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(54) STEEL PRODUCT AND METHOD OF MANUFACTURING THE SAME

(57) This invention relates to a steel product comprising a composition consisting of. in terms of weight percentages. wt. %:
C
0.025 - 0.065. preferably 0.025 - 0.055
Si
0.01 - 0.8. preferably 0.05 - 0.65
Mn
1.1 - 1.8. preferably 1.2 - 1.7
Al
0.005 - 0.12. preferably 0.02 - 0.08
Nb
0.005 - 0.1. preferably 0.01 - 0.06
Cu
0.6 - 1.5. preferably 0.6 - 1.2. more preferably 0.7 - 1.0
Cr
0.05 - 0.30. preferably 0.1 - 0.25
Ni

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0.2 - 1.1. preferably 0.3 - 1.1. more preferably 0.55 - 1.0
Ti
≤ 0.05. preferably ≤ 0.02. more preferably ≤ 0.005
Mo
0.1 - 0.3. preferably 0.15 - 0.25
V
0.01 - 0.2. preferably 0.02 - 0.13
B
0.0 - 0.001. preferably 0.0 - 0.00075. more preferably ≤ 0.0005
P
≤ 0.02. preferably ≤ 0.015. more preferably ≤ 0.01
S
≤ 0.015. preferably ≤ 0.01. more preferably ≤ 0.005
Ca
< 0.01 %. preferably < 0.004 %

remainder Fe and inevitable impurities, wherein a carbon equivalent CEN value for the steel product is CEN < 0.41. preferably CEN < 0.38. more preferably CEN < 0.35. and wherein the carbon equivalent CEN value is calculated from the composition. in wt.%. by using the following formula:

$$CEN= C+(0.75+0.25*\tanh(20*(C-0.12)))*(Si/24+Mn/6+Cu/15+Ni/20+(Cr+Mo+Nb+V)/5+5B).$$

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Description

TECHNICAL FIELD

[0001] The present invention relates to a hot-rolled steel product that can be used for example in pipe fittings in oil and gas industry.

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

BACKGROUND OF THE INVENTION

[0003] The present invention relates to a hot rolled steel product having an alloying concept especially suitable for manufacturing steel products such as high strength pipe fittings of varying dimension (sizes and wall thicknesses) that may contain multiple heat treatments such as austenitization(s), quenching, and tempering step(s).

[0004] Manufacturing of pipe fittings requires careful process control to achieve required product properties. The process typically contains multiple heat treatments such as austenitization(s), quenching, tempering, stress relieving(s), forming and welding steps and all these can have an influence on the final product properties. With the current steel products available on the market, however, yield strength requirements are not always satisfied in the final product. For example, based on National Energy Board of Canada report (2018), over the last 15 years several incidents have been reported in steel fittings and quality assurance programs have been inadequate.

[0005] Robustness to varying cooling rates during quenching is a key property for these steels. This is especially important for manufacturing of pipe fittings, which have varying wall thicknesses. In traditional low-carbon steel grades used for these applications (0.10 - 0.30 wt.% C), the varying cooling rates occurring in steel products during manufacturing of pipe fittings may lead to abrupt changes in the phase balances and the resulting mechanical properties, thus, for example, yield strength and/or impact toughness requirements are not always met in the final product. This may lead to an increased amount of rejections during product testing and possibly catastrophic failures during use. Furthermore, at present, it is not possible to achieve the required product properties, with a single alloy, over a wide thickness range even through a careful process control. Thus, there is a need for an alloy that is robust with regard to varying cooling rates.

SUMMARY OF THE INVENTION

[0006] In view of the state of art, it is a primary object of the invention to provide a hot-rolled 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 steel product that is more tolerable to different cooling rates during the manufacturing of a pipe fitting, for example.

[0007] The steel according to the invention is more tolerable to the changes in the manufacturing of a e.g. pipe fitting. This is achieved by effectively lowering the carbon content from typical 0.14-0.20 wt.% to 0.025-0.065 wt.% while increasing the alloying elements e.g. Cr, Mo, Cu and Ni. Especially, it has been demonstrated that a change in the cooling rate (during quenching) in higher carbon alloys can lead to undesired changes in the phase balances and mechanical properties. The inventors have surprisingly found that the lower carbon content combined with other alloying elements increase stability of mechanical properties over a wide range of wall thicknesses and cooling rates during quenching. Furthermore, even at the low carbon contents high yield strengths of above 550 MPa were achieved. In addition, the lower carbon content is generally seen as more favorable to weldability.

[0008] According to a first aspect of the invention, at least the primary object is achieved by a hot-rolled steel product according to claim 1. The steel product has a composition consisting of, in terms of weight percentages (wt.%):

C	0.025 - 0.065, preferably 0.025 - 0.055
Si	0.01 - 0.8, preferably 0.05 - 0.65
Mn	1.1 - 1.8, preferably 1.2 - 1.7
Al	0.005 - 0.12, preferably 0.02 - 0.08
Nb	0.005 - 0.1, preferably 0.01 - 0.06
Cu	0.6 - 1.5, preferably 0.6 - 1.2, more preferably 0.7 - 1.0
Cr	0.05 - 0.30, preferably 0.1 - 0.25
Ni	0.2 - 1.1, preferably 0.3 - 1.1, more preferably 0.55 - 1.0
Ti	≤ 0.05, preferably ≤ 0.02, more preferably ≤ 0.005
Mo	0.1 - 0.3, preferably 0.15 - 0.25
V	0.01 - 0.2, preferably 0.02 - 0.13

(continued)

B	0.0 - 0.001 , preferably 0.0 - 0.00075, more preferably ≤ 0.0005
P	≤ 0.02, preferably ≤ 0.015, more preferably ≤ 0.01
S	≤ 0.015, preferably ≤ 0.01, more preferably ≤ 0.005
Ca	< 0.01 , preferably < 0.004

remainder Fe and inevitable impurities, wherein a carbon equivalent CEN value of the steel alloy is CEN < 0.41, preferably CEN < 0.38, more preferably CEN < 0.35, and wherein the carbon equivalent CEN value is calculated from the composition, in wt.%, by using formula:

$$CEN = C+(0.75+0.25*\tanh(20*(C-0.12)))*(Si/24+Mn/6+Cu/15+Ni/20+(Cr+Mo+Nb+V)/5+5B).$$

[0009] Such a chemical composition is beneficial as it allows for formation of mainly granular bainitic microstructure even with slow cooling rates during the initial quenching in a quenching and tempering (Q&T) heat treatment.

[0010] The steel product has very low levels of C and limited Mn content. The low levels of C and limited levels of 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. 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.

[0011] Preferably, the hot-rolled steel product has a composition consisting of, in terms of weight percentages (wt. %):

C	0.025 - 0.055
Si	0.05 - 0.65
Mn	1.2 - 1.7
Al	0.02 - 0.08
Nb	0.01 - 0.06
Cu	0.7 - 1.0
Cr	0.1 - 0.25
Ni	0.55 - 1.0
Ti	≤ 0.005
Mo	0.15 - 0.25
V	0.02 - 0.13
B	≤ 0.0005
P	≤ 0.01
S	≤ 0.005
Ca	< 0.004

remainder Fe and inevitable impurities, wherein the carbon equivalent CEN value for the steel alloy is CEN < 0.41, preferably CEN < 0.38, more preferably CEN < 0.35, and wherein the carbon equivalent CEN value is calculated from the chemical composition, in wt.%, by using formula:

$$CEN = C+(0.75+0.25*\tanh(20*(C-0.12)))*(Si/24+Mn/6+Cu/15+Ni/20+(Cr+Mo+Nb+V)/5+5B).$$

[0012] Preferably, the steel product has a C/Mn ratio of, in wt.%, C/Mn < 0.041 and more preferably C/Mn < 0.034, wherein the amount of C and Mn are expressed in wt.%. For impact toughness, especially in the welded joint, it is beneficial that the C/Mn ratio is not too high.

