



(51) International Patent Classification:

C22C 38/04 (2006.01) C21D 1/18 (2006.01)
C22C 38/02 (2006.01) C21D 1/22 (2006.01)
C22C 38/14 (2006.01) C21D 1/19 (2006.01)
C22C 38/06 (2006.01) C21D 1/26 (2006.01)
C22C 38/00 (2006.01) B32B 15/01 (2006.01)
C22C 38/12 (2006.01) C22C 18/00 (2006.01)
C21D 9/46 (2006.01) C22C 18/04 (2006.01)
C21D 8/02 (2006.01) C23C 2/06 (2006.01)
C21D 6/00 (2006.01) C23C 2/40 (2006.01)

(21) International Application Number:

PCT/EP2024/065763

(22) International Filing Date:

07 June 2024 (07.06.2024)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

2350707-2 09 June 2023 (09.06.2023) SE

(71) Applicant: VOESTALPINE STAHL GMBH [AT/AT];
voestalpine Strasse 3, 4020 Linz (AT).

(72) Inventors: KRIZAN, Daniel; Europastrasse 12/3/23, 4020 Linz (AT). REHRL, Johannes; Kimmersdorfer Strasse 39, 4502 St. Marien (AT). KICKINGER, Christoph; Josefiberg 29, 3363 Ulmerfeld (AT).

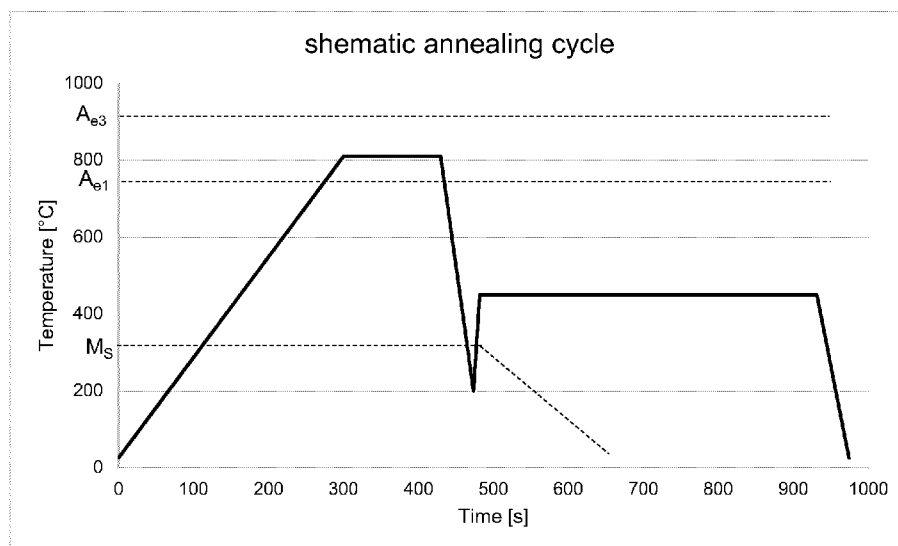
(74) Agent: AERA A/S; Niels Hemmingsens Gade 10, 5th floor, DK-1153 Copenhagen K (DK).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, MG, MK, MN, MU, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ,

(54) Title: A HIGH STRENGTH Q&P STEEL STRIP OR SHEET, AND A METHOD FOR PRODUCING THE SAME

Fig. 1



(57) Abstract: The invention relates to a high strength steel strip or sheet having: a composition comprising of the following elements in wt. %: C 0.10 – 0.30, Mn 1.5 – 3.0, Si 0.5 – 2.0, Al 0.03 – 0.50, Ti 0.01 – 0.10, B 0.002 – 0.008, optionally Nb, V, Cr, Mo, balance Fe apart from impurities, mechanical properties TS 980 – 1300 MPa, and optionally one or more of: YS 600 – 1100 MPa, HER ≥ 20 %, and TE ≥ 13 %, and a microstructure ϵ fulfilling in vol. %: Ferrite 5 – 50, tempered martensite 20 – 85, bainite 0 – 15, fresh martensite 0 – 10 and retained austenite 5 – 20. The invention also relates to a method for producing a high strength steel strip or sheet.

RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

- *with international search report (Art. 21(3))*
- *in black and white; the international application as filed contained color or greyscale and is available for download from PATENTSCOPE*

A HIGH STRENGTH Q&P STEEL STRIP OR SHEET, AND A METHOD FOR PRODUCING
THE SAME

TECHNICAL FIELD

- 5 The present invention relates to high strength steel strip or sheets suitable for applications in automobiles. In particular, the invention relates to cold rolled steel strip or sheets which have been produced by a process comprising intercritical annealing followed quenching and partitioning.

BACKGROUND ART

- 10 For a great variety of applications increased strength levels are a pre-requisite for light-weight constructions in the automotive industry, since car body mass reduction results in reduced fuel consumption.

Automotive body parts are often stamped out of sheet steels, forming complex structural members of
15 thin sheet. However, such parts cannot be produced from conventional high strength steels, because of a too low formability for complex structural parts. For this reason, multiphase Transformation Induced Plasticity aided steels (TRIP steels) have gained considerable interest in the last years, in particular for application in auto body structural parts.

- 20 TRIP steels possess a multi-phase microstructure, which includes a meta-stable retained austenite phase, which is capable of producing the TRIP effect. When the steel is deformed, the austenite transforms into martensite, which results in remarkable work hardening. This hardening effect acts to resist necking in the material and postpones failure in sheet forming operations. The microstructure of a TRIP steel can greatly alter its mechanical properties.

25

- Quenching & Partitioning (Q&P) is an annealing cycle which consists of a quenching and a partitioning step. In the quenching step, fully austenitized or intercritically annealed steels are quenched to a temperature between the martensite start temperature M_s and the martensite finish temperature M_F to reach a partial martensitic transformation. The quenched steels are then held at a
30 temperature either at or above the initial quenching temperature. Austenite that prevails after quenching is stabilized through carbon partitioning from martensite into the austenite during the partitioning.

- Liquid Metal Embrittlement(LME) is a phenomenon where certain metals like Al and steels undergo
35 brittle failure when stressed in contact with liquid metals like Zn, Sn, Pb, etc. One of the challenges in the welding industry is cracking due to LME observed on spot welds of Zn-coated High Strength Steel. Liquid zinc penetration results in a drastic reduction in the strength and ductility of the steel.

LME can occur when there is a contact between the solid material and the embrittling liquid metal.

