



(11)

EP 2 670 870 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:

20.01.2016 Bulletin 2016/03

(21) Application number: **12708776.5**

(22) Date of filing: **31.01.2012**

(51) Int Cl.:

C21C 7/10 (2006.01)	C21D 8/04 (2006.01)
C21D 9/48 (2006.01)	C22C 38/04 (2006.01)
C21D 8/02 (2006.01)	C22C 1/02 (2006.01)
C22C 38/06 (2006.01)	C22C 38/08 (2006.01)
C22C 38/12 (2006.01)	C22C 38/14 (2006.01)

(86) International application number:

PCT/EP2012/051566

(87) International publication number:

WO 2012/104306 (09.08.2012 Gazette 2012/32)

(54) **PROCESS FOR PRODUCING HIGH STRENGTH STEEL**

VERFAHREN ZUR HERSTELLUNG VON HOCHFESTEM STAHL

PROCÉDÉ DE FABRICATION D'ACIER À RÉSISTANCE ÉLEVÉE

(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**

(30) Priority: **31.01.2011 EP 11152816**
13.04.2011 EP 11162332

(43) Date of publication of application:
11.12.2013 Bulletin 2013/50

(73) Proprietor: **Tata Steel IJmuiden BV**
1951 JZ Velsen-Noord (NL)

(72) Inventors:

- **RICHARDS, Bernardus Johannes**
1970 CA IJmuiden (NL)

- **SCHAAR, Benno**
1970 CA IJmuiden (NL)
- **TIEKINK, Wouter Karel**
1970 CA IJmuiden (NL)

(74) Representative: **Bodin, Andre**
Tata Steel Nederland Technology B.V.
Group Intellectual Property Services
P.O. Box 10000 - 3G.37
1970 CA IJmuiden (NL)

(56) References cited:

EP-A1- 0 505 732	EP-A1- 1 323 837
EP-A1- 1 852 514	EP-A2- 0 556 834
WO-A1-2011/012242	JP-A- 2000 144 330

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 2 670 870 B1

Description

[0001] The present invention relates to a process for producing a high strength steel and to steel produced thereby.

[0002] High strength steels generally rely on carbon in one or more strengthening mechanisms. These mechanisms vary from the formation of pearlite to increase the strength, to the transformation of carbon containing austenite into martensite or bainite, e.g. in a heat treatment or carbon steels or the thermomechanical treatment of dual-phase, TRIP, complex phase steels, bainitic or martensitic steels, or to the formation of very fine carbide precipitates in HSLA steels possibly also resulting in a very fine microstructure as a result of thermomechanical rolling.

[0003] As the carbon content rises, steel has the ability to become harder and stronger through heat treating, but this also makes it less ductile. Regardless of the heat treatment, a higher carbon content reduces weldability. Welding of steels which derive their strength from a transformation product such as dual-phase and TRIP steels may be awkward as the heat input from the welding process may destroy the strength of the steel.

[0004] EP0556834 relates to a method of producing a high-strength steel sheet which exhibits good workability and which can be formed into a can having high strength by drawing with minimized earing. The properties are achieved by minimising the aluminium content needed for deoxidising and the aluminium in solid solution by keeping the oxygen to a low level.

[0005] It is an object of the invention to provide an alternative process for producing a high strength steel.

[0006] According to the first aspect a process is provided for producing a high strength steel, said process comprising:

- producing a vacuum-degassed steel melt in a steelmaking step comprising a ladle treatment comprising, by weight,
 - at most 0.02% carbon,
 - **at most 0.003% silicon.**
 - at most 0.010% nitrogen,
 - at most 0.10% phosphorus,
 - at most 0.020% sulphur,
 - at least 0.15% manganese,
 - at most 0.0045% boron,
 - at most 0.03% titanium,
 - at most 0.1% niobium,
 - at most 0.2% vanadium,
 - at most 3% chromium,
 - at most 6% nickel,
 - at most 1.5% molybdenum,
 - at most 0.005% calcium,
 - at most 0.006% zirconium,
 - at most 0.005% barium,
 - at most 0.005% strontium,
 - at most 0.05% in total of rare earth elements,
 - and balance iron and inevitable impurities,
- wherein a target oxygen content of the melt at the end of the ladle treatment of the melt is obtained by measuring the actual oxygen content of the melt followed by adding a suitable amount of aluminium and/or zirconium in a suitable form to the melt to bind oxygen wherein the target oxygen content of the melt at the end of the ladle treatment is at most 100 ppm;
- adding a second deoxidiser, after the oxygen activity at the end of the ladle treatment of at most 100 ppm is reached, to create fine particles and to bring down the dissolved oxygen in the steel in the ladle to 10 ppm or lower, wherein the second deoxidiser is one or more of Zr, Ca, Ba, Sr, Ti, Cr and Si;
- casting the steel thus produced in a continuous casting process to form a slab or strip;
- wherein said process provides a slab, strip or sheet of ultra-low-carbon steel comprising at most 0.002% of acid soluble aluminium and at most 0.004% silicon and a total oxygen content of at most 150 ppm.