[0013] In an embodiment, the steel product has the following microstructure in vol %:

Polygonal ferrite, PF: 50 ≤ PF ≤ 90,
Quasipolygonal ferrite, QPF: 5 ≤ QPF ≤ 35, more preferably 10 ≤ QPF ≤ 30, wherein
PF + QPF: 55 ≤ PF + QPF ≤ 95,
Granular bainite, GB: 1 ≤ GB ≤ 30, and
Carbon rich phases, CRP: 1 ≤ CRP ≤ 20, preferably 1 ≤ CRP ≤ 15, more preferably 1 ≤ CRP ≤ 10.

[0014] The steel product may herein be a hot-rolled steel product.

[0015] Such a microstructure is beneficial for the manufacturing of pipe fittings, because it has a significant amount of polygonal ferrite, which makes the steel product sufficiently soft for forming of a pipe fitting, for example. This allows for cold forming of relatively thick material thicknesses. For the hot rolled samples, the carbon rich phases comprise the sum of each individual sub structure i.e. MA-constituents, lath bainite and pearlite.

[0016] In some embodiments, the steel product has a yield strength (RP0.2) in the range of 300-600 MPa, preferably 350-550 MPa, and more preferably 370-520 MPa.

[0017] In some embodiments, the steel product has an ultimate tensile strength (Rm) in the range of 420-850 MPa, preferably 490-800 MPa, and more preferably 530-775 MPa.

[0018] In an embodiment, the steel product is a hot rolled steel plate having a thickness in the range of 4 mm to 100 mm, preferably 8 mm to 65 mm, more preferably 10 mm to 55 mm. These thickness ranges are relevant for the manufacturing of pipe fittings.

[0019] In some embodiments, the steel product has the following microstructure:

Polygonal ferrite (PF): 0 ≤ PF ≤ 10, preferably 0 ≤ PF ≤ 5, more preferably 0 ≤ PF ≤ 3,
Quasipolygonal ferrite (QPF): 1 ≤ QPF ≤ 35, preferably 1 ≤ QPF ≤ 25,
Granular bainite (GB): 50 ≤ GB ≤ 99, preferably 60 ≤ GB ≤ 95, more preferably 65 ≤ GB ≤ 90, and
Lath bainite (LB): 0 ≤ LB ≤ 20, preferably 2 ≤ LB ≤ 20.

[0020] The steel product may herein be a pipe fitting.

[0021] Such a microstructure comprising a significant amount of granular bainite, and a low amount of polygonal ferrite, is beneficial as it provides for great impact toughness values combined with high strength values.

[0022] In some embodiments, the steel product has the following yield strength (RP0.2) in the range of 550-800 MPa, preferably 550-750 MPa, more preferably 550-700 MPa.

[0023] In some embodiments, the steel product has an ultimate tensile strength (Rm) in the range of 580-900 MPa, preferably 600-850 MPa, and more preferably 640-820 MPa.

[0024] In some embodiments, the steel product has a Charpy-V impact toughness of at least 100 J/cm2, preferably at least 150 J/cm2 at a temperature of -46 °C when measured from 2 mm of surface of the steel product.

[0025] In some embodiments, the steel product is a pipe fitting.

[0026] In a second aspect, the present invention provides a method for manufacturing a hot-rolled steel product according to claim 13. The method comprises the following steps of:

- heating a steel slab to a temperature in the range of 950 °C to 1350 °C, the steel slab having the following composition:

  C 0.025 - 0.065, preferably 0.025 - 0.055
  Si 0.01 - 0.8, preferably 0.05 - 0.65
  Mn 1.1 - 1.8, preferably 1.2 - 1.7
  Al 0.005 - 0.12, preferably 0.02 - 0.08
  Nb 0.005 - 0.1, preferably 0.01 - 0.06
  Cu 0.6-1.5, preferably 0.6-1.2, more preferably 0.7-1.0
  Cr 0.0 - 0.30, preferably 0.0-0.25
  Ni 0.2 - 1.1, preferably 0.3-1.1, more preferably 0.55-1.0
  Ti ≤ 0.05, preferably ≤ 0.02, more preferably ≤ 0.005
  Mo 0.1 - 0.3, preferably 0.15 - 0.25
  V 0.0 - 0.2, more preferably 0.02 - 0.13
  B 0.0 - 0.001 , preferably 0.0 - 0.00075, more preferably ≤ 0.0005 P ≤ 0.02, preferably ≤ 0.015, more preferably ≤ 0.01
  S ≤ 0.015, preferably ≤ 0.01, more preferably ≤ 0.005
  Ca < 0.01 %, preferably < 0.004 %
  remainder Fe and inevitable impurities, wherein a carbon equivalent CEN value for the steel product is CEN < 0.41, preferably CEN < 0.38, more preferably CEN < 0.35, and
  wherein the carbon equivalent CEN value is calculated from the chemical composition, in wt.%, by using the

following formula:

$$\mathrm{CEN}= C+(0.75+0.25*\tanh(20*(C-0.12)))*(Si/24+Mn/6+Cu/15+Ni/20+(Cr+Mo+Nb+V)/5+5B);$$

- hot rolling the heated steel slab in a plurality of hot rolling passes for manufacturing a hot rolled steel product, wherein

  i) the steel slab is subjected to a plurality of rolling passes at a temperature above and/or below an austenite non-recrystallization temperature, in order to form a strip or a plate, wherein the final rolling temperature is above 850 °C, and

  ii) the steel strip or a plate from step (i) is cooled, preferably in air, down to room temperature.

[0027] Such a manufacturing method leads to a hot rolled steel product comprising a microstructure having a significant fraction of polygonal ferrite, which provides for a good starting microstructure for cold forming of a pipe fitting, for example.

[0028] In some embodiments the method further comprises the steps of:

- forming the steel strip or a plate into a steel product, such as a pipe fitting,
- subjecting the steel product from previous step to at least one austenitizing heat treatment at a temperature within the temperature range of 800 °C to 1000 °C for a time period of 5 minutes to 5 hours,
- cooling the steel product from the previous step, preferably by immersion-quenching in a suitable liquid medium,
- subjecting the steel product from the previous step to at least one tempering heat treatment at a temperature within the range of 540 °C to 690 °C for a time period of 5 minutes to 5 hours, and subsequently
- cooling the steel product to room temperature.

[0029] Such a method leads to a steel microstructure comprising a significant amount of granular bainite, and a low amount of polygonal ferrite. This is beneficial as such a microstructure provides for great impact toughness values combined with high strength values.

[0030] Further advantages and advantageous features of the invention are disclosed in the following description and in the dependent claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0031]

Figure 1a and 1b illustrate the microstructure of example steel C according to an embodiment of the invention, in the as-rolled condition and quenched and tempered condition, respectively.

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

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0032] The term "steel" is defined as an iron alloy containing carbon (C).

[0033] The term "ultimate tensile strength" (UTS, Rm) refers to the limit, at which the steel fractures under tension, thus the maximum tensile stress.

[0034] 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 %.

[0035] The term "Q&T" (quench and tempered) is a heat treatment wherein a steel is first fully austenitized, followed by quenching down to room temperature, and then heated to a tempering temperature, after which the steel is typically cooled down to room temperature in air. The quenching step may be conducted using several quenching media (e.g. air, water, water-polymer solution, oil).

[0036] The term "CR" (cooling rate) in this application refers to a cooling rate during the quenching step of a Q&T heat treatment.

[0037] The term "carbon equivalent equation" (CEN) in this application refers to a specific carbon equivalent equation:

$$CEN=C+(0.75+0.25*\tanh(20*(C-0.12)))*(Si/24+Mn/6+Cu/15+Ni/20+(Cr+Mo+Nb+V)/5+5B) \quad (1)$$

[0038] The alloying content of steel together with the processing parameters determines the microstructure, which in turn determines the mechanical properties of the steel.

[0039] 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, especially during welding. 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. The above-defined CEN carbon equivalent equation according to formula (1) was used to calculate the carbon equivalent values for the steels according to the present invention.

