

(19)



(11)

EP 3 719 148 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: **19167552.9**

(22) Date of filing: **05.04.2019**

(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:

- **Hemmilä, Mikko**
86400 Vihanti (FI)
- **Liimatainen, Tommi**
92130 Raahe (FI)
- **Virolainen, Esa**
90540 Oulu (FI)
- **Suikkanen, Pasi**
90400 Oulu (FI)

(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, 0.17 % to 0.38 % C, 0 % to 0.5 % Si, 0.1 % to 0.4 % Mn, 0.015 % to 0.15 % Al, 0.1 % to 0.6 % Cu, 0.2 % to 0.8 % Ni, 0.1 % to 1 % Cr, 0.01 % to 0.3 % Mo, 0 % to 0.005 % Nb, 0 % to 0.05 % Ti, 0 % to 0.2 % V, 0.0008

% to 0.005 % B, 0 % to 0.025 % P, 0.008 % or less S, 0.01 % or less N, 0 % to 0.01 % Ca, and the remainder being Fe and inevitable impurities, wherein the steel product has a Brinell hardness in the range of 420 - 580 HBW, and a corrosion index (ASTM G101-04) of at least 5.

EP 3 719 148 A1

Description

FIELD OF INVENTION

[0001] The present invention relates to a high-hardness steel strip product exhibiting excellent resistance to climatic corrosion, a good balance of high hardness and excellent mechanical properties such as impact strength and 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 are achieved due to the high hardness provided by the wear resistant steels. The benefits of wear resistant steels are even more crucial when the paint layer on a machine's outer surface is frequently exposed to mechanical stresses such as impacts which can cause scratch to paint layers.

[0004] Such high hardness in 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. To overcome these drawbacks related to brittleness, a tempering step after quench hardening is usually introduced, which however increases the processing efforts and costs.

[0005] 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. Usually, stress corrosion cracking starts as a pitting corrosion with hard-to-detect fine cracks penetrating into the material while most of the material surface appears intact. Stress corrosion cracking is classified as a catastrophic form of corrosion, as the detection of such fine cracks can be very difficult and the damage not easily predicted. There is a need of better approaches to decrease the carbon content without compromising the hardness or any of the other mechanical properties, such as impact strength, formability/bendability or resistance to stress corrosion cracking.

[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.

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

SUMMARY OF INVENTION

[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 resistance to climatic corrosion, guaranteed impact strength values and excellent

formability/bendability. The problem is solved by the combination of specific alloy designs with cost-efficient TMCP procedures which produces a metallographic microstructure comprising mainly martensite.

[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	0.17 - 0.38, preferably 0.21 - 0.35, more preferably 0.22 - 0.28
	Si	0 - 0.5, preferably 0.01 - 0.5, more preferably 0.03 - 0.25
	Mn	0.1 - 0.4, preferably 0.15 - 0.3
	Al	0.015 - 0.15
10	Cu	0.1 - 0.6, preferably 0.1 - 0.5, more preferably 0.1 - 0.35
	Ni	0 - 0.8, preferably 0.2 - 0.8
	Cr	0.1 - 1, preferably 0.3 - 1, more preferably 0.35 - 1, even more preferably 0.35 - 0.8
	Mo	0.01 - 0.3, preferably 0.03 - 0.3, more preferably 0.05 - 0.3
15	Nb	0 - 0.005
	Ti	0 - 0.05, preferably 0 - 0.035, more preferably 0 - 0.02
	V	0 - 0.2, preferably 0 - 0.06
	B	0.0005 - 0.005, preferably 0.0008 - 0.005
	P	0 - 0.025, preferably 0.001 - 0.025, more preferably 0.001 - 0.012
20	S	0 - 0.008, preferably 0 - 0.005
	N	0 - 0.01, preferably 0 - 0.005, more preferably 0 - 0.004
	Ca	0 - 0.01, preferably 0 - 0.005, more preferably 0.0008 - 0.003

25 remainder Fe and inevitable impurities.