Under certain conditions, the contact between the alloy and the liquid metal may result in a rapid penetration of the liquid phase along grain boundaries. In the absence of external stress, the

- 5 phenomenon is known as grain boundary penetration, and the associated thermodynamic driving force is the reduction of interfacial energy. Grain boundary penetration is observed if the condition $\gamma_{GB} \geq 2\gamma_{SL}$ is satisfied, where γ_{GB} is the grain boundary energy and γ_{SL} is the solid-liquid interface energy. In fact, higher γ_{GB} results in an increased driving force for the penetration.

- 10 High strength Si grades have a strong propensity to LME. An index that has been used in the industry gives that the relation $C + Si/4 \leq 0.4$ should be satisfied to ensure low propensity to LME (C and Si in weight %).

- EP 3 394 298 B1 discloses a process for the production of a high-strength steel sheet with intercritical single annealing and Q&P. The steel comprises 0.15 – 0.23 C, 2 – 2.8 Mn, 1.0 – 2.1 Si, 0.02 – 1.0 Al, 1.7 – 2.1 Si + Al, 0 – 0.035 Nb, 0 – 0.3 Mo, 0 – 0.4 Cr, balance Fe and impurities. B and Ti are not intentionally added, and B is therefore less than 0.0010 while Ti is limited to 0.05. The patent proposes two relations to reduce LME sensitivity: (1) $C + Si/10 \leq 0.3\%$ and (2) $Al \geq 6 \cdot (C + Mn/10) - 2.5\%$.

20

- EP 3 656 880 B1 discloses a process for the production of a high-strength steel sheet with intercritical single annealing and Q&P. The steel comprises 0.15 – 0.23 C, 1.4 – 2.6 Mn, 0.6 – 1.5 Si, 0.02 – 1.0 Al, 1.0 – 2.0 Si + Al, 0 – 0.035 Nb, 0 – 0.3 Mo, 0 – 0.3 Cr, balance Fe and impurities. B and Ti are not intentionally added, and B is therefore less than 0.0010 while Ti is limited to 0.05. The patent proposes two relations to reduce LME sensitivity: (1) $C + Si/10 \leq 0.3\%$ and (2) $Al \geq 6 \cdot (C + Mn/10) - 2.5\%$.

25

- EP 2 604 715 B1 discloses a process for the production of high-strength cold-rolled steel sheet. The steel sheet including 0.05 – 0.3 C, 0.3 – 2.5 Si, 0.5 – 3.5 Mn, 0.003 – 0.100 P, ≤ 0.02 S, 0.010 – 0.5 Al, optionally at least one element selected from Cr: 0.005 to 2.00, Mo: 0.005 to 2.00, V: 0.005 to 2.00, Ni: 0.005 to 2.00, and Cu: 0.005 to 2.00, optionally one or both of Ti: 0.01 to 0.20 and Nb: 0.01 to 0.20, optionally B: 0.0002 to 0.005, optionally one or both of Ca: 0.001 to 0.005 and REM: 0.001 to 0.005, and balance being iron and unavoidable impurities. The process comprises intercritical single annealing with Quenching & Partitioning, in which the average heating rate from 500°C to A_{e1} transformation point should be 10°C/s or more to suppress recrystallization during heating. This is to achieve a fine grain structure, which improves the crashworthiness. Not all facilities are capable of such high heating rates to the annealing and the high heating rates may also add extra costs.

30

35

EP 3 859 041 A1 discloses a High-strength cold-rolled steel sheet with Q&P cycle, full austenitic annealing followed by quenching and tempering. It suggests that if silicon exceeds 0.8 %, deterioration of physical properties of a weld portion due to formation of LME cracks cannot be prevented and surface characteristics and plating properties of the steel deteriorate. The document proposes an equation which should be fulfilled to avoid that LME resistance is deteriorated during spot welding: $C + (Si + Al)/5 \leq 0.35\%$.

It would be advantageous to improve LME resistance without restrictions on C, Si, and Al. Furthermore, it would be advantageous if production costs can be kept low, and that it is possible to produce the steel sheets in a wide variety of continuous annealing lines.

DISCLOSURE OF THE INVENTION

The present invention is directed to steel strip or sheets having a tensile strength of 980 – 1300 MPa. The steel strip or sheets are produced in a single annealing process of which the annealing cycle includes intercritical annealing, quenching to a temperature between $M_S - 20\text{ }^{\circ}\text{C}$ and M_F and partitioning at a temperature above the quenching temperature. By adding Ti+B to the composition, it is possible to be free of cracks longer than 300 μm in the heat affected zone of spot weld joints. The addition of B is believed to reduce the austenite/austenite interface energy such that $\gamma_{GB} < 2\gamma_{SL}$. Ti binds N so that B remains free to protect the austenitic grain boundaries. Ti and B are increased by a factor of 10 compared to normal impurity levels.

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 shows schematically the annealing cycle of the invention.

DETAILED DESCRIPTION

In a preferred embodiment the strip or sheet has a composition consisting of the following alloying elements (in wt. %):

C	0.10 – 0.30
Mn	1.5 – 3.0
Si	0.5 – 2.0
Al	0.03 – 0.50
Ti	0.01 – 0.10
B	0.002 – 0.008
Optionally	
Nb	≤ 0.1

V	≤ 0.1
Cr	≤ 0.8
Mo	≤ 0.2

balance Fe apart from impurities.

5

The composition is excluding any coatings applied to the strip or sheet.

The importance of the separate elements and their interaction with each other as well as the limitations of the chemical ingredients of the claimed alloy are briefly explained in the following. All percentages for the chemical composition of the steel are given in weight % (wt. %) throughout the description.

10

Upper and lower limits of the individual elements can be freely combined within the limits set out in the claims. The arithmetic precision of the numerical values can be increased by one or two digits for all values given in the present application. Hence, a value of given as e.g. 0.1 % can also be expressed as 0.10 or 0.100 %. The amounts of the microstructural constituents are given in volume % (vol. %).

15

C: 0.10 – 0.30 %

C stabilizes the austenite and is important for obtaining sufficient carbon within the retained austenite phase. C is also important for obtaining the desired strength level. Generally, an increase of the tensile strength in the order of 100 MPa per 0.1 % C can be expected. When C is too low it is difficult to attain a sufficient tensile strength. If C is too large the weldability is impaired. The upper limit is therefore 0.30 % and may be restricted to 0.29, 0.28, 0.27, 0.26, 0.25, 0.24, 0.23 or 0.22 %. The lower limit may be 0.10, 0.12, 0.14, or 0.16 %.

20

A preferred range is 0.16 – 0.22 %.

25

Si: 0.5 – 2.0 %

Si acts as a solid solution strengthening element and is important for securing the strength of the thin steel strip. Si suppresses the cementite precipitation and is essential for austenite stabilization.

