. Preferably, the hot-rolled steel strip product has a thickness of from 2 mm to 4 mm.

[0010] The hot-rolled steel strip product may have a tensile strength (R_m) of at least 1475 MPa, a yield strength ($R_{p0.2}$) of at least 1100 MPa, and an elongation (A_{50}) of at least 4%. Preferably, the hot-rolled steel strip product has a yield strength ($R_{p0.2}$) of at least 1200 MPa.

[0011] The hot-rolled steel strip product may have a time to fracture of at least 130 minutes (preferably at least 140 minutes, more preferably at least 150 minutes) when subjected to a constant load test, as described in the detailed description, at a load of 80% of the tensile strength of the hot-rolled steel strip.

[0012] The present disclosure further relates to a method for producing the hot-rolled steel strip product as described above. The method comprises the following steps:

providing a steel slab of a steel with the following composition, in percent by weight (wt.-%):

C	0.20 - 0.26,
Si	0.05 - 0.5,
Mn	0.2 - 0.8,
Cr	0.2 - 0.6,
Ni	0.2 - 0.5,
Al	0.015 - 0.065,
Ti	0.005 - 0.02,
B	0.001- 0.005,

optionally Cu <0.30,
optionally Mo <0.10,
optionally Nb <0.01,
optionally V <0.04,

balance Fe and unavoidable impurities;

wherein the unavoidable impurities P, S and N are limited to:

P	≤0.02,
S	≤0.005, and
N	≤0.0055;

- heating the steel slab to an austenitizing temperature of 1150 -1300 °C;
- hot-rolling the steel slab to a desired thickness from a temperature in the range of Ar3 to 1280 °C to a desired final thickness of the steel product, wherein the finish rolling temperature is in the range of 800 - 960 °C, preferably 860 - 950 °C;
- quenching the hot-rolled strip to a coiling temperature of 250 °C or less, preferably 150 °C or less, with an average cooling rate of at least 30 °C/s;
- optionally galvanizing the hot-rolled strip; and
- optionally temper annealing the hot-rolled strip at a temperature of 100 - 250 °C.

[0013] The present disclosure further provides an automotive component produced from the hot-rolled steel strip product as described above. The automotive component may be a reinforcement beam (such as a reinforcement beam for a battery pack), a chassis part, or a bumper beam, but is not limited thereto.

BRIEF DESCRIPTION OF DRAWINGS

[0014]

Fig. 1 represents a SEM image of a cross section of sample B, and

Fig. 2 represents an Inverse Pole Figure from EBSD measurement of sample D.

DETAILED DESCRIPTION

[0015] The invention will be described in more detail below with reference to exemplifying embodiments, experimental results and the accompanying drawings. The invention is however not limited to the exemplifying embodiments and/or experimental results discussed, and/or shown in the drawings, but may be varied within the scope of the appended claims.

[0016] It should be noted that when ranges are given in the present disclosure, said ranges include the respective end values of the specified range unless explicitly disclosed otherwise.

[0017] The present disclosure provides a hot-rolled steel strip product which is suitable for use in the manufacture of automotive components. The hot-rolled steel strip product has a tensile strength (R_m) above 1400 MPa and a microstructure comprising at least 90 % by volume of martensite. The steel has a composition comprising, in percent by weight (wt.-%):

C	0.20 - 0.26,
Si	0.05 - 0.5,
Mn	0.2 - 0.8,
Cr	0.2 - 0.6,
Ni	0.2 - 0.5,
Al	0.015 - 0.065,
Ti	0.005 - 0.02,
B	0.001- 0.005,

optionally Cu <0.30,
optionally Mo <0.10,
optionally Nb <0.01,
optionally V <0.04,

balance Fe and unavoidable impurities;
wherein the unavoidable impurities P, S and N are limited to:

P	≤0.02,
S	≤0.005, and
N	≤0.0055.

[0018] In the following, the importance of the separate elements and their interaction, as well as the limitations of constituent elements of in the composition of the steel strip product are briefly discussed. All percentages for the chemical composition are given in weight-% (wt.-%) unless explicitly disclosed otherwise. Upper and lower limits of the individual elements of the composition can be freely combined within the broadest limits set out in the claims, unless explicitly disclosed otherwise.

[0019] Furthermore, the microstructure of the hot-rolled steel strip product is described below. The amount of phase(s) in the microstructure is given in volume-% (vol.-%) throughout the present disclosure. It should here be recognized that a certain volume percentage is generally determined within this technical field by considering an area percentage of the relevant constituent component (phase) in a sample, said area percentage considered to correspond to the volume percentage.

Carbon: 0.20 - 0.26 wt.-%

[0020] Carbon increases strength by solid solution strengthening, and thus directly affect the strength level in martensitic structures. Carbon is also an austenite stabilizing element. Therefore, in the present steel, carbon is present in an amount of at least 0.20 wt.-% to reach the desired strength level for the steel strip product. Suitably, the steel comprises at least 0.21 wt.-% of carbon.

[0021] However, high contents of carbon may have a detrimental effect of weldability, toughness, formability and/or bendability, as well as resistance to stress corrosion cracking. Therefore, the steel comprises at most 0.26 wt.-% carbon. Suitably, the carbon content may be 0.25 wt.-% or less.