[0040] 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.

[0041] Another aspect where carbon equivalent equations may be used is to estimate a preheating temperature for welding. For the steel presented here, a low CEN value alone is not sufficient, as it also needs to be combined with a low C level.

[0042] Preferably, the CEN carbon equivalent value is CEN < 0.41, more preferably CEN < 0.38, even more preferably CEN < 0.35.

[0043] 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 element refers to weight percentage.

Carbon C is used in the range of 0.025 - 0.065%

[0044] Carbon is a critical element for achieving sufficient strength level in steel products as it contributes to various strengthening mechanisms like phase transformation products, solid solution strengthening and precipitation strengthening. However, excessive C alloying leads to undesirable weldability issues and reduces the impact toughness and formability of a steel by promoting transformation products rich in brittle microconstituents. Furthermore, excessive C alloying increases the strength of the steel too much.

[0045] Various carbon equivalents are commonly used to describe the sensitivity of steels for welding related cracking phenomena. The CEN formula (1) defined above is used for comparing alloy steels having wide variation in their chemical compositions.

[0046] Alloys having low CEN values are generally more crack resistant than those having high values. According to the formula (1), C has a large impact on the CEN end value i.e., steels that contain alloying elements other than carbon benefit from low carbon content.

[0047] Preferably, C is used in the range of 0.025 - 0.055%.

Silicon Si is used in the range of 0.01 - 0.8%

[0048] Si is effective as a deoxidizing or killing agent that can remove oxygen from the melt during a steelmaking process. Si alloying enhances strength by solid solution strengthening and increases austenite stability. Also, the presence of Si can stabilize residual austenite during welding. However, silicon content of higher than 0.8 % may unnecessarily increase carbon equivalent (CEN) value thereby decreasing weldability. Furthermore, surface quality of the hot-rolled steel may be deteriorated if Si is present in excess.

[0049] Preferably, Si is used in the range of 0.05 - 0.65 %, and more preferably 0.05 - 0.5 %.

Manganese Mn is used in the range of 1.1 - 1.8 %

[0050] Mn is an essential alloying element in improving both strength and low-temperature toughness. There is a rough relation between higher Mn content and higher strength level of the steel. Mn alloying enhances strength by solid solution strengthening, and increases strength by shifting phase transformations to lower temperatures.

[0051] However, alloying with Mn more than 1.8 % unnecessarily increases the CEN value thereby decreasing weldability. If the Mn content is too high, hardenability of the steel increases such that not only the heat-affect zone (HAZ) toughness is deteriorated, but also centerline segregation of the steel plate is promoted, and consequently the low-temperature toughness of the center of the steel plate is impaired.

[0052] Preferably, Mn is used in the range of 1.2 % to 1.7 %.

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

[0053] Al is an effective deoxidizing or killing agent that can remove oxygen from the melt during the steelmaking process, such as continuous casting. Al can also remove nitrogen by forming stable aluminum nitride (AlN) particles and provide grain refinement, which can further promote high toughness, especially at low temperatures. Furthermore, Al can stabilize residual austenite. However, excess Al may increase non-metallic inclusions thereby deteriorating cleanliness. Excess Al may promote formation of AlO line inclusions that may be detrimental to formability.

[0054] Preferably, Al is used in the range of 0.02 - 0.08 %. In some embodiments, a maximum Al limit may be 0.06 %, if for example, low aluminum oxide (AlO) content is preferred.

Niobium Nb is used in the range of 0.005 - 0.1 %

[0055] Nb forms carbides NbC and carbonitrides Nb(C,N). Nb is considered to be a major austenite grain refining element during re-austenitizing heat treatment and contributes to increased strength through precipitation strengthening during tempering.

[0056] Nb also contributes to the strengthening and toughening of steels in four ways during hot-rolling:

i) refining the austenite grain structure due to the pinning effect of Nb(C,N) during the reheating and soaking stage at high temperatures by introducing fine Nb(C, N) precipitates;
ii) retarding the recrystallization kinetics due to Nb solute drag effect at high temperatures (>1000°C) and preventing the occurrence of recrystallization due to strain induced precipitation at lower temperatures and thereby contributing to microstructural refinement;
iii) precipitation strengthening during and/or after γ-α transformation (or subsequent heat treatment); and
iv) retarding the phase transformation to lower temperatures giving rise to transformation hardening and toughening.

[0057] Yet, preferably, Nb addition should be limited to 0.08 % since further increase in Nb content does not have a pronounced effect on further increasing the strength and toughness. Excessive Nb can be harmful for HAZ toughness since Nb may promote the formation of coarse upper bainite structure by forming relatively unstable TiNbN or TiNb(C, N) precipitates.

[0058] Preferably, Nb is used in the range of 0.01 % to 0.06 %.

[0059] Copper Cu is used in the range of 0.6 - 1.5 %

[0060] Cu can promote low carbon bainitic structures and decrease polygonal ferrite fraction, cause solid solution strengthening and may contribute to precipitation strengthening. Cu may also increase austenite stability in the steel. Cu has also beneficial effects against hydrogen induced cracking (HIC) and sulfide stress corrosion cracking (SSCC).

[0061] When added in excessive amounts, Cu may deteriorate field weldability and the HAZ toughness. Furthermore, problems may arise in continuous casting with increased Cu alloying. Therefore, its upper limit is set to 1.5 %.

[0062] Preferably, Cu is used in the range of 0.6 - 1.2 %, and more preferably 0.7 - 1.0 %.

Chromium Cr is used in the range of 0.05 - 0.3 %

[0063] 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 enhances strength by solid solution strengthening and increases austenite stability by decreasing phase transformation temperatures during accelerated cooling.

[0064] However, if Cr is used in content above content 0.3 % the HAZ toughness as well as field weldability may be adversely affected.

[0065] Preferably, Cr is used in the range of 0.1 % to 0.25 %.

Nickel Ni is used in the range of 0.2 - 1.1 %

[0066] Ni is an alloying element that improves strength, low temperature toughness and HAZ toughness. Ni further prevents pitting corrosion, i.e. it reduces the number of initiation sites for stress corrosion cracking, especially when alloyed together with Cu.

[0067] Ni and Cu may be alloyed together to promote low temperature transformation products, and to provide solid solution strengthening. Also, alloying of Ni and Cu does not drastically influence the CEN value, as can be seen from equation (1).

[0068] If the steel has high amounts of Cu, Ni is needed in order to prevent surface defects from arising during hot rolling, especially when high temperatures (usually above 1100 °C) are used at the start of 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 %.

[0069] However, Ni contents of above 1.1 % would increase alloying costs too much without significant technical improvement. An excess of Ni may produce high viscosity iron oxide scales, which deteriorate surface quality of the steel product.

[0070] Ni is preferably used in the range of 0.3 - 1.1 %, and more preferably 0.55 -1.0 %.

Titanium Ti is used in an amount of ≤ 0.05 %

[0071] Ti is an optional alloying element. Ti may be added to bind free N that is harmful to toughness by forming stable titanium nitrides (TiN) together with niobium carbides (NbC) can efficiently prevent austenite grain growth in the reheating stage at high temperatures. TiN precipitates can further prevent grain coarsening in HAZ during welding thereby improving toughness.

[0072] However, if Ti content is too high, coarsening of TiN and precipitation hardening due to TiC formation may occur and the low-temperature toughness may be deteriorated. Therefore, it is necessary to restrict titanium to an amount of ≤ 0.05 %, preferably to an amount of ≤ 0.02 % and more preferably to an amount of ≤ 0.005 %.

[0073] However, Ti alloying is not mandatory as other alloying elements, such as Al, Nb and V, may also be alloyed to bind free nitrogen.

[0074] 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.

Molybdenum Mo is used in the range of 0.1 - 0.3%

[0075] Mo alloying is used to improve impact strength, low-temperature toughness and tempering resistance. The presence of Mo enhances strength by favoring formation of bainite, and via solid solution and precipitation strengthening. In general, lower Mo alloying is possible when manufacturing thinner steel products and increased Mo is preferred with increased thicknesses.

