

(19)



(11)

EP 3 719 149 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

07.10.2020 Bulletin 2020/41

(51) Int Cl.:

C21D 8/02 (2006.01)

C22C 38/04 (2006.01)

C22C 38/42 (2006.01)

C22C 38/44 (2006.01)

C22C 38/54 (2006.01)

(21) Application number: **19185759.8**

(22) Date of filing: **11.07.2019**

(84) Designated Contracting States:

**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR**

Designated Extension States:

BA ME

Designated Validation States:

KH MA MD TN

(71) Applicant: **SSAB Technology AB**

101 21 Stockholm (SE)

(72) Inventors:

- **Larsson, Magnus**
781 84 Borlänge (SE)
- **Gladh, Magnus**
781 84 Borlänge (SE)

(30) Priority: **05.04.2019 EP 19167552**

(74) Representative: **Valea AB**

Box 7086

103 87 Stockholm (SE)

(54) **HIGH-HARDNESS STEEL PRODUCT AND METHOD OF MANUFACTURING THE SAME**

(57) A hot-rolled steel strip product comprising a composition consisting of, in terms of weight percentages, 0.14 % to 0.35 % C, 0 % to 0.5 % Si, 0.05 % to 0.40 % Mn, 0.1 % or less Al, 0.1 % to 0.4 % Cu, 0.2 % to 0.9 % Ni, 0.2 % to 0.9 % Cr, 0.2 % or less Mo, 0.005 % or less Nb, 0.035 % or less Ti, 0.05 % or less V, 0.0005 %

to 0.0050 % B, 0.025 % or less P, 0.008 % or less S, 0.01 % or less N, 0.01 % or less Ca, and the remainder being Fe and inevitable impurities, wherein the steel product has a Brinell hardness in the range of 420 to 580 HBW.

EP 3 719 149 A1

Description

FIELD OF INVENTION

[0001] The present invention relates to a high-hardness steel strip product exhibiting a good balance of high hardness and excellent mechanical properties such as impact strength and formability/bendability. The present invention further relates to a method of manufacturing the high-hardness steel strip product.

BACKGROUND

[0002] High hardness has a direct effect on wear resistance of a steel product, the higher hardness the better wear resistance. By high hardness it is meant that the Brinell hardness is at least 450 HBW and especially in the range of 500 HBW to 650 HBW.

[0003] Wear resistant steels are also known as abrasion resistant steels. They are used in applications in which high resistance against abrasive and shock wear is required. Such applications can be found in e.g. mining and earth moving industry, and waste transportation. Wear resistant steels are used for instance in gravel truck's bodies and excavator buckets, whereby longer service time of the vehicle components is achieved due to the high hardness provided by the wear resistant steels.

[0004] Wear resistant steels can also function as structural steels for making construction components if the wear resistant steels have sufficient mechanical properties such as formability, weldability and fatigue resistance that comply with national standards. The advantage of using wear resistant steels in the structural part for construction purposes is that less welding is needed and the weight can be lowered.

[0005] Such high hardness in a steel product is typically obtained by martensitic microstructure produced by quench hardening steel alloy having high content of carbon (0.41-0.50 wt. %) after austenitization in the furnace. In this process steel plates are first hot-rolled, slowly cooled to room temperature from the hot-rolling heat, reheated to austenitization temperature, equalized and finally quench hardened. This process is hereinafter referred to as the reheating and quenching (RHQ) process. Examples of steels produced in this way are wear resistant steels disclosed in CN102199737 or some commercial wear resistant steels. Due to the relatively high content of carbon, which is required to achieve the desired hardness, the resulting martensite reaction causes significant internal residual stresses to the steel. This is because the higher the carbon content the higher the lattice distortion. Therefore, this type of steel is very brittle and can even crack during the quench hardening. Due to the high carbon content these steels have deteriorated impact strength, poor formability or bendability, and low resistance to stress corrosion cracking (SCC). Stress corrosion cracking is the cracking induced from the combined influence of tensile stress and a corrosive environment. To overcome these drawbacks, a tempering step after quench hardening can be introduced to improve mechanical properties. This however increases the processing efforts and costs.

[0006] CN102392186 and CN103820717 relate to RHQ steel plates having relatively low carbon content (0.25-0.30 wt. % in CN102392186; 0.22-0.29 wt. % in CN103820717) and also relatively low manganese content. A tempering step after quench hardening is required for making such RHQ steel plates, which inevitably increases the processing efforts and costs.

[0007] EP2695960 relates to an abrasion-resistant steel product exhibiting excellent resistance to stress corrosion cracking, which steel sheet can be made in a process where direct quenching (DQ) may be performed immediately after hot rolling, without the reheating treatment after hot rolling as in the RHQ process. The steel sheet of EP2695960 has a relatively low carbon content (0.20-0.30 wt. %) and a relatively high manganese content (0.40-1.20 wt. %). In order to increase the resistance to stress corrosion cracking, the base phase or main phase of the microstructure of the steel product of EP2695960 must be made of tempered martensite. On the other hand, the area fraction of untempered martensite is restricted to 10% or less because the resistance to stress corrosion cracking is reduced in the presence of untempered martensite. In balancing abrasion resistance and resistance to stress corrosion cracking, the steel product of EP2695960 has a surface hardness of 520 HBW or less.