Silicon: 0.05 - 0.5 wt.-%

[0022] Silicon has the beneficial effect of retarding formation of cementite and perlite and suppresses formation of coarse carbides. It also contributes to solid solution strengthening. Silicon is also effective as a deoxidizing agent or killing agent that can remove oxygen from the melt during a steelmaking process. Therefore, the composition of the present steel comprises at least 0.05 wt.-% of silicon. Suitably, silicon may be present in an amount of at least 0.10 wt.-%, preferably at least 0.15 wt.-%.

[0023] However, too high contents of silicon may cause scale issues which can impair fatigue properties of the steel strip product. Therefore, silicon is present in an amount of 0.5 wt.-% or less. Suitably, silicon may be present in an amount of 0.45 wt.-% or less, preferably 0.40 wt.-% or less.

Manganese: 0.2 - 0.8 wt.-%

[0024] Manganese has the beneficial effect of suppressing the ferrite transformation temperature as well as the ferrite transformation rate. Alloying with manganese lowers the martensite start temperature (M_s) and martensite finish temperature (M_f), which may suppress autotempering of martensite during quenching. Reduced autotempering of martensite leads to higher internal stresses that may enhance the risk for quench-induced cracking. However, a lower degree of autotempered martensite is beneficial for achieving higher hardness. Manganese also increases austenite hardenability and therefore enhances hardness. Therefore, manganese is present in an amount of at least 0.2 wt.-% to achieve desired hardenability. Suitably, manganese is present in an amount of at least 0.3 wt.-%, preferably at least 0.4 wt.-%.

[0025] However, too high contents of Mn may increase formation of manganese sulfides, which could induce formation of initiations sites for pitting corrosion and stress corrosion cracking. Also, high contents of manganese may increase risk for segregation during continuous casting, which in turn may lead to an inhomogeneous structure. Furthermore, too high contents of manganese may deteriorate formability and toughness. Therefore, manganese is present in an amount of at most 0.8 wt.-%. Suitably, the steel comprises manganese in an amount of 0.65 wt.-% or less.

Chromium: 0.2 - 0.6 wt.-%

[0026] Chromium in solid solution enhances strength and hardness by increasing austenite hardenability. Chromium also suppresses ferrite formation, in a manner similar to manganese. Therefore, chromium is present in an amount of at least 0.2 wt.-%.

[0027] However, high contents of chromium increases hot deformation resistances and limits the ability to roll thin and wide dimensions. Furthermore, an increase in the Cr content also leads to an increase in alloy cost. Therefore, chromium is present in an amount of 0.6 wt.-% or less.

Preferably chromium is present in an amount of 0.5 wt.-% or less .

Nickel: 0.2 - 0.6 wt.-%

[0028] Nickel is an alloying element that improves austenite hardenability, thereby increasing strength. Nickel also improves the ductility and is generally considered to increase toughness in martensitic steels. Therefore, nickel is present in an amount of at least 0.2 wt.-%.

[0029] However, nickel contents of above 0.5 wt.-% would unduly increase the alloying costs without significant technical improvement. Preferably, nickel is present in an amount of 0.4 wt.-% or less.

Aluminum: 0.015 - 0.065 wt.-%

[0030] Aluminum is an element frequently used in the steel industry as deoxidizing or killing agent that can remove oxygen from the melt during the steelmaking process. Moreover, aluminum removes nitrogen by forming stable aluminum

nitride particles and provides grain refinement, which is beneficial for toughness. Therefore, aluminum is present in an amount of at least 0.015 wt.-%.

[0031] However, an excess of aluminum may increase the amount of non-metallic inclusions, thereby deteriorating inner cleanliness of the steel. Therefore, aluminum is present in an amount of 0.065 wt.-% or less.

Titanium: 0.005 - 0.02 wt.-%

[0032] Titanium is used for binding free nitrogen by formation of titanium nitrides. Thereby, the risk for a reduction in toughness is reduced. Moreover, such titanium nitride particles can efficiently prevent austenite grain growth when the steel slab, during the manufacturing process, is heated to the austenitizing temperature. Thereby, titanium may reduce the risk for abnormal grain growth of the austenite grains. Moreover, formation of titanium nitrides suppresses precipitation of boron nitride, thereby leaving boron free to make its contribution to hardenability. Therefore, titanium is present in an amount of at least 0.005 wt.-%. Suitably, titanium is present in an amount of at least 0.006 wt.-%.

[0033] However, if the titanium content is too high, there is a risk of coarsening of titanium nitride and precipitation hardening due to formation of titanium carbides. This may in turn lead to a deterioration of toughness. Therefore, titanium is present in an amount of 0.02 wt.-% or less. Preferably, titanium is present in an amount of 0.015 wt.-% or less.

Boron: 0.001 - 0.005 wt.-%

[0034] Boron is a micro-alloying element used to increase hardenability. However, boron also has a tendency of forming boron nitrides. Therefore, in order to achieve effective alloying with boron, it is required that the steel comprises nitrogen stabilizing elements to prevent formation of boron nitride. As described above, titanium may be used for this purpose. The present steel comprises at least 10 ppm of boron to achieve desired hardenability.

[0035] At too high contents of boron, there is however a risk of deterioration of formability. Therefore, boron is present in an amount of 50 ppm or less. Preferably, boron is present in an amount of 40 ppm or less. More preferably, boron is present in an amount of 30 ppm or less.