[0007] With the process according to the invention a steel slab or strip can be produced having very clean grain boundaries. As a result, the recrystallisation temperature of the steel is much lower than conventional ultra-low carbon steels. This phenomenon is attributed to the extremely low levels of silicon and acid soluble aluminium in the final steel strip or sheet and the presence of finely dispersed manganese and/or iron oxide particles. As a result of the low recrystallisation temperature of the steel the annealing temperatures can be reduced as well, leading to a more economical process as well as a reduced tendency for grain growth in the product. The reduced annealing temperatures also prevent

sticking in batch annealing processes and reduce the risk of rupture in continuous annealing. A further advantage of the very clean grain boundaries is the strongly reduced susceptibility to corrosion on the grain boundaries. This is especially relevant for the application of the steel in the production of battery cases. The coating systems used in the production of batteries may be leaner (e.g. thinner coating layers or fewer coating layers) when using a substrate with a better corrosion resistance. For producing a mild cold-rolled steel from the slab or strip, the phosphorous content should be selected to be not greater than 0.025wt%, preferably at most 0.020%. A suitable maximum for silicon is 0.003%. The manganese content is at least 0.15% to attain a minimum strength increase caused by ODS. A preferable minimum value is 0.3% where the strength increase becomes significant. The maximum content is not limited technically, only economically. A suitable maximum value for the manganese content is 4%, but preferably the manganese content does not exceed 3%.

[0008] The essential difference with the conventional process for producing an ultra-low-carbon steel strip or sheet is that the ladle treatment of the melt during the vacuum-degassing step, e.g. in an RH-process, does not target a removal of the oxygen by killing it by adding excess aluminium to form alumina particles, but a process wherein the oxygen content of the melt is monitored and controlled, and a dedicated amount of aluminium is added so as to avoid the addition of excess aluminium to the melt which would be present in the final steel as acid soluble aluminium (i.e. in the form of metallic aluminium, not as alumina). It is therefore not an aluminium killed steel in the sense of EN10130. The addition of the precise amount of aluminium ensures that all alumina formed in the ladle treatment is removed from the melt prior to solidification during continuous casting, so that the resulting steel contains hardly any or no aluminium oxide, but instead it contains very small particles which form during the solidification in the mould. These particles are believed to be MnO-MnS rich types. Very small nanoparticles are created in the mould and the slab as well and these are believed to be Fe_xO_y -particles combined with Mn_xO_y -S. The generation of these oxide-containing nanoparticles leads to the so-called oxide dispersed strengthening (ODS). There may also be a contribution of the nanoparticles to strength increase by a precipitation hardening mechanism. The degassing of the molten steel may be made by any conventional methods such as the RH method, the RH-OB method, or in a vacuum tank degasser. The oxygen content of the liquid steel may be measured using expendable oxygen sensors to measure the melt's oxygen activity.

[0009] Instead of adding aluminium to reduce the oxygen activity to the required window at the ladle treatment, any other deoxidant may be used that can reach this window, i.e. 10 and 100 ppm oxygen activity at approximately 1600 °C, e.g. Ti, Zr, Ca, Sr, Ba etc.

[0010] The absence of metallic aluminium prevents the formation of aluminium-nitride precipitates at later stages of the process and therefore provides clean grain boundaries. Moreover, the absence of AlN also prevents many problems associated with the dissolution and precipitation characteristics of AlN in the hot strip process such as inhomogeneities of the microstructure and properties over length and width of the strip as a result of the difference in thermal path of different positions of the hot rolled strip in coiled form. There is no need to dissolve the AlN in the reheating furnace of a hot strip mill so a lower furnace temperature can be used, nor is there a need to use a high coiling temperature to allow the AlN to precipitate in the coil. This in turn leads to an improved pickling ability. The chemistry of the slab or strip results in the formation of finely dispersed oxides, comprising mainly manganese oxides. Of these inclusions, relatively large size inclusions act as nuclei for the recrystallisation during annealing of cold-rolled steel, while relatively small size inclusions may act to become appropriate barriers with respect to grain coarsening caused after the recrystallisation to thereby control the grain size of the steel.