[0076] However, Mo is a relatively expensive alloying element. Excess Mo alloying may, for example, increase strength unnecessarily, especially with thinner plates. Thus, Mo may be used up to 0.3 %.

[0077] Preferably, Mo is used in the range of 0.15 - 0.25 %.

Vanadium V is used in the range of 0.01 - 0.2 %

[0078] V contributes to increased strength through precipitation strengthening during tempering. V is a strong carbide and nitride former, and V(C,N) may also form and its solubility in austenite is higher than that of Nb or Ti. Thus, V alloying has potential for precipitation strengthening, because large quantities of V are dissolved and available for precipitation during tempering.

[0079] V levels of 0.02 - 0.03 % is generally alloyed to increase bainite fraction. V levels of more than 0.03 % are alloyed to provide sufficient precipitation strengthening for increased tempering resistance. However, an addition exceeding 0.2% V has substantial negative effects on weldability.

[0080] Preferably, V is used in the range of 0.02 - 0.13%.

Boron B may be present in the range of 0.0 - 0.001 %

[0081] B is not intentionally alloyed in these steels, as it may promote excessive formation of upper bainite structures, which could lead to deterioration of impact toughness. However, B may be present as an impurity. Furthermore, low-temperature toughness and HAZ toughness are rapidly deteriorated when the B content exceeds 0.0005 %.

[0082] Preferably, B is present in the range of 0.0 - 0.00075%, and more preferably in an amount of ≤ 0.0005 %.

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

[0083] Ca addition during a steelmaking process may be used 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.

[0084] However, for example, if S level is below 0.001 then Ca addition is not necessary. At such low S levels, MnS do not have a significant impact on mechanical properties and thus it is not mandatory to add Ca in order to remove excess S.

[0085] Preferably, Ca may be 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. In this Ca range, i.e., 0.001 - 0.004 %, the cleanliness of the steel is at an optimal level.

[0086] 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.

[0087] Unavoidable impurities may comprise phosphor P, sulfur S, and nitrogen N. Their contents in terms of weight percentages 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 $N < 0.0100$ %, more preferably $N < 0.0060$ %.

[0088] Other inevitable impurities may include hydrogen $H < 0.0004$ %, preferably $H < 0.0002$ %, oxygen $O < 0.01$%, 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.

[0089] The total amount of inevitable impurities should preferably be limited to 0.3%, more preferably to 0.2%, even more preferably to 0.1%.

[0090] The invented steel is more tolerable, with respect to mechanical properties, to the changes occurring in the heat treatments, especially different cooling rates during quenching, of steel products having varying dimensions such as pipe fittings. This is achieved by effectively lowering the carbon content from traditional low carbon range, such as 0.10 - 0.30 wt.% C, to about ≤ 0.055 wt.% C, while increasing the alloying elements Cr, Mo, Cu and Ni to satisfy sufficient mechanical properties. The effect of alloying is balanced so that cracking resistance evaluated via CEN formula is kept at a low level.

Manufacturing of a hot rolled steel product

[0091] 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, such as vacuum degassing, 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 may promote brittle cracking and thus decrease impact toughness.

[0092] The hot-rolled steel product may be a strip or preferably a plate with a typical thickness of 4 to 100 mm, preferably 8 mm to 65 mm and more preferably 10 to 55 mm. Typically, a strip is coiled after hot rolling whereas a plate is not coiled after hot rolling.

[0093] A method for manufacturing the hot-rolled steel product disclosed herein will now be described with reference to Figure 2.

[0094] In a first step 101, a steel slab with the above defined composition is heated to a target temperature in the range of 950 °C - 1350 °C, preferably 1050 °C - 1300 °C and more preferably 1150 °C - 1250 °C, for a period of 30 min to 10 hours, preferably 2 hours to 6 hours.

[0095] In a second step 102, the heated steel slab is hot rolled in a plurality of hot rolling passes.

[0096] The plurality of hot-rolling passes are carried out at a temperature above and/or below the austenite non-recrystallization temperature.

[0097] After the plurality of hot-rolling passes, the hot rolled steel product is cooled in a cooling step 103, preferably in air, down to room temperature such that a required microstructure is achieved. In another embodiment the hot rolled steel product from step 102 is subjected to accelerated continuous cooling down to room temperature.

[0098] In a fourth optional step 104, the hot rolled and cooled steel product may be tempered in order to obtain lower strength if needed. This may be especially relevant when the steel plate is subjected to accelerated continuous cooling in the cooling step 103.

[0099] In the heating stage of step 101 the slabs are heated to a discharging temperature in the range of 950 °C to 1350 °C, preferably 1050 °C to 1300 °C, and more preferably 1150 °C to 1250 °C, for a period of 30 min to 10 hours, preferably 2 hours to 6 hours. Higher temperatures enable better Nb dissolution into austenite.

[0100] 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.

[0101] The hot rolling steps may be carried out above the austenite non-recrystallization temperature (Tnr) and/or below the Tnr temperature. Typically, at the start of rolling, the rolling temperature is above Tnr and at the end of hot rolling, the rolling temperature may be below Tnr. The rolling temperature at the end of hot rolling may, however, also be above Tnr.

[0102] The final rolling temperature (FRT) at final rolling pass is typically in the range of 800 °C to 990 °C, preferably in the range of 840 °C to 960 °C.

[0103] The hot-rolled steel product in the cooling step 103 is cooled to room temperature. Preferably cooling is conducted in air. Alternatively, cooling may be conducted as accelerated continuous cooling or as a combination of air cooling and accelerated continuous cooling. High cooling rates after hot rolling may lead to an unnecessary strength increase of the steel. In such a case, the hot rolled steel product may be subjected to an optional tempering step in order to reduce the strength levels to allow for better formability.

[0104] Optionally, the fourth step 104 of heat treatment such as tempering or annealing is performed to reduce strength levels. Preferably, tempering is performed at a temperature in the range of 640 °C to 740 °C for 0.5 hour to 1 hour. However, the tempering treatment parameters may be different as well.

[0105] The hot rolled steel product of the present invention is manufactured by hot rolling a slab into a steel product, such as a plate or a sheet or a coil. In the as-rolled condition the invented steel remains sufficiently soft so that subsequent manufacturing processes such as forming and welding operations are easier to carry out without faults such as cracking in bending or in the weld heat-affected zone. The inventive steel has typically a yield strength of 300-600 MPa after hot rolling. The inventive steel has typically predominantly ferritic microstructure in the as-rolled condition as illustrated in Figure 1a.

[0106] Generally, during the 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.

[0107] 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.

[0108] 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.

[0109] 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.

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.

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 lower bainite, degenerated lower bainite, and upper bainite.

[0110] Some of the above microstructures typically contain martensite-austenite constituents. The area fractions of MA-constituents may be in some cases determined separately as well. In such cases, the combined area fraction of MA-constituents in the overall microstructure may, in terms of volume pecentages, be $\leq 3\%$, or preferably $\leq 2\ \%$.

[0111] The present invention aims at further developing the hot-rolled steel product and the manufacturing method thereof such that a new hot rolled steel product with uncompromised mechanical properties as well as economic advantages can be achieved.

[0112] The microstructure according to the present invention after hot rolling comprises, in terms of volume percentages, polygonal ferrite (PF): $50 \leq PF \leq 90$; quasi-polygonal ferrite (QPF): $5 \leq QPF \leq 35$, preferably $10 \leq QPF \leq 30$; granular bainite (GB): $1 \leq GB \leq 30$ and carbon rich phases, CRP: $1 \leq CRP \leq 20$, preferably $1 \leq CRP \leq 15$, more preferably $1 \leq CRP \leq 10$. The above microstructure relates to a steel product, which has been cooled slowly after hot rolling. If the steel would have been subjected to accelerated continuous cooling and tempering after hot rolling, the resulting microstructure then becomes tempered.