Copper: optionally up to 0.3 wt.-%

[0036] Copper may be added, for example for solid solution strengthening purposes, if desired. Copper may alternatively be present as a result of the raw material used for making the steel, in which case it may be considered as an unavoidable impurity. However, high contents of copper may lead to brittleness and are therefore not desired. For said reason, the copper content (if present) is limited to less than 0.3 wt.-%.

Molybdenum: optionally up to 0.1 wt.-%

[0037] Molybdenum may, if desired, be added to increase strength. However, addition of molybdenum is not essential to the present steel product and may increase the alloying costs. Therefore, the content of molybdenum (if present) is less than 0.10 wt.-%.

Niobium: optionally up to 0.01 wt.-%

[0038] Niobium may, if desired, be used for the purpose of increasing strength by grain refinement. However, niobium is not essential to the present steel product and may increase the alloying costs. Moreover, niobium may reduce formability and bendability and should therefore be restricted. Hence, the content of niobium (if present) is less than 0.01 wt.-%.

Vanadium: optionally up to 0.04 wt.-%

[0039] Vanadium may, if desired, be added for the purpose of increasing strength. However, vanadium is not essential to the steel product and may increase the alloying costs. Therefore, content of vanadium (if present) is in the present steel less than 0.04 wt.-%.

Unavoidable impurities

[0040] In the present disclosure, unavoidable impurities are considered to be impurities resulting from the manufacturing process and/or the raw material used.

[0041] One example of an unavoidable impurity is phosphorus (P). Low levels of phosphorous is beneficial for toughness and formability. Therefore, the phosphorus content is limited to at most 0.02 wt.-%. Another example of an unavoidable

impurity is sulfur, which should also be present in low amounts to avoid deterioration of toughness and formability. Sulphur may therefore be present in an amount of 0.005 wt.-% or less. Preferably, the sulfur content is equal to or less than 0.045 wt.-%. Nitrogen is another example of an unavoidable impurity. Nitrogen may also cause a reduction of toughness and formability if present in too high contents. Therefore, nitrogen is present in an amount of equal to or less than 0.0055 wt.-%. The nitrogen content may suitably be 40 ppm or less, preferably equal to or less than 35 ppm.

[0042] Yet another example of an unavoidable impurity is calcium (Ca) which may result from the manufacturing process since it is commonly added during the steelmaking process for refining, deoxidation, and desulphurization. An excessive amount of Ca should however be avoided to achieve a clean steel and avoid deterioration of the mechanical properties, in particular toughness and bendability. The calcium content is suitably limited to 0.005 wt.-% or less, preferably 0.003 wt.-% or less.

[0043] Other examples of unavoidable elements include hydrogen (H) and oxygen (O), where the latter may contribute to formation of impurities. The hydrogen content should preferably be limited to maximally 0.5 ppm. The oxygen content should preferably be limited to maximally 25 ppm.

Microstructure of hot-rolled steel strip product

[0044] The microstructure of the hot-rolled steel strip may be assessed by Scanning Electron Microscopy (SEM), combined with electron backscatter diffraction (EBSD) where applicable, as known in the art. When determining an amount and/or size of a constituent component of the microstructure, such as a phase, an image obtained via SEM of a cross-section of a representative sample is considered. The image analysis may be made manually by the skilled person and/or by usage of computer analysis as known in the art.

[0045] The hot-rolled steel strip product has a microstructure comprising at least 90 vol.-% of martensite. Preferably, the microstructure comprises at least 95 vol.-%, more preferably at least 98 vol.-%, of martensite. Here, it should be noted that normally occurring local variations in the surface zones of the strip as well as in the center area of the thickness of the strip may be present as a result of the manufacturing process. A representative fraction of martensite may therefore suitably be measured at $\frac{1}{4}$ thickness of the steel strip product.

[0046] The martensitic structure may be non-tempered, autotempered or tempered depending on the manufacturing process and/or other conditions that the hot-rolled steel strip product may be subjected to. For the purpose of increasing the resistance to hydrogen embrittlement, it is preferred that the microstructure comprises tempered martensite. It is within the normal routine of the person skilled in the art to, by investigating the microstructure, determine whether the martensite is non-tempered, autotempered or tempered. The presence of tempered martensite can be identified, during investigation of the microstructure, mainly by evenly dispersed formation of different carbides depending on the time-temperature pattern of the tempering. Thereby, tempered martensite may be identified in the microstructure of a sample by comparison with images of previous samples, tempered according to known time-temperature patterns.

[0047] In addition to martensite, the microstructure may comprise small amounts of bainite, retained austenite and/or carbides.

[0048] Furthermore, the average prior austenite grain size may be 50 μm or less. Preferably, the average prior austenite grain size of the strip steel product, is 30 μm or less or even 20 μm or less. The average prior austenite grain size is here determined according to ASTM E 112. Local variations in surface zone and center region may be present as a result of the manufacturing process. Therefore, a representative average prior austenite grain size may suitably be determined at $\frac{1}{4}$ thickness of the steel strip product.

Manufacturing of the hot-rolled steel strip product

[0049] In the following, the method for producing the hot-rolled steel strip product will be described in more detail.

[0050] The first step in the production of the hot-rolled steel strip product is to provide a steel slab of a steel with the above-described composition. The steel slab may for example be provided casting a melt of the composition by means of continuous casting, also known as strand casting.