[0011] The carbon content of the steel melt is preferably limited to at most 0.02% because when a higher carbon content is used, the carbon forms carbon monoxide in the manufacturing stage during which the steel is molten, and that CO in turn remains as blow-hole defects in the solidified steel. Moreover, the boiling effect may cause operational problems during casting. It should be noted that the silicon in the solidified steel may be present as silicon oxide and/or as metallic silicon. More preferably the carbon content is limited to 0.008%. Even more preferably the carbon content is limited to at most 0.0045% (i.e. 45 ppm).

[0012] In an embodiment the steel melt comprises 0.002% carbon and/or at most 0.003% silicon and/or the slab, strip or sheet comprises a total oxygen content of at most 100 ppm.

[0013] During casting very little and preferably no Al is left in the steel, and as a consequence the Si pick-up, which normally occurs according to the following reaction $\text{Al}_{\text{steel}} + \text{SiO}_2 \rightarrow \text{Al}_2\text{O}_3 + \text{Si}_{\text{steel}}$ does not occur due to the low Al-content.

[0014] A conventional process for producing an aluminium killed ultra-low-carbon steel strip or sheet results in an oxygen activity or dissolved oxygen content at the end of the ladle treatment of the melt, i.e. immediately prior to casting, of about 3 to 5 ppm. In the process according to the invention the target oxygen content of the melt at the end of the ladle treatment of the melt is preferably at least 10, or even more preferably 20 ppm. A preferable maximum target oxygen content of the melt at the end of the ladle treatment is 100, or even more preferably 80 ppm. It should be noted that the oxygen content of the melt may increase during the time between the end of the ladle treatment and the casting step. The total oxygen content of the slab or strip may therefore be at most 150 ppm, preferably at most 120 and even more preferably at most 100 ppm. The total oxygen content comprises oxides as well as oxygen in solution.

[0015] In an embodiment the target oxygen content of the melt at the end of the ladle treatment of the melt is at least

10 ppm. This minimum values ensures that sufficient manganese oxides are formed. To avoid too many large oxides and to avoid too much CO-formation, it is preferable that the target oxygen content is at most 100 ppm. The inventors found that a target oxygen content at the end of the ladle treatment between 10 and 70, provided a good compromise. A more preferable maximum value is at most 60 ppm or even at most 40 ppm. A suitable minimum target oxygen content of the melt at the end of the ladle treatment of the melt is at least 20 ppm. It is believed that the relatively high oxygen content of the steel melt prior to casting results in a low viscosity as a result of the high oxygen potential of the melt.

[0016] By steering the process on the oxygen content, rather than on the aluminium content the amount of acid soluble aluminium and the amount of silicon is as low as possible. It is preferable that the strip or sheet of ultra-low-carbon steel produced according to the invention comprises at most 0.001% or even at most 0.0005% of acid soluble aluminium and/or at most 0.003% or even 0.002% silicon. Even more preferable the silicon content is at most 0.001%. Ideally, there is no acid soluble aluminium and no silicon in the solidified steel.

[0017] This process produces a slab or strip suitable for producing a high strength. Depending on the alloying additions, the mechanical properties of the steel thus produced can be tailored.

[0018] Without dispersed oxides, normal polygonal ferrite grains form during cooling from the austenite region such as on the run-out table of a hot strip mill or after a high temperature annealing treatment. In the presence of finely dispersed oxides such as in the steel according to the invention, the oxides act as nucleation sites for the formation of ferrite leading to acicular ferrite and/or intragranular polygonal ferrite. This microstructure shows a significantly higher strength than the microstructure consisting of normal polygonal ferrite grains. This effect also occurs during the cooling after welding, and therefore the material to be welded together more easily retains its strength.

[0019] The acicular ferrite effect can be improved by adding elements such as Ti, Nb and V. Beside the known effects of precipitation hardening and retardation of the phase transformation, these elements will create additional oxides during solidification in the mould and slab. These oxides are small and stable. Ti, Nb and V partly use the MnO-s oxides (in the range of 0.5 to 1.2 μm) as a surface to grow on during solidification in the mould, thus changing the oxide surface of the original MnO into a surface which is very well suited for the acicular ferrite effect in the slab and hot strip mill.