[0011] Preferably, the aforementioned composition comprises, in terms of weight percentages (wt. %):

	Ti	0 - 0.005
	N	0 - 0.003

30

[0012] Preferably, the aforementioned composition comprises, in terms of weight percentages (wt. %):

	Ti	> 0.005 and $\leq$ 0.05
35	N	> 0.003 and $\leq$ 0.01

[0013] Preferably, $[Ni] > [Cu]/3$, and more preferably $[Ni] > [Cu]/2$, wherein

40 $[Ni]$ is the amount of Ni in the composition,
 $[Cu]$ is the amount of Cu in the composition.

[0014] The steel product is alloyed with the essential alloying elements Si, Cu, Ni and Cr, which provides good resistance against climatic corrosion and increases durability of a paint layer.

[0015] The steel product has a low content of Mn, which is important for improving impact toughness and bendability.

45 **[0016]** The Ca/S ratio is adjusted such that CaS cannot form thereby improving impact toughness and bendability. The Ca/S ratio is preferably in the range of 1 - 2, more preferably 1.1 - 1.7, and even more preferably 1.2 - 1.6.

[0017] 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.

50 **[0018]** 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.

[0019] In a second aspect, the present invention provides a method for manufacturing hot-rolled steel strip product comprising the following steps of

- 55
- providing a steel slab consisting of the chemical composition as mentioned previously in the Summary and according to any one of the claims 1 to 5;
 - heating the steel slab to the austenitizing temperature of 1200 - 1350 °C;

- hot-rolling to the desired thickness at a temperature in the range of Ar_3 to 1300°C, wherein the finish rolling temperature is in the range of 800 °C to 960 °C, preferably 870°C - 930°C, more preferably 885°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.

[0020] Optionally, a step of temper annealing is performed on the direct quenched and coiled strip 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.

[0021] The steel product is a steel strip having a thickness of 10 mm or less, preferably 8 mm or less, and more preferably 7 mm or less.

[0022] 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 $\frac{1}{4}$ thickness of the steel strip product. The martensitic structure may be untempered, autotempered and/or tempered. Preferably, the martensitic structure is not tempered. More preferably, the aforementioned microstructure comprises more than 10 vol. % untempered martensite. Preferably, the microstructure comprises 0 - 1 vol. % residual austenite, and more preferably 0 - 0.5 vol. % residual austenite. Typically, the microstructure also comprises bainite, ferrite and/or pearlite.

[0023] 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 $\frac{1}{4}$ thickness of the steel strip product.

[0024] 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.

[0025] The obtained steel product has a good balance of hardness and other mechanical properties such as improved resistance to climatic corrosion and excellent impact strength. 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, and more preferably 470 - 530 HBW;
- a corrosion index (ASTM G101-04) ≥ 5 , preferably ≥ 5.5 , and more preferably ≥ 6 ;
- a Charpy-V impact toughness of at least 34 J/cm² at a temperature of -20 °C or -40 °C.

[0026] The steel product exhibits excellent bendability or formability. The steel product has a minimum bending radius of 3.4 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 2.7 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.

[0027] The steel product has a good balance of high hardness and excellent mechanical properties such as impact strength and formability/bendability. Consequently, the steel product exhibits excellent resistance to climatic corrosion.

BRIEF DESCRIPTION OF DRAWINGS

[0028]

Figure 1 illustrates the microstructures.

DETAILED DESCRIPTION OF THE INVENTION

[0029] The term "steel" is defined as an iron alloy containing carbon (C).

[0030] The term climatic corrosion (a.k.a. atmospheric corrosion) refers to outdoor corrosion caused by local environmental conditions. Environmental conditions are formed from weather phenomena like rain and sunshine. They are also affected by different impurities in the air like chlorides from sea water and sulfur compounds coming from volcanic activity and industry or mining.

[0031] The term "Brinell hardness (HBW)" is a designation of hardness of steel. The Brinell hardness test is performed by pressing a 10 mm spherical tungsten carbide ball against a clean prepared surface using a 3000 kilogram force, producing an impression, measured and given a special numerical value.

[0032] The term "corrosion index (ASTM G101-04)" refers to the American Society for Testing and Materials (ASTM)

standard G101 which is currently the only available guide to quantify the atmospheric corrosion resistance of weathering steels as a function of their composition.

[0033] The term "accelerated continuous cooling (ACC)" refers to a process of accelerated cooling at a cooling rate down to a temperature without interruption.

[0034] The term "ultimate tensile strength (UTS, R_m)" refers to the limit, at which the steel fractures under tension, thus the maximum tensile stress.