However, if the content is too high, then too much silicon oxides will form on the strip surface, which may lead to cladding on the rolls in the CAL and, as a result thereof, to surface defects on

30

subsequently produced steel sheets. The upper limit is therefore 2.0 % and may be restricted to 1.9, 1.8, 1.7 or 1.6 %. The lower limit may be 0.5, 0.6, 0.7, or 0.8 %.

A preferred range is 0.8 – 1.6 %.

Mn: 1.5 – 3.0 %

35

Manganese is a solid solution strengthening element, which stabilises the austenite by lowering the M_s temperature and prevents ferrite and pearlite to be formed during cooling. In addition, Mn lowers the

Ae3 temperature and is important for the austenite stability. At too low contents it might be difficult to obtain the desired amount of retained austenite, a sufficient tensile strength, and the austenitizing temperature might be too high for conventional industrial annealing lines. In addition, at lower contents it may be difficult to avoid the formation of polygonal ferrite. However, if the amount of Mn is too high problems with segregation may occur because Mn accumulates in the liquid phase and causes banding, resulting in a potentially deteriorated workability. The upper limit may therefore be 3.0, 2.9, 2.8, 2.7 or 2.6 %. The lower limit may be 1.5, 1.6, 1.7, 1.8, 1.9, 2.0 or 2.1%. A preferred range is 2.1 – 2.6 %.

10 Al: 0.03 – 0.50 %

Additions of Al can increase the carbon content in the retained austenite. Al can also be used as a deoxidizer. Al, like Si, is not soluble in the cementite can therefore delay cementite formation during bainite formation and martensite tempering. An addition of Al can further improve galvanization and reduce the susceptibility to LME. The M_s temperature is also increased with increasing Al content. A drawback of Al is that it results in an increase of the Ae3 temperature. The upper limit may be 0.5, 0.4, 0.3, 0.2, 0.1%. The lower limit may be set to 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09, or 0.1 %. If Al is used for deoxidation only, the upper limit may be 0.10, 0.09, 0.08, 0.07 or 0.06 %. For securing a certain effect the lower level may set to 0.03 or 0.04 %. A preferred range is 0.03 – 0.1 %.

20

B: 0.002 – 0.008 %

The steel is alloyed with B to reduce the austenite/austenite interface energy (γ_{GB}) to prevent grain boundary penetration, i.e. $\gamma_{GB} < 2 \gamma_{SL}$. B suppresses the formation of ferrite and improves the weldability of the steel sheet. However, excessive amounts of B deteriorate the workability. The upper limit may be set to 0.08, 0.07, 0.06, 0.05, or 0.004 %. The lower limit may be set to 0.002 or 0.0025 %. A preferred range is 0.0025 – 0.004 %.

25

Ti: 0.01 – 0.10 %

Ti improves strength and toughness, because of its influence on the grain size by forming carbides, nitrides or carbonitrides. In this steel, Ti is primarily added to bind the nitrogen in the steel so that B remains free to protect the austenitic grain boundaries. The effect of Ti is saturated above 0.1 %. The upper limit may be set to 0.10, 0.09, 0.08, 0.07, 0.06, or 0.05 %. The lower limit may be set to 0.01, 0.015, 0.02, 0.03, 0.04, or 0.05 %. A preferred range is 0.015-0.050 %.

30

35 Optional limitations

The microalloying with Ti and B improves the weldability by reducing the LME sensitivity. This

makes it possible to avoid LME cracks even when one or more of the following conditions are not met:

(1) $C + Si/10 \leq 0.3\%$

(2) $Al \geq 6 \cdot (C + Mn/10) - 2.5\%$

5 (3) $C + (Si + Al)/5 \leq 0.35\%$.

Therefore a LME resistant steel can be produced where $C + Si/10 > 0.3\%$ and/or $Al < 6 \cdot (C + Mn/10) - 2.5\%$ and/or $C + (Si + Al)/5 > 0.35\%$. The content in weight % of each element.

10 Optional elements

Nb: $\leq 0.1\%$

Nb is commonly used in low alloyed steels for improving strength and toughness, because of its influence on the grain size. Nb increases the strength elongation balance by refining the matrix microstructure and the retained austenite phase due to precipitation of NbC. The steel may contain Nb
15 in an amount of $\leq 0.1\%$. The upper limit may be restricted to 0.09, 0.07, 0.05, 0.03, 0.01, or 0.005 %. A lower limit may be 0.001, 0.01, or 0.05 %. A deliberate addition of Nb is not necessary according to the present invention.

V: $\leq 0.1\%$

20 The function of V is similar to that of Nb in that it contributes to precipitation hardening and grain refinement. The steel may contain V in an amount of $\leq 0.1\%$. The upper limit may be restricted to 0.09, 0.07, 0.05, 0.03, or 0.01 %. A lower limit may be 0.001, 0.01, or 0.05 %. A deliberate addition of V is not necessary according to the present invention.

25 Cr: $\leq 0.8\%$

Cr is effective in increasing the strength of the steel sheet. Cr is an element that forms ferrite and retards the formation of pearlite and bainite. The A_{e3} temperature and the M_s temperature are only slightly lowered with increasing Cr content. Cr results in an increased amount of stabilized retained austenite. Too much Cr may impair the surface finish of the steel. The amount of Cr is limited to
30 0.8 %. The upper limit may be 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, 0.1 or 0.05 %. The lower limit may be 0.01, 0.03, 0.05, 0.07, 0.10, 0.15, 0.20 or 0.25 %. Preferably, a deliberate addition of Cr is not conducted according to the present invention.

Mo $\leq 0.2\%$

35 Molybdenum is a powerful hardenability agent. It may further enhance the benefits of NbC precipitates by reducing the carbide coarsening kinetics. The steel may therefore contain Mo in an amount up to 0.2 %. Mo delays the decomposition of austenite and stabilizes the retained austenite.

Amounts of more than 0.2 % result in high costs. The upper limit may be restricted to 0.2, 0.1, 0.05, 0.01 %. The lowest amount may be set to 0.001, 0.005, 0.01, 0.02, 0.03, 0.04 or 0.05 %. A deliberate addition of Mo is not necessary according to the present invention.

5 Impurities

The following impurities may optionally be limited as disclosed below.

Ca: ≤ 0.05 %

Ca could be used for the modification of the non-metallic inclusions. The upper limit is 0.05% and may be set to 0.04, 0.03, 0.01, or 0.005 %. A deliberate addition of Ca is not necessary according to the present invention.

Cu: ≤ 0.1 %

Cu is an undesired impurity element that is restricted to ≤ 0.1 % by careful selection of the scrap used. The upper limit is 0.1% and may be further restricted to 0.05 %.