SUMMARY OF INVENTION

[0008] The present invention extends the utilization of the cost-effective thermomechanically controlled processing (TMCP) in conjunction with direct quenching (DQ) and possibly also tempering to produce a high-hardness steel strip product exhibiting excellent formability/bendability and impact strength values.

[0009] In view of the state of art, the object of the present invention is to solve the problem of providing a high-hardness steel strip product exhibiting excellent formability/bendability and impact strength values. The problem is solved by the combination of specific alloy designs with cost-efficient TMCP procedures which produces a metallographic microstructure comprising mainly martensite.

EP 3 719 149 A1

[0010] In a first aspect, the present invention provides a hot-rolled steel strip product comprising a composition consisting of, in terms of weight percentages (wt. %):

5	C	0.14 - 0.35, preferably 0.17 - 0.31, more preferably 0.20 - 0.28
	Si	0 - 0.5, preferably 0.01 - 0.50, more preferably 0.03 - 0.25
	Mn	0.05 - 0.40, preferably 0.05 - 0.30
	Al	0 - 0.1, preferably 0 - 0.08
	Cu	0.1 - 0.4, preferably 0.10 - 0.35
10	Ni	0.2 - 0.9, preferably 0.3 - 0.8, more preferably 0.3 - 0.7
	Cr	0.2 - 0.9, preferably 0.3 - 0.8, more preferably 0.3 - 0.7
	Mo	0 - 0.2, preferably 0 - 0.1
	Nb	0 - 0.005
	Ti	0 - 0.035
15	V	0 - 0.05
	B	0.0005 - 0.0050, preferably 0.0008 - 0.0040
	P	0 - 0.025, preferably 0 - 0.020
	S	0 - 0.008, preferably 0 - 0.005
20	N	0 - 0.01, preferably 0 - 0.005
	Ca	0 - 0.01, preferably 0 - 0.005, more preferably 0 - 0.003

remainder Fe and inevitable impurities.

[0011] The steel product has a low content of Mn, which is important for improving impact toughness and bendability.

25 **[0012]** The levels of Cr and Ni are set to improve hardenability. The level of Ni is further set to improve impact toughness and formability.

[0013] The level of Nb should be restricted to the lowest possible to increase formability or bendability of the steel product. Elements such as Nb may be present as residual contents that are not purposefully added.

30 **[0014]** The difference between residual contents and unavoidable impurities is that residual contents are controlled quantities of alloying elements, which are not considered to be impurities. A residual content as normally controlled by an industrial process does not have an essential effect upon the alloy.

[0015] In a second aspect, the present invention provides a method for manufacturing hot-rolled steel strip product comprising the following steps of

- providing a steel slab consisting of, in terms of weight percentages (wt. %):

35	C	0.14 - 0.35, preferably 0.17 - 0.31, more preferably 0.20 - 0.28
	Si	0 - 0.5, preferably 0.01 - 0.50, more preferably 0.03 - 0.25
	Mn	0.05 - 0.40, preferably 0.05 - 0.30
	Al	0 - 0.1, preferably 0 - 0.08
40	Cu	0.1 - 0.4, preferably 0.10 - 0.35
	Ni	0.2 - 0.9, preferably 0.3 - 0.8, more preferably 0.3 - 0.7
	Cr	0.2 - 0.9, preferably 0.3 - 0.8, more preferably 0.3 - 0.7
	Mo	0 - 0.2, preferably 0 - 0.1
45	Nb	0 - 0.005
	Ti	0 - 0.035
	V	0 - 0.05
	B	0.0005 - 0.0050, preferably 0.0008 - 0.0040
50	P	0 - 0.025, preferably 0 - 0.020
	S	0 - 0.008, preferably 0 - 0.005
	N	0 - 0.01, preferably 0 - 0.005
	Ca	0 - 0.01, preferably 0 - 0.005, more preferably 0 - 0.003

55 remainder Fe and inevitable impurities;

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

- hot-rolling to the desired thickness at a temperature in the range of A_{r3} to 1250°C, wherein the finish rolling temperature is in the range of 800 °C to 960 °C, preferably 870°C - 940°C, more preferably 880°C - 930°C; and

- direct quenching the hot-rolled steel strip product to a cooling end and coiling temperature of 450 °C or less, preferably 250 °C or less, more preferably 150 °C or less, and even more preferably 100 °C or less.

[0016] Optionally, a step of temper annealing is performed on the direct quenched product at a temperature in the range of 150 °C - 250 °C. However, the step of temper annealing is not required according to the present invention.

[0017] The steel product is a steel strip having a thickness of 10 mm or less, preferably 8 mm or less.

[0018] The obtained steel product has a microstructure comprising, in terms of volume percentages (vol. %), at least 90 vol. % martensite, preferably at least 95 vol. % martensite, and more preferably at least 98 vol. % martensite, measured from ¼ thickness of the steel strip product. The martensitic structure may be untempered, autotempered and/or tempered. Typically, the microstructure also comprises retained austenite, bainite, ferrite and/or cementite.

[0019] The obtained steel product has a prior austenite grain size of 50 µm or less, preferably 30 µm or less, more preferably 20 µm or less, measured from ¼ thickness of the steel strip product.