[0035] 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 %.

[0036] 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 (A_{50}) and 80 mm (A_{80}).

[0037] 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.

[0038] The term "bendability" refers to the ratio of R_i and the sheet thickness (t).

[0039] The alloying content of steel together with the processing parameters determines the microstructure which in turn determines the mechanical properties of the steel.

[0040] 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 0.17 % to 0.38 %.

[0041] 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 0.17 % to 0.38% depending on targeted hardness. If the carbon content is less than 0.17%, it is difficult to achieve a Brinell hardness of more than 420 HBW. 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 0.38 %.

[0042] Preferably, C is used in the range of 0.21 % to 0.35 %, and more preferably 0.22 % to 0.28 %.

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

[0043] 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 residual 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 Si is present in excess.

[0044] As previously mentioned, Si is an important alloying element for providing sufficient hardness and good resistance to climatic corrosion, and for increasing durability of a paint layer. Preferably, Si is used in the range of 0.01 % to 0.5 %, and more preferably 0.03 % to 0.25 %.

Manganese Mn is used in the range of 0.1 % to 0.4 %.

[0045] 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 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.

[0046] Mn alloying also 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.

[0047] Thus, Mn is used in an amount of at least 0.1 % to ensure hardenability, but not more than 0.4 % 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 0.15 % to 0.3 %.

Aluminum Al is used in the range of 0.015 % to 0.15 %.

[0048] Al is effective as a deoxidizing or killing agent that can remove oxygen from the melt during a steelmaking process. Al also removes N by forming stable AlN particles and provides grain refinement, which is beneficial to high toughness, especially at low temperatures. Also Al stabilizes residual austenite. However, an excess of Al may increase non-metallic inclusions thereby deteriorating cleanliness.

Copper Cu is used in the range of 0.1 % to 0.6 %.

[0049] 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 0.6%.

[0050] As previously mentioned, Cu is an important alloying element for providing sufficient hardness and good resistance to climatic corrosion, and for increasing durability of a paint layer. Preferably, Cu is used in the range of 0.1 % to 0.5 %, and more preferably 0.1 % to 0.35 %.

Nickel Ni is used in an amount of 0.8 % or less.

[0051] Ni is used to avoid quench induced cracking and also to improve low temperature toughness. Ni is an alloying element that improves austenite hardenability thereby increasing strength with no or marginal loss of impact toughness and/or 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 0.8 % 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.

[0052] As previously mentioned, Ni is an important alloying element for providing sufficient hardness and good resistance to climatic corrosion with no or marginal loss of impact toughness, and for increasing durability of a paint layer. Ni is preferably used in the range of 0.2 % to 0.8 %.

Chromium Cr is used in the range of 0.1 % to 1 %.

[0053] 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 1 % the HAZ toughness as well as field weldability may be adversely affected.

[0054] As previously mentioned, Cr is an important alloying element for providing sufficient hardness and good resistance to climatic corrosion with no or marginal loss of impact toughness, and for increasing durability of a paint layer. Preferably, Cr is used in the range of 0.3 % to 1 %, more preferably 0.35 % to 1 %, and even more preferably 0.35 % to 0.8 %.

Molybdenum Mo is used in the range of 0.01 % to 0.3 %.

[0055] 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 0.3 % 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.

[0056] Preferably, Mo is used in the range of 0.03 % to 0.3 %, and more preferably 0.05 % to 0.3 %.

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

[0057] 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 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 0.05 % or less.

[0058] 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 HAZ during welding thereby improving toughness. TiN formation suppresses BN precipitation, thereby leaving B free to make its contribution to hardenability. For this purpose, the ratio of Ti/N is at least 3.4. However, if Ti content is too high, coarsening of TiN and precipitation hardening due to TiC develop and the low-temperature toughness may be deteriorated. Therefore, it is necessary to restrict titanium so that it is less than 0.05%.

[0059] Preferably, Ti is used in an amount of 0.035 % or less, and more preferably 0.02 % or less. If the steel product has a low nitrogen content of 0.003 % or less, it is unnecessary to add Ti to ensure the boron hardenability effect, and the Ti content can be as low as 0.005 % or less. If the nitrogen content is more than 0.003 % but no more than 0.01%, the Ti content can be more than 0.005 % but no more than 0.05%.

