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- **DUPREZ, Lode**
B-9160 Lockeren (BE)
- **MINAMBRES, Javier**
Leioa 48940 Bizkaia (ES)
- **HERNANDEZ, Jacques**
F-13310 Saint Martin de Crau (FR)

(71) Applicant: **ArcelorMittal France**
93200 Saint Denis (FR)

(74) Representative: **Plaisant, Sophie Marie**
ArcelorMittal France
ArcelorMittal R&D
Intellectual Property
1-5 rue Luigi Cherubini
93200 Saint-Denis (FR)

(72) Inventors:
• **ANTONISSEN, Joachim**
B-9971 Lembeke (BE)

(54) **Hot rolled steel and enamelled steel sheet free of fish scale defect**

(57) The invention deals with a hot rolled and enamelled steel sheet free of fish scale defects, comprising, in % by weight:

C: 0.02 - 0.1 %
Mn : 0.3 - 1%
Al : 0.1 - - 0.4 %
Si : 0 - 0.3%
B : 0,002 - 0.01%
Nb: 0 - 0.1%
V : 0 - 0.08%
Ni : 0 - 0,35 %
Cu : 0 - 0,25 %
N: < 0.04 %
P : < 0,03 %
S : < 0.03 %

the balance being iron and unavoidable impurities due to smelting, said steel sheet having a thickness T_h and having being coiled at a temperature T_{coiling} , after being hot rolled, said composition comprising moreover a boron content B above or equal to B_{min} defined according to the following relationship :

$$B_{\text{min}} (\text{ppm}) = 60 - (12 \times T_h(\text{mm})) + (T_{\text{coiling}}(^{\circ}\text{C}) / 18)$$

and with a manufacturing process of said sheet.

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Description

[0001] The present invention deals with a hot-rolled steel sheet, which can be used for industrial silos and tanks, shower tubs and other sanitary wares, and for building facades and claddings manufacture, without being limited to such use.

[0002] The manufacturers of those products already use hot rolled or cold-rolled enamelled steel sheet in their process, because of structural, hygienic and endurance requirements. However, the hot rolled steel grades employed for such use have to go through expensive and environmentally unfriendly surface pre-treatment in order to make it suitable for enamelling and especially two side enamelling.

[0003] The enamelling operation consists in depositing an enamel layer either in liquid or in powdery form and in firing this layer around 830°C. This enamel layer must adhere firmly to the steel sheet and present a good surface appearance.

[0004] In particular, if the pre-treatment of the hot rolled steel sheet is not performed properly, a defect called "fish scale" may appear which consists in "fish scale" like cracks all over the enamel coating.

[0005] This defect is due to the accumulation of hydrogen and the resulting pressure build-up at the interface between steel and enamel during the cooling down phase of the firing operation. During firing, the hydrogen solubility in the steel increases and water present in the furnace atmosphere dissolves in the enamel and migrates to the enamel / steel interface, where it decomposes into hydrogen and oxygen atoms. During subsequent cooling, the hydrogen solubility in steel decreases and the enamel solidifies. Due to the decreasing solubility, the excess hydrogen migrates to the enamel / steel interface without being able to escape as the enamel has turned solid. Besides the hydrogen introduced through the water contained in the furnace atmosphere, further hydrogen pick-up can arise from the water present in the enamel formulation as well as from the oxido-reduction reactions between enamel and steel.

[0006] The hydrogen pressure consequently increases at the interface and finally the enamel cracks creating fish scales.

[0007] The purpose of the invention therefore is to offer an improved hot rolled steel material, suitable for enamelling and especially two-side enamelling without environmentally unfriendly pre-treatment, generating no fish scales defect after enamelling, with a good adherence of the enamel layer on the steel sheet, said steel sheet presenting at the same time the required mechanical characteristics.

