(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 4 116 445 A1**

(12) # EUROPEAN PATENT APPLICATION

(43) Date of publication:
11.01.2023 Bulletin 2023/02

(21) Application number: **22183442.7**

(22) Date of filing: **06.07.2022**

(51) International Patent Classification (IPC):
C21D 1/19 $^{(2006.01)}$ ***C21D 1/25*** $^{(2006.01)}$
C21D 1/26 $^{(2006.01)}$ ***C21D 8/02*** $^{(2006.01)}$
C21D 9/46 $^{(2006.01)}$ ***C22C 38/00*** $^{(2006.01)}$
C22C 38/02 $^{(2006.01)}$ ***C22C 38/04*** $^{(2006.01)}$
C22C 38/42 $^{(2006.01)}$ ***C22C 38/44*** $^{(2006.01)}$
C22C 38/46 $^{(2006.01)}$ ***C22C 38/48*** $^{(2006.01)}$
C22C 38/50 $^{(2006.01)}$ ***C22C 38/54*** $^{(2006.01)}$
C22C 38/06 $^{(2006.01)}$

(52) Cooperative Patent Classification (CPC):
**C21D 1/19; C21D 1/25; C21D 1/26; C21D 8/0226;
C21D 8/0263; C21D 9/46; C22C 38/001;
C22C 38/002; C22C 38/02; C22C 38/04;
C22C 38/06; C22C 38/42; C22C 38/44;
C22C 38/46; C22C 38/48;** (Cont.)

(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

(30) Priority: **08.07.2021 EP 21184520**

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(54) # HOT-ROLLED WEATHER RESISTANT STEEL PRODUCT AND METHOD OF MANUFACTURING THE SAME

(57) This invention relates to a hot-rolled weather resistant steel product comprising a composition consisting of, in terms of weight percentages (wt. %): C 0.015 - 0.045, Si 0.15 - 0.75, Mn 0.8 - 1.6, Al 0.005 - 0.12, Nb 0.0 - 0.08, Cu 0.2 - 1.0, Cr 0.35 - 1.0, Ni 0.01 - 1.0, Ti 0.0 - 0.12, Mo > 0.05 - 0.35, V 0.0 - 0.14, B < 0.0006, $P \leq 0.035$, $S \leq 0.025$, W optionally < 0.1 %, Co optionally < 0.1 %, N < 0.0200 %, H < 0.0004 %, O < 0.0100 %, Ca < 0.01 %, REM < 0.1 %, and remainder Fe and inevitable impurities. Said steel product has a microstructure comprising a matrix consisting of, in terms of volume percentages (vol. %), measured at ¼ thickness: Polygonal ferrite (PF): $0 \leq PF \leq 10$, Quasipolygonal ferrite (QPF): $5 \leq QPF \leq 36$, Granular bainite (GB): $20 \leq GB \leq 70$, Lath bainite (LB): $16 \leq LB \leq 80$, Retained austenite (RA): $RA \leq 2$, Martensite/austenite constituents (MA): $MA \leq 5$, Pearlite (P): $P \leq 5$, and GB+LB > 50 %,

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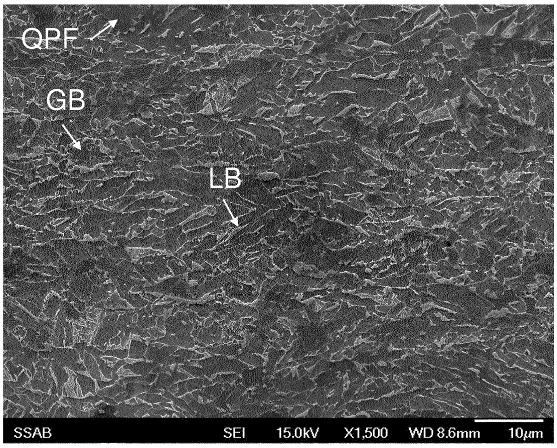


Fig. 1

(52) Cooperative Patent Classification (CPC): (Cont.)
C22C 38/50; C22C 38/54; C21D 2211/001;
C21D 2211/002; C21D 2211/005;
C21D 2211/008; C21D 2211/009

Description

TECHNICAL FIELD

[0001] The present invention relates to a hot-rolled weather resistant steel product that can be used in bridge construction and industrial plant support structures, for example.

[0002] The present invention further relates to a method for manufacturing a hot-rolled weather resistant steel product.

BACKGROUND OF THE INVENTION

[0003] A general trend in steel development is towards higher strength and low-temperature impact toughness combined with good weldability. Conventional weathering steels are typically normalized. Strength of these steels comes mainly from solid solution strengthening. The conventional weathering steels commonly exhibit low strength levels, 355 MPa yield strength, combined with rather poor impact toughness properties at low temperatures. These properties do not meet the requirements set by applications for these steels where higher strength combined with good impact toughness properties, good weldability and high resistance to post weld heat treatment (PWHT) are currently required.

[0004] In the past, weathering steels with greater strength levels have been produced using thermomechanically controlled processing (TMCP). The conventional TMCP weathering steels, exhibiting yield strength levels above 460 MPa, are traditionally manufactured by using relative high carbon (C) levels (0.07 - 0.12 %) combined with TMCP. However, due the high carbon levels, impact toughness and welding properties are not optimized. Generally, conventional TMCP weathering steels exhibit mainly fine grained polygonal ferritic microstructure, which is precipitation strengthened by utilizing microalloying elements. Thermomechanical processing of these weathering steels classically consists of three stages. During a first rough rolling stage, austenite grain size is refined due to repeated cycles of the recrystallization process. In a second controlled rolling stage, the austenite is deformed in the non-recrystallization temperature regime, which brings significant refinement to the final polygonal ferrite microstructure. Finally, a third stage of accelerated cooling can be applied to further refine the resulting polygonal ferrite grain size.

[0005] The application of accelerated cooling is, nevertheless, challenging for the conventional TMCP weathering steels due to the elevated C levels. For example, thin plates with high C levels are difficult to produce using accelerated cooling since this may lead to undesired microstructures. In order to circumvent this, high alloying strategy in combination with air cooling is frequently used for the conventional TMCP weathering steels. Increased alloying has disadvantages as it impairs impact toughness for both the base material and HAZ (heat affected zone), deteriorates weldability and increases costs.

[0006] Furthermore, accelerated cooling combined with conventional C levels may produce large martensite/austenite (MA) constituents in polygonal ferrite matrix. The MA constituents exhibit high hardness and are brittle. The presence of these MA constituents typically deteriorates impact toughness. Furthermore, at very high cooling rates even conventional TMCP weathering steels with sufficient hardenability may form some fraction of brittle upper bainite, which is also harmful for impact toughness and formability.

SUMMARY OF THE INVENTION

[0007] In view of the state of art, it is a primary object of the invention to provide a hot-rolled weather resistant steel product, which is in at least some aspect improved with respect to known such steel products. In particular, it is an object of the present invention to solve the problem of providing a hot-rolled weather resistant steel product exhibiting excellent resistance to climatic corrosion, guaranteed impact strength values and excellent formability/bendability and weldability combined with low carbon levels. According to a first aspect of the invention, at least the primary object is achieved by a hot-rolled weather resistant steel product according to claim 1. The steel product has a composition consisting of, in terms of weight percentages (wt. %):

C	0.015 - 0.045, preferably 0.025 - 0.045, more preferably 0.025 - 0.040
Si	0.15 - 0.75, preferably 0.30 - 0.75, more preferably 0.50 - 0.70
Mn	0.8 - 1.6, preferably 1.0 - 1.5, more preferably 1.2 - 1.4
Al	0.005 - 0.12, preferably 0.015 - 0.10, more preferably 0.02 - 0.06
Nb	0.0 - 0.08, preferably 0.005 - 0.06, more preferably 0.02 - 0.04
Cu	0.2 - 1.0, preferably 0.2 - 0.6, more preferably 0.25 - 0.45
Cr	0.35 - 1.0, preferably 0.35 - 0.85, more preferably 0.50 - 0.70
Ni	0.01 - 1.0, preferably 0.07 - 0.65, more preferably 0.10 - 0.25
Ti	0.0 - 0.12, preferably 0.005 - 0.030, more preferably 0.010 - 0.020

(continued)

Mo	> 0.05 - 0.35, preferably > 0.05 - 0.30, more preferably > 0.05 - 0.15
V	0.0 - 0.14, preferably 0.0 - 0.08, more preferably less than 0.03
B	< 0.0006
P	≤ 0.035, preferably ≤ 0.015, more preferably ≤ 0.010
S	≤ 0.025, preferably ≤ 0.010, more preferably ≤ 0.003
W optionally	< 0.1 %
Co optionally	< 0.1 %
N	< 0.0200 %, preferably N < 0.0060 %
H	< 0.0004 %, preferably H < 0.0002 %
O	< 0.0100 %
Ca	< 0.01 %, preferably 0.001 - 0.004 %
REM	< 0.1 %

remainder Fe and inevitable impurities, wherein the steel product has a microstructure comprising a matrix consisting of, in terms of volume percentages (vol. %), measured at ¼ thickness:

Polygonal ferrite (PF):
0 ≤ PF ≤ 10, preferably 0 ≤ PF ≤ 5
Quasipolygonal ferrite (QPF):
5 ≤ QPF ≤ 36, preferably 5 ≤ QPF ≤ 32, more preferably 5 ≤ QPF ≤ 30
Granular bainite (GB):
20 ≤ GB ≤ 70, preferably 23 ≤ GB ≤ 65, more preferably 26 ≤ GB ≤ 60
Lath bainite (LB):
16 ≤ LB ≤ 80, preferably 20 ≤ LB ≤ 75, more preferably 27 ≤ LB ≤ 70
Retained austenite (RA):
RA ≤ 2, preferably ≤ 0.5, more preferably ≤ 0.1
Martensite/austenite constituents (MA):
MA ≤ 12, preferably MA ≤ 8, more preferably ≤ 5
Pearlite (P):

P ≤ 5, preferably P ≤ 2, more preferably P ≤ 1, wherein
GB+LB > 50 %, preferably GB+LB > 65 %.