Ni: ≤ 0.2 %

Ni is also an undesired impurity element that is restricted to ≤ 0.2 % by careful selection of the scrap used. The upper limit is 0.2% and may be further restricted to 0.1 or 0.05 %.

Other impurity elements may be comprised in the steel in normal occurring amounts. However, it is preferred to limit the amounts of P, S, As, Zr, Sn to the following optional maximum contents:

P: ≤ 0.05 , ≤ 0.04 , ≤ 0.03 or ≤ 0.02 %

S: ≤ 0.05 , ≤ 0.03 , ≤ 0.01 , ≤ 0.005 or ≤ 0.001 %

As: ≤ 0.020 , or ≤ 0.010 %

Zr: ≤ 0.010 , or ≤ 0.006 %

Sn: ≤ 0.030 , or ≤ 0.015 %

Oxygen and hydrogen can further be limited to

O: ≤ 0.001 , or ≤ 0.0003 %

H: ≤ 0.0050 , or ≤ 0.0020 %

It is also preferred to control the nitrogen content to the range:

N: ≤ 0.015 %, preferably 0.001 - 0.008 %

35 Mechanical properties

The steel should fulfil the following condition on the tensile strength:

TS, Tensile Strength (R_m) 980 – 1300 MPa

And optionally one or more of the following mechanical properties:

YS, Yield Strength ($R_{p0.2}$) 600 – 1100 MPa

HER, Hole Expansion

Ratio (λ) ≥ 20 %

5 TE, Total

Elongation (A_{80}) ≥ 13 %

Preferably, all these requirements are fulfilled at the same time.

Different strength grades may be produced having the following mechanical properties:

10

Steel grades	980	1180
TS, Tensile Strength (R_m)	980 – 1100 MPa	1180 – 1300 MPa
YS, Yield Strength ($R_{p0.2}$)	600 – 850 MPa	850 – 1100 MPa
HER, Hole Expansion Ratio (λ)	> 20 %	> 30 %
TE, Total Elongation (A_{80})	> 18 %	> 13 %

The strip or sheet thickness of the final product may be 0.1 – 4 mm, preferably 0.5 – 3 mm. The strip or sheet width may be 500 – 2000 mm, preferably 700 – 1750 mm in non-slit condition.

15

Preferably, the sheet or strip is provided with at least one spot welded joint, each having a heat affected zone around it, wherein the heat affected zone/s are free of cracks longer than 300 μm .

Microstructure

20 The microstructural constituents are in the following expressed in volume % (vol. %).

Ferrite	5 – 50
tempered martensite	20 – 85
bainite	0 – 15
fresh martensite	0 – 10
25 retained austenite (RA)	5 – 20

Each of the phases in the list above may balance the microstructure.

Preferably, the average grain diameter is in the range of 3 – 30 μm , more preferably 5 – 25 μm , most preferably 5 – 25 μm . The average grain size can be determined using the intercept procedure

30 described in ASTM E112-13(2021) “Standard Test Methods for Determining Average Grain Size”.

Ferrite is the sum of intercritical and proeutectoid ferrite and should be between 5 – 50 vol. %. The lower limit may be 5, 10, 15, or 20 vol. %. The upper limit may be 50, 40 or 30 vol %. A preferred range for grade 980 is 20-40 vol. % and for grade 1180 a preferred range is 10 – 30 vol. %.

- 5 Tempered martensite is martensite from the quenching step that is tempered in the partitioning step. The lower limit of tempered martensite may be 20, 25, 30, 35, or 40 vol. %. The upper limit may be 85, 70, 60, or 50 vol %. A preferred range is 30 – 70 vol. %. A more preferred range for grade 980 is 30-60 vol. %, and for grade 1180 a more preferred range is 40 – 70 vol. %.

10

The steel may contain bainite. The upper limit of bainite may be 15, 10, 5, or 0 vol %. The lower limit may be 0, 5, or 10 vol %. A preferred range for grade 980 is 5 – 10 vol. % and for grade 1180 a preferred range is 0 – 10 vol. %.

- 15 Fresh martensite can be formed upon final cooling after quenching and partitioning. The upper limit of fresh martensite may be 10 or 5 vol.%. A preferred range is 0 – 5 vol. %.

Retained austenite is a prerequisite for obtaining the desired TRIP effect. The amount of retained austenite should be in the range of 5 – 20 vol %, preferably 10 – 20 vol %.

20

The steel grades 980 and 1180 may be limited to the following microstructures which includes rpefred ranges for each phase.

Steel grades	980	1180
Ferrite (vol. %)	20 – 40	10 – 30
Tempered Martensite (vol. %)	30 – 60	40 – 70
Bainite (vol. %)	5 – 10	0 – 10
RA (vol. %)	10 – 20	10 – 20
Fresh Martensite (vol. %)	0 – 5	0 – 5

- 25 Definitions

Temperatures are given in degrees Celsius throughout the description.

Ae1 refers to the temperature at which austenite begins to form in a steel and Ae3 temperature is the temperature at which the steel becomes fully austenitic. Ae1 and Ae3 are calculated by means of

- 30 ThermoCalc 2022 TCFE 12.

M_s temperature is calculated using the M_s formula found in S. Kaar, K. Steineder, R. Schneider, D. Krizan and C. Sommitsch: „New M_s -formula for exact microstructural prediction of modern 3rd generation AHSS chemistries”, Scr. Mater., Vol. 200, 2021, 113923.

5
$$M_s = 692 - 502 * (C + 0.86 * N)^{0.5} - 37 * Mn - 14 * Si + 20 * Al - 11 * Cr$$

The M_s formula uses the content in weight % of each element.

M_F formula is derived from Koistinen-Marburger equation found in (Koistinen, D. and Marburger, R: “A general equation prescribing the extent of the austenite-martensite transformation in pure iron-carbon alloys and plain carbon steels”, Acta Metall, 7, 1959, pp. 59 – 60):

10
$$M_F = M_s + [\ln(1 - f_M)]/0.011,$$

where the fraction of martensite f_M is 0.95.

The microstructure, including the amount of each phase, can be identified in scanning electron microscope (SEM) using 2000 times magnification. Preferably by cutting out a sample from a steel plate and polishing a cross section of a plate parallel to the rolling direction. The microstructure should be taken from ¼ of the thickness. The surface can be etched to make the phases easier to identify.

However, the amount of retained austenite is preferably determined by means of the saturation magnetization method described in detail in Proc. Int. Conf. on TRIP-aided high strength ferrous alloys (2002), Ghent, Belgium, p. 61 – 64.

The R_m , $R_{p0.2}$ values as well as the total and/or uniform elongation are derived in accordance with the Industrial Standard DIN EN ISO 6892-1, wherein the samples with a gauge length of 80 mm are taken in the longitudinal direction of the strip.