[0008] To solve this problem, a first object of the invention is a hot rolled and enamelled steel sheet free of fish scale defects, comprising, in % by weight:

C: 0.02 - 0.1 %
 Mn : 0.3 - 1 %
 Al: 0.1 - 0.4 %
 Si : 0 - 0.3%
 B: 0,002 - 0.01 %
 Nb: 0 - 0.1%
 V : 0 - 0.08%
 Ni : 0 - 0,35 %
 Cu : 0 - 0,25 %
 N: < 0.04 %
 P : < 0,03 %
 S : < 0.03 %

the balance being iron and unavoidable impurities due to smelting, said steel sheet having a thickness Th and having being coiled at a temperature T_{coiling}, after being hot rolled, said composition comprising moreover a boron content B above or equal to Bmin defined according to the following relationship :

$$B_{min} \text{ (ppm)} = 60 - (12 \times Th(\text{mm})) + (T_{coiling}(\text{°C}) / 18)$$

[0009] In a preferred embodiment, the hot rolled and enamelled steel sheet according to the invention comprises, in % by weight:

C : 0.04 - 0.08 %
 Mn : 0.6 - 1 %
 Al : 0.1 - 0.4 %
 Si : 0,1 - 0.3%

Nb: 0.03 - 0.1%
V: 0.02 - 0.06%
Ni : 0 - 0,35 %
Cu : 0 - 0,25 %
N: < 0.04 %
P : < 0,03 %
S : < 0.03 %
B ≥ Bmin

[0010] In another preferred embodiment, the hot rolled and enamelled steel sheet according to the invention, comprises, in % by weight:

C : 0.04 - 0.08 %
Mn : 0.3 - 0.7 %
Al : 0.1 - 0.4 %
Si : 0 - 0.1%
Ni : 0 - 0,35 %
Cu : 0 - 0,25 %
N : < 0.04 %
P : < 0,03 %
S : < 0.03 %
B ≥ Bmin

[0011] The hot rolled and enamelled steel sheet according to the invention may present a thickness between 1.3 and 3 mm and a yield strength under 320 MPa and a tensile strength above 290 MPa, for use as a shower tub.

[0012] It may also present a thickness between 2 and 10 mm and a yield strength above 320 MPa and a tensile strength above 400 MPa, for use as tank or an industrial silo.

[0013] It can also present a thickness between 1.5 and 3 mm and a yield strength above 275 MPa and a tensile strength above 430 MPa, for use as a building cladding or facade.

[0014] Another object of the invention consists in a method of manufacturing of a hot rolled and enamelled steel sheet according to the invention, consisting in:

- smelting a steel which composition is according to the invention,
- casting said steel composition into a slab and hot rolling said slab into a hot rolled steel sheet presenting a thickness under 10 mm,
- coiling said hot rolled steel sheet at a temperature comprised between 380 and 650°C,
- degreasing and/or shot blasting said hot rolled steel sheet,
- depositing at least an enamel layer under liquid or powdery form on at least one side of said hot rolled sheet,
- optionally drying said enamel layer and
- firing the said enamel layer.

[0015] In a preferred embodiment, the enamelling is performed on both sides of said hot rolled sheet.

[0016] The present inventors discovered that the presence of free boron was essential in avoiding fish scale defect. This free boron can be regulated by alloying the steel composition with enough aluminium and generating a precipitation of AlN precipitates, protecting the boron from precipitating with nitrogen.

[0017] Without willing to be bound by any theory, it is believed that the free boron can act as hydrogen trap during enamelling forming boron hydrides and preventing hydrogen to migrate to the coating surface.

[0018] Other characteristics and advantages of the invention will appear through the detailed description which will follow, only given as a mere example.

[0019] The steel composition comprises carbon in an amount of 0.02 to 0.1 %. This element improves the mechanical characteristics of the steel but must be limited so as not to impair the weldability of the steel. Moreover, a higher level of carbon would jeopardize the deep-drawing ability of the steel, which is especially required for the sanitary wares application. Finally elevated carbon contents are known to cause pin defects on enameled parts due to CO₂ production.

[0020] The steel composition comprises manganese in an amount of 0.3 to 1 % and preferably of 0.55 to 1%. This element improves the mechanical characteristics of the steel but must be limited so as not to impair the weldability of the steel or the deep-drawing properties of the steel sheet. Additionally, large amounts of manganese are known to affect negatively the enamel adherence.

[0021] The steel composition comprises aluminium in an amount of 0.1 to 0.4 % and preferably of 0.12 to 0.3%. This

element is used as a deoxidizing element during smelting. In the present invention, it plays an essential role in protecting boron from the nitrogen, by forming precipitates of AlN with this element.