[0008] Preferably, the hot-rolled weather resistant steel product has a composition consisting of, in terms of weight percentages (wt. %):

C	0.025 - 0.040
Si	0.50 - 0.70
Mn	1.2 - 1.4
Al	0.02 - 0.06
Nb	0.02 - 0.04
Cu	0.25 - 0.45
Cr	0.50 - 0.70
Ni	0.10 - 0.25
Ti	0.010 - 0.020
Mo	> 0.05 - 0.15
V	0.0 - 0.03
B	< 0.0006
P	≤ 0.010
S	≤ 0.003
W optionally	< 0.1 %
Co optionally	< 0.1 %
N	< 0.0060 %

(continued)

H	< 0.0002 %
O	< 0.0100 %
Ca	0.001 - 0.004 %
REM	< 0.1 %

remainder Fe and inevitable impurities wherein
the steel product has a microstructure comprising a matrix consisting of, in terms of volume percentages (vol. %), measured at ¼ thickness:

Polygonal ferrite (PF): $0 \leq PF \leq 5$
Quasipolygonal ferrite (QPF): $5 \leq QPF \leq 30$
Granular bainite (GB): $26 \leq GB \leq 60$
Lath bainite (LB): $27 \leq LB \leq 70$
Retained austenite (RA): $RA \leq 0.1$
Martensite/austenite constituents (MA): ≤ 5
Pearlite (P): $P \leq 1$, wherein
GB+LB > 65 %.

[0009] The weather resistant steel product has very low levels of C and limited Mn content. The low levels of C and Mn are important for improving impact toughness, formability and weldability. The combined content of C and Mn should however be above a certain level to ensure a sufficient amount of granular bainite in the microstructure. The microstructure is then further strengthened via other alloying elements, such as Mo, which promote formation of lath bainite. Excessive C and Mn contents decrease the bainite phase transformation start temperature (Bs) thus making it challenging to form granular bainite. Furthermore, undesired bainitic microstructures, such as brittle upper bainite, are more easily formed.

[0010] Preferably, the minimum value of equation C+Mn/6 for the aforementioned steel product is 0.15, more preferably 0.20 and even more preferably 0.24. Furthermore, the maximum value of equation C+Mn/6 for the aforementioned steel composition is preferably 0.31, more preferably 0.29 and even more preferably 0.27.

[0011] In order to ensure good impact toughness and formability, it is desirable to keep inclusion size small. Preferably, the weather resistant steel product comprises non-metallic inclusions having a median inclusion size below 4 μm in diameter, wherein 95 % of the total amount of the inclusions are less than or equal to 5.8 μm in diameter.

[0012] The weather resistant steel product is alloyed with the essential alloying elements Si, Cu, Ni and Cr, which provide good resistance against climatic corrosion. Preferably, the corrosion index of the present steel product is at least 5, more preferably at least 6, and even more preferably at least 6.5, according to standard ASTM G101-04:

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

[0013] With great climatic corrosion resistance i.e. great weathering properties, the need for painting and maintenance is reduced thus improving the environmental friendliness of the steels according to the invention.

[0014] The weather resistant steel product according to the present invention has a good combination of strength and impact toughness. Preferably, the weather resistant steel product has a yield strength (Rp0.2) in the range of 500-650 MPa, more preferably 520-625 MPa, and even more preferably 540-599 MPa. Furthermore, the aforementioned steel product preferably has an ultimate tensile strength (Rm) in the range of 570-850 MPa, more preferably 610-830 MPa, and even more preferably 660-810 MPa. The preferred yield ratio for the inventive steel is in the range of 0.65-0.90.

[0015] Preferably, Charpy-V impact toughness measured from 2 mm of a surface of the weather resistant steel product is at least 150 J/cm^2, more preferably at least 200 J/cm^2, even more preferably at least 250 J/cm^2 measured at a temperature of -60 °C.

[0016] Carbon equivalent equations are frequently used to describe a steel's tendency to form hard, low transformation temperature phases, such as brittle upper bainite or martensite upon cooling. The presence of these phases may lead to undesired brittle fracture. Generally, the higher the carbon equivalent value, the higher the tendency to form said phases. Two different and commonly well-known carbon equivalent equations were used to calculate the carbon equivalent values for the steels according to the present invention:

CEV equation:

$$CEV = \%C + \frac{\%Mn}{6} + \frac{\%Cr+\%Mo+\%V}{5} + \frac{\%Cu+\%Ni}{15}$$

Pcm equation:

$$Pcm = \%C + \frac{\%Si}{30} + \frac{\%Mn+\%Cu+\%Cr}{20} + \frac{\%Ni}{60} + \frac{\%Mo}{15} + \frac{\%V}{10} + 5\%B$$

[0017] The alloying strategy needs to be lean in order to ensure good welding properties and to prevent cracking during cooling of the weld. The inventors have also noticed that when the alloy carbon content is very low, good impact toughness values may be obtained even at higher carbon equivalent values. Generally, the lower the C content, the higher the carbon equivalent may be while still maintaining good impact toughness values. Another aspect where carbon equivalent equations may be used is to estimate a pre-heating temperature for welding.

[0018] Preferably, Pcm carbon equivalent value is Pcm < 0.25, more preferably Pcm < 0.23, even more preferably Pcm < 0.21, and/or CEV carbon equivalent value is CEV < 0.56, more preferably CEV < 0.54, even more preferably CEV < 0.52, for the aforementioned steel product.

[0019] Preferably, the weather resistant steel product has a thickness in the range of 2 mm to 100 mm, more preferably 6 mm to 70 mm, and even more preferably 8 to 40 mm. The weather resistant steel product exhibits excellent formability, such as bendability. Preferably, the weather resistant steel product has, in the longitudinal or transverse direction, a minimum bending radius of 3.0 t or less, more preferably 1.5 t or less, and even more preferably 1.0 t or less, wherein t is the thickness of the steel product.

[0020] In a second aspect, the present invention provides a method for manufacturing a hot-rolled weather resistant steel product according to claim 14. The method comprises the following steps of:

- heating a steel slab with the composition according to the first aspect of the invention to a temperature in the range of 1100 °C - 1300 °C, and preferably 1100 - 1250 °C;
- hot rolling the heated steel slab in a plurality of hot rolling passes, wherein

    i. the steel slab is subjected to a first plurality of rolling passes at a temperature above the austenite non-recrystallization temperature
    ii. the steel slab from step (i) is cooled down to a temperature below the austenite non-recrystallization temperature
    iii. the steel slab from step (ii) is subjected to a second plurality of rolling passes at a temperature below the austenite non-recrystallization temperature, wherein the reduction ratio of the second plurality of rolling passes is at least 1.5, preferably at least 1.8, more preferably 2.2 or more, and wherein the final rolling temperature is in the range of 760 °C to 990 °C, preferable the final rolling temperature is in the range of 800 °C to 950 °C;

- accelerated continuous cooling at a cooling rate of at least 5 °C/s, preferably at least 10 °C/s, and more preferably at least 15 °C/s to a cooling stop temperature of 250 - 350 °C or 351 - 450 °C or 451 - 550 °C or 551 - 650 °C; and
- optionally, tempering at a temperature in the range of 580 °C to 640 °C for 0.5 hour to 1.5 hour.

[0021] The optional step of tempering is not mandatory according to the present invention. The method for manufacturing a hot-rolled weather resistant steel product according to the second aspect combines a specific alloy design with cost-efficient TMCP procedures, which produces a metallographic microstructure comprising quasi-polygonal ferrite, granular bainite and lath bainite, as main phases leading to great weathering and mechanical properties with improved weldability.

BRIEF DESCRIPTION OF THE DRAWINGS

[0022]

Figure 1 illustrates the microstructure of Example steel 8,

Figure 2 is a flow chart schematically illustrating a method according to an embodiment of the invention.

Figure 3 plots yield strength and A5 total elongation for samples before and after a post-weld heat treatment for example steel 15,

Figure 4 plots ultimate tensile strength for samples before and after a post-weld heat treatment for example steel 15, and

Figure 5 plots Charpy V-notch test temperature as a function of impact energy per cm^2 for example steel 15.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0023] The term "steel" is defined as an iron alloy containing carbon (C).

[0024] 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, industry or mining.

[0025] The term "corrosion index (ASTM G101-04)" refers to the American Society for Testing and Materials (ASTM) standard G101 which is a widely used guide to quantify the atmospheric corrosion resistance of weathering steels as a function of their composition.

[0026] The term "accelerated continuous cooling (ACC)" refers to a process of accelerated cooling at a cooling rate down to a cooling stop temperature without interruption.

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

[0028] The term "yield strength (YS, Rp0.2)" 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. Common gauge lengths are 50 mm (A50), 80 mm (A80) and A5. A5 elongation refers to permanent elongation for proportional specimens with length L0 equal to 5 times diameter.

[0030] The term "minimum bending radius (Ri)" is used to refer to the minimum radius of bending that can be applied to a test sheet without occurrence of cracks. Bendability testing method for the inventive steels is described afterward.

[0031] The term "bendability" refers to the ratio of Ri and the sheet thickness (t).

[0032] The alloying content of steel together with the processing parameters determines the microstructure, which in turn determines the mechanical properties of the steel.

[0033] 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 detail, wherein % of each component refers to weight percentage.

Carbon C is used in the range of 0.015-0.045%

[0034] C alloying increases strength of steel by solid solution and precipitation strengthening, and hence C content largely determines the strength level of the steel product. C also has a strong impact on formation of different phases. For example, low C levels enable formation of quasi-polygonal ferrite and granular bainite and tough, low carbon lath bainite. C is used in the range of 0.015 % to 0.045% depending on targeted strength. C has detrimental effects on impact toughness, weldability, formability or bendability, and resistance to stress corrosion cracking. Therefore, C content is set to not more than 0.045%.

[0035] Preferably, C is used in the range of 0.025-0.045%, and more preferably 0.025-0.040%.