[0020] The aspect ratio of a prior austenite grain structure is one of the factors affecting a steel product's impact toughness and bendability. In order to improve impact toughness, the prior austenite grain structure should have an aspect ratio of at least 1.5, preferably at least 2, and more preferably at least 3. In order to improve bendability, the prior austenite grain structure should have an aspect ratio of 7 or less, preferably 5 or less, and more preferably 1.5 or less. The obtained steel product according to the present invention has a prior austenite grain structure with an aspect ratio in the range of 1.5 - 7, preferably 1.5 - 5, and more preferably 2 - 5, which ensures that a good balance of excellent impact toughness and excellent bendability can be achieved.

[0021] The steel product has a good balance of high hardness and excellent mechanical properties such as impact strength and formability/bendability.

[0022] The steel product has at least one of the following mechanical properties:

a Brinell hardness in the range of 420 - 580 HBW, preferably 450 - 550 HBW, more preferably 460 - 530 HBW, and even more preferably 470 - 530 HBW;

a Charpy-V impact toughness of at least 50 J/cm² at a temperature of -40 °C.

[0023] The steel product exhibits excellent bendability or formability. The steel product has a minimum bending radius of 3.2 t or less in a measurement direction longitudinal to the rolling direction wherein the bending axis is longitudinal to rolling direction; a minimum bending radius of 2.5 t or less in a measurement direction transversal to the rolling direction wherein the bending axis is transversal to rolling direction; and wherein t is the thickness of the steel strip product.

DETAILED DESCRIPTION OF THE INVENTION

[0024] The term "steel" is defined as an iron alloy containing carbon (C).

[0025] The term "Brinell hardness (HBW)" is a designation of hardness of steel. The Brinell hardness test is performed by pressing a spherical tungsten carbide ball with a diameter of 10 mm against a clean prepared surface of a metal sheet using a 3000 kilogram force, producing an impression, measured and given a special numerical value. A spherical tungsten carbide ball with a diameter of 5 mm and a load of 750 kilogram force are applied to test samples with thinner gauges, e.g. 3 mm in thickness.

[0026] The term "gauge" refers generally to a measure of the thickness of a metal sheet.

[0027] The term "ultimate tensile strength (UTS, R_m)" refers to the limit, at which the steel fractures under tension, thus the maximum tensile stress.

[0028] The term "yield strength (YS, R_{p0.2})" refers to 0.2 % offset yield strength defined as the amount of stress that will result in a plastic strain of 0.2 %.

[0029] The term "total elongation (TEL)" refers to the percentage by which the material can be stretched before it breaks; a rough indicator of formability, usually expressed as a percentage over a fixed gauge length of the measuring extensometer. Two common gauge lengths are 50 mm (A50) and 80 mm (A80).

[0030] The term "minimum bending radius (R_i)" is used to refer to the minimum radius of bending that can be applied to a test sheet without occurrence of cracks.

[0031] The term "bendability" refers to the ratio of R_i and the sheet thickness (t). The term "bendability" can also be used interchangeably with "formability" in the context of the current description.

[0032] The term "heat-affected zone (HAZ)" refers to a non-melted area of a metal material that has experienced changes in its material properties as a result of exposure to high temperatures. The alterations in material properties are usually a result of welding or high-heat cutting procedures. The HAZ is identified as the area between the weld or cut and the base metal material. These areas can vary in size and severity depending on the properties of the materials involved, the intensity and concentration of heat, and the process employed.

[0033] The alloying content of steel together with the processing parameters determines the microstructure which in turn determines the mechanical properties of the steel.

[0034] Alloy design is one of the first issues to be considered when developing a steel product with targeted mechanical properties. Next the chemical composition according to the present invention is described in more details, wherein % of each component refers to weight percentage.

Carbon C is used in the range of 0.14 % to 0.35 %.

[0035] C alloying increases strength of steel by solid solution strengthening, and hence C content determines the strength level. C is used in the range of 0.14 % to 0.35 % depending on targeted hardness. If the carbon content is less than 0.14%, it is difficult to achieve a Brinell hardness of more than 420 HBW. C is also an austenite stabilizing element. However, C has detrimental effects on weldability, impact toughness, formability or bendability, and resistance to stress corrosion cracking. Therefore, C content is set to not more than 0.35 %.

[0036] Preferably, C is used in the range of 0.17 % to 0.31 %, and more preferably 0.20 % to 0.28 %.

Silicon Si is used in an amount of 0.5 % or less.

[0037] Si is added to the composition to facilitate formation of a protective oxide layer under corrosive climate conditions, which provides good resistance against climatic corrosion and increases the durability of a paint layer that is easily damaged or removed from machines surfaces due to wear. Si is effective as a deoxidizing or killing agent that can remove oxygen from the melt during a steelmaking process. Si alloying enhances strength by solid solution strengthening, and enhances hardness by increasing austenite hardenability. Also the presence of Si can stabilize retained austenite. However, silicon content of higher than 0.5 % may unnecessarily increase carbon equivalent (CE) value thereby weakening the weldability. Furthermore, surface quality may be deteriorated if the Si level is excessively high.

[0038] Preferably, Si is used in the range of 0.01 % to 0.50 %, and more preferably 0.03 % to 0.25 %.

Manganese Mn is used in the range of 0.05 % to 0.40 %.

[0039] Mn alloying lowers martensite start temperature (M_s) and martensite finish temperature (M_f), which can suppress autotempering of martensite during quenching. Reduced autotempering of martensite leads to higher internal stresses that may enhance the risk for quench-induced cracking or distortion of shape. Although a lower degree of autotempered martensitic microstructures is beneficial to higher hardness, its negative effects on impact strength should not be underestimated.