[0113] Volume fractions of phase constituents were determined from planar sections by using Scanning Electron Microscopy, SEM, micrographs, and both point counting methodology and image analysis. 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 carbon rich phases, respectively. For the hot rolled samples, the carbon rich phases comprise the sum of each individual sub structure (i.e. MA-constituents, lath bainite and pearlite). Finally, the fraction of each constituent was obtained by dividing the number of points in the given phase constituent by the total number of grid points.

[0114] The purpose of the hot rolled steel product according to the invention is to provide a relatively soft starting microstructure with reduced strength in order to enable easier manufacturing of, for example, pipe fittings. The above microstructure enables improved formability (bending, cold and hot forming, welding, cutting, etc.) of the steel material before subsequent heat treatments, such as quenching and tempering (Q&T). When slow cooling after hot rolling is applied as discussed above, the need for tempering after hot rolling becomes unnecessary.

Manufacturing of a pipe fitting

[0115] The steel of the invention and manufactured as described above may be used for example in manufacturing of pipe fittings. In general, during manufacturing of a pipe fitting, the steel may be formed in many ways, such as hot forming or preferably cold forming, welding and cutting, etc. The process may also include several heat treatments and typically at least one quenching and tempering heat treatment at the end of manufacturing.

[0116] In an embodiment where Q&T heat treatment is carried out to the pipe fitting formed from the steel of the invention, austenitizing is always carried out at 800 °C to 1000 °C for 5 minutes to 5 hours, and preferably at 880 to 940°C for 1 to 2 hours, wherein the holding time starts when the steel component has reached the target temperature. Holding time also depends on the thickness of the steel. A general rule of 1 hour of holding in furnace per 1 inch or 25.4 mm of thickness may be applied. Sometimes holding times of less than 5 minutes may be used, such as with induction heating. In such cases, the holding temperature should be higher, preferably 880-1000 °C, to ensure full austenitization.

[0117] The purpose of the austenization step is to ensure homogenous austenitic microstructure for subsequent processing. Heat treatment below this temperature range, or shorter holding times, may result in partial austenitization, whereas heat treatment above this temperature range, or longer heat treatment, leads to coarse and uneven microstructure. Both lead to inferior mechanical properties.

[0118] Following the austenitization heat treatment, the steel component is cooled, preferably immersion-quenched, in a suitable medium, such as a clean water bath, so that the microstructure achieved at room temperature is predominantly granular bainitic, having little or no brittle secondary phases like martensitic-austenitic microconstituents, coarse pearlite, or aligned coarse cementite phases. In the invented steel, this type of microstructure is achieved over various cooling rates of resulting from quenching to air, oil or water. Generally, quenching to air results in the slowest cooling rate, and quenching to water results in the fastest cooling rate, while oil quenching results in an intermediate cooling rate.

[0119] Finally, the steel component is subsequently tempered in the range 540 °C to 690 °C for 5 minutes to 5 hours, preferably 580 to 650°C for 1 to 2 hours, wherein the holding time starts when the steel component has reached the target temperature, and cooled to room temperature. Holding time also depends on the thickness of the steel component. A general rule of 1 hour of holding in furnace per 1 inch of thickness may be applied. Sometimes holding times of less than 5 minutes may be used, such as with induction heating. In such cases, the holding temperature should be higher, preferably 600 - 690 °C.

[0120] In the forming of a pipe fitting, the hot rolled steel product from step 103 or 104, is first formed into a pipe fitting in a forming step 105. During the following Q&T treatment, the steel is first annealed in an annealing step 106 to a temperature where the microstructure is fully austenitic. During the subsequent quenching step 107, a microstructure comprising quasi-polygonal ferrite, granular bainite, lath bainite, and possibly small amounts of polygonal ferrite, cementite and MA constituents is formed. The final microstructure and phase fractions after quenching depend on the cooling rate and composition of the steel. In the subsequent tempering step 108, the steel is tempered at a tempering temperature for a given time. During the tempering step, the microstructure is tempered, and (e.g. V, Nb, Mo) precipitation occurs. Thus, the resulting microstructure after the Q&T treatment is a tempered, mainly bainitic microstructure strengthened via precipitation strengthening. In the final cooling step 109 the tempered steel product is cooled to room temperature.

[0121] In the tempering stage, the final strength of the steel product level is attained. Tempering outside the temperature and time ranges mentioned above may lead to yield strength levels outside the target range of 550-800 MPa. The inventive steel product has typically a yield strength of 550-800 MPa after quenched and tempered (Q&T) processing combined with an impact toughness of at least 100 J/cm^2 measured at -46°C, preferably at least 150 J/cm^2, and more preferably 200 J/cm^2.

[0122] 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 together with fine-grained quasi-polygonal ferrite lead to the formation of substantial amounts of high angle boundaries between the interfaces of granular bainitic ferrite and quasi-polygonal ferrite. Thus, for the inventive steels in the Q&T condition, generally a bainitic microstructure is not enough. It is important that the main bainitic phase of the inventive steels in the Q&T condition is granular bainite.

[0123] The presence of martensite is not allowed as one of the main phases in the inventive steels, especially in the Q&T condition. If martensite is present, it should be restricted to the MA constituents and the size of the MA constituents should be as small as possible to promote good impact toughness properties. Phase fraction of polygonal ferrite should also be kept as small as possible in the Q&T condition. The strength of polygonal ferrite is low when combined with a bainitic phase. Therefore, large fractions of polygonal ferrite would lead to decreased strength of the steel. In addition, MA constituents in polygonal ferrite typically form at the grain boundaries of the polygonal ferrite and are typically larger in size thus deteriorating impact toughness.

[0124] The granular bainite dominated 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, for the most part, to the granular bainitic part of the microstructure. Low C content further reduces the size of MA constituents in the steel according to the present invention.

[0125] If a 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 dominated, fine microstructures exhibit improved impact toughness.

[0126] The combination of correct alloying (especially Cu and Ni together with Nb, V and Mo) combined with low C levels and mainly granular bainitic matrix gives the steel product great strength combined with outstanding impact toughness and tolerance to different cooling rates during Q&T heat treatment.

[0127] 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 A-Z

[0128] Examples from the inventive steels A-D and reference steels X and Z were prepared with chemical compositions according to Table 1. During the preparation, every alloy was melted, cast and hot-rolled to various thicknesses. A majority of the example steels were then subsequently Q&T processed according to previously described processing parameters to simulate the heat treatment practices of pipe fitting manufacturing.

Alloying of hot rolled steel

[0129] Table 1 illustrates the chemical compositions for the inventive steels according to Examples A-D as well as for the reference examples X and Z. It can be seen from Table 1, that the reference examples have increased C and generally decreased Cu and Ni alloying compared to the inventive examples. From Table 1, it is seen that the inventive example steels have very low carbon contents and lowest calculated CEN. Unlike in the reference alloys, the inventive alloys combine Cr, Mo, Cu and Ni alloying with low C contents.

[0130] The reference alloy Z has a high C content and additional alloying of Cr and Mo, but the resulting CEN value is still high. Furthermore, the reference alloy X has medium C content level with high Ni content, minor Cu addition and relatively low CEN.

Processing and mechanical properties of the hot rolled steel

[0131] Table 2 illustrates the processing parameters and mechanical properties for the inventive steels as well as for the reference example in the hot rolled condition. Steel slabs were first annealed to fully austenitize the slab followed by hot rolling wherein the last pass was conducted at the final rolling temperature (FRT) shown in the table. Finally, the hot rolled plate was cooled to room temperature in air, except for inventive example B2, for which an insulated cooling method was used. For the full-scale experiments, a batch of 105 tons was melted, cast and hot rolled. For the laboratory experiments, a smaller batch of 60 kg was melted, cast and hot rolled.

[0132] For the inventive examples, yield strengths range from 376 MPa to 503 MPa and tensile strengths range from 545 MPa to 703 MPa. For the full-scale inventive examples impact toughness levels of 166-358 J/cm^2 were measured. For the reference example, yield strength is 474 MPa and tensile strength is 617 MPa.