The hole expansion ratio (λ) is determined by the hole expansion test according to ISO/WD 16630:2009 (E). In this test a conical punch having an apex of 60° is forced into a 10 mm diameter punched hole made in a steel sheet having the size of 100 x 100 mm². The test is stopped as soon as the first crack is determined, and the hole diameter is measured in two directions orthogonal to each other. The arithmetic mean value is used for the calculation.

The hole expanding ratio (λ) in % is calculated as follows:

35
$$\lambda = (D_h - D_o)/D_o \times 100$$

wherein D_0 is the diameter of the hole at the beginning (10 mm) and D_h is the diameter of the hole after the test.

LME Crack length can be determined by the following method. First a maximum current $I_{\max}$ is determined in accordance with the standardized test described in SEP1220-2 (Stahl Eisen Prüfblätter) – for the standard two sheet combination. In a second step a three-sheet combination subjected to RSW (resistant spot welded joint) at the same current ($I_{\max}$) but at a welding time five times longer in order to increase the heat input. For each combination 8 spots are welded and the occurrence of the cracks in the Heat Affected Zone (HAZ) are manually examined in a light optical microscope on metallographically prepared samples.

The formula $\gamma_{GB} \geq 2\gamma_{SL}$ is described in the publications Journal of Materials Science 14 (1979) 1-18; “Review Liquid metal embrittlement”, and Progress in Materials Science 121 (2021) 100798; “Pathway to understand liquid metal embrittlement (LME) in Fe-Zn couple: From fundamentals toward application”. These are incorporated by reference.

Unless otherwise specified, parameter values throughout the description including the Examples are determined by the methods given in this section.

Production of a cold rolled strip.

A cold rolled steel strip may be produced by the following steps:

- a) Making steel slabs with the composition defined above. The steel slabs may e.g. be produced by converter melting or in an electric steel plant and secondary metallurgy to finalise the composition
- b) The slabs are hot rolled in austenitic range to a hot rolled strip. Preferably by reheating the slab to a temperature between 1000 °C and 1280 °C. Preferably rolling the slab completely in the austenitic range wherein the hot rolling finishing temperature is greater than or equal to 850 °C to obtain the hot rolled steel strip.
- c) Thereafter, the hot rolled strip may be coiled at a coiling temperature in the range of 400 – 700 °C.
- d) Optionally subjecting the coiled strip to a scale removal process, such as pickling.
- e) Optionally annealing at a temperature in the range of 450 – 950 °C. Preferably batch annealing at 450 – 650 °C, for a duration of 2 – 30 h, more preferably 5 – 20 h. The strip may alternatively be continuously annealed at temperature in the range of 650 – 950 °C for 10 – 200 s.
- f) Optionally subjecting the annealed strip to a scale removal process, such as pickling.
- g) Thereafter cold rolling the annealed steel strip at a reduction rate between 20 – 90 %, preferably around 50 – 70 % reduction.

The steps a) – g) of producing the cold rolled strip described above are examples on how the cold rolled strip can be produced. The invention may also be applied to cold rolled strips that are produced under similar but different processing conditions as known in the art.

5

Intercritical annealing with Quenching and Partitioning

- h) Providing a cold rolled steel strip to a continuous annealing line, the steel strip having a composition as suggested above.
- i) heating the strip to an annealing temperature (T_{an}) between $Ae1$ and $Ae3$, preferably between $Ae1 + 20\text{ }^{\circ}\text{C}$ and $Ae3 - 20\text{ }^{\circ}\text{C}$. In the range of $500\text{ }^{\circ}\text{C}$ to the annealing temperature (T_{an}), the heating rate ($HR1$) is $< 10\text{ }^{\circ}\text{C/s}$, preferably $< 5\text{ }^{\circ}\text{C/s}$.
- j) soaking for $10 - 300\text{ s}$ (t_{an}) at the annealing temperature (T_{an}). The annealing temperature (T_{an}) and soaking time are controlled to reach a desired amount of intercritical ferrite and austenite.
- k) cooling the strip at a rate ($CR1$) of $5 - 100\text{ }^{\circ}\text{C/s}$, preferably $10 - 50\text{ }^{\circ}\text{C/s}$, to a first quenching temperature (T_q) between M_F and $(M_S - 20)\text{ }^{\circ}\text{C}$. The lower limit may further be restricted to the highest of M_F and value chosen from $150, 160, 170$, and $180\text{ }^{\circ}\text{C}$. The upper limit may further be restricted to $M_S - 30, M_S - 40, M_S - 50, M_S - 60, M_S - 70, M_S - 80, M_S - 90$, or $M_S - 100\text{ }^{\circ}\text{C}$. The cooling rate ($CR1$) may further be restricted to $< 20\text{ }^{\circ}\text{C/s}$.
- l) heating the cooled strip at a rate ($HR2$) of $10 - 100\text{ }^{\circ}\text{C/s}$, preferably $20 - 50\text{ }^{\circ}\text{C/s}$, to a first partitioning temperature (T_p) in the range of the first quenching temperature (T_q) $+ 10\text{ }^{\circ}\text{C}$ to $500\text{ }^{\circ}\text{C}$ and partitioning the strip for $20 - 1000\text{ s}$ (t_p). Preferably the first partitioning temperature (T_q) is above M_S . The upper limit may be restricted to $500, 480, 450, 430$, or $410\text{ }^{\circ}\text{C}$. The lower limit may be restricted to $260, 280, 300, 320, 340, 360$, or $380\text{ }^{\circ}\text{C}$.
- m) cooling the strip to a temperature below $50\text{ }^{\circ}\text{C}$, preferably to room temperature, at a rate ($CR2$) of $1 - 50\text{ }^{\circ}\text{C/s}$.
- n) optionally applying a coating though galvanising, galvannealing, electro galvanising, or physical vapor deposition.
- o) resistance spot welding of sheets from the strip.

Optional coating

The steel sheet or strip may optionally be coated and comprise a zinc or a zinc-alloy coating. The coating can e.g. be applied by:

- Electrogalvanizing (EG) including electroplating.
- Physical Vapor Deposition (PVD).
- Hot Dip Galvanizing (HDG) in a Hot Dip Galvanizing Line, in which the strip is immersed in a molten zinc bath at the end of the final partitioning (step n). A Hot Dip Galvanizing Line can be the same line as a Continuous Annealing Line with added hot dip coating.

- 5 - Galvannealing (GA) in a Galvannealing line, which is the similar as the Hot Dip Galvanizing Line with the addition of an annealing step following the hot dip coating. I.e. processed the same way as the Continuous Annealing Line, but including galvannealing at the end of the final partitioning (step n). Galvannealing is a combination of galvanizing and annealing around 480 – 560°C in order to facilitate a higher degree of Fe in the ZnFe coating.