[0040] Mn alloying enhances strength by solid solution strengthening, and enhances hardness by increasing austenite hardenability. However, if the Mn content is too high, hardenability of the steel will increase at the expense of impact toughness. Excessive Mn alloying may also lead to C-Mn segregation and formation of MnS, which could induce formation of initiation sites for pitting corrosion and stress corrosion cracking.

[0041] Thus, Mn is used in an amount of at least 0.05 % to ensure hardenability, but not more than 0.40 % to avoid the harmful effects as described above and to ensure excellent mechanical properties such as impact strength and bendability. Preferably, a low level of Mn is used in the range of 0.05 % to 0.30 % to further improve the bendability.

Aluminum Al is used in the range of 0.1 % or less.

[0042] Al is effective as a deoxidizing or killing agent that can remove oxygen from the melt during a steelmaking process. Al removes N by forming stable AlN particles and provides grain refinement, which is beneficial to high toughness. Also, Al stabilizes retained austenite. However, an excess of Al may increase non-metallic inclusions thereby deteriorating cleanliness.

[0043] Preferably, Al is used in the range of 0.08 % or less.

Copper Cu is used in the range of 0.1 % to 0.4 %.

[0044] Cu is added to the composition to facilitate formation of a protective oxide layer under corrosive climate conditions, which provides good resistance against climatic corrosion and increases the durability of a paint layer that is easily damaged or removed from machines surfaces due to wear. Cu may promote formation of low carbon bainitic structures, cause solid solution strengthening and contribute to precipitation strengthening. Cu may also have beneficial effects of inhibiting stress corrosion cracking. When added in excessive amounts, Cu deteriorates field weldability and the heat affected zone (HAZ) toughness. Therefore, the upper limit of Cu is set to 0.4 %.

[0045] Preferably, Cu is used in the range of 0.10 % to 0.35 %.

Nickel Ni is used in the range of 0.2 % to 0.9 %.

[0046] Ni is used to avoid quench induced cracking and also to improve toughness and formability. Ni is an alloying element that improves austenite hardenability thereby increasing strength with no or marginal loss of impact toughness and/or heat-affected zone (HAZ) toughness. Ni also improves surface quality thereby preventing pitting corrosion, *i.e.* initiation site for stress corrosion cracking. Ni is added to the composition to facilitate formation of a protective oxide layer under corrosive climate conditions, which provides good resistance against climatic corrosion and increases the durability of a paint layer that is easily damaged or removed from machines surfaces due to wear. However, nickel contents of above 0.9 % would increase alloying costs too much without significant technical improvement. An excess of Ni may produce high viscosity iron oxide scales which deteriorate surface quality of the steel product. Higher Ni contents also have negative impacts on weldability due to increased CE value and cracking sensitivity coefficient.

[0047] Ni is preferably used in the range of 0.3 % to 0.8 %, and more preferably 0.3 % to 0.7 %.

Chromium Cr is used in the range of 0.2 % to 0.9 %.

[0048] Cr is added to the composition to facilitate formation of a protective oxide layer under corrosive climate conditions, which provides good resistance against climatic corrosion and increases the durability of a paint layer that is easily damaged or removed from machines surfaces due to wear. Cr alloying provides better resistance against pitting corrosion thereby preventing stress corrosion cracking at an early stage. As mid-strength carbide forming element Cr increases the strength of both the base steel and weld with marginal expense of impact toughness. Cr alloying also enhances strength and hardness by increasing austenite hardenability. However, if Cr is used in an amount above 0.9 % the heat-affected zone (HAZ) toughness as well as field weldability may be adversely affected.

[0049] Preferably, Cr is used in the range of 0.3 % to 0.8 %, and more preferably 0.3 % to 0.7 %.

Molybdenum Mo is used in the range of 0.2 % or less.

[0050] Mo alloying improves impact strength, low-temperature toughness and tempering resistance. The presence of Mo enhances strength and hardness by increasing austenite hardenability. Mo can be added to the composition to provide hardenability in place of Mn. In the case of B alloying, Mo is usually required to ensure the effectiveness of B. However, Mo is not an economically acceptable alloying element. If Mo is used in an amount of above 0.2 % toughness may be deteriorated thereby increasing the risk of brittleness. An excessive amount of Mo may also reduce the effect of B. Furthermore, the inventors have noticed that Mo alloying retards recrystallization of austenite thereby increasing the aspect ratio of a prior austenite grain structure. Therefore, the level of Mo content should be carefully controlled to prevent excessive elongation of the prior austenite grains which may deteriorate bendability of the steel product.

[0051] Preferably, Mo is used in the range of 0.1 % or less.

Niobium Nb is used in an amount of 0.005 % or less.

[0052] Nb forms carbides NbC and carbonitrides Nb(C,N). Nb is considered to be the major grain refining element. Nb contributes to strengthening and toughening of steels. Yet, Nb addition should be limited to 0.005 % since an excess of Nb deteriorates bendability, in particular when direct quenching is applied and/or when Mo is present in the composition. Furthermore, Nb can be harmful for heat-affected zone (HAZ) toughness since Nb may promote the formation of coarse upper bainite structure by forming relatively unstable TiNbN or TiNb(C,N) precipitates. The level of Nb should be restricted to the lowest possible to increase formability or bendability of the steel product.

Titanium Ti is used in an amount of 0.035 % or less.