Vanadium V is used in an amount of 0.2 % or less.

[0060] V has substantially the same but smaller effects as Nb. V_4C_3 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 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 0.2 % V has negative effects on weldability and hardenability.

[0061] Preferably, V is used in an amount of 0.06 % or less.

Boron B is used in the range of 0.0005 % to 0.005 %.

[0062] B is a well-established microalloying element to increase hardenability. The most effective B alloying would preferably require the presence of Ti in an amount of at least 3.42 N to prevent formation of BN. In the presence of an amount of 0.003 % or less nitrogen, the Ti content can be lowered to 0.005 % or less, which is beneficial to low-temperature toughness. Hardenability deteriorates if the B content exceeds 0.005 %.

[0063] Preferably, B is used in the range of 0.0008 % to 0.005 %.

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

[0064] 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 SCC resistance.

[0065] Preferably, Ca is used in an amount of 0.005 % or less, and more preferably 0.0008 % to 0.003 % to ensure excellent mechanical properties such as impact strength and bendability.

[0066] The Ca/S ratio is adjusted such that CaS cannot form thereby improving impact toughness and bendability. The inventors have noticed that, in general, during the steelmaking process the optimal Ca/S ratio is in the range of 1 - 2, preferably 1.1 - 1.7, and more preferably 1.2 - 1.6 for clean steel.

[0067] Unavoidable impurities can be phosphor P, sulfur S, nitrogen N. Their content in terms of weight percentages (wt. %) is preferably defined as follows:

P	0 - 0.025, preferably 0.001 - 0.025, more preferably 0.001 - 0.012
S	0 - 0.008, preferably 0 - 0.005, more preferably 0 - 0.002
N	0 - 0.01, preferably 0 - 0.005, more preferably 0 - 0.004

5

[0068] 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.

10

[0069] 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.

[0070] The first step is to provide a steel slab by means of, for instance a process of continuous casting, also known as strand casting.

15

[0071] In the reheating stage, the steel slab is heated to the austenitizing temperature of 1200 - 1350 °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.

[0072] 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.

20

[0073] In the hot rolling stage the slab is hot rolled to the desired thickness at a temperature in the range of Ar3 to 1300°C, wherein the finish rolling temperature (FRT) is in the range of 800 °C to 960 °C, preferably 870°C - 930°C, more preferably 885°C - 930°C.

25

[0074] 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.

30

[0075] 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.

[0076] The obtained steel strip product has a thickness of 10 mm or less, preferably 8 mm or less, more preferably 7 mm or less.

35

[0077] 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.

[0078] 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.

40

[0079] 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 martensitic structure is not tempered. More preferably, the aforementioned microstructure comprises more than 10 vol. % untempered martensite. Preferably, the microstructure comprises 0 - 1 vol. % residual austenite, and more preferably 0 - 0.5 vol. % residual austenite. Typically, the microstructure also comprises bainite, ferrite and/or pearlite.

45

[0080] Optionally, an extra step of temper annealing is performed at a temperature in the range of 150 °C - 250 °C.

[0081] The steel strip product has a good balance of hardness and other mechanical properties such as excellent impact strength, improved resistance to climatic corrosion and excellent formability/bendability.

50

[0082] The steel strip product has a high Brinell hardness in the range of 420 - 580 HBW, preferably 450 - 550 HBW, and more preferably 470 - 530 HBW.

[0083] The steel strip product has a corrosion index (ASTM G101-04) of at least 5, preferably at least 5.5, and more preferably at least 6, which indicates improved resistance against climatic corrosion. The durability of a paint layer is increased and the repainting interval can be 1.5 - 2 times longer by using the steel product of the invention.

55

[0084] The corrosion index (ASTM G101-04) is used for estimating long term atmospheric corrosion of low alloy steels in various environments. The corrosion index (ASTM G101-04) equation is formed with a statistical method from long term outdoor corrosion exposure tests, which equation is represented as follows.

$$I_{\text{ASTMG101}} = 26.01(\% \text{Cu}) + 3.88(\% \text{Ni}) + 1.20(\% \text{Cr}) + 1.49(\% \text{Si}) + 17.28(\% \text{P}) - 7.29(\% \text{Cu})(\% \text{Ni}) - 9.10(\% \text{Ni})(\% \text{P}) - 33.39(\% \text{Cu})^2$$

[0085] The steel strip product with high hardness has a Charpy-V impact toughness of at least 34 J/cm² at a temperature of -20 °C or -40 °C thereby fulfilling the conventional impact strength requirements.