[0051] Thereafter, the steel slab is heated to an austenitizing temperature of from 1150 to 1300 °C (including the end values of the range). The temperature to which the steel slab is heated is important for controlling the austenite grain growth. An increase in the temperature to which the steel slab is heated can cause dissolution of alloy precipitates and result in grain coarsening and/or abnormal grain growth.

[0052] The steel slab is, after the above-described heating step, hot-rolled to the desired thickness of the finished product. The desired thickness may be within the range of 1.5 mm to 6 mm, preferably 2 mm to 4 mm, but is not limited thereto. At the start of said hot-rolling, the temperature of the steel slab is in the range of Ar3 to 1280 °C. Ar3 is the temperature at which austenite begins to transform into ferrite during cooling. It should also be noted that Ar3 is dependent of the actual chemical composition of the steel. The skilled person is well aware of methods for determining Ar3 for a particular composition, and this will therefore not be further described in the present disclosure. The finish rolling tem-

perature if the hot-rolling step is in the range of from 800 °C to 960 °C, preferably 860 to 950 °C.

[0053] The hot-rolled strip is thereafter quenched to a temperature at which it is, or at least may be, coiled. In other words, it is quenched to a coiling temperature. The coiling temperature is 250 °C or less. Preferably, the hot-rolled strip is quenched to a coiling temperature of 150 °C or less. The average cooling rate during said quenching is at least 30 °C/seconds. Said average cooling rate is determined by considering the temperature range from finish rolling temperature to the coiling temperature and the total time for said quenching between these temperatures, if following an arbitrary point of the hot-rolled strip in the longitudinal direction of the strip.

[0054] It should here be noted that the cooling rate during said quenching will vary over the quenching step. Usually, the cooling rate is larger at the start of the quenching step (i.e. at higher temperatures) than at the end of the quenching step. As an example, the cooling rate may be as high as about 300 °C/second in the quenched region down to 500 °C.

[0055] The above-described quenching of the hot-rolled strip is suitably initiated shortly after hot-rolling to ensure desired microstructure and mechanical properties. Preferably, quenching is initiated within about 10 seconds from the hot-rolling step, although longer times may also be plausible.

[0056] The steel strip product may after the quenching step be coiled, and allowed to cool down to room temperature.

[0057] If desired, the hot-rolled steel strip product may thereafter be subjected to one or more further processing steps. For example, the hot-rolled steel strip product may be galvanized whereby it is provided with a corrosion protective layer on the surface of the hot-rolled steel strip. This may for example be performed through electro-galvanizing or a similar process that does not substantially alter the properties of the hot-rolled steel strip product in a way that the properties are not met afterwards.

[0058] Additionally, or alternatively, the hot-rolled steel strip product may be subjected to low temperature temper annealing. More specifically, the hot-rolled steel strip product may be subjected to temper annealing at a temperature of from 100 °C to 250 °C. The appropriate duration of such a low temperature annealing depends on various factors, such as whether it is performed on the hot-rolled steel strip in coiled or un-coiled form. As an example, in case the low temperature temper annealing is performed on a coiled hot-rolled steel strip, the duration may suitably be at least 2 hours to ensure that all the material reaches the intended temperature, whereas in uncoiled condition the duration may be considerably shorter, such as in the order of a few minutes or less. There is no upper limit for the duration of the low temperature temper annealing process since the temperature is sufficiently low so as to not negatively affect the properties of the hot-rolled steel strip product, and is thus in practice rather limited by process economy. The low temperature temper annealing is beneficial since it may further improve the resistance of the hot-rolled steel strip product to hydrogen embrittlement. This is due to the low temperature temper annealing reducing defects in the crystal lattice of the hot-rolled steel strip product. Furthermore, although the low temperature temper annealing may lead to a slight reduction in the tensile strength, it may also result in an increase in yield strength which is advantageous.

Properties of the hot-rolled strip product

[0059] The hot-rolled steel strip product according to the present disclosure has a tensile strength, R_m , above 1400 MPa. More specifically, the hot-rolled steel strip may have a tensile strength of at least 1475 MPa. The tensile strength is however typically less than 1750 MPa. Moreover, the hot-rolled steel strip product may have a yield strength, $R_{p0.2}$ of at least 1100 MPa. Preferably, the yield strength is at least 1200 MPa. The yield strength is however typically less than 1550 MPa. The hot rolled steel strip product may also have an elongation to fracture, A_{50} , of at least 4%, preferably at least 5% or even 6% or higher. The tensile strength, yield strength and elongation may be determined according to SS-EN ISO 6892-1. These tensile properties make the hot-rolled steel strip highly suitable for used in automotive applications.

[0060] The hot-rolled steel strip product also has good formability, which is important when seeking to produce for example various automotive components. The formability may for example be quantified by the bendability of the hot-rolled steel strip product. The hot-rolled steel strip product according to the present disclosure may have a bendability R_i/t , determined by subjecting a test piece of the hot-rolled steel strip product to plastic deformation by three-point bending (with one single stroke) until a specified angle 90° of the bend is reached after unloading, of 4.0 or less, wherein R_i is the inner radius and t is the thickness of the hot-rolled steel strip product.

[0061] The hot-rolled steel strip product also has high toughness. More specifically, the toughness measured on a sub sized specimen (1/4 sized specimen) in longitudinal direction is at least 15 J at -40 °C, preferably at least 20 J at -40 °C, when determined according to SS-EN ISO 148-1.