Silicon Si is used in the range of 0.15-0.75%

[0036] Si is an effective deoxidizing or killing agent that can remove oxygen from the melt during a steelmaking process. Si also improves steel’s internal cleanliness at the melt shop. Si is an essential element for promoting weathering properties in weathering steels. Si alloying enhances strength by e.g. solid solution strengthening and by decreasing phase transformation temperatures during accelerated cooling. For these reasons, at least 0.15% Si is used to ensure good weathering properties.

[0037] However, silicon content of higher than 0.75 % may unnecessarily increase carbon equivalent (Pcm) value thereby weakening weldability. In addition, surface quality may be deteriorated if excess Si is present. Furthermore, increasing Si alloying stabilizes M/A constituents, which may deteriorate impact toughness, especially at ICCGHAZ (Intercritical Coarse Grain Heat Affected Zone). Si also enlarges the A1-A3 temperature range wherein ICCGHAZ forms. This further increases the possibility of formation of stable, carbon enriched constituents, such as M/A constituents.

[0038] Therefore, in order to ensure good weldability and good ICCGHAZ impact toughness, the maximum value of equation C+Si/30 is below 0.07 preferably below 0.068 and more preferably below 0.065.

[0039] Preferably, Si is used in the range of 0.30-0.75%, and more preferably 0.5-0.7%.

Manganese Mn is used in the range of 0.8-1.6%

[0040] Mn is an essential element improving the balance between strength and low-temperature toughness. Mn alloying enhances strength by solid solution strengthening and by decreasing phase transformation temperatures during accelerated cooling. Mn also promotes formation of bainite. This is important for ensuring sufficient strength of the steel product and hence a minimum content of Mn of 0.8% is required.

[0041] On the other hand, if the Mn content is too high, it may promote segregation in the steel product and consequently the low-temperature toughness of the center of the steel plate is impaired. Alloying with Mn more than 1.6 % unnecessarily increases the CEV and Pcm values thereby weakening weldability by increasing the need for preheating before welding. In addition, increasing Mn levels may deteriorate especially the heat-affect zone (HAZ) toughness.

[0042] Preferably, Mn is used in the range of 1.0-1.5%, and more preferably 1.2-1.4%.

Aluminum Al is used in the range of 0.005-0.12%

[0043] Al is an effective deoxidizing or killing agent that can remove oxygen from the melt during a steelmaking process. Al also removes nitrogen by forming stable AIN particles and provides grain refinement, which promotes high toughness, especially at low temperatures. Furthermore, Al stabilizes residual austenite. However, excess Al may increase non-metallic inclusions thereby deteriorating cleanliness. Excess Al may promote formation of AIO line inclusions that may be detrimental to formability.

[0044] Preferably, Al is used in the range of 0.015-0.10%, and more preferably 0.02-0.06%.

Niobium Nb is used in the range of 0.0-0.08%

[0045] Nb is an optional alloying element. Nb forms carbides NbC and carbonitrides Nb(C,N). Nb may be useful in grain refinement as it is considered to be a major grain-refining element during austenite-to-ferrite phase transformation after hot-rolling. Nb also contributes to strengthening and toughening of steels, and to formation of the desired phase structure in the steel product. Yet, if Nb is alloyed, Nb addition should be limited to 0.08 % since an excess of Nb does not significantly improve strength of the steel. Furthermore, Nb can be harmful for HAZ toughness since Nb may promote formation of coarse upper bainite structure by forming relatively unstable TiNbN or TiNb(C,N) precipitates.

[0046] Preferably, if alloyed, Nb is used in the range of 0.005-0.06%, and more preferably 0.02-0.04%.

[0047] In some embodiments, the inventive steel may be absent of Nb, excluding inevitable impurity levels i.e. Nb is not purposefully alloyed in the steel. In such a case, grain size may be refined by other means, such as by altering processing parameters and/or by changing other alloying element ratios.

[0048] Nb alloying enables wider processing windows and easier processing of the inventive steel product. However, it is also possible to produce the inventive steel without any Nballoying. This, however, requires more careful process control.

[0049] For example, if Nb is not purposefully alloyed, processing parameters and alloying should be optimized in such a way that the structure of the steel does not preferably recrystallize before accelerated cooling. Furthermore, rolling temperature should be preferably reduced and reduction ratio below recrystallization temperature needs to be sufficiently high. Finally, finish rolling temperature should preferably be lower than when Nb is alloyed.

[0050] In case the structure of the steel recrystallizes before the accelerated cooling, the grain size should preferably be as small as possible. This can be achieved with sufficiently high reduction rates during hot rolling, especially at the end of hot rolling. In addition, grain growth after the end of rolling and before the start of accelerated cooling should be minimized. This can be achieved by initiating accelerated cooling as soon as possible after end of hot rolling.

[0051] Accelerated cooling should also be controlled in such a way that the microstructure of the Nb-free steel product corresponds to the Nb-alloyed steel product in order to enable as similar as possible mechanical properties.

[0052] Furthermore, other alloying elements should also be optimized in such a way that the microstructure corresponds to the inventive steel, as described in claim 1.

Copper Cu is used in the range of 0.2-1.0%

[0053] 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. Cu may promote formation of low carbon bainitic structures, promote solid solution strengthening and contribute to precipitation strengthening.

[0054] Cu may also have beneficial effects of inhibiting stress corrosion cracking. When added in excessive amounts, Cu deteriorates field weldability and the HAZ toughness. Therefore, the upper limit of Cu is set to 1.0%.

[0055] Preferably, Cu is used in the range of 0.2-0.6%, and more preferably 0.25-0.45%.

Chromium Cr is used in the range of 0.35-1.0%

[0056] 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. Cr alloying provides better resistance against pitting corrosion, thereby preventing stress corrosion cracking at an early stage.

[0057] 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 by solid solution strengthening and by decreasing phase transformation temperatures during accelerated cooling. However, if Cr is used in an amount above 1.0 % the HAZ toughness as well as field weldability may be adversely affected.

[0058] 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. Cr alloying also promotes bainite formation. Therefore, Cr is preferably used in the range of 0.35-0.85%, more preferably 0.5-0.70%.

Nickel Ni is used in the range of 0.01-1.0%

[0059] Ni is used to improve low temperature toughness. Ni is an alloying element that improves strength with no or marginal loss of impact toughness and/or HAZ toughness. Ni also improves surface quality. Ni also prevents pitting corrosion, i.e. it reduces the number of initiation sites for stress corrosion cracking, especially when Cu is used. Ni is also added to the composition to facilitate formation of a protective oxide layer under corrosive climate conditions, which provides good resistance against climatic corrosion.

[0060] However, Ni contents of above 1.0 % would increase alloying costs too much without significant technical improvement. An excess of Ni may produce high viscosity iron oxide scales, which deteriorates surface quality of the steel product. Ni contents above 1.0 % also have negative impacts on weldability due to increased CE value and cracking sensitivity coefficient.

[0061] If the steel has high amounts of Cu, Ni is needed in order to prevent surface defects from arising during hot rolling. As a general rule, a Ni content of at least 30% of the Cu content is needed to prevent the defects, and preferably even more. Ni alloying may be needed when the Cu content is more than 0.20%.

[0062] As previously mentioned, Ni is an important alloying element for providing sufficient strength and good resistance to climatic corrosion with no or marginal loss of impact toughness. Ni is preferably used in the range of 0.07-0.65%, and more preferably 0.10-0.25%.

Titanium Ti is used in the range of 0.0-0.12%

[0063] Ti is an optional alloying element. Ti is added to bind free nitrogen N, which is harmful to toughness, by forming stable TiN that 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. At elevated C and Ti levels, the forming TiC may contribute to strength of the steel via precipitate strengthening.

[0064] However, Ti alloying is not mandatory as other alloying elements, such as Al, Nb and V, may also be alloyed to bind free nitrogen.

[0065] Preferably, if Ti is not alloyed, Nb alloying is increased. In such a case, Nb alloying should be at least 0.02%. Alternatively, V alloying may be increased to a minimum amount of 0.08%. Alternatively, Al alloying may also be increased in a minimum amount of 0.02%. Each of Nb, V and Al may be alloyed either separately, or in a combination of two or more of Nb, V and Al.

[0066] Preferably, if Ti is used, it is used in the range of 0.005-0.030%, and more preferably 0.010-0.020%, if HAZ impact toughness needs to be improved.

Molybdenum Mo is used in the range of > 0.05-0.35%

[0067] Mo alloying is used to improve strength, low-temperature toughness and tempering resistance. The presence of Mo enhances strength by favoring formation of bainite, especially lath bainite, by lowering phase transformation temperatures, and via solid solution strengthening. The combination of Mo alloying and low C content also prevents the formation of brittle martensite thus improving e.g. impact toughness properties, wherein the improvement in impact toughness is mainly contributed to formation of tough, low-carbon granular bainite and low-carbon lath bainite.

[0068] However, Mo is a relatively expensive alloying element. Excess Mo alloying may, for example, increase strength unnecessarily and complicate process control, especially with thinner plates. Mo may be used up to 0.35 %. In such a case the potential excess strength increase should be compensated by reducing other alloying elements and by adjusting process parameters.

[0069] Preferably, Mo is used in the range of > 0.05-0.30 %, and more preferably in the range of > 0.05-0.15 %.

Vanadium V is used in the range of 0.0-0.14%

[0070] V is an optional alloying element. V has substantially the same but smaller effects as Nb. 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. If the steel product is tempered or PWHT is applied, then a minimum V alloying of 0.01% may be preferably applied to prevent softening during these treatments. In the example steels herein, V alloying has been replaced by Nb and Ti alloying illustrating the optionality of V alloying. However, even though V is not purposefully alloyed, it may still be present as an inevitable impurity, such as in an amount of 0.007%, as is the case with the example steels.

[0071] However, an addition exceeding 0.14% V has substantial negative effects on weldability. Furthermore, increasing V alloying stabilizes M/A constituents, which may deteriorate impact toughness, especially at ICCGHAZ. V increases the possibility of nucleation sites for carbon enriched constituents, such as M/A constituents. Furthermore, V slows C diffusion in retained austenite thus stabilizing M/A constituents. In addition, V prevents M/A constituents from softening during tempering via formation of V precipitates. Therefore, in order to ensure good weldability and good ICCGHAZ impact toughness, V is preferably alloyed less than 0.03 %.