[0022] The steel composition may comprise silicon in an amount of up to 0.3 %, which acts as a deoxidizing element in the same way as aluminium. This element also contributes to the mechanical characteristics of the steel.

[0023] The steel composition comprises boron, preferably in an amount of 0.002 to 0.01 %. As explained above, this essential element act as a hydrogen trap provided it is present under un-combined form (also called free boron). The total amount of boron must be above or equal to B_{min} defined by the following relationship:

$$B_{min} \text{ (ppm)} = 60 - (12 \times Th(\text{mm})) + (T_{\text{coiling}}(^{\circ}\text{C}) / 18)$$

[0024] Th represents the thickness of the steel sheet before being enameled and T_{coiling} the coiling temperature of the sheet after the hot rolling operation. When the total boron amount is above or equal to this minimum value, the necessary quantity of free boron atoms will be present in the steel sheet so as to avoid fish scale defect.

[0025] Without willing to be bound by any theory, the thickness dependency could probably be explained as follows. The absolute amount of hydrogen which is pumped into the steel during enamelling depends only of the surface area to be coated and is therefore thickness independent. The absolute amount of hydrogen traps (free boron) available is however directly linked to the volume of the steel sheet, which is the product of thickness and surface area. The same relative amount of free boron therefore leads to a higher absolute number of hydrogen traps in a thick sheet compared to a thin one.

[0026] The steel composition may comprise niobium in an amount of up to 0.1 % or vanadium in an amount of up to 0.08% and preferably 0.01 to 0.08%, and most preferably in an amount of 0.02 to 0.06%, to strengthen the steel by refining the grain size.

[0027] The steel composition may comprise nickel in an amount of up to 0.35 % which has the effect of improving the adhesion of the enamel layer.

[0028] The steel composition may comprise copper in an amount of up to 0.25 %, which has the effect of improving the adhesion of the enamel layer.

[0029] The steel composition may comprise nitrogen in an amount of up to 0.04 %. This element is present as an impurity resulting of smelting. It can also be added by renituration to strengthen the steel.

[0030] The steel composition may comprise phosphor and sulphur in an amount of up to 0.03 %. These elements are impurities coming from the smelting and should be reduced as much as possible because of their detrimental effect on the steel properties.

[0031] To produce a hot rolled steel sheet according to the invention, the man skilled in the art may use a classical process of production including smelting the steel composition with the help of an electric furnace, by example. The liquid steel can then be continuously cast into slabs of a thickness of 60 to 250 mm, depending on the casting process employed.

[0032] The slab can then be hot rolled to obtain a hot rolled steel sheet presenting a thickness varying between 1.3 and 10 mm. The hot rolling operation can take place after reheating at a temperature generally above 1150°C, the hot rolling being finished at a temperature above 800°C.

[0033] The hot rolling stand can also be put in line with the casting of a thin slab, no reheating being then necessary.

[0034] After the hot rolling operation, the steel sheet gets cooled and coiled at a temperature called T_{coiling}.

[0035] In both cases, the coiling temperature of the hot rolled steel sheet must be controlled carefully as the formation of AlN or BN precipitates mostly occurs during this operation. According to the invention, the coiling temperature should be chosen between 380 and 650°C, and preferably between 380 and 590°C, depending on the thickness Th of the steel sheet and on its boron content.

[0036] The microstructure of the steel sheet according to the invention consists preferably in a mixture of ferrite and perlite, as it allows reaching the mechanical characteristics desired for the main applications of this product.

[0037] However, it is clear that the effect of the free boron does not depend on this microstructure and could be obtained also with another one, like a purely ferritic one.

Examples

1. Enamelling properties

[0038] The enamel tests have been performed on rectangular sheets of 100 x 120 mm in which two holes have been drilled at the top to allow suspending the samples in the enamelling furnace.

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[0039] Prior to the application of the enamel, the samples were pickled and cleaned in a vapour phase degreasing unit (Kerry Ultrasonics using HFE-72DE degreasing liquid from 3M) which consists in three phases:

- ultrasonic degreasing during 180 s
- vapour phase degreasing during 90s
- drying during 60s.