[0062] Hydrogen embrittlement is a phenomenon that may occur when a steel is exposed to hydrogen dissolving and diffusing into the steel in combination with stresses. Hydrogen embrittlement may lead to loss in ductility and/or toughness. Moreover, hydrogen embrittlement may lead to a reduction in load bearing capacity even below the yield strength. Hydrogen could be introduced to the steel during the steelmaking process, further processes such as electro galvanizing processes or the like, or during use of the steel. Moreover, hydrogen embrittlement is more common for high strength grades with tensile strength above 1200 MPa and the risk generally increases with increasing strength due to higher

amount of defects in the crystal lattice. Hydrogen embrittlement is often a concern within the automotive industry, primarily since it may lead to fracture without any reasonably detectable warning. The hot-rolled steel strip product according to the present disclosure has good resistance to hydrogen embrittlement despite the fact that it also has high strength.

[0063] Resistance to hydrogen embrittlement may be investigated by using a Constant Load Test (CLT), wherein a test specimen is subjected to a constant tensile load in the range of 40-80% of tensile strength while introducing hydrogen to the specimen and measuring time to fracture. It should here be noted such a test is not standardized and is sensitive to variations, for example with regard to nature/quality of cut edge of specimen, hydrogen source etc. Therefore, when resistance to hydrogen embrittlement is quantified in the present disclosure, it is in relation to a constant load test being performed as described in the following.

Constant Load Test (CLT)

[0064]

- A test specimen is cut from the hot-rolled steel strip product by means of a conventional workshop shearer, using the settings of shear angle between 1.3-1.9° and clearance 15°, to a width 10 mm and length >200 mm of the specimen, the length being parallel to the rolling direction of the hot-rolled strip product.
- The test specimen is thereafter partly arranged in a container in such a way that the specimen may be subjected to an electrolyte over a portion of the specimen while being clamped at the respective longitudinal ends for the purpose of being subjected to a tensile load. At least 44 ml of electrolyte consisting of 0.5 molar Na₂SO₄ is used, the electrolyte covering a total length of 60 mm of the longitudinal cut edge of the specimen, wherein 30 mm is on each side of the specimen.
- The specimen is subjected to a tensile load at 80% of the tensile strength of the hot-rolled steel strip product and an electrical current is applied to the electrolyte when said tensile load has been reached. By means of a potentiostat, a current density of 0.2 mA/mm² is kept constant throughout the test. Mapping of time starts once the specified load is reached and the electrical current is applied. The test is finished, and time stopped, when the specimen fractures.

[0065] The hot-rolled steel strip product according to the present disclosure may have a resistance to hydrogen embrittlement, if tested according to the Constant Load Test as described above, of at least 130 minutes when subjected to a load of 80% of the tensile strength. Preferably, the resistance to hydrogen embrittlement is at least 140 minutes, and more preferably at least 150 minutes, if tested according to the Constant Load Test as described above.

Experimental results

[0066] Six different alloys, with chemical compositions as specified in Table 1, were tested.

Table 1. Chemical composition of tested materials in wt.%, balance being Fe.

Element	Alloy 1	Alloy 2	Alloy 3*	Alloy 4*	Alloy 5*	Alloy 6*
C	0.220	0.232	0.267	0.211	0.229	0.238
Si	0.195	0.214	0.009	0.161	0.179	0.172
Mn	0.500	0.480	0.390	0.690	0.200	0.200
P	0.011	0.005	0.009	0.010	0.007	0.006
S	0.0031	0.001	0.004	0.001	0.001	0.002
N	0.0014	0.0023	0.0051	0.0037	0.0024	0.0024
Cr	0.303	0.299	0.022	0.590	0.390	0.375
Ni	0.303	0.303	0.034	0.500	0.510	0.493
Al	0.053	0.046	0.029	0.049	0.051	0.055
Ti	0.011	0.012	0.031	0.003	0.002	0.002
B	0.0022	0.0016	0.0052	0.0012	0.0011	0.0011
Cu	0.004	0.010	0.158	0.010	0.160	0.160
Mo	0.003	0.055	0.002	0.045	0.050	0.048

(continued)

Element	Alloy 1	Alloy 2	Alloy 3*	Alloy 4*	Alloy 5*	Alloy 6*
Nb	0.000	0.001	0.000	0.010	0.001	0.001
V	0.008	0.008	0.007	0.013	0.010	0.010
Ca	0.0001	0.0019	0.0001	0.0003	0.0008	0.0012
* Comparative example						

[0067] The alloys were produced in full scale charges of 100-200 tonnes and cast by continuous casting to slabs. The slabs were reheated to a reheating temperature (i.e. austenitizing temperature) with a holding time of at least 30 minutes at said temperature. The slabs were thereafter subjected to hot rolling, to a final sheet thickness, from the reheating temperature to a finishing rolling temperature, followed by quenching to a coiling temperature of lower than 150 °C. Some of the hot-rolled strips were subjected to tempering. Where tempering was performed, this was made with the hot-rolled strip in coiled condition except for Alloy 3 (sample L), where tempering was performed on a lab scale. The parameters of the processing steps for the respective samples are specified in Table 2. The average cooling rate specified in Table 2 was calculated by dividing the temperature range from the finish rolling temperature to the coiling temperature with the duration for the material to pass these measured temperatures.

[0068] Samples of the hot-rolled steel strips were subjected to various tests as specified below. The results of the tests performed are also specified in Table 2.