[0053] TiC precipitates are able to deeply trap a significant amount of hydrogen H, which decreases the H diffusivity in the materials and removes some of the detrimental H from the microstructure to prevent stress corrosion cracking. Ti is also added to bind free N that is harmful to toughness by forming stable TiN that together with NbC can efficiently prevent austenite grain growth in the reheating stage at high temperatures. TiN precipitates can further prevent grain coarsening in the heat-affected zone (HAZ) during welding thereby improving toughness. TiN formation suppresses BN precipitation, thereby leaving B free to make its contribution to hardenability. However, if Ti content is too high, coarsening of TiN and precipitation hardening due to TiC develop and toughness may be deteriorated. Therefore, it is necessary to restrict Ti so that it does not exceed 0.035%.

Vanadium V is used in an amount of 0.05 % or less.

[0054] V has substantially the same but smaller effects as Nb. V₄C₃ precipitates are able to deeply trap a significant amount of hydrogen H, which decreases the H diffusivity in the materials and removes some of the detrimental H from the microstructure to prevent hydrogen induced cracking (HIC). V is a strong carbide and nitride former, but V(C,N) can also form and its solubility in austenite is higher than that of Nb or Ti. Thus, V alloying has potential for dispersion and precipitation strengthening, because large quantities of V are dissolved and available for precipitation in ferrite. However, an addition of more than 0.05 % V has negative effects on weldability, hardenability and alloying cost.

Boron B is used in the range of 0.0005 % to 0.0050 %.

[0055] B is a well-established microalloying element to increase hardenability. Boron can be added to retard phosphorus segregation to grain boundaries thereby reducing embrittlement during welding in the heat-affected zone (HAZ). Effective B alloying requires the presence of Ti to prevent formation of BN. In the presence of B, Ti content can be lowered to be less than 0.02%, which is beneficial for toughness. However, hardenability deteriorates if the B content exceeds 0.005 %.

[0056] Preferably, B is used in the range of 0.0008 % to 0.0040 %.

Calcium Ca is used in an amount of 0.01 % or less.

[0057] Ca addition during a steelmaking process is for refining, deoxidation, desulphurization, and control of shape, size and distribution of oxide and sulphide inclusions. Ca is usually added to improve subsequent coating. However, an excessive amount of Ca should be avoided to achieve clean steel thereby preventing the formation of calcium sulfide (CaS) or calcium oxide (CaO) or mixture of these (CaOS) that may deteriorate the mechanical properties such as bendability and stress corrosion cracking (SCC) resistance.

[0058] Preferably, Ca is used in an amount of 0.005 % or less, and more preferably 0.003 % or less to ensure excellent mechanical properties such as impact strength and bendability.

[0059] Unavoidable impurities can be phosphorus P, sulfur S and nitrogen N. Their content in terms of weight percentages (wt. %) is preferably defined as follows:

P	0 - 0.025, preferably 0 - 0.020
S	0 - 0.008, preferably 0 - 0.005
N	0 - 0.01, preferably 0 - 0.005

[0060] Other inevitable impurities may be hydrogen H, oxygen O and rare earth metals (REM) or the like. Their contents are limited in order to ensure excellent mechanical properties, such as impact toughness.

[0061] The steel product with the targeted mechanical properties is produced in a process that determines a specific microstructure which in turn dictates the mechanical properties of the steel product.

[0062] The first step is to provide a steel slab by means of, for instance a process of continuous casting, also known as strand casting.

[0063] In the reheating stage, the steel slab is heated to the austenitizing temperature of 1150 - 1300 °C, and thereafter subjected to a temperature equalizing step that may take 30 to 150 minutes. The reheating and equalizing steps are important for controlling the austenite grain growth. An increase in the heating temperature can cause dissolution and coarsening of alloy precipitates, which may result in abnormal grain growth.

[0064] The final steel product has a prior austenite grain size of 50 μm or less, preferably 30 μm or less, more preferably 20 μm or less, measured from ¼ thickness of the steel strip product.

[0065] In the hot rolling stage the slab is hot rolled to the desired thickness at a temperature in the range of Ar₃ to 1250°C, wherein the finish rolling temperature (FRT) is in the range of 800 °C to 960 °C, preferably 870°C - 940°C, more preferably 880°C - 930°C.

[0066] The aspect ratio of a prior austenite grain structure is one of the factors affecting a steel product's impact toughness and bendability. In order to improve impact toughness, the prior austenite grain structure should have an aspect ratio of at least 1.5, preferably at least 2, and more preferably at least 3. In order to improve bendability, the prior austenite grain structure should have an aspect ratio of 7 or less, preferably 5 or less, and more preferably 1.5 or less. A desired aspect ratio of prior austenite grains can be achieved by adjusting a number of parameters such as finish rolling temperature, strain/deformation, strain rate, and/or alloying with the elements such as Mo that retard recrystallization of austenite.

[0067] The obtained steel product according to the present invention has a prior austenite grain structure with an aspect ratio in the range of 1.5 - 7, preferably 1.5 - 5, and more preferably 2 - 5, which ensures that a good balance of

excellent impact toughness and excellent bendability can be achieved.

[0068] The obtained steel strip product has a thickness of 10 mm or less, preferably 8 mm or less.