Processing and mechanical properties of the Q&T heat treated steel

[0133] Table 3 lists Q&T heat treatment parameters and the resulting mechanical properties and shows the effects of various heat treatments on the mechanical properties of the example and reference steels. All the samples were processed similarly with the biggest difference being in cooling rate resulting from quenching to different liquid quenching media. The results demonstrate that only the inventive steels satisfy simultaneously the yield strength, tensile strength, and toughness criteria over the range of cooling rates (CR) experienced in Q&T process.

[0134] In both the laboratory and full-scale experiments, steel coupons were heat treated and their temperature history was recorded via thermocouples. Austenitization and tempering heat treatments were carried out in open air laboratory furnaces. Several quenching media were utilized to provide a range of cooling rates for the quenching condition (i.e. water, air, and oil). It is worth noting that also the thickness of the steel sample had an effect on the cooling rate. Generally, the thicker the steel sample, the lower the resulting cooling rate. Furthermore, cooling rate increases from air to oil to water, with water providing the highest cooling rate for the quenching media used.

[0135] The mechanical properties of both the hot rolled samples and the Q&T heat treated samples were tested according to ASTM A370 for test pieces. For the full scale examples, the test pieces were cut perpendicular to the rolling direction. For the laboratory examples, the test pieces were cut parallel to the rolling direction. All tensile tests were carried out at room temperature and each individual test is reported.

[0136] The Charpy V impact toughness values were evaluated at 0°C for the hot rolled condition and -46°C for the Q&T condition according to SFS-EN ISO 148-1:2016 standard except for the full scale specimens, which were tested according to ASTM E23. The results show an average of three test pieces, which were cut perpendicular to the rolling direction.

[0137] The inventive alloys have a very robust performance to the changes in the cooling rate. For the inventive examples yield strengths of 562-692 MPa, tensile strengths of 657-800 MPa and impact toughness values of 113-370 J/cm^2 were measured. The results show that despite varying cooling rates, all mechanical properties are on a great level. Furthermore, it is noticeable that even with low carbon contents of 0.031-0.044 %, high yield strengths of above 550 MPa are achieved.

[0138] Conversely, the reference alloys struggle to meet the criteria when there are changes in the cooling rate. For the reference examples yield strengths of 544-869 MPa, tensile strengths of 714-904 MPa and impact toughness values of 19-71 J/cm^2 were measured.

[0139] Reference alloy X has inferior yield strength in the air quenched condition (544 MPa) and excessive yield strength at the water quenched condition (869 MPa) indicating that the yield strength of the steel varies greatly with cooling rate, thus making the alloy not robust with regard to cooling rate. Furthermore, impact toughness is insufficient regardless of the cooling rate. The results also show for the reference alloy X that the low CEN value alone (< 0.40) is not enough to provide sufficient toughness.

[0140] The reference alloy Z meets strength requirements at the tested cooling rates resulting from air and oil quenching, but impact toughness of the alloy is insufficiently low at both cooling rates and in fact impact toughness generally decreases with increasing cooling rate for alloy Z.

Microstructure

[0141] 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. Finally, specimens were etched with 2% Nital.

[0142] 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, lath-like bainite, martensite-austenite constituents and pearlite, 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.

[0143] Phase fractions of the inventive steels no. 1, 18, 19 and 22 are shown in Tables 4 and 5 in different heat treatment conditions, as an example. The phase fractions in Tables 4 and 5 were determined with point counting methodology.

[0144] For the hot rolled samples, it can be seen that the dominant microstructure is polygonal ferrite with small fractions of quasi-polygonal ferrite and granular bainite. In addition, coarse carbon rich phases containing different fractions of MA-constituents, lath bainite and pearlite, were also identified. The carbon rich phases refer to carbon rich areas occurring in combination with polygonal ferrite dominated microstructures. For the hot rolled samples, the carbon rich phases comprise the sum of each individual sub structure (i.e. MA-constituents, lath bainite and pearlite). The different fractions of MA-constituents, lath bainite and pearlite were not determined separately, as their mutual fractions are not essential for the inventive steel in the hot rolled condition.

[0145] For the Q&T heat treated samples, it can be seen that the dominant microstructure is granular bainite with small fractions of quasi-polygonal ferrite and lath bainite. For the Q&T heat treated samples, carbon rich phases have not been determined separately since they are counted to be part of the other phases. For example, granular bainite typically contains, by definition, some fraction of MA-constituents but the fraction of the MA-constituents in granular bainite was not separately determined.

[0146] Figure 1a illustrates the microstructure of Example steel 1 in the hot rolled condition and Figure 1b illustrates the microstructure of Example steel 1 in the Q&T condition. In Figures 1a and 1b, denotations of PF, QPF and GB refer to the corresponding phases of polygonal ferrite (PF), quasi-polygonal ferrite (QPF) granular bainite (GB) and lath bainite (LB).

[0147] It is to be understood that the present invention is not limited to the embodiments described above; rather, the skilled person will recognize that many changes and modifications may be made within the scope of the appended claims.

Table 1

Steel	C	Si	Mn	P	S	Al	Nb	V	Cu	Cr	Ni	Mo	Ti	B	Ca	CEN	Remark
A	0.035	0.510	1.600	<0.01	0.0032	0.060	0.030	0.060	0.780	0.230	0.940	0.200	<0.001	<0.0005	<0.004	0.29	Inv.
B	0.031	0.650	1.410	<0.01	0.0032	0.060	0.040	0.030	0.810	0.190	0.840	0.200	<0.001	<0.0005	<0.004	0.26	Inv.
C	0.039	0.444	1.490	0.006	0.0011	0.041	0.031	0.062	0.773	0.204	0.900	0.192	0.003	0.0005	0.002	0.27	Inv.
D	0.044	0.500	1.680	<0.01	0.0036	0.060	0.040	0.100	0.950	0.220	0.880	0.210	<0.001	<0.0005	<0.004	0.32	Inv.
X	0.086	0.530	1.580	<0.01	0.0038	0.040	0.040	0.100	0.290	0.220	0.910	0.210	<0.001	<0.0005	<0.004	0.37	Ref.
Z	0.142	0.450	1.550	0.012	0.0012	0.040	0.040	0.100	0.010	0.220	0.300	0.200	0.006	0.0005	<0.004	0.48	Ref.

Table 2

Materials					Hot-rolling parameters				Mechanical properties		
Alloy		Sample	Slab thickness (mm)	Final thickness (mm)	Rolling method	Annealing Temperature (°C)	Finish rolling temperature (°C)	Cooling method	YS (MPa)	TS (MPa)	CVN (J/cm^2)
Inventive	A	5	110	35	Laboratory	1140	950	air	502	733	-
	A	6	110	35	Laboratory	1140	950	air	503	729	
	B	10	65	16	Laboratory	1200	950	Insulated cooling	376	545	-
	B	11	65	16	Laboratory	1200	950	Insulated cooling	383	554	
	C	13	210	13	Full scale	1230	930	air	457	676	310
	C	15	210	20	Full scale	1230	930	air	471	678	285
	C	17	210	30	Full scale	1230	880	air	453	677	305
	C	19	210	35	Full scale	1230	880	air	455	668	288
	C	21	210	40	Full scale	1230	880	air	487	666	358
	C	23	210	45	Full scale	1230	880	air	482	661	166