[0086] The steel strip product exhibits excellent bendability or formability. The steel product has a minimum bending radius of 3.4 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 2.7 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.

[0087] 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.

[0088] The chemical compositions used for producing the tested steel strip products are presented in Table 1.

[0089] The manufacturing conditions for producing the tested steel strip products are presented in Table 2.

[0090] The mechanical properties of the tested steel strip products are presented in Table 3.

Microstructure

[0091] 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 - 4 all have a main phase of at least 90 vol. % martensite. Figure 1 is an SEM image on the RD-ND plane from ¼ thickness of the steel strip no. 1, where the prior austenite grain boundaries are visualized. The prior austenite grain structure of the steel strip no. 1 has an aspect ratio of 3.4.

Brinell hardness HBW

[0092] The Brinell hardness test is performed by pressing a 10 mm spherical tungsten carbide ball against a clean prepared surface using a 3000 kilogram force, producing an impression, measured and given a special numerical value. 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 - 4 exhibits a Brinell harness in the range of 475 - 491 HBW. The comparative example no. 5 exhibits a Brinell harness of 486 HBW while the comparative example no. 6 exhibits a Brinell harness of 469 HBW.

Corrosion index (ASTM G101-04)

[0093] The corrosion index (ASTM G101-04) is calculated based on the American Society for Testing and Materials (ASTM) standard G101. As shown in Table 3, each one of the inventive examples no. 1 - 4 has a corrosion index (ASTM G101-04) of at least 5.28. On the other hand, the comparative examples no. 5 and 6 have a much lower corrosion index (ASTM G101-04) of 3.4 and 1.04 respectively.

Charpy-V impact toughness

[0094] The impact toughness values at -20 °C or -40 °C were obtained by Charpy V-notch tests according to the ASME (American Society of Mechanical Engineers) Standards. The inventive examples no. 1 and 2 have a Charpy-V impact toughness of 63 J/cm² and 45 J/cm² respectively at a temperature of -20 °C (Table 3). Each one of the inventive examples no. 1 - 4 has a Charpy-V impact toughness in the range of 38 - 120 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 - 4 has a Charpy-V impact toughness in the range of 58 - 105 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 - 4 is improved compared to the comparative example no. 6. The comparative example no. 5 has a better Charpy-V impact toughness values than the inventive examples no. 1 and 2 at the expense of bendability.

Elongation

[0095] Elongation was determined according ASTM E8 standard using transverse specimens of a produced batch of 2000 ton of plates. The mean value of total elongation (A₅₀) of the inventive examples no. 1 and 2 is 11.6 and 11.3

respectively (Table 3), which is better than the comparative examples no. 5 and 6 having a mean A_{50} value of 10.1 and 9.1 respectively. The comparative examples no. 5 and 6 have better A_{50} values than the inventive examples no. 3 and 4 at the expense of Charpy-V impact toughness.

5 Bendability

[0096] 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.

[0097] According to the bend tests, each one of the inventive examples no. 1 - 4 has a minimum bending radius of 3.3 t or less in a measurement direction longitudinal to the rolling direction; a minimum bending radius of 2.6 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 example no. 5 exhibits lower bendability with a minimum bending radius of 3.7 t in a measurement direction longitudinal to the rolling direction and a minimum bending radius of 2.2 t in a measurement direction transversal to the rolling direction.

20 Yield strength

[0098] Yield strength was determined according ASTM E8 standard using transverse specimens of a produced batch of 2000 ton of plates. Each one of the inventive examples no. 1 - 4 has a mean value of yield strength ($R_{p0.2}$) in the range of 1302 MPa to 1399 MPa, measured in the longitudinal direction (Table 3). The comparative examples no. 5 and 6 have a mean value of yield strength ($R_{p0.2}$) of 1262 MPa and 1338 MPa respectively, measured in the longitudinal direction (Table 3).