[0040] The HFE-72DE degreasing liquid from 3M contains 68-72% in volume of 1,2-trans dichloroethylene, 4 to 16% of ethyl nonafluoroisobutyl ether, 4-16% of ethyl nonafluorobutyl ether, 2-8% of methyl nonafluoroisobutyl ether and 1-8% of methyl nonafluorobutyl ether.

[0041] The enamel used was Ferro 2290 which is an enamel known to be sensitive to fish scale defect and contains no adhesion promoting additives.

[0042] The top of each rectangular sample was covered with enamel on one side while the bottom was coated on both sides, by using a wet spray booth, with a thickness layer between 100 and 150 μm . Firing of the enamelled samples was performed in a tunnel furnace at 840°C during 6 minutes and 30 seconds for the 6mm thick samples and during 3 minutes and 30 seconds for the 3.5mm thick samples.

[0043] After the enamelling, the aspect of each sample was visually and mechanically evaluated.

[0044] For the evaluation of fish scale defect, a semi-quantitative ranking was used, in which a score of 5 means that the sample coating is covered by fish scale defect, while a score of 0 is given to an a steel sheet showing no fish scale defect. This evaluation was performed immediately after the firing of the enamel layer and after holding for 96 hours in a furnace at 70°C.

2. Mechanical properties

[0045] The enamelled samples were submitted to a determination of their tensile properties according to the standard EN 10002-1 on an electro-mechanical testing machine Zwick Z250.

3. Samples

[0046] The tested samples had the following composition (in wt %):

Steel	C %	Mn %	Si %	Ni %	Cu %	Al %	B %	N %	P %	S %
B134	0.06	0.5	0.03	0.25	0.15	0.08	0	0.016	0.02	0.02
B135	0.06	0.5	0.03	0.25	0.15	0.12	0	0.016	0.02	0.02
B136	0.06	0.5	0.03	0.25	0.15	0.16	0	0.016	0.02	0.02
B137	0.06	0.5	0.03	0.25	0.15	0.16	0.002	0.016	0.02	0.02
B138	0.06	0.5	0.03	0.25	0.15	0.16	0.004	0.016	0.02	0.02
B139	0.06	0.5	0.03	0.25	0.15	0.16	0.006	0.016	0.02	0.02
A120	0.06	0.5	0.03	0.25	0.15	0.16	0.008	0.016	0.02	0.02
S001	0.03	0.2	0.03	0.24	0.15	0.17	0.006	0.016	0.015	0.003

[0047] Based on those compositions, several samples were produced with some variations in the process parameters of manufacturing:

Trial	Steel	Thickness (mm)	Coiling temperature (°C)	B min (ppm) (1)
1	B134	3.5	580	50
2	B135	3.5	580	50
3	B136	3.5	580	50
4	B137	3.5	580	50
5	B138	3.5	580	50

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(continued)

Trial	Steel	Thickness (mm)	Coiling temperature (°C)	B min (ppm) (1)
6	B139	3.5	580	50
7	A120	3.5	580	50
8	B138	3.5	400	40
9	B139	3.5	400	40
10	B136	6.0	580	20
11	B137	6.0	580	20
12	B138	6.0	580	20
13	B139	6.0	580	20
14	A120	6.0	580	20
15	S001	3.0	560	55
(1) calculated according to formula				

4. Results of the trials

[0048]

Trial	Steel	Fish scale after firing	Fish scale 96 h after firing	TS (MPa)	YS (MPa)
1	B134	0	<u>3</u>	nd	nd
2	B135	0	<u>2</u>	nd	nd
3	B136	0	<u>2</u>	nd	nd
4	B137	0	<u>2</u>	376	281
5	B138	0	<u>4</u>	375	285
6*	B139	0	0	377	279
7*	A120	0	0	390	276
8*	B138	0	1	388	297
9*	B139	0	1	386	291
10	B136	0	<u>4</u>	nd	nd
11*	B137	0	0	364	251
12*	B138	0	0	372	250
13*	B139	0	0	369	246
14*	A120	0	0	394	262
15*	S001	0	0	390	316
• * : according to the invention • nd : not determined					

[0049] As can be seen from that table, none of the trials with composition containing no boron gave good results in terms of fish scale defect (B134, 135 and 136 and trials 1 to 3 and 10), whatever the thickness or the coiling temperature used.