[0072] Furthermore, an excess V alloying also increases cost unnecessarily.

[0073] Preferably, V is used in the range of 0.0-0.08%, and more preferably in an amount of less than 0.03%.

Boron B may be present in amounts of less than 0.0006%

[0074] B is not an essential alloying element according to the present invention and B is generally present only as an impurity. Furthermore, B alloying may even be detrimental to the mechanical properties of the steel product. B strongly increases hardenability thus leading to presence of brittle phases and decreased elongation.

Calcium Ca may be present in amounts of less than 0.01%

[0075] Ca addition during a steelmaking process is for refining, deoxidation, desulphurization, and control of shape, size and distribution of oxide and sulphide inclusions. 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.

[0076] Preferably, Ca is used in an amount of 0.01 % or less, and more preferably 0.001-0.004% to ensure excellent mechanical properties such as impact strength and bendability.

[0077] 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.

[0078] Unavoidable impurities may comprise phosphor P, sulfur S, and nitrogen N. Their contents in terms of weight percentages (wt. %) are preferably defined as follows:

$P \leq 0.035$, preferably ≤ 0.015, more preferably ≤ 0.010
$S \leq 0.025$, preferably ≤ 0.010, more preferably ≤ 0.003
$N < 0.0200$ %, preferably $N < 0.0060$ %

[0079] Other inevitable impurities may include hydrogen H (< 0.0004 %, preferably H < 0.0002 %), oxygen O (<0.0100 %) and rare earth metals (REM) (<0.1%) or the like, and Tungsten W (<0.1%) and Cobalt Co (<0.1%). Their contents are limited in order to ensure excellent mechanical properties, such as impact toughness.

[0080] The total amount of inevitable impurities should preferably be limited to 0.3%, more preferably to 0.2%, even more preferably to 0.1%.

[0081] Clean steelmaking practice may be applied to minimize unavoidable impurities that may appear as non-metallic inclusions. Clean steelmaking practices commonly include e.g. ladle treatments and careful control of continuous casting process to prevent oxidation of the steel. Non-metallic inclusions disrupt the homogeneity of structure, so their influence on the mechanical and other properties can be considerable. During deformation triggered by flatting, forging and/or stamping, non-metallic inclusions can cause cracks and fatigue failure in steel. The inventors have noticed that, in the present invention, great mechanical properties are achieved when the median inclusion size is set below 4 μm in equivalent circle diameter. Furthermore, 95 % of the total amount of the inclusions are less than or equal to 5.8 μm in equivalent circle diameter.

[0082] The hot-rolled weather resistant steel product may be a strip or preferably a plate with a typical thickness of 2 to 100 mm, preferably 6 mm to 70 mm and more preferably 8 to 40 mm. Typically, a strip is coiled after hot rolling whereas a plate is not coiled after hot rolling.

[0083] The parameters of TMCP are regulated for achieving the optimal microstructure with the chemical composition.

[0084] A method for manufacturing the hot rolled weather resistant steel product disclosed herein will now be described with reference to figure 2.

[0085] In a first step 101, a steel slab with the above defined composition is heated to a temperature in the range of 1100 °C - 1300 °C.

[0086] In a second step 102, the heated steel slab is hot rolled in a plurality of hot rolling passes. This step includes a plurality of sub-steps (i), (ii) and (iii) carried out subsequently.

[0087] In the first sub-step (i), the steel slab is subjected to a first plurality of rolling passes at a temperature above the austenite non-recrystallization temperature.

[0088] In the second sub-step (ii), the steel slab from sub-step (i) is cooled down to a temperature below the austenite non-recrystallization temperature.

[0089] In the third sub-step (iii), the steel slab from step (ii) is subjected to a second plurality of rolling passes at a temperature below the austenite non-recrystallization temperature. The reduction ratio of the second plurality of rolling passes is at least 1.5. The final rolling temperature is in the range of 760 °C to 990 °C.

[0090] In a third step 103, the hot-rolled steel product is subjected to accelerated continuous cooling at a cooling rate of at least 5 °C/s, to a cooling stop temperature of 250 - 350 °C. In an optional fourth step 104, the cooled steel product is tempered at a temperature in the range of 580 °C to 640 °C for 0.5 hour to 1.5 hour.

[0091] In the heating stage of step 101, the slabs are heated to a discharging temperature in the range of 1100 °C to 1300 °C, preferably 1100 °C to 1250 °C, and typically 1140 °C, which is important for controlling the austenite grain growth. An increase in the heating temperature can cause excessive dissolution and coarsening of microalloy precipitates, which can result in abnormal grain growth.

[0092] In the hot rolling stage of step 102, the slab is hot rolled with a typical pass schedule of 10-20 hot rolling passes, for example 16-18 passes, depending on the thickness of the slab and the final product. Preferably, the amount of rolling passes is kept as low as possible to ensure high reduction of a single rolling pass. Furthermore, the accumulative reduction ratio is preferably in the range of 2 to 35 at the end of the hot rolling stage.

[0093] The first hot rolling process in sub-step (i) is carried out above the austenite non-recrystallization temperature (Tnr) and then the slab is cooled down in sub-step (ii) to a temperature below Tnr before controlled rolling passes are carried out below Tnr in sub-step (iii). Controlled rolling refers to controlling the temperature range wherein the rolling passes take place. This temperature range is typically between the Tnr and a set final rolling temperature (FRT), wherein FRT is below Tnr. Controlled rolling at a temperature below the austenite non-recrystallization temperature causes the austenite grains to elongate and creates initiation sites for ferrite grains.

[0094] For the inventive steels, the FRT target range is preferably set high enough to avoid formation of deformed polygonal ferrite during controlled rolling. The formation of deformed polygonal ferrite is undesirable as it would decrease the fraction of granular bainite and lath bainite and could result in inferior mechanical properties, such as decreased strength.

[0095] Pancaked austenite grains are formed thereby accumulating a strain (i.e. dislocation) in austenite grains that can promote ferrite grain refinement by acting as a nucleation site for austenite to ferrite transformation. The controlled rolling ratio of at least 1.5, preferably at least 1.8, and more preferably at least 2.2, ensures that austenite grains are sufficiently deformed. The controlled rolling reduction of 2.2 may be achieved with 4 to 10 rolling passes. The most prominent consequence of deformation in the austenite non-recrystallization region is the improvement in toughness properties.

[0096] The final rolling temperature is typically in the range of 760 °C to 990 °C, preferably in the range of 800 °C to 950 °C, which contributes to the refinement of microstructure. The hot-rolled product is in the step 103 cooled by accelerated continuous cooling to a cooling stop temperature of 250 - 350 °C or 351 - 450 °C or 451 - 550 °C or 551 - 650 °C, at a cooling rate of at least 5 °C/s, preferably at least 10 °C/s, and more preferably at least 15 °C/s. Cooling stop temperatures below 250 °C may result in formation of undesired phase structure, which may adversely impact mechanical properties. The ferrite grain refinement is promoted during the fast accelerated cooling from a temperature above the Ar3 to the cooling stop temperature. Low-temperature transformation microstructures such as bainite are also formed during the accelerated cooling step. The correct cooling stop temperature is defined based on desired strength and the thickness of the steel product.

[0097] Optionally, the subsequent step 104 of heat treatment such as tempering or annealing is performed for fine tuning the microstructure. Preferably, tempering is performed at a temperature in the range of 580 °C to 640 °C for 0.5 hour to 1.5 hour.

[0098] Generally, during the accelerated continuous cooling the polygonal ferrite transformation takes place first, followed by the quasi-polygonal ferrite transformation, bainite transformation and martensite/austenite-islands forming consecutively at decreasing temperatures. The final steel product has a mixed microstructure mainly based on quasipolygonal ferrite, granular bainite and lath bainite, wherein the combined fraction of granular bainite and lath bainite is more than 50 %.

[0099] In the following, these four ferrite morphologies are briefly described:

1. Polygonal ferrite (PF) exhibits roughly equiaxed grains with smooth boundaries.

2. Quasi-polygonal ferrite (QPF) forms during continuous cooling at temperatures lower than transformation into polygonal ferrite. Formation of QPF requires that the cooling rate is high enough and that the steel carbon content is low enough.

[0100] When cooling is rapid enough the partitioning of carbon in the two-phase field is minimized and austenite can transform into ferrite without composition change. Thus, coarse-grained ferrite that is also known as massive ferrite is formed by a formation mechanism known as massive transformation. This means that the atomic mobility is limited to an interface region and is a predominantly interface-controlled reaction that involves localized diffusion.

[0101] QPF grains have highly irregular and undulating grain boundaries and they contain substructure. Furthermore, due to the absence of characteristic crystallographic orientation relationship between parent and product phases, QPF grains can grow rapidly without regard for prior-austenite boundaries.

[0102] 3. Granular bainite (GB) exhibits sheaves of elongated ferrite crystals (granular or equiaxed shapes) with low disorientations and a high dislocation density, containing roughly equiaxed islands of MA constituents.

[0103] 4. Lath bainite (LB), in this context, refers to all bainitic phases that form at temperatures below the transformation temperature of granular bainite. Lath bainite includes bainitic ferrite that is in the form of laths. Said ferrite may have carbides (cementite) or MA constituents precipitated within the bainitic ferrite. With regard to the present invention, the term lath bainite typically includes structures such as low-carbon lower bainite, degenerated low-carbon lower bainite, and low-carbon upper bainite.

[0104] The present invention aims at further developing the weather resistant steel and the manufacturing method thereof such that a new steel product with uncompromised mechanical properties as well as economic advantages can be achieved.