Tensile strength

[0099] Tensile strength was determined according ASTM E8 standard using transverse specimens of a produced batch of 2000 ton of plates. Each one of the inventive examples no. 1 - 4 has a mean value of ultimate tensile strength (R_m) in the range of 1509 MPa to 1566 MPa, measured in the longitudinal direction (Table 3). The comparative examples no. 5 and 6 have a mean value of ultimate tensile strength (R_m) of 1550 MPa and 1552 MPa respectively, measured in the longitudinal direction (Table 3).

Table 1. Chemical compositions (wt. %).

Steel type	C	Si	Mn	P	S	Al	Cu	Ni	Cr	Mo	Nb	Ti	V	B	Ca (ppm)	N (ppm)	Remarks
A	0,251	0,098	0,246	0,008	0,0016	0,094	0,30	0,493	0,718	0,098	0	0,016	0,04	0,0018	23	39	Inventive example
B	0,23	0,179	0,200	0,007	-0,0006	0,051	0,16	0,51	0,39	0,05	0,001	0,002	0,01	0,0011	8	24	Inventive example
C	0,233	0,179	0,714	0,009	0,0006	0,035	0,009	0,506	0,713	0,067	0	0,017	0,008	0,0017	21	31	Comparative example
D	0,262	0,175	1,19	0,008	0,0002	0,048	0,01	0,035	0,212	0,005	0	0,015	0,008	0,0014	30	21	Comparative example

Table 2. Manufacturing conditions

Steel strip no.	Steel type	Strip thickness (mm)	Hot rolling		Cooling rate (°C/s)	Colling temperature (°C)	Temper annealing		Remarks
			Heating temperature (°C)	FRT (°C)			Heating temperature (°C)	Holding time (h)	
1	A	6	1280	895	70	50	-	-	Inventive example
2	A	6	1280	925	70	50	-	-	Inventive example
3	B	6	1280	900	-	50	200	8	Inventive example
4	B	3	1280	905	-	50	200	8	Inventive example
5	C	6	1280	870	55	50	-	-	Comparative example
6	D	6	1280	915	55	50	-	-	Comparative example

Table 3. Mechanical properties

Steel strip no.	Steel type	Corr. Index	HBW	R _{p0.2} (L) (MPa)	R _m (L) (MPa)	A ₅₀	ChV (-20) T (J/cm ²)	ChV (-40) L (J/cm ²)	ChV (-40) T (J/cm ²)	Bending r/t		Remarks
										longit.	transv.	
1	A	6.74	487	1399	1566	11,6	63	63	80	3,3	2,0	Inventive example
2	A	6.74	491	1337	1529	11,3	45	38	58	3,0	2,0	Inventive example
3	B	5.28	475	1355	1509	6,9	-	120	83	2,3	1,3	Inventive example
4	B	5.28	487	1302	1549	8,8	-	120	105	2,6	2,6	Inventive example
5	C	3.40	486	1262	1550	9,4	73	68	83	3,7	2,2	Comparative example
6	D	1.04	469	1338	1552	10,0	32	30	42	-	-	Comparative example

Claims

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

5	C	0.17 - 0.38, preferably 0.21 - 0.35, more preferably 0.22 - 0.28
	Si	0 - 0.5, preferably 0.01 - 0.5, more preferably 0.03 - 0.25
	Mn	0.1 - 0.4, preferably 0.15 - 0.3
	Al	0.015 - 0.15
10	Cu	0.1 - 0.6, preferably 0.1 - 0.5, more preferably 0.1 - 0.35
	Ni	0 - 0.8, preferably 0.2 - 0.8
	Cr	0.1 - 1, preferably 0.3 - 1, more preferably 0.35 - 1, even more preferably 0.35 - 0.8
	Mo	0.01 - 0.3, preferably 0.03 - 0.3, more preferably 0.05 - 0.3
	Nb	0 - 0.005
15	Ti	0 - 0.05, preferably 0 - 0.035, more preferably 0 - 0.02
	V	0 - 0.2, preferably 0 - 0.06
	B	0.0005 - 0.005, preferably 0.0008 - 0.005
	P	0 - 0.025, preferably 0.001 - 0.025, more preferably 0.001 - 0.012
20	S	0 - 0.008, preferably 0 - 0.005, more preferably 0 - 0.002
	N	0 - 0.01, preferably 0 - 0.005, more preferably 0 - 0.004
	Ca	0 - 0.01, preferably 0 - 0.005, more preferably 0.0008 - 0.003

25 remainder Fe and inevitable impurities, wherein the steel product has a Brinell hardness in the range of 420 - 580 HBW, and a corrosion index (ASTM G101-04) of at least 5.

