



(86) **Date de dépôt PCT/PCT Filing Date:** 2011/04/08
(87) **Date publication PCT/PCT Publication Date:** 2012/10/11
(45) **Date de délivrance/Issue Date:** 2016/06/07
(85) **Entrée phase nationale/National Entry:** 2013/10/04
(86) **N° demande PCT/PCT Application No.:** EP 2011/055477
(87) **N° publication PCT/PCT Publication No.:** 2012/136270

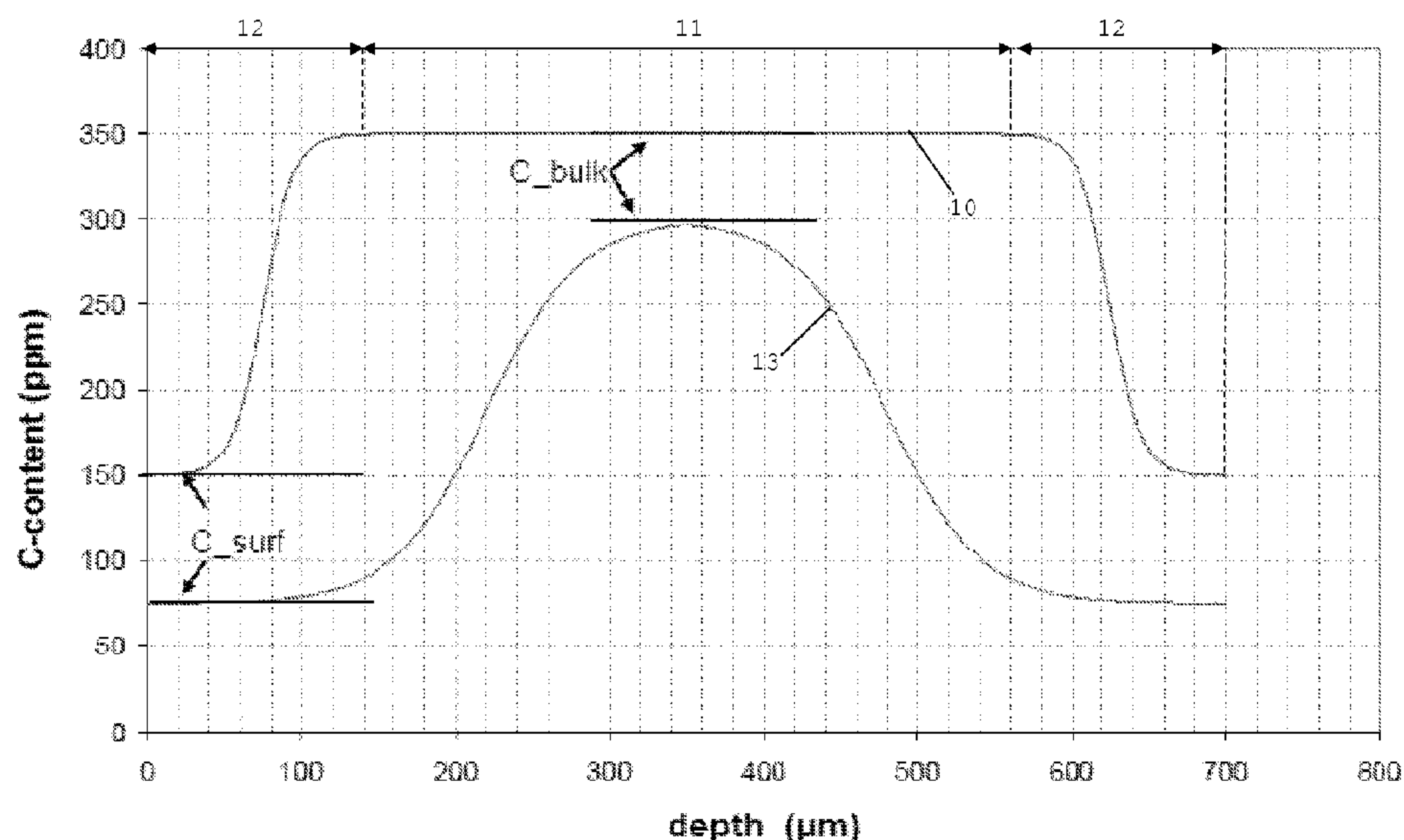
(51) **Cl.Int./Int.Cl.** **C21D 3/04** (2006.01),
C21D 8/02 (2006.01), **C21D 9/46** (2006.01),
C21D 9/56 (2006.01)