[0069] The hot-rolled steel strip product is direct quenched to a cooling end and coiling temperature of 450 °C or less, preferably 250 °C or less, more preferably 150 °C or less, and even more preferably 100 °C or less. The cooling rate is at least 30 °C/s.

[0070] The direct quenched steel strip product is coiled at temperature of 450 °C or less, preferably 250 °C or less, more preferably 150 °C or less, and even more preferably 100 °C or less.

[0071] The obtained steel strip product has a microstructure comprising, in terms of volume percentages (vol. %), at least 90 vol. % martensite, preferably at least 95 vol. % martensite, and more preferably at least 98 vol. % martensite, measured from ¼ thickness of the steel strip product. The martensitic structure may be untempered, autotempered and/or tempered. Preferably, the microstructure comprises 1 vol. % or less retained austenite, and more preferably 0.5 vol. % or less retained austenite. Typically, the microstructure also comprises bainite, ferrite, pearlite and/or cementite.

[0072] Optionally, an extra step of temper annealing is performed at a temperature in the range of 150 °C - 250 °C.

[0073] The steel strip product has a good balance of hardness and other mechanical properties such as excellent impact strength and excellent formability/bendability.

[0074] The steel strip product has a high Brinell hardness in the range of 420 - 580 HBW, preferably 450 - 550 HBW, more preferably 460 - 530 HBW, and even more preferably 470 - 530 HBW.

[0075] The steel strip product with high hardness has a Charpy-V impact toughness of at least 50 J/cm² at a temperature of -40 °C thereby fulfilling the conventional impact strength requirements.

[0076] The steel strip product exhibits excellent bendability or formability. The steel product has a minimum bending radius (R_t) of 3.2 t or less in a measurement direction longitudinal to the rolling direction wherein the bending axis is longitudinal to rolling direction; a minimum bending radius (R_t) of 2.5 t or less in a measurement direction transversal to the rolling direction wherein the bending axis is transversal to rolling direction; and wherein t is the thickness of the steel strip product.

[0077] The following examples further describe and demonstrate embodiments within the scope of the present invention. The examples are given solely for the purpose of illustration and are not to be construed as limitations of the present invention, as many variations thereof are possible without departing from the scope of the invention.

[0078] The chemical compositions used for producing the tested steel strip products are presented in Table 1. Steel types A - C are the inventive compositions according to the present disclosure. Steel types D and E are comparative compositions which comprise a relatively high Mn content of 1.20 wt. % and 1.19 wt. % respectively (Table 1).

[0079] The manufacturing conditions for producing the tested steel strip products are presented in Table 2.

[0080] The mechanical properties of the tested steel strip products are presented in Table 3.

Microstructure

[0081] Microstructure can be characterized from SEM micrographs and the volume fraction can be determined using point counting or image analysis method. The microstructures of the tested inventive examples no. 1 - 3 all have a main phase of martensite in an amount of at least 90 vol. %.

Brinell hardness HBW

[0082] The Brinell hardness test is performed by pressing a spherical tungsten carbide ball with a diameter of 10 mm against a clean prepared surface of the steel strip samples with a thickness of 6 mm using a 3000 kilogram force, producing an impression, measured and given a special numerical value. For the strip samples with a thickness of 3 mm, a spherical tungsten carbide ball with a diameter of 5 mm and a load of 750 kilogram force are applied. The measurement is done perpendicular to the upper surface of the steel sheet at 10 - 15 % depth from the steel surface. As shown in Table 3, each one of the inventive examples no. 1 - 3 exhibits a Brinell hardness in the range of 467 - 489 HBW. The comparative examples no. 4 exhibits a Brinell hardness of 485 HBW while the comparative example no. 5 exhibits a Brinell hardness of 502 HBW.

Charpy-V impact toughness

[0083] The impact toughness values at -40 °C are obtained by Charpy V-notch tests according to the ISO 148 standard. Each one of the inventive examples no. 1 - 3 has a Charpy-V impact toughness in the range of 78 - 118 J/cm² at a temperature of -40 °C if the measurement direction is longitudinal to the rolling direction. Each one of the inventive examples no. 1 - 3 has a Charpy-V impact toughness in the range of 65 - 90 J/cm² at a temperature of -40 °C if the measurement direction is transversal to the rolling direction. The impact toughness of the inventive examples no. 1 - 3 is improved compared to the comparative examples no. 4 and 5.

Elongation

[0084] Elongation was determined according ISO 6892 standard using longitudinal specimens. The mean value of total elongation (A80) of the inventive examples no. 1, 2 and 3 is 4.5, 7.6 and 7.7 respectively (Table 3). The comparative examples no. 4 and 5 have better elongation values than the inventive examples no. 1 - 3 at the expense of Charpy-V impact toughness and bendability.

Bendability

[0085] The bend test consists of 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. The limit of bendability (R/t) for a material can be identified in a test series if a minimum of 3 m bending length, without any defects, is fulfilled with the same punch radius (R) both longitudinally and transversally. Cracks, surface necking marks and flat bends (significant necking) are registered as defects.

[0086] According to the bend tests, each one of the inventive examples no. 1 - 3 has a minimum bending radius (R_i) of 2.8 t or less in a measurement direction longitudinal to the rolling direction; a minimum bending radius (R_i) of 2.0 t or less in a measurement direction transversal to the rolling direction; and wherein t is the thickness of the steel strip product (Table 3). The comparative examples no. 4 and 5 exhibit a minimum bending radius (R_i) of 3.7 t and 3.3 t respectively in a measurement direction longitudinal to the rolling direction, and a minimum bending radius (R_i) of 3.0 t and 2.7 t respectively in a measurement direction transversal to the rolling direction (Table 3).