Tensile testing

[0069] Yield strength ($R_{p0.2}$), tensile strength (R_m) and total elongation (A50) were determined through tensile testing according to SS-EN ISO 6892-1. The samples were longitudinal to rolling direction.

Bendability

[0070] Bendability was tested by subjecting a test piece to plastic deformation by three-point bending, with one single stroke, until a specified angle 90 ° of the bend is reached after unloading. The inspection and assessment of the bends is a continuous process during the whole test series. This is to be able to decide if the punch radius (R) should be increased, maintained or decreased. Bendability was tested with the bend parallel with rolling direction, and the result is given as inner radius (Ri) divided by sample thickness (t). The limit of bendability (Ri/t) was identified in a test series when a consistent bend radius, without any defects, is fulfilled with the same punch radius (R). Here, cracks, surface necking marks and flat bends (significant necking) were considered as defects.

[0071] The bend test was performed according to SS-EN ISO 7438.

Impact toughness

[0072] Impact toughness (Charpy V-notch) was tested according to SS-EN ISO 148-1 with sample direction according to rolling direction.

Constant Load Test

[0073] Resistance to hydrogen embrittlement was tested using a Constant Load Test (CLT) during which the test specimens were subjected to a load of 80% of tensile strength. Three different specimens for each sample (condition) were tested to ensure consistency, and the result is presented in Table 2 as the average of the three samples.

Microstructure characterization

[0074] Metallographic cross sections were extracted from material in tempered condition, hot mounted in conductive phenolic resin, ground and polished to a 1 µm surface finish, either etched or further polished using colloidal silica. The etched and further polished sample were examined using a scanning electron microscope (SEM) equipped for electron backscatter diffraction (EBSD) respectively.

[0075] During investigation of the microstructure, it was confirmed that all of the tested samples contained well above 90 vol-% martensite.

[0076] Figure 1 represents an example of a SEM image of a cross section of Sample No. B at about ¼ of the thickness.

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The cross-section was taken essentially parallel to the rolling direction. Figure 2 represents Inverse Pole Figure from EBSD measurement of Sample No. D, at about $\frac{1}{4}$ of the thickness, also taken with the cross-section essentially parallel to the rolling direction.

[0077] Prior austenite grain size (PAGS) was estimated according to ASTM E 112, giving an average size below 50 μm for all samples. For example, an average size of 14.6 μm was obtained for Sample No. B, and 16.4 μm was obtained for Sample No. D.

[0078] From the test results, it can be seen that tempering clearly contributes to improved hydrogen embrittlement resistance. Sample No. J has twice as long time to fracture compared to Sample No. I and the same for Sample No. L compared to Sample No. K. The results referring to constant load testing also show that alloying with more than 0.3% Ni does not further improve resistance to hydrogen embrittlement, compare Sample No. B and Sample No. J versus Sample No. M and Sample No. O. Lower Ni content is beneficial from a cost perspective.

Table 2. Samples, processing conditions thereof and test results

No.	Comp.	Reheating temp. [°C]	Finishing rolling temp. [°C]	Sheet thickness [mm]	Average cooling rate [°C/s]	Tempering treatment	Yield strength Rp02 [MPa]	Tensile strength Rm [MPa]	Elongation on Aso [%]	Charpy V [J] Longitudinal (-40°C)	Bendability [R/t] Longitudinal	CLT [min] 80% of Rm Longitudinal
A	Alloy 1	1250	881	3.0	47	N.A.	1205	1573	7.7	18	2.5	*
B	Alloy 1	1250	881	3.0	47	200°C/8h	1331	1539	7.2	18	3.0	166
C	Alloy 1	1250	929	3.0	62	N.A.	1139	1498	7.8	18	2.5	*
D	Alloy 1	1250	929	3.0	62	200°C/8h	1259	1477	7.7	20	3.0	*
E	Alloy 2	1250	895	3.2	53	N.A.	1229	1582	8.0	19	3.5	*
F	Alloy 2	1250	895	3.2	53	200°C/8h	1328	1532	7.0	22	3.5	*
G	Alloy 2	1250	935	3.0	68	N.A.	1172	1522	8.2	20	3.5	*
H	Alloy 2	1250	935	3.0	68	200°C/8h	1278	1489	7.0	20	3.4	*
I	Alloy 2	1250	897	3.0	57	N.A.	1234	1589	7.8	18	3.3	77
J	Alloy 2	1250	897	3.0	57	200°C/8h	1351	1553	6.4	21	3.3	147
K	Alloy 3	1250	891	3.0	49	N.A.	1445	1659	6.0	6	2.5	36
L	Alloy 3	1250	891	3.0	49	200°C/4h	1488	1575	6.0	7	3.7	70
M	Alloy 4	1250	892	3.0	53	200°C/8h	1452	1624	6.5	21	*	137
N	Alloy 5	1250	906	3.0	62	200°C/8h	1378	1562	6.0	24	3.2	
O	Alloy 6	1250	905	3.0	62	200°C/8h	1400	1584	5.5	18	2.9	129
[*] Not tested												

Claims

1. A hot-rolled steel strip product with a tensile strength (R_m) above 1400 MPa and having a microstructure comprising at least 90% by volume of martensite, the steel having a composition comprising, in percent by weight (wt.-%):

C	0.20 - 0.26
Si	0.05 - 0.5,
Mn	0.2 - 0.8,
Cr	0.2 - 0.6,
Ni	0.2 - 0.5,
Al	0.015 - 0.065,
Ti	0.005 - 0.02,
B	0.001- 0.005,

optionally Cu <0.30,
optionally Mo <0.10,
optionally Nb <0.01,
optionally V <0.04,

balance Fe and unavoidable impurities;
wherein the unavoidable impurities P, S and N are limited to:

P	≤ 0.02 ,
S	≤ 0.005 , and
N	≤ 0.0055 .