(72) **Inventeurs/Inventors:**
VAN STEENBERGE, NELE, BE;
LEVEAUX, MARC, FR;
DUPREZ, LODE, BE;
GOUSSELOT, PHILIPPE, FR

(73) **Propriétaire/Owner:**
ARCELORMITTAL INVESTIGACION Y DESARROLLO
SL, ES

(74) **Agent:** SMART & BIGGAR

(54) **Titre : FEUILLE D'ACIER APPROPRIÉE POUR UN EMAILLAGE ET PROCÉDE DE FABRICATION D'UNE TELLE FEUILLE**
(54) **Title: A STEEL SHEET SUITABLE FOR ENAMELLING AND METHOD FOR PRODUCING SUCH A SHEET**



(57) **Abrégé/Abstract:**

The present invention is related to a rolled steel sheet suitable for enamelling, said sheet having a carbon profile, defined by a gradient in the C-level from a level $C_{surface}$ at least one surface of the sheet, to a level C_{bulk} in the bulk of the sheet, C_{bulk} being higher than $C_{surface}$, and With I - C_{bulk} higher than 0 and lower than or equal to 0.08wt%, - $C_{surface}$ between 0 and 0.015wt%, - Al between 0.012wt% and 0.07wt%, Mn between 0.12wt% and 0.45wt%, 0 lower than 0.01wt% and optionally : - Cu between 0.025wt% and 0.1wt%, - S between 0.008wt% and 0.04wt%, - Ca between 0.0005wt% and 0.005wt%, the balance being Fe and incidental impurities, and wherein the depth where the C-level reaches $(C_{bulk} + C_{surface})/2$ 12, is higher than 75μm. The invention is equally related to a method for producing said steel sheet.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
11 October 2012 (11.10.2012)

WIPO | PCT

(10) International Publication Number
WO 2012/136270 A1

(51) International Patent Classification:

C21D 3/04 (2006.01) *C21D 9/46* (2006.01)
C21D 8/02 (2006.01) *C21D 9/56* (2006.01)

(21) International Application Number:

PCT/EP2011/055477

(22) International Filing Date:

8 April 2011 (08.04.2011)

(25) Filing Language:

English

(26) Publication Language:

English

(71) Applicant (for all designated States except US): **ARCELORMITTAL INVESTIGACIÓN Y DESARROLLO SL** [ES/ES]; CL/Chavarri, 6, E-48910 Sestao Bizkaia (ES).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **VAN STEENBERGE, Nele** [BE/BE]; Kortrijksesteenweg 199, B-9000 Gent (BE). **LEVEAUX, Marc** [FR/FR]; 26 Avenue Foch, F-59700 Marcq-En-Baroeul (FR). **DUPREZ, Lode** [BE/BE]; Beerveldestraat 37, B-9160 Lokeren (BE). **GOUSSELOT, Philippe** [FR/FR]; 1 Rue Virginie du Verger, F-57070 Metz (FR).

(74) Agent: pronovem - Office Van Malderen; Ave Josse Goffin 158, B-1082 Brussels (BE).