Yield strength

[0087] Yield strength was determined according ISO 6892 standard using longitudinal specimens. Each one of the inventive examples no. 1 - 3 has a mean value of yield strength ($R_{p0.2}$) in the range of 1310 MPa to 1413 MPa measured in the longitudinal direction (Table 3). The comparative examples no. 4 and 5 have a mean value of yield strength ($R_{p0.2}$) of 1375 MPa and 1397 MPa respectively, measured in the longitudinal direction (Table 3).

Tensile strength

[0088] Ultimate tensile strength (R_m) was determined according ISO 6892 standard using longitudinal specimens. Each one of the inventive examples no. 1 - 3 has a mean value of ultimate tensile strength (R_m) in the range of 1511 MPa to 1609 MPa, measured in the longitudinal direction (Table 3). The comparative examples no. 4 and 5 have a mean value of ultimate tensile strength (R_m) of 1617 MPa and 1654 MPa respectively, measured in the longitudinal direction (Table 3).

Table 1. Chemical compositions (wt. %).

Steel type	C	Si	Mn	P	S	N	Cr	Ni	Cu	Mo	Al	Nb	V	Ti	B	Ca
1A	0.2390	0.1720	0.2000	0.0100	0.0018	0.0028	0.3840	0.4760	0.1600	0.0580	0.0550	0.0010	0.0150	0.0020	0.0011	0.0013
1B	0.2290	0.1790	0.2000	0.0070	0.0006	0.0024	0.3900	0.5100	0.1600	0.0500	0.0510	0.0010	0.0100	0.0020	0.0011	0.0008
1C	0.2500	0.1770	0.2000	0.0070	0.0006	0.0022	0.4000	0.5000	0.1500	0.0140	0.0580	0.0010	0.0090	0.0020	0.0011	0.0008
2D	0.2290	0.1740	1.2000	0.0090	0.0005	0.0023	0.2100	0.0600	0.0100	0.0230	0.0390	0.0010	0.0090	0.0100	0.0015	0.0007
2E	0.2550	0.1770	1.1900	0.0100	0.0007	0.0026	0.2000	0.0500	0.0100	0.0340	0.0390	0.0010	0.0090	0.0090	0.0013	0.0007
1 inventive composition																
2 comparative composition																

Table 2. Manufacturing conditions

Steel strip no.	Steel type	Strip thickness (mm)	Hot rolling			Cooling		Temper annealing		Remarks
			Heating temp. (°C)	RT (°C)	FRT (°C)	Cooling temp. (°C)	Cooling rate (°C/s)	Annealing temp. (°C)	Holding time (h)	
1	A	3	1250	1130	890	< 100	262	200	8	inventive example
2	B	6	1200	1100	900	< 100	127	200	8	inventive example
3	C	6	1210	1090	890	< 100	128	-	-	inventive example
4	D	3	1270	1140	905	< 100	290	-	-	comparative example
5	E	6	1230	1090	905	< 100	142	-	-	comparative example

Table 3. Mechanical properties

Steel strip no	Steel type	Strip thickness (mm)	R _{p0.2} (L) (MPa)	R _m (L) (MPa)	A80 (L) (%)	HBW	ChV (-40) (J/cm ²)		Bending (R _p /t)		Remarks
							Longit.	Transv.	Longit.	Transv.	
1	A	3	1413	1609	4.5	488	105	90	2.6	2.0	inventive example
2	B	6	1310	1511	7.6	467	118	85	2.3	1.3	inventive example
3	C	6	1334	1582	7.7	489	78	65	2.8	1.7	inventive example
4	D	3	1375	1617	6.3	485	-	-	3.7	3.0	comparative example
5	E	6	1397	1654	8.0	502	58	50	3.3	2.7	comparative example

Claims

1. A hot-rolled steel strip product comprising a composition consisting of, in terms of weight percentages (wt. %):

5	C	0.14 - 0.35, preferably 0.17 - 0.31, more preferably 0.20 - 0.28
	Si	0 - 0.5, preferably 0.01 - 0.50, more preferably 0.03 - 0.25
	Mn	0.05 - 0.40, preferably 0.05 - 0.30
	Al	0 - 0.1, preferably 0 - 0.08
10	Cu	0.1 - 0.4, preferably 0.10 - 0.35
	Ni	0.2 - 0.9, preferably 0.3 - 0.8, more preferably 0.3 - 0.7
	Cr	0.2 - 0.9, preferably 0.3 - 0.8, more preferably 0.3 - 0.7
	Mo	0 - 0.2, preferably 0 - 0.1
	Nb	0 - 0.005
15	Ti	0 - 0.035
	V	0 - 0.05
	B	0.0005 - 0.0050, preferably 0.0008 - 0.0040
	P	0 - 0.025, preferably 0 - 0.020
20	S	0 - 0.008, preferably 0 - 0.005
	N	0 - 0.01, preferably 0 - 0.005
	Ca	0 - 0.01, preferably 0 - 0.005, more preferably 0 - 0.003

remainder Fe and inevitable impurities, wherein the steel product has a Brinell hardness in the range of 420 - 580 HBW.