2. The hot-rolled steel strip product according to claim 1, having a microstructure comprising at least 95 % by volume of martensite, preferably at least 98 % by volume of martensite.
3. The hot-rolled steel strip product according to any one of the preceding claims, having a thickness of from 1.5 mm to 6 mm, preferably from 2 mm to 4 mm.
4. The hot-rolled steel strip product according to any one of the preceding claims, comprising 0.20 - 0.25 wt.-% C, preferably 0.21 - 0.25 wt.-% C.
5. The hot-rolled steel strip product according to any one of the preceding claims, comprising 0.10 - 0.45 wt.-% Si, preferably 0.15 - 0.40 wt.-% Si.
6. The hot-rolled steel strip product according to any one of the preceding claims, comprising 0.3 - 0.8 wt.-% Mn, preferably 0.4 - 0.65 wt.-% Mn.
7. The hot-rolled steel strip product according to any one of the preceding claims, comprising 0.2 - 0.5 wt.-% Cr.
8. The hot-rolled steel strip product according to any one of the preceding claims, comprising 0.2 - 0.4 wt.-% Ni.
9. The hot-rolled steel strip product according to any one of the preceding claims, comprising 0.006-0.015 wt.-% Ti.
10. The hot-rolled steel strip product according to any one of the preceding claims, comprising 0.001 - 0.004 wt.-% B, preferably 0.001 - 0.003 wt.-% B.
11. The hot-rolled steel strip product according to any one of the preceding claims, wherein the martensite is tempered.
12. The hot-rolled steel strip product according to any one of the preceding claims, having a tensile strength (R_m) of at least 1475 MPa, a yield strength ($R_{p0.2}$) of at least 1100 MPa, and an elongation (A_{50}) of at least 4%; preferably wherein the hot rolled steel strip product has a yield strength ($R_{p0.2}$) of at least 1200 MPa.

13. The hot-rolled steel strip product according to any one of the preceding claims, having a time to fracture of at least 130 minutes when subjected to a constant load test, as described in the detailed description, at a load of 80% of the tensile strength of the hot-rolled steel strip product.

5 14. A method for producing the hot-rolled steel strip product according to any one of the preceding claims, the method comprising:

providing a steel slab having the composition;

heating the steel slab to an austenitizing temperature of 1150 -1300 °C;

10 hot-rolling the steel slab to a desired thickness from a temperature in the range of Ar3 to 1280 °C to a desired final thickness of the steel product, wherein the finish rolling temperature is in the range of 800 - 960 °C, preferably 860 - 950 °C;

quenching the hot-rolled strip to a coiling temperature of 250 °C or less, preferably 150 °C or less, with an average cooling rate of at least 30°C/s;

15 optionally galvanizing the hot-rolled strip;

optionally temper annealing the hot-rolled strip at a temperature of 100 - 250 °C.

15. An automotive component produced from the hot-rolled steel strip product according to any one of claims 1 to 13.

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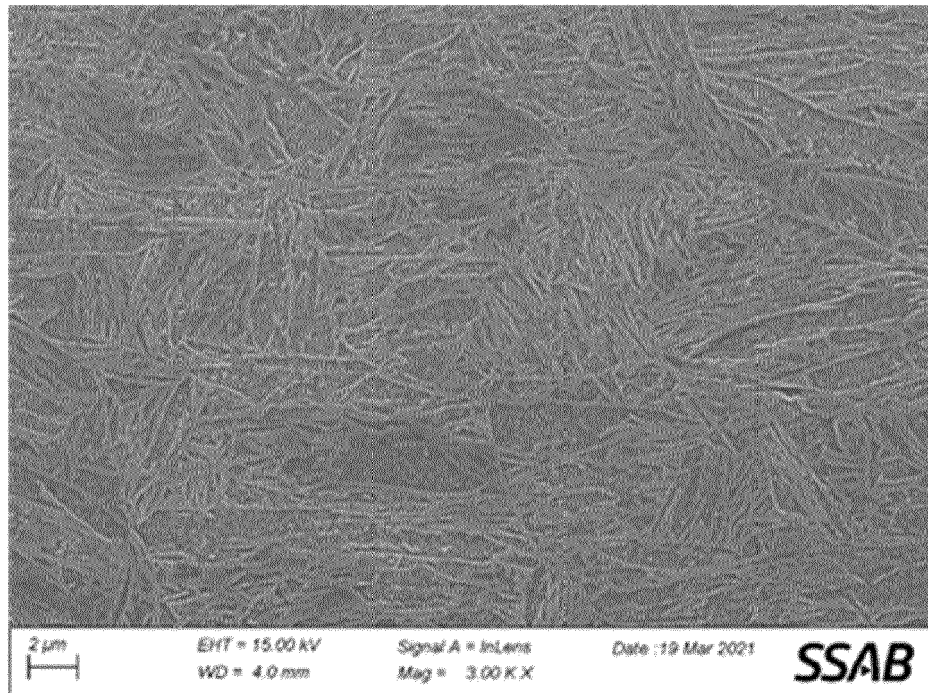