[0020] Another way to make the acicular ferrite is to bring small nuclei in the liquid melt before the steel enters the tundish or add the nuclei in the tundish. This is not done by the addition of oxides but by the addition of a "deoxidiser" which is known **not** to create clusters: e.g. Zr, Ca, Ba, Sr, Ti, Cr, and/or Si. Cluster of oxides will float out of the steel and will make the process unstable in respect of the steel properties (e.g. alumina cluster formation should be avoided). The nuclei will act as a promoter of particle-growth during the subsequent casting and solidification into 0.5 - 1.2 μm sized particles, which can exhibit excellent acicular ferrite properties e.g. when Ba was used as the nuclei creating agent. Calcium, Ba or Sr, which are a vapour at steelmaking temperatures, can be injected by cored wire or by lance and the oxides that are formed are in the size of 0.1 to 1.2 μm , but fine oxides (<100 nm) can be created as well in this operation.

[0021] After solidification the majority of the total oxygen is in the form of oxides in the range of 0.6 to 1.2 μm , having compositions which vary from MO/Mn-O-S (M = deoxidiser). The sulphur content in the steel is preferably at most 120 ppm, but it may be as low as 30 or even 20 ppm to create more pure oxides over oxysulphides during casting and solidification). The deoxidiser is added in the liquid steel, preferably in an RH(-OB) where the oxygen can be tuned easily to the required level and Ca, Ba or Sr can be added in the RH vessel with high precision or can be added in the lance ("KTB" lance), but a simple stirring station or a ladle furnace can be used as well using a lance or cored wire as the injection technique. It would even be possible to do the whole operation in a tundish but smoke, dirt and fumes may create health problems in the tundish area of the caster, so this method is not preferable.

[0022] Cr can act as an oxide creator (ODS) but does not help very much in the micro alloying effect to strength (Cr < 0.2 wt%). Zr and Ti have a very strong oxide effect, and the oxygen control (oxygen activity control = dissolved oxygen) in the tundish, which is usually set during the ladle treatment, needs to be controlled within strict limits (for Ti between 15 and 60 ppm O activity, for Zr between 5 and 25 ppm O activity). Ti and Zr also create some C and N micro alloying properties because traces stay dissolved in the steel. Boron can be used when needed but will hardly exhibit any ODS effects as the formation of nitrides takes precedence (BN).

[0023] In an embodiment a second deoxidiser is added after the oxygen activity at the end of the ladle treatment is set to the required value; this new deoxidiser creates fine particles and, in some cases a small amount of clusters, which will float from the steel to the slag: new deoxidisers such as Zr, Ce, Ti, Ba and even Si may be used to bring the dissolved oxygen to 10 ppm or even lower (e.g. for Zr contents of 50 ppm or lower, the required oxygen activity will in some cases be 3 ppm or lower at the ladle treatment facility. The fine oxides that were formed in the liquid steel will not float because they are too small to float, and Ce_xO_y (in combination with CeO_2 -s) has the advantage of the high density inclusions density is approximately 6 kg/l, which will prevent flotation of 1 μm sized particles during ladle treatment. Zr will create ZrO_y oxides with a density of about 4 to 5 kg/l and will show a lower tendency of flotation than e.g. alumina, titania or silica/manganese silicates. Ba can be used also to create the nano-sized particles, but Ba exhibits a too high vapour pressure to be added to the steel in a standard way.

[0024] In an embodiment the second deoxidiser is added by injecting a cored wire under high stirring conditions in a stirring station or ladle furnace treatment. The highly stirred melt in combination with the extra stirring supplied by the

vaporizing alloy from the cored wire will create ideal circumstances to make very fine nano sized particles in the oxygen containing steels.

[0025] Although the method of the invention can be very well performed in conventional thick slab casting (slab thickness generally between 150 and 350 mm) a thin slab caster is the preferred option to cast the high strength steels, because of the faster solidification and the temperature levelling after casting and before rolling will create optimal precipitates for strength. A calcium treatment may be avoided because the high oxygen steels do not need any help to prevent clogging at a thin slab caster. Alternatively a strip caster (cast strip thickness < 10 mm) can be used and the advantage is here the controlled high solidification rate.

[0026] In an embodiment of the process the steel slab or strip comprises

- at most 5 ppm B, or wherein the steel comprises between 10 and 30 ppm B and/or
- at most 0.002% carbon and/or
- between 0.0012 and 0.0030% nitrogen.

[0027] In an embodiment the process comprises hot-rolling the slab at a temperature above Ar_3 to obtain a hot-rolled strip.