A zinc alloy coating may comprise in weight %:

Mg 0.1 – 10

Al 0.1 – 10

10 Optionally one or more of:

Bi, Pb, Sn, Sb, Si, Ti, Ca, Mn, La, Ce, Cr, Ni and Zr in a total amount of 0.01 – 1.0

Balance Zn and impurities.

A galvannealed coating may contain 5 – 20 wt.% of diffused Fe.

15

Other coating composition known in the art can be applied.

EXAMPLES

Ten alloys L1 – L10 were produced by conventional metallurgy by converter melting and secondary metallurgy. The compositions of the alloys (elements are in [wt%]) are shown in table 1, further elements were present only as impurities, and below the lowest levels specified in the present

- 5 description. L1 – L3, and L8 are reference grades with low Ti and B. The inventive samples L4 – L7 and L9 – L10 all had a substantial addition of Ti and B.

Table 1

Alloy	C	Si	Mn	Mo	Nb	Al	Ti	B	N	Invention Y/N
<i>L1</i>	0.202	1.45	2.53	0.08	0.002	0.06	0.003	0.0003	0.005	N
<i>L2</i>	0.203	1.51	2.51	0.08	0.002	0.05	0.004	0.0003	0.004	N
<i>L3</i>	0.213	1.46	2.53	0.08	0.002	0.06	0.003	0.0003	0.006	N
<i>L4</i>	0.195	1.47	2.47	0.01	0.002	0.05	0.028	0.0032	0.005	Y
<i>L5</i>	0.200	1.45	2.46	0.01	0.003	0.05	0.029	0.0050	0.004	Y
<i>L6</i>	0.200	1.48	2.49	0.01	0.003	0.06	0.028	0.0023	0.003	Y
<i>L7</i>	0.173	1.44	2.62	0.01	0.003	0.06	0.028	0.0032	0.004	Y
<i>L8</i>	0.172	1.48	2.37	0.01	0.022	0.05	0.003	0.0003	0.005	N
<i>L9</i>	0.174	1.51	2.36	0.01	0.020	0.05	0.028	0.0033	0.003	Y
<i>L10</i>	0.172	1.49	2.37	0.01	0.021	0.05	0.029	0.0065	0.004	Y
Alloy	Ae1	Ae3	M _F	M _S						
<i>L1</i>	662	818	78	351						
<i>L2</i>	664	819	78	350						
<i>L3</i>	656	815	72	344						
<i>L4</i>	670	821	84	357						
<i>L5</i>	670	820	83	355						
<i>L6</i>	670	821	82	354						
<i>L7</i>	660	823	93	365						
<i>L8</i>	665	831	101	373						
<i>L9</i>	672	834	101	373						
<i>L10</i>	671	833	101	374						

- The alloys L1 – L10 were continuously cast and cut into slabs. The slabs were reheated and hot rolled
- 10 in austenitic range to a thickness of about 2.8 mm. The hot rolling finishing temperature was about 900 °C. The hot rolled steel strips were thereafter coiled at a coiling temperature of 550 °C. The coiled hot rolled strips were pickled and batch annealed at about 560 °C for 10 hours in order to reduce the tensile strength of the hot rolled strip and thereby reducing the cold rolling forces. The strips were thereafter cold rolled in a five-stand cold rolling mill to a final thickness of about 1.4 mm.
- 15 The steels were subjected to Intercritical annealing with Quenching and Partitioning in a continuous annealing line. The process values are shown in Table 2 and the annealing cycle is schematically shown in Fig. 1.

Table 2

Alloy	HR1	Tan °C	tan s	CR1 °C/s	Tq °C	HR2 °C/s	Tp °C	tp s	Invention Y/N
<i>L1</i>	2.7	810	130	14	200	30	450	450	N
<i>L2</i>	2.9	830	120	14	240	30	450	420	N
<i>L3</i>	2.0	820	175	11	200	25	450	600	N
<i>L4</i>	3.5	820	100	18	210	35	420	340	Y
<i>L4</i>	2.1	820	170	10	220	20	420	300	Y
<i>L5</i>	2.9	820	120	15	210	30	420	420	Y
<i>L6</i>	2.8	810	130	14	210	29	420	440	Y
<i>L7</i>	2.9	820	120	15	210	30	420	420	Y
<i>L8</i>	2.3	780	175	10	210	22	400	600	N
<i>L9</i>	2.3	780	175	10	210	22	400	600	Y
<i>L10</i>	2.3	780	175	10	210	22	400	600	Y

Different properties were determined, and the results are shown in Table 3. The mechanical properties - Yield strength, Tensile strength, Uniform Elongation, Total Elongation, Hole Expansion Ratio are similar for the reference grades L1 – L3; L8 compared to the inventive grades L4 – L7; L9 – L10.

5

Also, the amounts of each phase of the microstructures were similar. The retained austenite is shown in the table 3. The other microstructural phases were checked that they were within the defined boundaries of respective steel grade 980, 1180. The average grain diameter of the microstructure was around 15 μm for each steel grade 980, 1180.

10

Table 3

Strength level	Alloy	YS MPa	TS MPa	UE %	TE %	RA %	HER %	mean crack length μm	Invention Y/N
1180	<i>L1</i>	896	1245	11.1	14.9	13	38	1391	N
	<i>L2</i>	932	1265	10.0	13.8	12	50	1518	N
	<i>L3</i>	947	1229	10.8	15.0	12	43	1173	N
	<i>L4</i>	894	1193	12.4	15.9	14	45	220	Y
	<i>L4</i>	989	1190	11.4	15.6	12	49	197	Y
	<i>L5</i>	981	1223	11.7	15.7	13	46	186	Y
	<i>L6</i>	971	1220	12.3	16.1	13	54	203	Y
	<i>L7</i>	991	1187	10.9	14.7	12	57	211	Y
980	<i>L8</i>	618	1044	16.6	20.7	17	31	914	N
	<i>L9</i>	652	1025	16.7	20.9	17	30	185	Y
	<i>L10</i>	658	1032	16.5	20.5	16	32	180	Y

The LME Crack length was determined in a two step test. First, the maximum current I_{max} was determined in accordance with the standardized test described in SEP1220-2 (Stahl Eisen Prüfblätter) for the standard two sheet combination. In the second step a three-sheet combination was subjected to RSW (resistant spot welded joint) at the same current (I_{max}) but the welding time was five times in

15

order to increase the heat input. For each combination 8 spots were welded and the occurrence of cracks in the Heat Affected Zone (HAZ) was manually examined in a light optical microscope on metallographically prepared samples.