Fig. 1

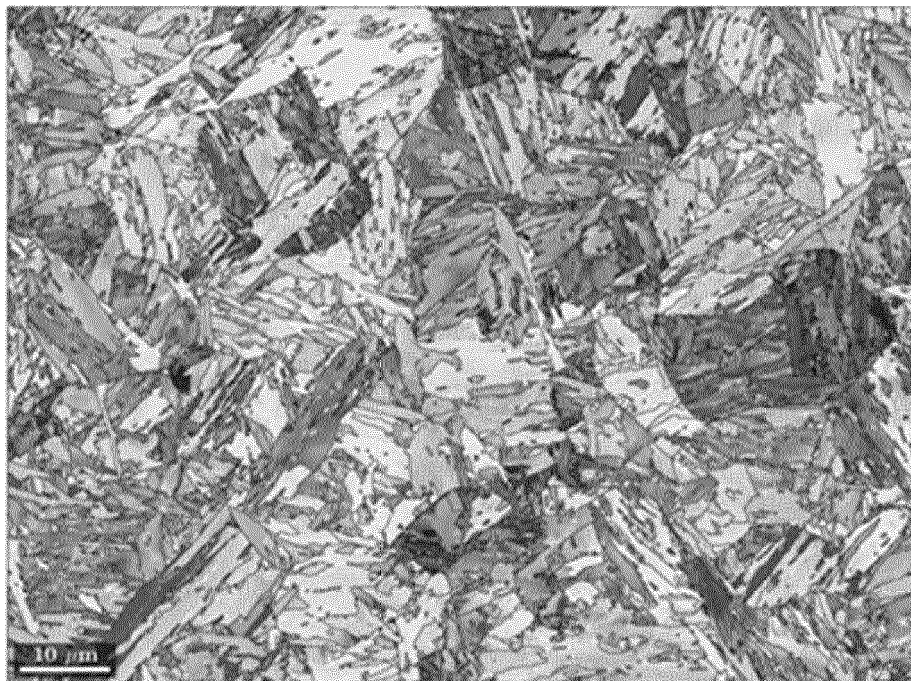


Fig. 2



EUROPEAN SEARCH REPORT

Application Number

EP 21 20 7843

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	EP 3 719 149 A1 (SSAB TECHNOLOGY AB [SE]) 7 October 2020 (2020-10-07) * paragraphs [0003], [0008], [0084], [0087], [0088]; claims 1, 5, 9; tables 1-3, ex. 1-3 *	1-15	INV. C21D8/02 C22C38/02 C22C38/04 C22C38/06 C22C38/08
A	US 2015/140358 A1 (YOKOYAMA TAKAFUMI [JP] ET AL) 21 May 2015 (2015-05-21) * paragraph [0001]; tables 1, ex. J *	1-15	C23C2/02 C23C2/06 C21D8/04 C22C38/42
A	EP 2 647 730 A2 (RAUTARUUKKI OYJ [FI]) 9 October 2013 (2013-10-09) * paragraphs [0001], [0005], [0098]; claim 1 *	1-15	
A	JP 4 874434 B1 (NIPPON STEEL CORP) 15 February 2012 (2012-02-15) * abstract; tables 1, ex. C and L *	1-15	
A	JP 2009 030093 A (JFE STEEL KK) 12 February 2009 (2009-02-12) * abstract; tables 1, ex. B *	1-15	TECHNICAL FIELDS SEARCHED (IPC) C22C C21D C23C

The present search report has been drawn up for all claims

Place of search

The Hague

Date of completion of the search

13 April 2022

Examiner

Chebeleu, Alice

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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 A : technological background
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 D : document cited in the application
 L : document cited for other reasons

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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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45

50

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 3719149	A1	07-10-2020	CA 3135141 A1	08-10-2020
			CA 3135144 A1	08-10-2020
			CN 113785078 A	10-12-2021
			CN 113785079 A	10-12-2021
			EP 3719148 A1	07-10-2020
			EP 3719149 A1	07-10-2020
			KR 20210149123 A	08-12-2021
			WO 2020201437 A1	08-10-2020
			WO 2020201438 A1	08-10-2020

US 2015140358	A1	21-05-2015	BR 112014024879 B1	22-01-2019
			CN 104364408 A	18-02-2015
			EP 2835440 A1	11-02-2015
			ES 2699996 T3	13-02-2019
			JP 5339005 B1	13-11-2013
			JP WO2013150669 A1	17-12-2015
			KR 20150000897 A	05-01-2015
			KR 20160121599 A	19-10-2016
			MX 366776 B	23-07-2019
			PL 2835440 T3	28-02-2019
			US 2015140358 A1	21-05-2015
			WO 2013150669 A1	10-10-2013

EP 2647730	A2	09-10-2013	EP 2647730 A2	09-10-2013
			ES 2738631 T3	24-01-2020
			PL 2647730 T3	31-12-2019

JP 4874434	B1	15-02-2012	BR 112012020436 A2	12-12-2017
			CN 102666885 A	12-09-2012
			JP 4874434 B1	15-02-2012
			JP WO2011099408 A1	13-06-2013
			WO 2011099408 A1	18-08-2011

JP 2009030093	A	12-02-2009	JP 5145804 B2	20-02-2013
			JP 2009030093 A	12-02-2009