[0105] The microstructure according to the present invention comprises, in terms of volume percentages, polygonal ferrite (PF): $0 \leq PF \leq 10$, preferably $0 \leq PF \leq 5$; quasi-polygonal ferrite (QPF): $5 \leq QPF \leq 36$, preferably $5 \leq QPF \leq 32$, more preferably $5 \leq QPF \leq 30$; granular bainite (GB): $20 \leq GB \leq 70$, preferably $23 \leq GB \leq 65$, more preferably $26 \leq GB \leq 60$; lath bainite (LB): $16 \leq LB \leq 80$, preferably $20 \leq LB \leq 75$, more preferably $27 \leq LB \leq 70$; retained austenite (RA): $RA \leq 2$, preferably ≤ 0.5, more preferably ≤ 0.1. Occasionally, islands of martensite/austenite (MA) constituents can be detected in the microstructure. If present, martensite/austenite constituent (MA) fractions are: $MA \leq 12$, preferably $MA \leq 8$, more preferably ≤ 5. Furthermore, the microstructure may comprise pearlite (P). If present, pearlite fractions are: $P \leq 5$, preferably $P \leq 2$, more preferably $P \leq 1$.

[0106] The broadest phase fraction ranges were determined by a computational model using a large experimental data set, including data that is outside the scope of this patent. The inventors have noticed that the modeled phase fractions and resulting strength levels correspond well with the experimentally determined values for the inventive steels.

[0107] Good toughness of steels, and especially low ductile-to-brittle transition temperature (DBTT), is often associated with a high density of high angle boundaries. Such high angle boundaries are usually present in the microstructure and are beneficial, because these boundaries act as obstacles for cleavage crack propagation. Microstructures comprising a significant fraction of granular bainite and lath bainite together with fine-grained quasipolygonal ferrite lead to the formation of substantial amounts of high angle boundaries between the interfaces of bainitic ferrites (mainly granular bainite and lath bainite) and quasi-polygonal ferrite. In addition, lath bainite generally exhibits a large fraction of high angle boundaries. Thus, for the inventive steels, generally bainitic microstructure is not enough. It is important that the main bainitic ferrites of the inventive steels are low-carbon granular bainite and low-carbon lath bainite. Preferably, the inventive steel product comprises a matrix that is essentially bainitic through a thickness of the steel product. Low-carbon lath bainite is beneficial in the microstructure of the inventive steels, since it enhances strength while maintaining good impact toughness levels. On the contrary, highcarbon lath bainite would increase strength but deteriorate impact toughness.

[0108] The presence of martensite is not allowed as one of the main phases in the inventive steels. If martensite is present, it should be restricted to the MA constituents and the size of the MA constituents should as small as possible to promote good impact toughness properties. Phase fraction of polygonal ferrite should also be kept as small as possible. The strength of polygonal ferrite is low when combined with bainitic ferrite. Therefore, large fractions of polygonal ferrite would lead to decreased strength of the steel. In addition, MA constituents in polygonal ferrite are typically larger in size thus deteriorating impact toughness.

[0109] The granular bainite containing microstructures also reduce the size and fraction of MA constituents. This is beneficial, as large islands of MA constituents are considered to be favourable nucleation sites for brittle fracture. The distribution of MA constituents is preferably restricted to the granular bainitic ferrite part of the microstructure. Low C content further reduces the size of MA constituents in the steel according to the present invention.

[0110] Generally, lath bainite does not contain large fractions of MA constituents in the inventive steels. This is due to the low carbon content of the inventive steels and accelerated cooling, during which carbon does not have time to diffuse and form MA constituents.

[0111] If the cleavage microcrack is initiated in the vicinity of MA constituents, the propagation of this microcrack is easily blunted and temporarily halted due to the adjacent high angle boundary. For a microcrack to reach the critical length, beyond which the microcrack can propagate in an unstable manner, more energy is required to connect and link the neighboring microcracks by e.g. rotation of the short microcracks in a shearing mode. Therefore, the steels with granular bainite and lath bainite containing microstructures having small grain size exhibit improved impact toughness and especially low DBTT.

[0112] The steel product may have a yield strength (Rp0.2) in the range of 500-650 MPa, preferably 520-625 MPa, and more preferably 540-599 MPa; and an ultimate tensile strength (Rm) in the range of 570-850 MPa, preferably 610-830 MPa, and more preferably 660-810 MPa; while the yield ratio may be in the range of 0.65-0.90. The steel product may have a Charpy-V impact toughness of at least 150 J/cm2, preferably at least 200 J/cm2, more preferably at least 250 J/cm^2 at a temperature of -60 °C. The steel product may have a minimum bending radius of 3.0 t or less, preferably 1.5 t or less, more preferably 1.0 t in the longitudinal or transverse direction, and wherein t is the thickness of the steel product.

[0113] The combination of correct alloying (mainly Si, Cr, Cu and Ni for weathering properties), including low C levels and presence of Mo, with a a matrix containing mainly low-carbon granular bainite and low-carbon lath bainite, gives the steel product great strength combined with outstanding impact toughness and weathering properties.

[0114] 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.

EXAMPLES 1-21

[0115] The following chapters relate to Examples 1-21. Examples 1-19 are inventive examples and Examples 20-21 are comparative examples. The examples were obtained from industrial scale rolling tests.

Alloying and processing

[0116] Table 1 illustrates the chemical compositions for the inventive steels according to Examples 1-19 as well as for the comparative examples 20 and 21. It can be seen from Table 1, that the comparative examples have increased C and Ni alloying compared to the inventive examples. Furthermore, the comparative examples do not have Mo alloying.

[0117] Table 2 illustrates the processing parameters for the inventive steels as well as for the comparative examples. The final rolling temperature FRT for the comparative examples was lower than for the inventive examples.

[0118] Table 3 illustrates the carbon equivalent and corrosion index values for the inventive examples and comparative example. Similar carbon equivalent and corrosion index values were determined for the comparative examples.

Microstructure

[0119] Plate head and tail end quarter-thickness microstructures were studied on sections containing the rolling direction (RD) and the normal direction (ND). Microstructures were characterized using Field Emission Scanning Electron Microscopy (FESEM) JEOL JSM-7000F. Samples were mounted in a conductive resin and mechanically polished to 1 μm. The final polishing step was conducted with MD-Chem polishing cloth and non-drying 0.04 μm colloidal silica suspension using 10 N force and 120 s polishing time. Finally, specimens were etched in 2% Nital. Volume fractions of phase constituents were determined from planar sections by using SEM micrographs, and both point counting methodology and image analysis as well. A complete grid of points was drawn, and points were registered to obtain the number of points in polygonal ferrite, quasi-polygonal ferrite, granular bainite and lath-like bainite, respectively. Finally, the fraction of each constituent was obtained by dividing the number of points in given phase constituent by the total number of grid points.

[0120] To characterize the inclusion structure, energy dispersive spectrometer analysis was applied at 15kV and 3.5nA. The data were acquired and analyzed using Oxford INCA software. The working distance was 10mm and each inclusion was measured for 1 second live time. The scanning area was estimated to be sufficiently large for reliable inclusion feature analysis and measurement covered area from the plate top surface to the bottom surface.

[0121] Phase fractions of the inventive steels no. 4 and 8 are shown in Table 4, as an example. The phase fractions in Table 4 were determined with point counting methodology. It can be seen that the dominant microstructures are granular bainite and lath bainite with a smaller fractions of quasi-polygonal ferrite and polygonal ferrite.

[0122] Figure 1 illustrates the microstructure of Example steel 8. In Figure 1, denotations of QPF, GB and LB refer to the corresponding phases of quasi-polygonal ferrite (QPF), granular bainite (GB) and lath bainite (LB).

Yield strength

[0123] Yield strength was determined according to SFS-EN ISO 6892-1:2019 standard using transverse specimens of a production batch of 300 ton of plates. The measured yield strength (Rp0.2) values in the transverse direction range from 504 MPa to 588 MPa, for the steels according to the invention, as can be seen from Table 5. Yield strength levels ranging from 504 to 539 MPa were measured for the comparative examples.

Ultimate tensile strength

[0124] Ultimate tensile strength was determined according to SFS-EN ISO 6892-1:2019 standard using transverse specimens of a production batch of 300 ton of plates. The measured ultimate tensile strength (Rm) values in the transverse direction range from 617 MPa to 800 MPa, for the steels according to the invention, as can be seen from Table 5. Ultimate tensile strength levels ranging from 650 to 704 MPa were measured for the comparative examples.

Yield ratio

[0125] The ratio between yield strength and ultimate tensile strength, i.e. the yield ratio (YR) is also shown in Table 5. For the inventive examples, the yield ratio ranges from 0.68 to 0.89 while yield ratios ranging from 0.77 to 0.78 were determined for the comparative examples.

Total elongation

[0126] Total elongation was determined according to SFS-EN ISO 6892-1:2019 standard using transverse specimens of a production batch of 300 ton of plates. The measured A5 total elongation values in the transverse direction range from 16 % to 23,8 %, for the steels according to the invention, as can be seen from Table 5. Total elongation levels of 19 % were measured for both of the comparative examples.

Charpy-V impact toughness

[0127] The impact toughness values at temperatures -40 °C, -50 °C and -60 °C were obtained by Charpy V-notch tests according to the SFS-EN ISO 148-1:2016 standard. The impact toughness values were measured using 10 mm x 5-10 mm longitudinal specimens taken from 2 mm of a surface of the weather resistant steel product of a production batch of plates manufactured from three heats of 300 tons in total.

[0128] Table 5 shows that the mean impact toughness values range from 303 J/cm^2 to 442 J/cm^2 at -60 °C for the steels according to the invention. The impact toughness values for comparative examples are at significantly lower level of 108 and 119 J/cm^2 at a temperature of -60 °C, for examples 20 and 21 respectively, regardless of the lower FRT used for the comparative examples. As known in the field, generally, lowering FRT yields better impact toughness values. It is also noteworthy that for the inventive examples, the impact toughness levels do not significantly decrease with decreasing test temperature.

Bendability

[0129] 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 where a minimum amount of three test samples (16*300*300 mm), 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.

[0130] According to the bend tests, the inventive plates have a minimum bending radius (Ri) 1.0 times plate thickness (t), i.e. Ri = 1.0 t, in both longitudinal and transverse directions.

PWHT-resistance

[0131] Generally, steels with mainly bainitic microstructures exhibit good resistance to softening after a post-weld heat treatment (PWHT). The inventive steels have good resistance to softening after a PWHT especially due to Cr, Mo, Cu and Nb alloying and mainly bainitic microstructure.