- 5 Remarkable differences in the LME Crack length were observed. It was found that there was not any HAZ cracks longer than 300 μm in any of the samples L4 – L7 and L9 – L10 (in the inventive samples) The 1180 grades had a reduction from 1360.7 μm ($\pm 174.5\mu\text{m}$) of the reference alloys L1 – L3 to 201.5 μm ($\pm 14.2\mu\text{m}$) of the inventive alloys L4 – L7. The 980 grades had a reduction from 914 μm of the reference alloy L8 to 182.5 μm ($\pm 2.5\mu\text{m}$) of the inventive alloys L9 – L10.

10

Hence, by adding Ti+B to the alloy and subjecting it to an intercritical annealing cycle with Q&P process, it is possible to be free of cracks longer than 300 μm in the heat affected zone of spot weld joints.

CLAIMS

1. A high strength steel strip or sheet having:

5 i) a composition consisting of the following elements in wt. %:

C	0.10 – 0.30
Mn	1.5 – 3.0
Si	0.5 – 2.0
Al	0.03 – 0.50
10 Ti	0.01 – 0.10
B	0.002 – 0.008
Optionally	
Nb	≤ 0.1
V	≤ 0.1
15 Cr	≤ 0.8
Mo	≤ 0.2

balance Fe apart from impurities;

20 ii) TS, Tensile Strength (R_m) 980 – 1300 MPa

and optionally at least one of:

YS, Yield Strength ($R_{p0.2}$) 600 – 1100 MPa

HER, Hole Expansion

Ratio (λ) ≥ 20 %

TE, Total Elongation (A_{80}) ≥ 13 %

25 wherein the R_m , $R_{p0.2}$ values as well as the total elongation are derived in accordance with the Industrial Standard DIN EN ISO 6892-1 including samples with a gauge length of 80 mm are taken in the longitudinal direction of the strip, and the hole expansion ratio (λ) is determined by the hole expansion test according to ISO/WD 16630:2009 (E).

30 iii) microstructure fulfilling the following requirements in vol. %:

Ferrite	5 – 50
tempered martensite	20 – 85
bainite	0 – 15
fresh martensite	0 – 10
35 retained austenite	5 – 20

2. The steel strip or sheet according to claim 1, comprising at least one spot welded joint, each having a heat affected zone around it, wherein the heat affected zone/s are free of cracks longer than 300 μm .

3. The steel strip or sheet according to claim 1 or 2, wherein the microstructure fulfils at least one of the following requirements in vol. %, preferably all the requirements:

Ferrite	20 – 40
tempered martensite	30 – 60
bainite	5 – 10
fresh martensite	0 – 5
retained austenite	10 – 20

4. The steel strip or sheet according to claim 3, wherein one or more of the following mechanical properties are fulfilled:

TS, Tensile Strength (R_m)	980 – 1100 MPa
YS, Yield Strength ($R_{p0.2}$)	600 – 850 MPa
HER, Hole Expansion	
Ratio (λ)	$\geq 20 \%$
TE, Total Elongation (A_{80})	$\geq 18 \%$

5. The steel strip or sheet according to claim 1 or 2, wherein the microstructure fulfils at least one of the following requirements in vol. %, preferably all the requirements:

Ferrite	10 – 30
tempered martensite	40 – 70
bainite	0 – 10
fresh martensite	0 – 5
retained austenite	10 – 20

6. The steel strip or sheet according to claim 5, wherein one or more of the following mechanical properties are fulfilled:

TS, Tensile Strength (R_m)	1180 – 1300 MPa
YS, Yield Strength ($R_{p0.2}$)	850 – 1100 MPa
HER, Hole Expansion	
Ratio (λ)	$\geq 30 \%$
TE, Total Elongation (A_{80})	$\geq 13 \%$

7. The high strength steel strip or sheet according to any one of the preceding claims having a composition consisting of the following alloying elements (in wt. %):

5	C	0.16 – 0.22
	Si	0.8 – 1.6
	Mn	2.1 – 2.6
	Al	0.03 – 0.1
	Ti	0.015 – 0.050
10	B	0.0025 – 0.004
	Optionally	
	Nb	≤ 0.1
	V	≤ 0.1
	Cr	≤ 0.8
15	Mo	≤ 0.2
	balance Fe apart from impurities.	

8. The high strength steel strip or sheet according to any one of the preceding claims comprising a zinc alloy coating.

20

9. The high strength steel strip or sheet according to claim 8 wherein the zinc alloy coating comprises in weight %:

Mg	0.1 – 10
Al	0.1 – 10

- 25 Optionally one or more of: Bi, Pb, Sn, Sb, Si, Ti, Ca, Mn, La, Ce, Cr, Ni and Zr in a total amount of 0.01 – 1.0
Balance Zn and impurities.

10. A method for producing a high strength steel strip or sheet according to any one of claims 1 – 9. comprising:

30

- h) providing a cold rolled steel strip having a composition as defined in any one of claims 1-9,
- i) heating the strip to an annealing temperature (T_{an}) between Ae_1 and Ae_3 , wherein in the range of 500 °C to the annealing temperature (T_{an}), the heating rate (HR1) is < 10 °C/s.
- j) soaking for 10 – 300 s (t_{an}) at the annealing temperature (T_{an}),