[0028] In an embodiment the process comprises

- cold-rolling the hot-rolled strip with a cold rolling reduction of between 40 and 96% to obtain an intermediate cold-rolled strip;
- annealing the intermediate cold-rolled strip;
- optionally subjecting the intermediate cold-rolled strip to a second cold rolling down to a final sheet thickness;
- optionally cutting the strip into sheets or blanks;

[0029] The invention will now be illustrated by means of non-limitative examples. Continuously cast slabs were produced of the steel grades listed in table 1. Table 1 gives two soft ULC compositions (with and without B) which show a 50 to 100 MPa ODS strengthening after subjecting it to a conventional cold rolling and annealing treatment. Table 2 shows high strength steel composition by composition in 1/1000 wt.% except C, Ca and N in ppm, composition in mould, except Ot and Oact.

Table 1: Composition in 1/1000 wt.% except C, N and B in ppm, composition in mould, except Ot, Oact_RH and Oact.

ID	C	Mn	P	S	Si	Al	Al _{sol}	N	Cu	Cr	Nb	Ni	V	Mo	Sn	B	Ti	Oact_RH	Oact	Ot
1138	20	181	11	9	1	3	<1	19	23	20	0	18	0	1	3	15	1	23	70	75
1140	15	175	12	8	0	1	<1	18	22	23	0	20	1	3	3	0	1	12	35	55
Oact_RH: oxygen activity after vacuum degassing Oact : tundish oxygen activity Ot: slab total oxygen content																				

Table 2. High strength steel composition by composition in 1/1000 wt. % except C, N and Ca in ppm, composition in mould, except Ot and Oact.

sample	C ppm	Mn	P	S	Si	Al tot	Al sol	Cu	Cr	Ni	Mo	Nb	V	Ti	N ppm	Ca ppm	Oact	Ot
A	25	1267	15	8	3	3	0	25	23	20	5	25	1	1	28	0	24	78
B	21	2512	14	7	2	2	0	23	22	24	3	2	75	2	67	1	21	74
C	28	1176	15	8	3	3	0	18	19	23	1	10	2	25	48	0	19	47
D	35	2967	18	9	5	2	0	21	18	21	0	32	75	8	74	1	29	38
E	18	826	13	9	0	3	0	19	72	20	1	14	1	1	21	0	46	51
F	31	1245	26	8	2	2	0	24	26	18	1	31	2	1	35	26	23	62
G	32	1184	14	8	2	1	0 Zr=0.0021	28	27	21	0	74	62	1	68	16	12	41
H	23	523	74	8	1	2	0	24	25	19	0	42	1	2	28	0	41	65
12713	30	524	3	4	4	3	0	7	30	13	5	1	1	1	19	1	41	65
Oact: tundish oxygen activity																		
Ot: slab total oxygen content																		

Claims

1. Process for producing a high strength steel said process comprising:

- producing a vacuum-degassed steel melt in a steelmaking step comprising a ladle treatment comprising, by weight,

- at most 0.02% carbon,
- at most 0.003% silicon
- at most 0.010% nitrogen,
- at most 0.10% phosphorus,
- at most 0.020% sulphur,
- at least 0.15% and at most 4% manganese,
- at most 0.0045% boron,
- at most 0.03% titanium,
- at most 0.1% niobium,
- at most 0.2% vanadium,
- at most 3% chromium,
- at most 6% nickel,
- at most 1.5% molybdenum,
- at most 0.005% calcium,
- at most 0.006% zirconium,
- at most 0.005% barium,
- at most 0.005% strontium,
- at most 0.05% in total of rare earth elements, such as cerium,
- and balance iron and inevitable impurities,

- wherein a target oxygen content of the melt at the end of the ladle treatment of the melt is obtained by measuring the actual oxygen content of the melt followed by adding a suitable amount of aluminium and/or zirconium in a suitable form to the melt to bind oxygen wherein the target oxygen content of the melt at the end of the ladle treatment is at most 100 ppm;

- adding a second deoxidiser, after the oxygen activity at the end the ladle treatment of at most 100 ppm is reached, to create fine particles and to bring down the dissolved oxygen in the steel in the ladle to 10 ppm or lower, wherein the second deoxidiser is one or more of Zr, Ca, Ba, Sr, Ti, Cr and Si;

- casting the steel thus produced in a continuous casting process to form a slab or strip;

- wherein said process provides a slab, strip or sheet of ultra-low-carbon steel comprising at most 0.002% of acid soluble aluminium and at most 0.004% silicon and a total oxygen content of at most 150 ppm.