Table 3

Materials						Heat treatments					Mechanical properties		
Alloy		Sample	THK (mm)	Rolling method	Condition	Temp 1 (°C)	Time 1 (min)	Cooling method	Temp 2 (°C)	Time 2 (min)	YS (MPa)	TS (MPa)	CVN (J/cm^2)
Inventive	A	1	13	Laboratory	Q & T	925	33	oil	630	33	577	679	199
	A	2	13	Laboratory	Q & T	925	33	oil	630	33	575	674	
	A	3	35	Laboratory	Q & T	925	140	water	630	140	663	742	155
	A	4	35	Laboratory	Q & T	925	140	water	630	140	664	744	
	B	7	13	Laboratory	Q & T	925	33	water	630	33	645	718	210
	B	8	13	Laboratory	Q & T	925	33	oil	630	33	562	657	239
	B	9	13	Laboratory	Q & T	925	33	oil	630	33	562	658	
	C	12	13	Full scale	Q & T	925	33	water	630	33	620	704	347
	C	14	20	Full scale	Q & T	925	50	water	630	50	617	701	284
	C	16	30	Full scale	Q & T	925	75	water	630	75	615	698	326
	C	18	35	Full scale	Q & T	925	88	water	630	88	591	701	348
	C	18-2	35	Full scale	Q & T	925	83	oil	630	83	590	675	301
	C	20	40	Full scale	Q & T	925	100	water	630	100	604	685	370
	C	22	45	Full scale	Q & T	925	112	water	630	112	601	686	354
	C	22-2	45	Full scale	Q & T	925	106	oil	630	106	581	668	318
	D	24	13	Laboratory	Q & T	925	33	air	630	33	584	741	115
	D	25	13	Laboratory	Q & T	925	33	air	630	33	577	741	
	D	26	13	Laboratory	Q & T	925	33	oil	630	33	660	769	113
	D	27	13	Laboratory	Q & T	925	33	oil	630	33	692	800	

Ref	X	30	13	Laboratory	Q & T	925	33	air	630	33	544	714	68
	X	31	13	Laboratory	Q & T	925	33	air	630	33	546	722	
	X	32	13	Laboratory	Q & T	925	33	oil	630	33	673	787	71
	X	33	13	Laboratory	Q & T	925	33	oil	630	33	675	783	
	X	34	13	Laboratory	Q & T	925	33	water	630	33	852	904	40
	X	35	13	Laboratory	Q & T	925	33	water	630	33	869	904	
	Z	40	35	Full scale	Q & T	925	84	air	630	84	576	706	19
	Z	41	35	Full scale	Q & T	925	84	air	630	84	570	708	
	Z	42	35	Full scale	Q & T	925	84	oil	630	84	702	800	21
	Z	43	35	Full scale	Q & T	925	84	oil	630	84	701	800	

Table 4

Alloy. sample	PF %	QPF %	GB%	C-rich phases %	Remarks
C 19	63	16	14	7	Full scale. as rolled

Table 5

Alloy. sample	PF %	QPF %	GB%	LB %	Remarks
A 1	1	15	80	4	Laboratory. Q&T
C 18-2	1	20	68	11	Full scale. Q&T
C 22	1	11	82	6	Full scale. Q&T

Claims

1. A steel product comprising a composition consisting of, in terms of weight percentages, wt. %:

C	0.025 - 0.065, preferably 0.025 - 0.055
Si	0.01 - 0.8, preferably 0.05 - 0.65
Mn	1.1 - 1.8, preferably 1.2 - 1.7
Al	0.005 - 0.12, preferably 0.02 - 0.08
Nb	0.005 - 0.1, preferably 0.01 - 0.06
Cu	0.6 - 1.5, preferably 0.6 - 1.2, more preferably 0.7 - 1.0
Cr	0.05 - 0.30, preferably 0.1 - 0.25
Ni	0.2 - 1.1, preferably 0.3 - 1.1, more preferably 0.55 - 1.0
Ti	≤ 0.05, preferably ≤ 0.02, more preferably ≤ 0.005
Mo	0.1 - 0.3, preferably 0.15 - 0.25
V	0.01 - 0.2, preferably 0.02 - 0.13
B	0.0 - 0.001, preferably 0.0 - 0.00075, more preferably ≤ 0.0005
P	≤ 0.02, preferably ≤ 0.015, more preferably ≤ 0.01
S	≤ 0.015, preferably ≤ 0.01, more preferably ≤ 0.005
Ca	< 0.01, preferably < 0.004

remainder Fe and inevitable impurities, wherein a carbon equivalent CEN value for the steel product is $\mathrm{CEN} < 0.41$, preferably $\mathrm{CEN} < 0.38$, more preferably $\mathrm{CEN} < 0.35$, and wherein the carbon equivalent CEN value is calculated from the composition, in wt.%, by using the following formula:

$$\mathrm{CEN}=\mathrm{C}+(0.75+0.25*\tanh(20*(\mathrm{C}-0.12)))*(\mathrm{Si}/24+\mathrm{Mn}/6+\mathrm{Cu}/15+\mathrm{Ni}/20+(\mathrm{Cr}+\mathrm{Mo}+\mathrm{Nb}+\mathrm{V})/5+5\mathrm{B}).$$

2. The steel product of claim 1, wherein the composition consists of, in terms of wt. %:

C	0.025 - 0.055
Si	0.05 - 0.65
Mn	1.2 - 1.7
Al	0.02 - 0.08
Nb	0.01 - 0.06
Cu	0.7 - 1.0
Cr	0.1 - 0.25
Ni	0.55 - 1.0
Ti	≤ 0.005
Mo	0.15 - 0.25
V	0.02 - 0.13
B	≤ 0.0005
P	≤ 0.01
S	≤ 0.005

(continued)

Ca	< 0.004

remainder Fe and inevitable impurities, wherein the carbon equivalent CEN value for the steel product is CEN < 0.35.

3. The steel product according any one of claims 1-2, wherein the steel product has a C/Mn ratio of, in wt.%: C/Mn < 0.041 and preferably C/Mn < 0.034.

4. The steel product according to any one of claims 1-3 having the following microstructure in volume percentages, vol. %:

Polygonal ferrite. PF: $50 \leq PF \leq 90$,
Quasipolygonal ferrite. QPF: $5 \leq QPF \leq 35$, preferably $10 \leq QPF \leq 30$, wherein
PF + QPF: $55 \leq PF + QPF \leq 95$,
Granular bainite. GB: $1 \leq GB \leq 30$, and
Carbon rich phases. CRP: $1 \leq CRP \leq 20$, preferably $1 \leq CRP \leq 15$, more preferably $1 \leq CRP \leq 10$.

5. The steel product according any one of the preceding claims, having a yield strength (Rp0.2) in the range of 300-600 MPa, preferably 350-550 MPa. and more preferably 370-520 MPa.

6. The steel product according any one of the preceding claims having an ultimate tensile strength (Rm) in the range of 420-850 MPa, preferably 490-800 MPa, and more preferably 530-775 MPa.

7. The steel product according to any one of the preceding claims, wherein the steel product is a hot rolled steel plate having a thickness in the range of 4 mm to 100 mm. preferably 8 mm to 65 mm, more preferably 10 mm to 55 mm.

8. The steel product according to any one of claims 1-3 having the following microstructure in volume percentages, vol. %:

Polygonal ferrite (PF): $0 \leq PF \leq 10$, preferably $0 \leq PF \leq 5$, more preferably $0 \leq PF \leq 3$,
Quasipolygonal ferrite (QPF): $1 \leq QPF \leq 35$, preferably $1 \leq QPF \leq 25$.
Granular bainite (GB): $50 \leq GB \leq 99$, preferably $60 \leq GB \leq 95$, more preferably $65 \leq GB \leq 90$, and
Lath bainite (LB): $0 \leq LB \leq 20$, preferably $2 \leq LB \leq 20$

9. The steel product according to claim 8 having
a yield strength (RP0.2) in the range of 550-800 MPa, preferably 550-750 MPa, and more preferably 550-700 MPa.

10. The steel product according to claim 8 or 9 having
an ultimate tensile strength (Rm) in the range of 580-900 MPa, preferably 600-850 MPa, and more preferably 640-820 MPa.

11. The steel product according to any one of claims 8-10 having
a Charpy-V impact toughness of at least 100 J/cm2, preferably at least 150 J/cm2 at a temperature of -46 °C when measured from 2 mm of a surface of the steel product.