30 2. The steel product according to claim 1, wherein the amount of Ti is in the range of 0 - 0.005 wt. % when the amount of N is in the range of 0 - 0.003 wt. %.

3. The steel product according to claim 1, wherein the amount of Ti is more than 0.005 wt. % and not more than 0.05 wt. % when the amount of N is more than 0.003 wt. % and not more than 0.01 wt. %.

35 4. The steel product according to any one of the preceding claims wherein $[Ni] > [Cu]/3$, preferably $[Ni] > [Cu]/2$, and wherein

$[Ni]$ is the amount of Ni in the composition,
 $[Cu]$ is the amount of Cu in the composition.

40 5. The steel product according to any one of the preceding claims, wherein the Ca/S ratio is in the range of 1 - 2, preferably 1.1 - 1.7, and more preferably 1.2 - 1.6.

45 6. The steel product according to any one of the preceding claims, wherein the steel product has a Brinell hardness in the range of 450 - 550 HBW, preferably 470 - 530 HBW.

7. The steel product according to any one of the preceding claims, wherein the steel product has a corrosion index (ASTM G101-04) of at least 5.5, preferably at least 6.

50 8. The steel product according to any one of the preceding claims, wherein the steel product has a Charpy-V impact toughness of at least 34 J/cm² at a temperature of - 20 °C or -40 °C in transversal and/or longitudinal direction.

55 9. The steel product according to any one of the preceding claims, wherein the steel product has a minimum bending radius of 3.4 t or less in a measurement direction longitudinal to the rolling direction; a minimum bending radius of 2.7 t or less in a measurement direction transversal to the rolling direction; and wherein t is the thickness of the steel strip product.

10. 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	≥ 90, preferably ≥ 95, more preferably ≥ 98
residual austenite	0 - 1, preferably 0 - 0.5

5

remainder bainite, ferrite and/or pearlite.

11. 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.

10

12. 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, more preferably 2 - 5.

13. The steel product according to any one of the preceding claims, wherein the steel strip product has a thickness of 10 mm or less, preferably 8 mm or less, and more preferably 7 mm or less.

15

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

20

- providing a steel slab consisting of the chemical composition according to any one of the claims 1 to 5;
- heating the steel slab to the austenitizing temperature of 1200 - 1350 °C;
- hot-rolling to the desired thickness at a temperature in the range of Ar3 to 1300°C, wherein the finish rolling temperature is in the range of 800 °C to 960 °C, preferably 870°C - 930°C, more preferably 885 - 930 °C;
- 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; and
- optionally, temper annealing at a temperature in the range of 150 °C - 250 °C.