2. Process according to any one of the preceding claims wherein the steel slab or strip comprises

- at most 0.008% carbon, preferably at most 0.0045%.

3. Process according to claim 1 or 2, wherein the steel slab, strip or sheet comprises a total oxygen content of at most 100 ppm.

4. Process according to any one of the preceding claims, wherein the target oxygen content of the melt at the end of the ladle treatment of the melt is at least 10 ppm.

5. Process according to any one of the preceding claims, wherein the target oxygen content of the melt at the end of the ladle treatment of the melt is at most 70 ppm, preferably at most 60 ppm.

6. Process according to any one of the preceding claims wherein the process provides a strip or sheet of ultra-low-carbon steel comprising at most 0.001% of acid soluble aluminium and/or at most 0.002% silicon.

7. Process according to any one of the preceding claims wherein the steel comprises at most 3% manganese.

8. Process according to any one of the preceding claims wherein the steel slab or strip comprises

- at most 5 ppm B, or wherein the steel comprises between 10 and 30 ppm B and/or
- at most 0.002% carbon and/or
- between 0.0012 and 0.0030% nitrogen.

9. Process according to any one of the preceding claims wherein the steel slab is cast in a thin slab caster or a strip caster.

10. Process according to any one of the preceding claims wherein the steel slab or strip comprises

- hot-rolling the slab at a temperature above Ar3 to obtain a hot-rolled strip;

11. Process according to claim 10 wherein the finely dispersed particles act as nucleation sites for the formation of ferrite leading to acicular ferrite and/or intragranular polygonal ferrite in the hot-rolled strip.

12. Process according to claim 11 wherein the finely dispersed particles are selected from Zr, Ca, Ba, Sr, Ti, Cr, and/or Si, and form oxides.

13. Process according to any one of claims 10 to 12 comprising

- cold-rolling the hot-rolled strip with a cold rolling reduction of between 40 and 96% to obtain an intermediate cold-rolled strip;
- annealing the intermediate cold-rolled strip;
- optionally subjecting the intermediate cold-rolled strip to a second cold rolling down to a final sheet thickness;
- optionally cutting the strip into sheets or blanks;

Patentansprüche

1. Verfahren zum Produzieren eines hochfesten Stahls, Folgendes beinhaltend:

- Produzieren einer vakuumentgasten Stahlschmelze in einem Stahlerzeugungsschritt, beinhaltend eine Pfannenbehandlung, beinhaltend, nach Gewicht,

- maximal 0.02 % Kohlenstoff,
- maximal 0.003 % Silizium,
- maximal 0.010 % Stickstoff,
- maximal 0.10 % Phosphor,
- maximal 0.020 % Schwefel,
- mindestens 0.15 % und maximal 4 % Mangan,
- maximal 0.0045 % Bor,
- maximal 0.03 % Titan,
- maximal 0.1 % Niobium,
- maximal 0.2 % Vanadium,
- maximal 3 % Chrom,
- maximal 6 % Nickel,
- maximal 1.5 % Molybdän,
- maximal 0.005 % Calcium,
- maximal 0.006 % Zirkon,
- maximal 0.005 % Barium,
- maximal 0.005 % Strontium,
- maximal 0.05 %, insgesamt, seltene Erdelemente, wie Cer,
- Rest Eisen und unvermeidbare Verunreinigungen,

- wobei ein Sauerstoffzielanteil der Schmelze am Ende der Pfannenbehandlung der Schmelze erhalten wird durch Messen des tatsächlichen Sauerstoffanteils der Schmelze, gefolgt durch Hinzufügen einer geeigneten Menge von Aluminium und/oder Zirkon in einer geeigneten Form zur Schmelze, um Sauerstoff zu binden, wobei der Sauerstoffzielanteil am Ende der Pfannenbehandlung maximal 100 ppm beträgt;

- Hinzufügen eines zweiten Desoxidationsmittels, nachdem am Ende der Pfannenbehandlung die Sauerstoffaktivität von maximal 100 ppm erreicht wird, um Feinpartikel zu erzeugen und den gelösten Sauerstoff im Stahl

in der Pfanne auf 10 ppm oder niedriger herunter zubringen, wobei das zweite Desoxidationsmittel eines oder mehr von Zr, Ca, Ba, Sr, Ti, Cr und Si ist;

- Gießen des so produzierten Stahls in einem Stranggießverfahren, um eine Bramme oder ein Band zu bilden;
- wobei das Verfahren eine Bramme, ein Band oder ein Blech bereitstellt aus Stahl mit sehr geringem Kohlenstoffanteil mit maximal 0.002 % säurelöslichem Aluminium und mit maximal 0.004 % Silizium und einem Gesamtsauerstoffanteil von maximal 150 ppm.