[0132] By way of example, example steel 15 was subjected to post-weld heat treatment (PWHT) at 600 °C for 1.25 hour. Plate thickness of the tested example was 32 mm. Tensile properties were tested according to SFS-EN ISO 6892-1:2019 and impact toughness properties were tested according to SFS-EN ISO 148-1:2016. The impact toughness values were measured using 10 mm x 10 mm longitudinal specimens taken from 2 mm of a surface of the weather resistant steel product at temperatures of -40 °C, -50 °C and - 60 °C.

[0133] Figure 3 plots yield strength and A5 total elongation for samples before and after a post-weld heat treatment for example steel 15. Data points on the left were obtained after subjecting the example steel 15 to a tempering treatment for 1.25 hr at 600 °C and the right most data point represents an as-rolled sample, to which no PWHT was conducted.

[0134] Figure 4 plots ultimate tensile strength for samples before and after a post-weld heat treatment for example steel 15. Data points on the left were obtained after subjecting the example steel 15 to a tempering treatment for 1.25 hr at 600 °C and the right most data point represents an as-rolled sample, to which no PWHT was conducted.

[0135] Figure 5 plots Charpy V-notch test temperature as a function of impact energy per cm^2 for example steel 15. Data points with symbol (I) were obtained after subjecting the example steel 15 to a tempering treatment for 1.25 hr at 600 °C and data points with symbol (J) represent an as-rolled sample, to which no PWHT was conducted.

[0136] Yield strength levels range from 601 MPa to 652 MPa, ultimate tensile strength levels range from 724 MPa to 774 MPa, A5 total elongation levels range from 20.2 % to 22.8 % and impact toughness levels range from 246 J/cm^2 to 342 J/cm^2 for the PWHT-treated sample. Yield strength, ultimate tensile strength, A5 total elongation and impact toughness's for the as-rolled sample were 550MPa, 718 MPa, 18% and 293-398 J/cm2, respectively. The test data shows that excellent tensile and impact toughness properties are maintained even after a post weld heat treatment.

Weldability

[0137] Weldability testing was performed on a 25 mm-thick plate with composition of Example steel no 13. The weldability testing was performed by welding three butt joints using test pieces of 25 mm x 200 mm x 1000 mm in size. The test pieces were cut from the plate along the principal rolling direction so that the 1000 mm long butt welds were parallel to rolling direction. The joints were welded with single wire submerged arc welding process no 121 using heat input of 3.0 kJ/mm. No preheating before welding of the plate was used. Interpass temperature was in the range of 100 °C and 150 °C. The butt joints were welded using half V-groove preparation with 60° groove angle. The selected welding consumable for the SAW process Bavaria BF10 MV + S2NiCu.

[0138] Table 6 shows the welding process parameters and impact toughness values at the weld as well as at 1 and 2 mm from the fusion line towards the base material tested at -50 °C. The results show that good impact toughness levels are maintained for the welded steel product as well impact energies ranging from 65 J to 228 J combined with good ultimate tensile strength level of 676 MPa.

Table 1

Steel	C	Si	Mn	P	S	Al	Nb	V	Cu	Cr	Ni	N	Mo	Ti	Ca	B	Remarks
1	0,043	0,611	1,35	0,005	0,001	0,031	0,032	0,007	0,295	0,646	0,613	0,005	0,240	0,009	0,0028	0,0004	Inv.
2	0,038	0,604	1,35	0,005	0,001	0,030	0,031	0,007	0,289	0,642	0,615	0,004	0,240	0,012	0,0018	0,0004	Inv.
3	0,035	0,581	1,27	0,008	0,001	0,032	0,032	0,007	0,280	0,603	0,152	0,004	0,084	0,015	0,0015	0,0005	Inv.
4	0,043	0,611	1,35	0,005	0,001	0,031	0,032	0,007	0,295	0,646	0,613	0,005	0,240	0,009	0,0028	0,0004	Inv.
5	0,043	0,611	1,35	0,005	0,001	0,031	0,032	0,007	0,295	0,646	0,613	0,005	0,240	0,009	0,0028	0,0004	Inv.
6	0,034	0,577	1,29	0,006	0,001	0,032	0,031	0,008	0,289	0,607	0,154	0,004	0,077	0,014	0,0022	0,0003	Inv.
7	0,043	0,611	1,35	0,005	0,001	0,031	0,032	0,007	0,295	0,646	0,613	0,005	0,240	0,009	0,0028	0,0004	Inv.
8	0,043	0,611	1,35	0,005	0,001	0,031	0,032	0,007	0,295	0,646	0,613	0,005	0,240	0,009	0,0028	0,0004	Inv.
9	0,043	0,611	1,35	0,005	0,001	0,031	0,032	0,007	0,295	0,646	0,613	0,005	0,240	0,009	0,0028	0,0004	Inv.
10	0,043	0,611	1,35	0,005	0,001	0,031	0,032	0,007	0,295	0,646	0,613	0,005	0,240	0,009	0,0028	0,0004	Inv.
11	0,035	0,581	1,27	0,008	0,001	0,032	0,032	0,007	0,280	0,603	0,152	0,004	0,084	0,015	0,0015	0,0005	Inv.
12	0,035	0,581	1,27	0,008	0,001	0,032	0,032	0,007	0,280	0,603	0,152	0,004	0,084	0,015	0,0015	0,0005	Inv.
13	0,043	0,611	1,35	0,005	0,001	0,031	0,032	0,007	0,295	0,646	0,613	0,005	0,240	0,009	0,0028	0,0004	Inv.
14	0,038	0,604	1,35	0,005	0,001	0,030	0,031	0,007	0,289	0,642	0,615	0,004	0,240	0,012	0,0018	0,0004	Inv.
15	0,038	0,604	1,35	0,005	0,001	0,030	0,031	0,007	0,289	0,642	0,615	0,004	0,240	0,012	0,0018	0,0004	Inv.
16	0,035	0,581	1,27	0,008	0,001	0,032	0,032	0,007	0,280	0,603	0,152	0,004	0,084	0,015	0,0015	0,0005	Inv.
17	0,035	0,581	1,27	0,008	0,001	0,032	0,032	0,007	0,280	0,603	0,152	0,004	0,084	0,015	0,0015	0,0005	Inv.
18	0,038	0,604	1,35	0,005	0,001	0,030	0,031	0,007	0,289	0,642	0,615	0,004	0,240	0,012	0,0018	0,0004	Inv.
19	0,035	0,581	1,27	0,008	0,001	0,032	0,032	0,007	0,280	0,603	0,152	0,004	0,084	0,015	0,0015	0,0005	Inv.
20	0,08	0,25	1,49	0,009	0,0002	0,046	0,035	0,01	0,276	0,055	0,744	0,0031	0,005	0,013	0,0024	0,0003	Comp. Ex. Comp.
21	0,07	0,261	1,52	0,015	0,002	0,036	0,037	0,007	0,301	0,055	0,762	0,0035	0,006	0,014	0,0015	0,0005	Ex.

Table 2

Steel	Reheating T [°C]	FRT [°C]	CR ratio	Cooling end T [°C]	Cooling rate [°C/s]	Remarks
1	1169	880	2,2	425	40	Inv.
2	1164	930	2,5	600	30	Inv.
3	1166	880	2,2	500	20	Inv.
4	1171	880	2,5	275	40	Inv.
5	1158	880	2,5	425	40	Inv.
6	1167	880	2,5	500	45	Inv.
7	1158	880	2,3	275	40	Inv.
8	1173	880	2,3	350	40	Inv.
9	1175	880	2,3	425	40	Inv.
10	1161	880	2,3	600	30	Inv.
11	1163	880	2,3	500	40	Inv.
12	1168	880	2,3	400	40	Inv.
13	1176	840	2,5	275	20	Inv.
14	1164	840	2,5	450	20	Inv.
15	1164	840	2,5	350	20	Inv.
16	1163	840	2,5	400	15	Inv.
17	1167	840	2,5	500	15	Inv.
18	1164	840	2,6	500	15	Inv.
19	1168	840	2,6	425	15	Inv.
20	1140	743	2	530	10	Comp. Ex.
21	1140	717	2	530	10	Comp. Ex.

Table 3

Steel	CEV	PCM	ASTM G101	Remarks
1	0,5071	0,2068	7,5714	Inv.
2	0,5011	0,2011	7,5474	Inv.
3	0,4143	0,1734	6,6610	Inv.
4	0,5071	0,2068	7,5714	Inv.
5	0,5071	0,2068	7,5714	Inv.
6	0,4169	0,1725	6,6846	Inv.
7	0,5071	0,2068	7,5714	Inv.
8	0,5071	0,2068	7,5714	Inv.
9	0,5071	0,2068	7,5714	Inv.
10	0,5071	0,2068	7,5714	Inv.
11	0,4169	0,1725	6,6846	Inv.
12	0,4169	0,1725	6,6846	Inv.
13	0,5071	0,2068	7,5714	Inv.
14	0,5011	0,2011	7,5474	Inv.
15	0,5011	0,2011	7,5474	Inv.
16	0,4169	0,1725	6,6846	Inv.
17	0,4169	0,1725	6,6846	Inv.
18	0,5011	0,2011	7,5474	Inv.
19	0,4169	0,1725	6,6846	Inv.
20	0,4103	0,1946	6,5581	Comp. Ex.
21	0,4078	0,1888	6,6984	Comp. Ex.