25

30

35

40

45

50

55

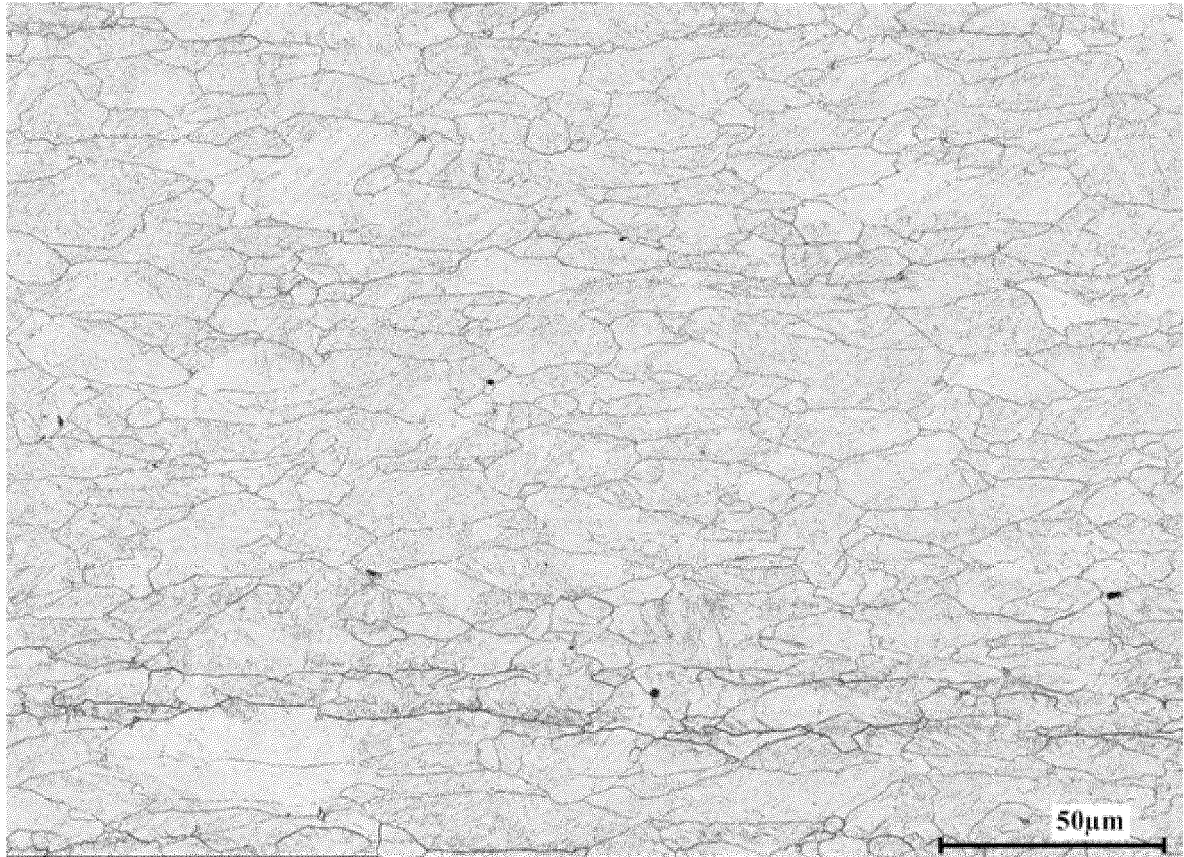


Figure 1



EUROPEAN SEARCH REPORT

Application Number
EP 19 16 7552

5

10

15

20

25

30

35

40

45

50

55

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 * -----	1-14	INV. C21D8/02 C22C38/04 C22C38/42 C22C38/44 C22C38/54
A	US 2014/096875 A1 (UEDA KEIJI [JP] ET AL) 10 April 2014 (2014-04-10) * claims 1-10; tables 1.1-3.4 * -----	1-14	
A	EP 2 778 239 A1 (TENARIS COILED TUBES LLC [US]) 17 September 2014 (2014-09-17) * claims 1-22; tables A1-C2 * -----	1-14	
			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 25 July 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			

 1
EPO FORM 1503 03.02 (P04C01)

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

EP 19 16 7552

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.

25-07-2019

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 2009030093 A	12-02-2009	JP 5145804 B2	20-02-2013
		JP 2009030093 A	12-02-2009

US 2014096875 A1	10-04-2014	AU 2012233198 A1	03-10-2013
		BR 112013025040 A2	27-12-2016
		CL 2013002758 A1	25-04-2014
		CN 103459634 A	18-12-2013
		EP 2695960 A1	12-02-2014
		JP 5553081 B2	16-07-2014
		JP 2012214890 A	08-11-2012
		KR 20130133035 A	05-12-2013
		MX 341765 B	02-09-2016
		PE 17392014 A1	26-11-2014
		US 2014096875 A1	10-04-2014
		WO 2012133911 A1	04-10-2012

EP 2778239 A1	17-09-2014	BR 102014006157 A2	26-01-2016
		CA 2845471 A1	14-09-2014
		CN 104046918 A	17-09-2014
		EP 2778239 A1	17-09-2014
		JP 6431675 B2	28-11-2018
		JP 2014208888 A	06-11-2014
		MX 360596 B	09-11-2018
		RU 2014109873 A	20-09-2015
		RU 2018127869 A	13-03-2019
		US 2014272448 A1	18-09-2014
		US 2017335421 A1	23-11-2017
		US 2018051353 A1	22-02-2018
		US 2018223384 A1	09-08-2018

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 [0004]
- CN 102392186 [0006]
- CN 103820717 [0006]
- EP 2695960 A [0007]