2. Verfahren gemäß einem der vorhergehenden Ansprüche, wobei die Stahlbramme oder das Stahlband maximal 0.008 % Kohlenstoff, vorzugsweise maximal 0.0045 % beinhaltet

3. Verfahren gemäß Anspruch 1 oder 2, wobei die Stahlbramme, das Stahlband oder das Stahlblech einen Sauerstoffanteil von maximal 100 ppm beinhaltet.

4. Verfahren gemäß einem der vorhergehenden Ansprüche, wobei der Sauerstoffzielanteil der Schmelze am Ende der Pfannenbehandlung der Schmelze mindestens 10 ppm beträgt.

5. Verfahren gemäß einem der vorhergehenden Ansprüche, wobei der Sauerstoffzielanteil der Schmelze am Ende der Pfannenbehandlung der Schmelze maximal 70 ppm, vorzugsweise maximal 60 ppm, beträgt.

6. Verfahren gemäß einem der vorhergehenden Ansprüche, wobei das Verfahren ein Band oder Blech aus Stahl mit sehr geringem Kohlenstoffanteil bereitstellt, beinhaltend maximal 0.001 % säurelösliches Aluminium und/oder maximal 0.002 % Silizium.

7. Verfahren gemäß einem der vorhergehenden Ansprüche, wobei der Stahl maximal 3 % Mangan beinhaltet.

8. Verfahren gemäß einem der vorhergehenden Ansprüche, wobei die Stahlbramme oder das Stahlband beinhaltet

- maximal 5 ppm B, oder wobei der Stahl zwischen 10 und 30 ppm B beinhaltet und/oder

- maximal 0.002 % Kohlenstoff und/oder

- zwischen 0.0012 und 0.0030 % Stickstoff.

9. Verfahren gemäß einem der vorhergehenden Ansprüche, wobei die Stahlbramme in einer Dünnbrammengießanlage oder einer Bandgießanlage gegossen wird.

10. Verfahren gemäß einem der vorhergehenden Ansprüche, wobei die Stahlbramme oder das Stahlband beinhaltet

- Warmwalzen der Bramme bei einer Temperatur über Ar3, um ein warmgewalztes Band zu erhalten;

11. Verfahren gemäß Anspruch 10, wobei die fein verteilten Partikel als Kristallisationskeime für die Bildung von Ferrit wirken, was zu nadelförmigem Ferrit und/oder intragranularem polygonalem Ferrit im warmgewalzten Band führt.

12. Verfahren gemäß Anspruch 11, wobei die fein verteilten Partikel 10 aus Zr, Ca, Ba, Sr, Ti, Cr und/oder Si ausgewählt sind und Oxide bilden.

13. Verfahren gemäß einem der Ansprüche 10 bis 12, beinhaltend:

- Kaltwalzen des warmgewalzten Bands mit einer Kaltwalzreduktion zwischen 40 und 96 %, um ein kaltgewalztes Zwischenband zu erhalten;

- Glühen des kaltgewalzten Zwischenbands;

- optional Unterwerfen des kaltgewalzten Zwischenbands einem zweiten Kaltwalzen hinunter auf eine endgültige Blechdicke;

- optional Schneiden des Bands in Bleche oder Rohlinge.

Revendications

1. Procédé pour la production d'un acier à résistance élevée, ledit procédé comprenant:

EP 2 670 870 B1

- la production d'une coulée d'acier dégazée sous vide dans le cadre d'une étape sidérurgique comportant un traitement en poche comprenant, en poids:

- au plus 0.02% de carbone,
- au plus 0.003% de silicium,
- au plus 0.010% d'azote,
- au plus 0.10% de phosphore,
- au plus 0.020% de soufre,
- au moins 0.15% et au plus 4% de manganèse,
- au plus 0.0045% de bore,
- au plus 0.03% de titane,
- au plus 0.1% de niobium,
- au plus 0.2% de vanadium,
- au plus 3% de chrome,
- au plus 6% de nickel,
- au plus 1.5% de molybdène,
- au plus 0.005% de calcium,
- au plus 0.006% de zirconium,
- au plus 0.005% de baryum,
- au plus 0.005% de strontium,
- au plus 0.05% d'éléments de terres rares, par exemple du cérium,
- le restant étant du fer et des impuretés inévitables,