[0050] At a coiling temperature of 580°C and a thickness of 3.5 mm, a minimum of 50 ppm of total boron was necessary to avoid fish scale appearance.

[0051] If the coiling temperature is reduced to 400°C with the same thickness, the minimum amount of total boron decreases to 40 ppm in order to avoid fish scale defect.

[0052] With a coiling temperature of 580°C and an increased thickness of 6 mm, the minimum amount of total boron decreases to 20 ppm in order to avoid fish scale defect.

5 **Claims**

1. Hot rolled and enamelled steel sheet free of fish scale defects, comprising, in % by weight:

10 C: 0.02 - 0.1 %
Mn : 0.3 - 1 %
Al: 0.1 - 0.4 %
Si : 0 - 0.3%
B: 0,002 - 0.01 %
15 Nb: 0 - 0.1%
V : 0 - 0.08%
Ni : 0 - 0,35 %
Cu : 0 - 0,25 %
N: < 0.04 %
20 P : < 0,03 %
S : < 0.03 %

the balance being iron and unavoidable impurities due to smelting, said steel sheet having a thickness Th and having being coiled at a temperature T_{coiling}, after being hot rolled, said composition moreover comprising a boron content B above or equal to Bmin defined according to the following relationship :

25

$$B_{min} \text{ (ppm)} = 60 - (12 \times Th(\text{mm})) + (T_{coiling}(\text{°C}) / 18)$$

30 2. Hot rolled and enamelled steel sheet according to claim 1 or 2, comprising, in % by weight:

C : 0.04 - 0.08 %
Mn : 0.6 - 1 %
Al : 0.1 - 0.4 %
35 Si : 0,1 - 0.3%
Nb: 0.03 - 0.1%
V: 0.02 - 0.06%
Ni : 0 - 0,35 %
Cu : 0 - 0,25 %
40 N: < 0.04 %
P : < 0,03 %
S : < 0.03 %
B ≥ Bmin

45 3. Hot rolled and enamelled steel sheet according to claim 1 or 2, comprising, in % by weight:

C : 0.04 - 0.08 %
Mn : 0.3 - 0.7 %
Al : 0.1 - 0.4 %
50 Si : 0 - 0.1%
Ni : 0 - 0,35 %
Cu : 0 - 0,25 %
N : < 0.04 %
P : < 0,03 %
55 S : < 0.03 %
B ≥ Bmin

4. Hot rolled and enamelled steel sheet according to anyone of claims 1 to 3, presenting a thickness between 1.3 and

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3 mm and a yield strength under 320 MPa and a tensile strength above 290 MPa, for use as a shower tube.

5 **5.** Hot rolled and enamelled steel sheet according to anyone of claims 1 to 3, presenting a thickness between 2 and 10 mm and a yield strength above 320 MPa and a tensile strength above 400 MPa, for use as tank or an industrial silo.

6. Hot rolled and enamelled steel sheet according to anyone of claims 1 to 3, presenting a thickness between 1.5 and 3 mm and a yield strength above 275 MPa and a tensile strength above 430 MPa, for use as a building cladding or facade.

10 **7.** Method of manufacturing of a hot rolled and enamelled steel sheet according to anyone of claims 1 to 6, consisting in :

- smelting as steel which composition is according to the composition of claims 1 to 3,
- casting said steel composition into a slab and hot rolling said slab into a hot rolled steel sheet presenting a thickness under 10 mm,
- 15 - coiling said hot rolled steel sheet at a temperature comprised between 380 and 650°C,
- degreasing and/or shot blasting said hot rolled steel sheet,
- depositing at least an enamel layer under liquid or powdery form on at least one side of said hot rolled sheet,
- optionally drying said enamel layer and
- 20 - firing the said enamel layer.

8. Method of manufacturing according to claim 7, wherein enamelling is performed on both sides of said hot rolled sheet.



EUROPEAN SEARCH REPORT

Application Number
EP 08 29 0664

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Place of search Munich		Date of completion of the search 9 December 2008	Examiner Rolle, Susett
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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