12. The steel product of any one of claims 8-11 wherein the steel product is a pipe fitting.

13. A method for manufacturing a steel product comprising the following steps of

- heating a steel slab having the composition according to claim 1 to a temperature in the range of 950 °C to 1350 °C;
- hot rolling the heated steel slab in a plurality of hot rolling passes to produce a hot rolled steel product, wherein

    i) the steel slab is subjected to a plurality of hot rolling passes at a temperature above and/or below an austenite non-recrystallization temperature in order to form a strip or a plate, wherein the final rolling temperature is above 850 °C, and
    ii) the steel strip or plate from step (i) is cooled, preferably in air, down to room temperature.

14. The method of according to claim 13, further comprising the steps of:

- forming the steel strip or plate into a steel product, such as a pipe fitting,
- subjecting the formed steel product from the previous step to at least one austenitizing heat treatment at a temperature within the temperature range of 800 °C to 1000 °C for a time period of 5 minutes to 5 hours,
- cooling the heated steel product from the previous step, preferably by immersion-quenching in a suitable liquid medium,
- subjecting the cooled steel product from the previous step to at least one tempering heat treatment at a temperature within the range of 540 °C to 690 °C for a time period of 5 minutes to 5 hours, and subsequently
- cooling the tempered steel product to room temperature.

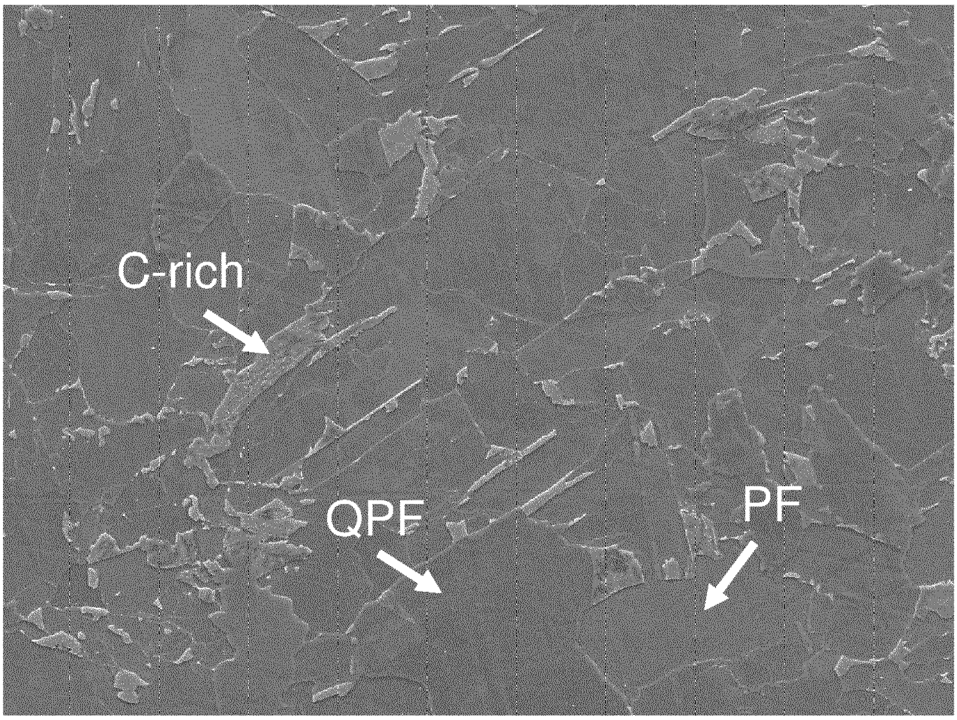

Fig. 1a

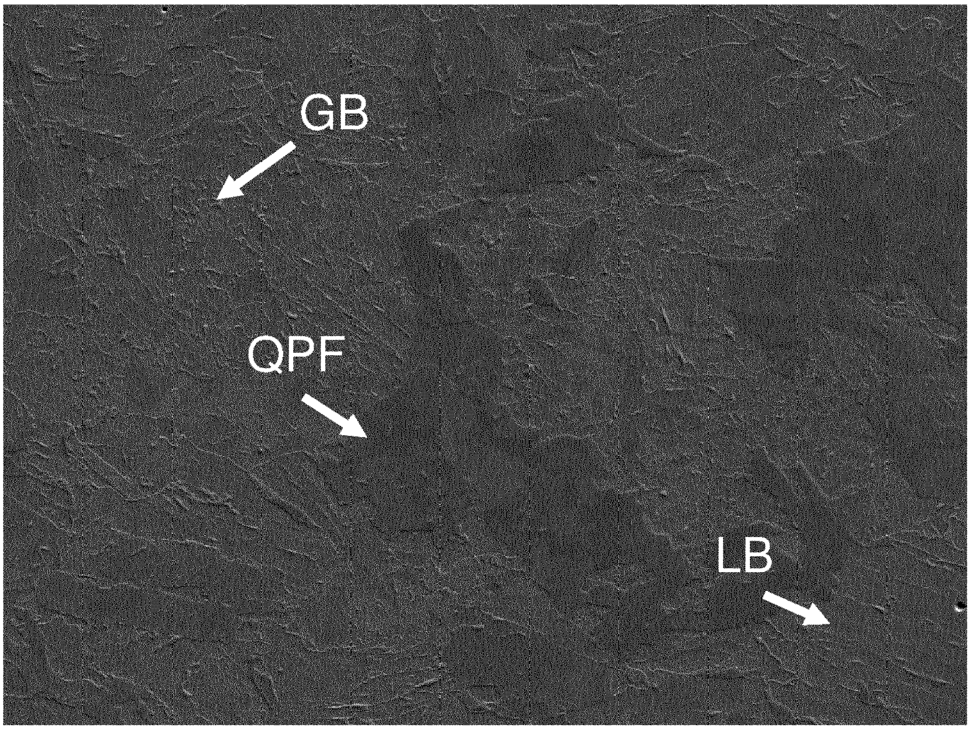

Fig. 1b

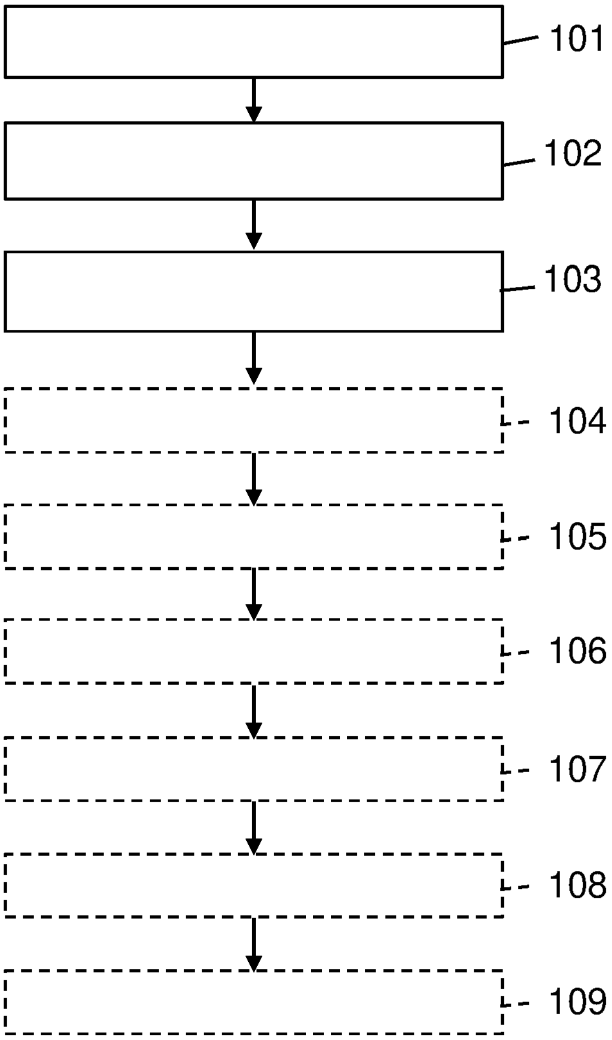

Fig. 2

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EUROPEAN SEARCH REPORT

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
The Hague	10 October 2023	Vlassi, Eleni

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Place of search	Date of completion of the search	Examiner
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