Table 4

Steel	PF %	QPF %	GB %	LB %	Remarks
4	1	10	37	52	Inv ex
8	0	9	31	59	Inv ex

Table 5

Steel	YS (MPa)	TS (MPa)	YR	A5	Energy [J/cm^2,-40°C]	Energy [J/cm^2,-50°C]	Energy [J/cm^2,-60°C]	Remarks
1	547	719	0,76	18,6	335,8	330,8	308,3	Inv.
2	516	712	0,72	20,5	305,8	305,8	303,3	Inv.
3	518	629	0,82	23,8	335,0	339,2	364,2	Inv.
4	569	795	0,72	18,3	348,9	359,4	354,4	Inv.
5	560	768	0,73	16,5	398,9	414,4	416,1	Inv.
6	543	635	0,86	23	442,2	436,1	442,2	Inv.
7	588	796	0,74	17,6	385,0	350,8	312,9	Inv.
8	582	747	0,78	16	417,1	331,7	384,2	Inv.
9	568	730	0,78	21,5	427,5	398,3	384,2	Inv.
10	506	749	0,68	20,8	352,5	335,0	315,4	Inv.
11	563	672	0,84	19	384,6	351,7	324,2	Inv.
12	571	644	0,89	20,8	416,3	434,6	434,6	Inv.
13	582	800	0,73	18,6	352,5	340,4	355,8	Inv.
14	563	760	0,74	18,9	375,0	365,8	385,8	Inv.
15	580	772	0,75	17,4	380,0	372,5	373,8	Inv.
16	525	657	0,80	22,4	431,7	412,5	411,7	Inv.
17	509	617	0,82	22,9	457,1	435,4	384,2	Inv.
18	539	704	0,77	20,5	395,8	410,4	378,3	Inv.
19	504	650	0,78	22	392,9	390,4	321,7	Inv.
20	552	637	0,86	19,0	-	-	108	Comp. Ex.
21	542	628	0,86	19,0			119	Comp. Ex.

Table 6

Steel	Welding Process	Welding Energy (kJ/mm)	PWHT	Welding Consumable	Preheating	TS (MPa)	CVN, -50 °C, weld, ave. (J)	CVN, -50 °C, FL+1, ave. (J)	CVN, -50 °C, FL+2, ave. (J)	Remarks
13	121/SAW	3,00	No	Bavaria BF10 MV + S2NiCu	RT	676	65	182	228	Inv. ex

Claims

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

C	0.015 - 0.045, preferably 0.025 - 0.045, more preferably 0.025 - 0.040
Si	0.15 - 0.75, preferably 0.30 - 0.75, more preferably 0.50 - 0.70
Mn	0.8 - 1.6, preferably 1.0 - 1.5, more preferably 1.2 - 1.4
Al	0.005 - 0.12, preferably 0.015 - 0.10, more preferably 0.02 - 0.06
Nb	0.0 - 0.08, preferably 0.005 - 0.06, more preferably 0.02 - 0.04
Cu	0.2 - 1.0, preferably 0.2 - 0.6, more preferably 0.25 - 0.45
Cr	0.35 - 1.0, preferably 0.35 - 0.85, more preferably 0.50 - 0.70
Ni	0.01 - 1.0, preferably 0.07 - 0.65, more preferably 0.10 - 0.25
Ti	0.0 - 0.12, preferably 0.005 - 0.030, more preferably 0.010 - 0.020
Mo	> 0.05 - 0.35, preferably > 0.05 - 0.30, more preferably > 0.05 - 0.15
V	0.0 - 0.14, preferably 0.0 - 0.08, more preferably less than 0.03
B	< 0.0006
P	≤ 0.035, preferably ≤ 0.015, more preferably ≤ 0.010
S	≤ 0.025, preferably ≤ 0.010, more preferably ≤ 0.003
W optionally	< 0.1 %
Co optionally	< 0.1 %
N	< 0.0200 %, preferably N < 0.0060 %
H	< 0.0004 %, preferably H < 0.0002 %
0	< 0.0100 %
Ca	< 0.01 %, preferably 0.001 - 0.004 %
REM	< 0.1 %

remainder Fe and inevitable impurities, wherein the steel product has a microstructure comprising a matrix consisting of, in terms of volume percentages (vol. %), measured at ¼ thickness:

Polygonal ferrite (PF): 0 ≤ PF ≤ 10, preferably 0 ≤ PF ≤ 5
Quasipolygonal ferrite (QPF): 5 ≤ QPF ≤ 36, preferably 5 ≤ QPF ≤ 32, more preferably 5 ≤ QPF ≤ 30
Granular bainite (GB): 20 ≤ GB ≤ 70, preferably 23 ≤ GB ≤ 65, more preferably 26 ≤ GB ≤ 60
Lath bainite (LB): 16 ≤ LB ≤ 80, preferably 20 ≤ LB ≤ 75, more preferably 27 ≤ LB ≤ 70
Retained austenite (RA): RA ≤ 2, preferably ≤ 0.5, more preferably ≤ 0.1
Martensite/austenite constituents (MA): MA ≤ 12, preferably MA ≤ 8, more preferably ≤ 5
Pearlite (P): P ≤ 5, preferably P ≤ 2, more preferably P ≤ 1, wherein
GB+LB > 50 %, preferably GB+LB > 65 %.

2. The hot-rolled weather resistant steel product according to claim 1 wherein the steel product has a composition consisting of, in terms of weight percentages (wt. %):

C	0.025 - 0.040
Si	0.50 - 0.70
Mn	1.2 - 1.4
Al	0.02 - 0.06
Nb	0.02 - 0.04
Cu	0.25 - 0.45
Cr	0.50 - 0.70
Ni	0.10 - 0.25
Ti	0.010 - 0.020
Mo	> 0.05 - 0.15
V	0.0 - 0.03
B	< 0.0006
P	≤ 0.010

(continued)

S	$\leq$ 0.003
W optionally	< 0.1 %
Co optionally	< 0.1 %
N	< 0.0060 %
H	< 0.0002 %
O	< 0.0100 %
Ca	0.001 - 0.004 %
REM	< 0.1 %

remainder Fe and inevitable impurities wherein
the steel product has a microstructure comprising a matrix consisting of, in terms of volume percentages (vol. %), measured at ¼ thickness:

Polygonal ferrite (PF): $0 \leq PF \leq 5$
Quasipolygonal ferrite (QPF): $5 \leq QPF \leq 30$
Granular bainite (GB): $26 \leq GB \leq 60$
Lath bainite (LB): $27 \leq LB \leq 70$
Retained austenite (RA): $RA \leq 0.1$
Martensite/austenite constituents (MA): ≤ 5
Pearlite (P): $P \leq 1$, wherein
GB+LB > 65 %.

3. The hot rolled weather resistant steel product according to claim 1 or 2, wherein
the minimum value of equation C+Mn/6 for the steel composition is 0.15, preferably 0.20 and more preferably 0.24.

4. The hot rolled weather resistant steel product according to any one of claims 1-3, wherein the maximum value of equation C+Mn/6 for the steel composition is 0.31, preferably 0.29 and more preferably 0.27.

5. The hot rolled weather resistant steel product according to any one of claims 1-4, wherein the maximum value of equation C+Si/30 for the steel composition is below 0.11, preferably below 0.09 and more preferably below 0.07.

6. The hot rolled weather resistant steel product according to any one of claims 1-4, wherein the steel product comprises non-metallic inclusions having a median inclusion size below 4 μm in diameter, and wherein 95 % of the total amount of the inclusions are less than or equal to 5.8 μm in diameter.

7. The hot-rolled weather resistant steel product according to any one of claims 1-5, wherein the corrosion index of the steel product is at least 5, preferably at least 6, and more preferably at least 6.5, according to ASTM G101-04.

8. The hot-rolled weather resistant steel product according to any one of claims 1-6 wherein the steel product has a yield strength (Rp0.2) in the range of 500-650 MPa, preferably 520-625 MPa, and more preferably 540-599 MPa.

9. The hot-rolled weather resistant steel product according to any one of claims 1-7 wherein the steel product has an ultimate tensile strength (Rm) in the range of 570-850 MPa, preferably 610-830 MPa, and more preferably 660-810 MPa.

10. The hot-rolled weather resistant steel product according to any one of claims 1-8 wherein the steel product has a yield ratio in the range of 0.65-0.90.

11. The hot rolled weather resistant steel product according to any one of claims 1-9, wherein Charpy-V impact toughness measured from 2 mm of a surface of the steel product is at least 150 J/cm^2, preferably at least 200 J/cm^2, more preferably at least 250 J/cm^2 measured at a temperature of -60 °C.

12. The hot rolled weather resistant steel product according to any one of claims 1-10, wherein

Pcm carbon equivalent value is Pcm < 0.25, preferably Pcm < 0.23, more preferably Pcm < 0.21, and/or

CEV carbon equivalent value is CEV < 0.56, preferably CEV < 0.54, more preferably CEV < 0.52.

13. The hot rolled weather resistant steel product according to any one of claims 1-11, wherein the steel product has a thickness in the range of 2 mm to 100 mm, preferably 6 mm to 70 mm, and more preferably 8 to 40 mm.

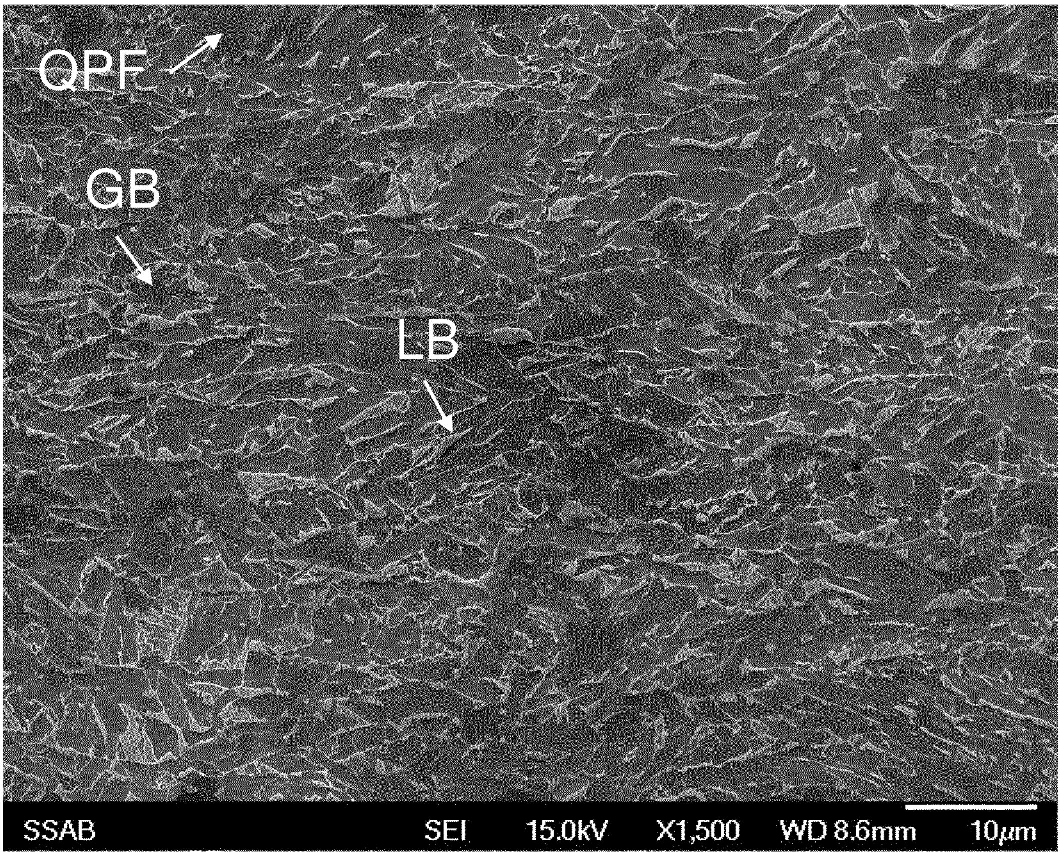
14. The hot rolled weather resistant steel product according to any one of claims 1-12, wherein the steel product has, in the longitudinal or transverse direction, a minimum bending radius of 3.0 t or less, preferably 2.0 t or less, more preferably 1.0 t or less, and wherein t is the thickness of the steel product.