2. The steel product according to claim 1, wherein the steel product has a Brinell hardness in the range of 450 - 550 HBW, preferably 460 - 530 HBW, and more preferably 470 - 530 HBW.

3. The steel product according to claim 1 or 2, wherein the steel product has a Charpy-V impact toughness of at least 50 J/cm² at a temperature of -40 °C.

4. The steel product according to any one of the preceding claims, wherein the steel product has a minimum bending radius of 3.2 t or less in a measurement direction longitudinal to the rolling direction; a minimum bending radius of 2.5 t or less in a measurement direction transversal to the rolling direction; and wherein t is the thickness of the steel strip product.

5. The steel product according to any one of the preceding claims, wherein the steel product has a microstructure consisting of, in terms of volume percentages (vol. %), martensite in an amount of at least 90 vol. %, preferably at least 95 vol. % and more preferably at least 98 vol. %; and remainder being retained austenite, bainite, ferrite, pearlite and/or cementite.

6. The steel product according to any one of the preceding claims, wherein the steel product has a prior austenite grain size of 50 μm or less, preferably 30 μm or less, more preferably 20 μm or less.

7. The steel product according to any one of the preceding claims, wherein the steel product has a prior austenite grain structure with an aspect ratio in the range of 1.5 - 7, preferably 1.5 - 5, and more preferably 2 - 5.

8. The steel product according to any one of the preceding claims, wherein the steel strip product has a thickness of 10 mm or less, and preferably 8 mm or less.

9. A method for manufacturing the steel product according to any one of the preceding claims comprising the following steps of

- providing a steel slab consisting of the chemical composition according to claim 1;
- heating the steel slab to the austenitizing temperature of 1150 - 1300 °C;
- hot-rolling to the desired thickness at a temperature in the range of Ar₃ to 1250°C, wherein the finish rolling temperature is in the range of 800 °C to 960 °C, preferably 870°C - 940°C, more preferably 880°C - 930°C;
- direct quenching the hot-rolled steel strip product to a cooling end and coiling temperature of 450 °C or less,

EP 3 719 149 A1

preferably 250 °C or less, more preferably 150 °C or less, and even more preferably 100 °C or less; and
- optionally, temper annealing at a temperature in the range of 150 °C - 250 °C.

5

10

15

20

25

30

35

40

45

50

55



EUROPEAN SEARCH REPORT

 Application Number
 EP 19 18 5759

5

10

15

20

25

30

35

40

45

50

55

1

EPO FORM 1503 03.82 (P04C01)

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	JP 2009 030093 A (JFE STEEL KK) 12 February 2009 (2009-02-12) * abstract; example B; tables 1,2 * -----	1-9	INV. C21D8/02 C22C38/04 C22C38/42 C22C38/44 C22C38/54
X	JP 4 874434 B1 (NIPPON STEEL CORP) 15 February 2012 (2012-02-15) * paragraph [0062]; claims 1,2; example L; tables 1-4 * -----	1-9	
X	EP 2 578 705 A1 (NIPPON STEEL & SUMITOMO METAL CORP [JP]) 10 April 2013 (2013-04-10) * claims 1-9; example F; tables 1,2 * -----	1-9	
A	WO 2015/007723 A1 (RAUTARUUKKI OYJ [FI]) 22 January 2015 (2015-01-22) * pages 15-17; claims 1-17 * -----	1-9	
A	EP 2 778 239 A1 (TENARIS COILED TUBES LLC [US]) 17 September 2014 (2014-09-17) * claims 1-22; tables A1-C2 * -----	1-9	
			TECHNICAL FIELDS SEARCHED (IPC)
			C21D C22C
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 6 August 2019	Examiner Catana, Cosmin
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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

EP 19 18 5759

5 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
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

06-08-2019

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 2009030093 A	12-02-2009	JP 5145804 B2 JP 2009030093 A	20-02-2013 12-02-2009
JP 4874434 B1	15-02-2012	BR 112012020436 A2 CN 102666885 A JP 4874434 B1 JP W02011099408 A1 WO 2011099408 A1	12-12-2017 12-09-2012 15-02-2012 13-06-2013 18-08-2011
EP 2578705 A1	10-04-2013	CA 2800991 A1 CN 103261451 A EP 2578705 A1 ES 2691209 T3 JP 5234226 B2 JP W02011152447 A1 KR 20130020811 A PL 2578705 T3 TR 201815837 T4 TW 201217199 A US 2013086965 A1 WO 2011152447 A1	08-12-2011 21-08-2013 10-04-2013 26-11-2018 10-07-2013 01-08-2013 28-02-2013 29-03-2019 21-11-2018 01-05-2012 11-04-2013 08-12-2011
WO 2015007723 A1	22-01-2015	NONE	
EP 2778239 A1	17-09-2014	BR 102014006157 A2 CA 2845471 A1 CN 104046918 A EP 2778239 A1 JP 6431675 B2 JP 2014208888 A MX 360596 B RU 2014109873 A RU 2018127869 A US 2014272448 A1 US 2017335421 A1 US 2018051353 A1 US 2018223384 A1	26-01-2016 14-09-2014 17-09-2014 17-09-2014 28-11-2018 06-11-2014 09-11-2018 20-09-2015 13-03-2019 18-09-2014 23-11-2017 22-02-2018 09-08-2018

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- CN 102199737 [0005]
- CN 102392186 [0006]
- CN 103820717 [0006]
- EP 2695960 A [0007]