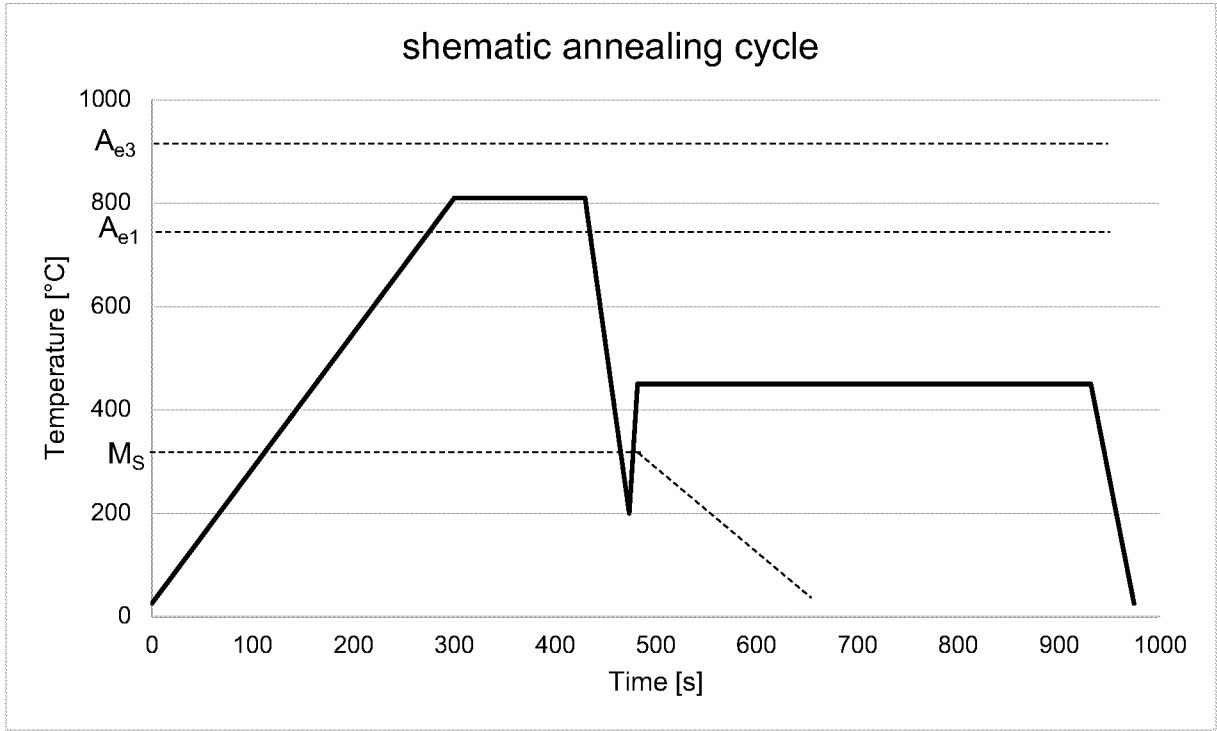
- 35 k) cooling the strip at a rate (CR1) of 10 – 100 °C/s to a quenching temperature (T_q) between M_F and ($M_S - 20$) °C,

- l) heating the cooled strip at a rate (HR2) of 10 – 100 °C/s to a partitioning temperature (Tp) in the range of the quenching temperature (Tq) + 10 °C to 500 °C. and partitioning the strip for 20 – 1000 s (tp),
- m) cooling the strip to a temperature below 50 °C at a rate (CR2) of 1 – 50 °C/s,
- 5 n) optionally applying a coating though galvanising, galvannealing, electro galvanising, or physical vapor deposition, and
- o) resistance spot welding of sheets cut from the strip.

11. The method according to claim 10, wherein the cold rolled steel strip is produced by the following steps:

- a) making steel slabs with a composition as defined in any one of claim 1-9,
- b) hot rolling in austenitic range to a hot rolled strip,
- c) coiling the hot rolled strip at a coiling temperature in the range of 400 – 700 °C,
- d) optionally subjecting the coiled strip to a scale removal process, such as pickling,
- 15 e) optionally annealing at a temperature in the range of 450 – 950 °C,
- f) optionally subjecting the annealed strip to a scale removal process, such as pickling,
- g) cold rolling the strip at a reduction rate between 20 – 90 %.

Fig. 1



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/065763

A. CLASSIFICATION OF SUBJECT MATTER					
INV.	C22C38/04	C22C38/02	C22C38/14	C22C38/06	C22C38/00
	C22C38/12	C21D9/46	C21D8/02	C21D6/00	C21D1/18
	C21D1/22	C21D1/19	C21D1/26	B32B15/01	C22C18/00
According to International Patent Classification (IPC) or to both national classification and IPC					
B. FIELDS SEARCHED					
Minimum documentation searched (classification system followed by classification symbols) C22C C21D B32B C23C					
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched					
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data					
C. DOCUMENTS CONSIDERED TO BE RELEVANT					
Category*	Citation of document, with indication, where appropriate, of the relevant passages				Relevant to claim No.
X	CN 113 416 888 A (ANGANG STEEL CO LTD) 21 September 2021 (2021-09-21)				1, 2, 7 - 11
A	the whole document				3 - 6

X	US 2017/145534 A1 (TAKASHIMA KATSUTOSHI [JP] ET AL) 25 May 2017 (2017-05-25)				1, 2, 7 - 11
A	claims 1-7 tables 1-6 paragraphs [0007] - [0085]				3 - 6

A	WO 2023/080632 A1 (POSCO CO LTD [KR]) 11 May 2023 (2023-05-11) claims 1-15 paragraphs [0030] - [0285] tables 1-3				1 - 11

	- / - -				
☒ Further documents are listed in the continuation of Box C.					
☒ See patent family annex.					
* Special categories of cited documents :					
"A" document defining the general state of the art which is not considered to be of particular relevance			"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention		
"E" earlier application or patent but published on or after the international filing date			"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone		
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)			"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art		
"O" document referring to an oral disclosure, use, exhibition or other means			"&" document member of the same patent family		
"P" document published prior to the international filing date but later than the priority date claimed					
Date of the actual completion of the international search			Date of mailing of the international search report		
26 August 2024			11/09/2024		
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016			Authorized officer Vlassi, Eleni		

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2024/065763

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	KR 2022 0019867 A (POSCO [KR]) 18 February 2022 (2022-02-18) the whole document -----	1 - 11
A	EP 3 859 041 A1 (POSCO [KR]) 4 August 2021 (2021-08-04) cited in the application claims 1-13 paragraphs [0007] - [0073] tables 1-4 -----	1 - 11
A	KR 2023 0082600 A (POSCO CO LTD [KR]) 8 June 2023 (2023-06-08) the whole document -----	1 - 11
A	US 2022/112575 A1 (REHRL JOHANNES [AT] ET AL) 14 April 2022 (2022-04-14) claims 1-10 paragraphs [0010] - [0079] -----	1 - 11

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2024/065763

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
CN 113416888	A	21-09-2021	NONE	

US 2017145534	A1	25-05-2017	CN 106170574 A	30-11-2016
			EP 3128027 A1	08-02-2017
			JP 5888471 B1	22-03-2016
			JP WO2015151419 A1	13-04-2017
			US 2017145534 A1	25-05-2017
			WO 2015151419 A1	08-10-2015

WO 2023080632	A1	11-05-2023	CN 118202081 A	14-06-2024
			EP 4428262 A1	11-09-2024
			KR 20230066166 A	15-05-2023
			WO 2023080632 A1	11-05-2023

KR 20220019867	A	18-02-2022	NONE	

EP 3859041	A1	04-08-2021	EP 3859041 A1	04-08-2021
			KR 20200036759 A	07-04-2020

KR 20230082600	A	08-06-2023	KR 20220086233 A	23-06-2022
			KR 20230082600 A	08-06-2023
			KR 20230082601 A	08-06-2023

US 2022112575	A1	14-04-2022	CN 113316649 A	27-08-2021
			US 2022112575 A1	14-04-2022
			WO 2020151856 A1	30-07-2020