15. A method for manufacturing the hot rolled weather resistant steel product according to any one of the preceding claims 1-13 comprising the following steps of

- heating (101) a steel slab with the composition according to claim 1 to a temperature in the range of 1100 °C - 1300 °C, and preferably 1100 - 1250 °C;
- hot rolling (102) the heated steel slab in a plurality of hot rolling passes, wherein

  i. the steel slab is subjected to a first plurality of rolling passes at a temperature above the austenite non-recrystallization temperature,
  ii. the steel slab from step (i) is cooled down to a temperature below the austenite non-recrystallization temperature,
  iii. the steel slab from step (ii) is subjected to a second plurality of rolling passes at a temperature below the austenite non-recrystallization temperature, wherein the reduction ratio of the second plurality of rolling passes is at least 1.5, preferably at least 1.8, more preferably 2.2 or more, and wherein the final rolling temperature is in the range of 760 °C to 990 °C, preferable the final rolling temperature is in the range of 800 °C to 950 °C;

- accelerated continuous cooling (103) at a cooling rate of at least 5 °C/s, preferably at least 10 °C/s, and more preferably at least 15 °C/s to a cooling stop temperature of 250 - 350 °C or 351 - 450 °C or 451 - 550 °C or 551 - 650 °C; and
- optionally, tempering (104) at a temperature in the range of 580 °C to 640 °C for 0.5 hour to 1.5 hour.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LB
SSAB
SEI
15.0kV
X1,500
WD 8.6mm
10μm

Fig. 1

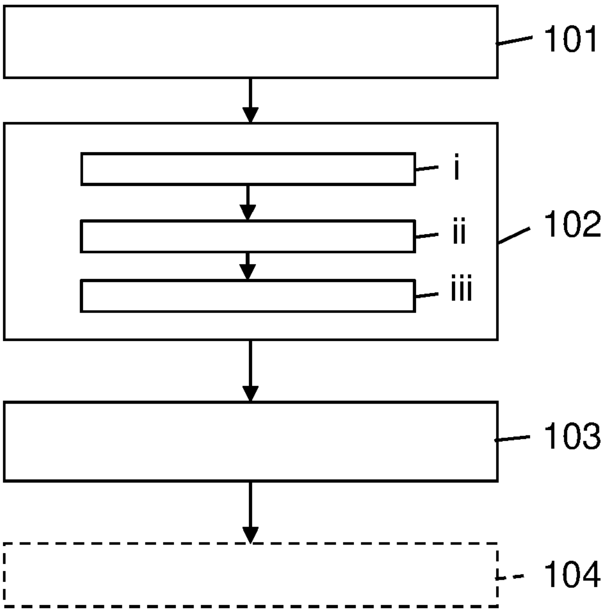
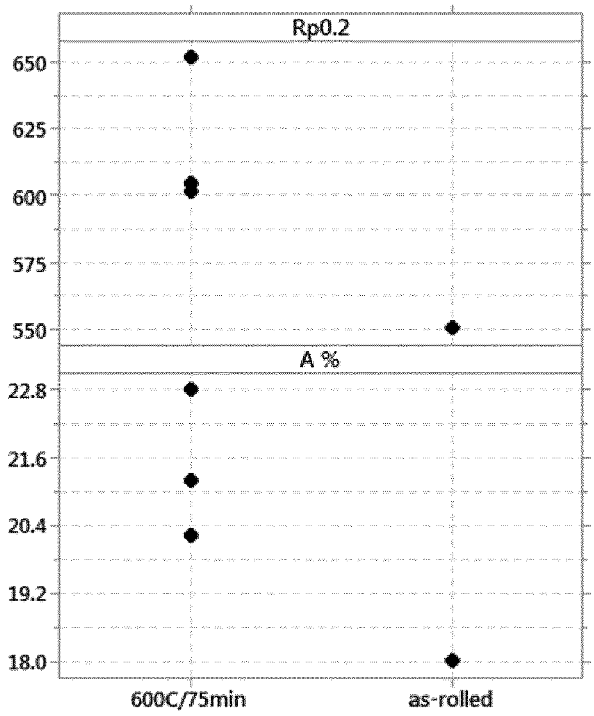

101
i
ii
iii
102
103
104

Fig. 2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625
600
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550
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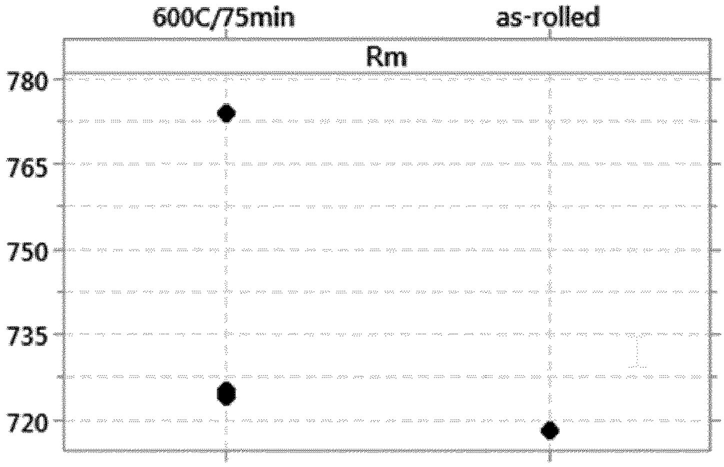
21.6
20.4
19.2
18.0
600C/75min
as-rolled

Fig. 3


600C/75min
as-rolled
Rm
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765
750
735
720

Fig. 4

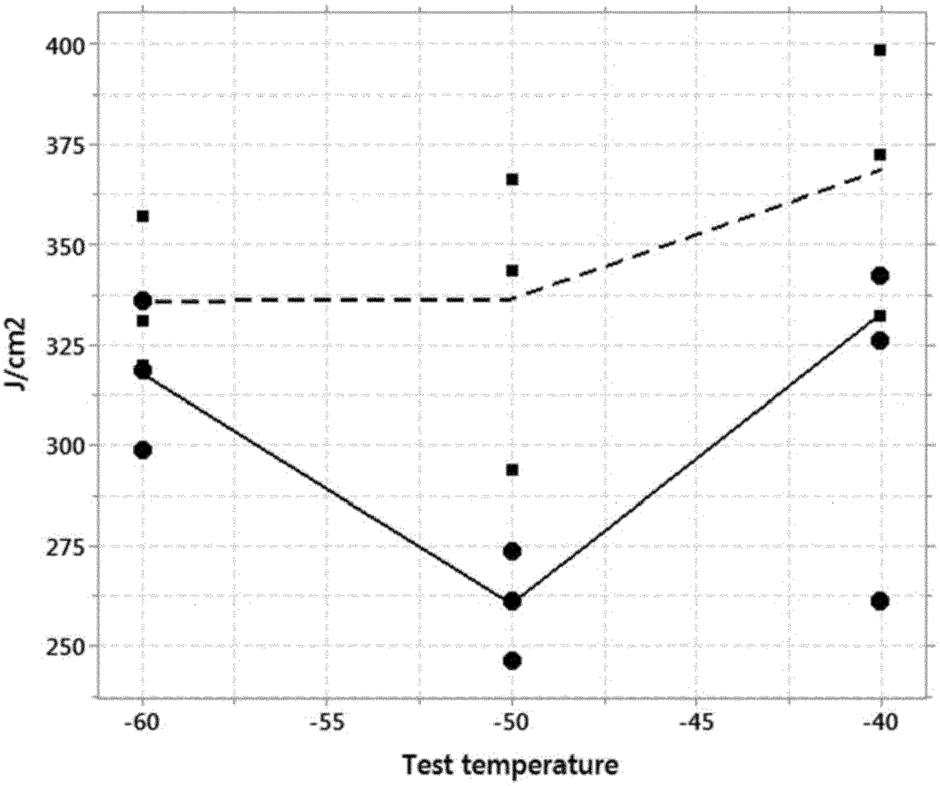
400
375
350
325
300
275
250
J/cm2
-60
-55
-50
-45
-40
Test temperature

Fig. 5

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EUROPEAN SEARCH REPORT

Application Number
EP 22 18 3442

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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A	* title, Table 1, Fig. 1, pg. 36 * -----	2	
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-/--

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	23 November 2022	Abrasonis, Gintautas

1

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Application Number
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The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
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EUROPEAN SEARCH REPORT

Application Number
EP 22 18 3442

DOCUMENTS CONSIDERED TO BE RELEVANT

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TECHNICAL FIELDS SEARCHED (IPC)

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	23 November 2022	Abrasonis, Gintautas

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23-11-2022

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