- une teneur cible en oxygène de la coulée à la fin du traitement en poche de celle-ci s'obtenant en mesurant la teneur effective en oxygène de la coulée, puis en ajoutant, à la coulée, une quantité appropriée d'aluminium et/ou de zirconium sous une forme appropriée afin de lier l'oxygène, la teneur cible en oxygène de la coulée, à la fin du traitement en poche, étant au plus 100 ppm ;

- l'adjonction d'un deuxième désoxydant, lorsque l'activité d'oxygène à la fin du traitement en poche atteint au plus 100 ppm, pour la création de fines particules et baisser l'oxygène dissous dans l'acier, dans la poche, jusqu'à 10 ppm, voire moins, le deuxième désoxydant étant un ou plusieurs des suivants: Zr, Ca, Ba, Sr, Ti, Cr et Si ;

- le moulage de l'acier ainsi produit dans un procédé à coulée continue pour la formation d'une brame ou d'un feuillard ;

- ledit procédé permettant d'obtenir une brame, un feuillard ou une tôle d'acier à très faible teneur en carbone, comprenant au plus 0.002% d'aluminium soluble dans l'acier et au plus 0.004% de silicium, et une teneur totale en oxygène de 150 ppm au plus.

2. Un procédé selon une quelconque des revendications précédentes, la brame ou le feuillard d'acier comprenant au plus 0.008% de carbone, de préférence au plus 0.0045%.

3. Un procédé selon la revendication 1 ou 2, la brame, le feuillard ou la tôle d'acier présentant une teneur totale en oxygène de 100 ppm au plus.

4. Un procédé selon une quelconque des revendications précédentes, la teneur cible en oxygène de la coulée à la fin du traitement en poche de la coulée étant au moins 10 ppm.

5. Un procédé selon une quelconque des revendications précédentes, la teneur cible en oxygène de la coulée à la fin du traitement en poche de la coulée étant au plus 70 ppm, et de préférence au plus 60 ppm.

6. Un procédé selon une quelconque des revendications précédentes, le procédé produisant un feuillard ou une tôle d'acier à très faible teneur en carbone comprenant au plus 0.001% d'aluminium soluble dans l'acier et/ou au plus 0.002% de silicium.

7. Un procédé selon une quelconque des revendications précédentes, l'acier comprenant au plus 3% de manganèse.

8. Un procédé selon une quelconque des revendications précédentes, la brame ou le feuillard d'acier comprenant

- au plus 5 ppm de B, ou l'acier présentant une teneur en B comprise entre 10 et 30 ppm et/ou

EP 2 670 870 B1

- au plus 0.002% de carbone et/ou
- de 0.0012 à 0.0030% d'azote.

- 5 **9.** Un procédé selon une quelconque des revendications précédentes, la brame d'acier étant moulée sous forme de coulées de rames minces ou de bandes en continu.
- 10.** Un procédé selon une quelconque des revendications précédentes, la brame ou le feuillard d'acier comprenant le laminage à chaud de la brame à une température supérieure à Ar3 pour obtenir un feuillard laminé à chaud.
- 10 **11.** Un procédé selon la revendication 10, les particules finement dispersées se comportant comme des sites de nucléation pour la formation de ferrite, portant à de la ferrite aciculaire et/ou de la ferrite polygonale intra-granulaire dans le feuillard laminé à chaud.
- 15 **12.** Un procédé selon la revendication 11, les particules finement dispersées 10 étant sélectionnées parmi les suivants: Zr, Ca, Ba, Sr, Ti, Cr et/ou Si, et formant des oxydes.
- 13.** Un procédé selon une quelconque des revendications 10 à 12, comprenant
- 20 - le laminage à froid du feuillard laminé à chaud, avec une réduction par laminage à froid comprise entre 40 et 96% pour obtenir un feuillard laminé à froid intermédiaire ;
- 25 - le recuit du feuillard laminé à froid intermédiaire ;
- 30 - en option la soumission du feuillard d'acier laminé à froid à un deuxième laminage à froid jusqu'à l'épaisseur finale de la tôle ;
- 35 - en option le découpage du feuillard en tôles ou en flans.
- 40
- 45
- 50
- 55

REFERENCES CITED IN THE DESCRIPTION

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

Patent documents cited in the description

- EP 0556834 A [0004]