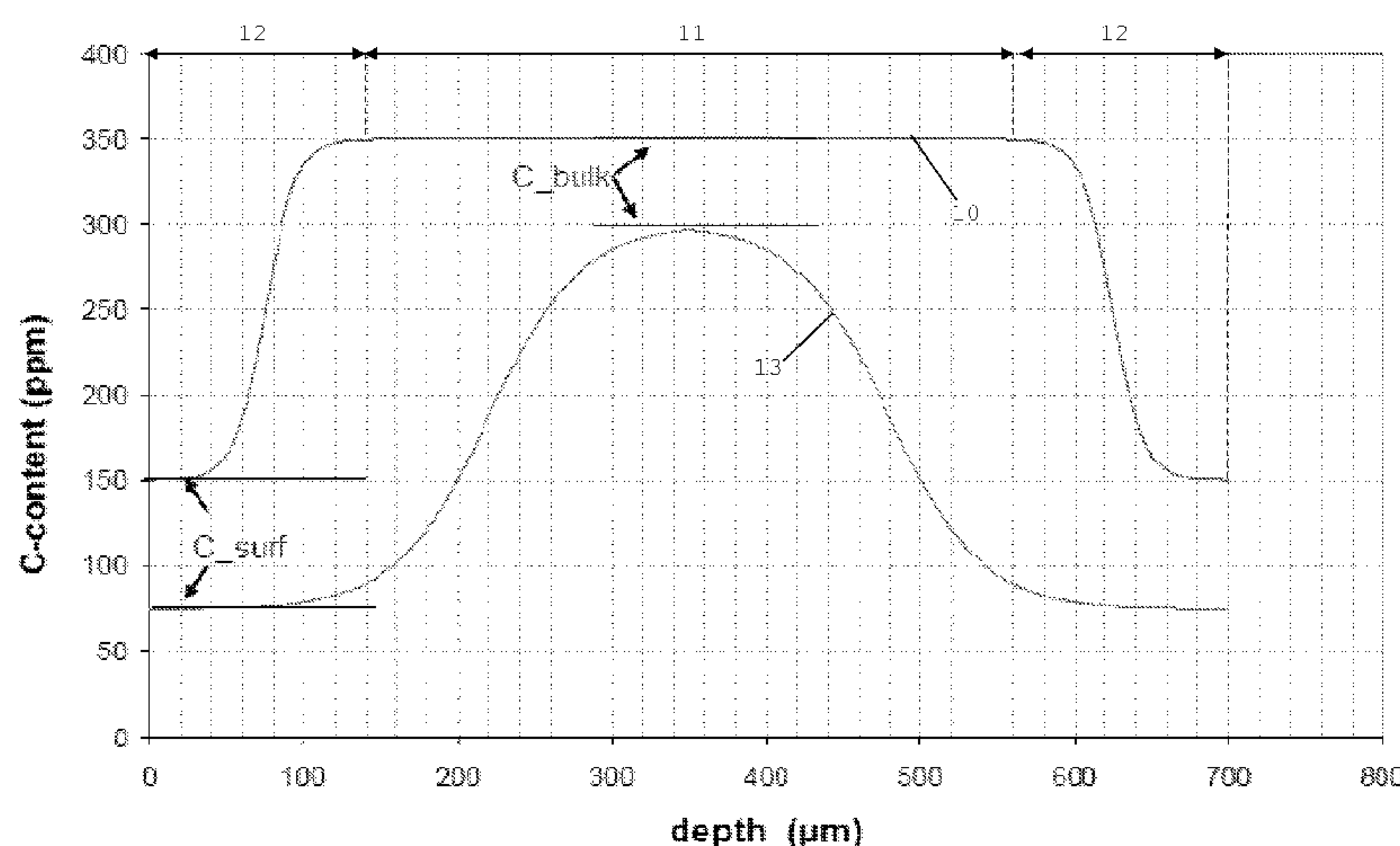
(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG,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

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: A STEEL SHEET SUITABLE FOR ENAMELLING AND METHOD FOR PRODUCING SUCH A SHEET



F-C. 1

(57) Abstract: The present invention is related to a rolled steel sheet suitable for enamelling, said sheet having a carbon profile, defined by a gradient in the C-level from a level C_{surface} at least one surface of the sheet, to a level C_{bulk} in the bulk of the sheet, C_{bulk} being higher than C_{surface} , and With I - C_{bulk} higher than 0 and lower than or equal to 0.08wt%, - C_{surface} between 0 and 0.015wt%, - A1 between 0.012wt% and 0.07wt%, Mn between 0.12wt% and 0.45wt%, 0 lower than 0.01wt% and optionally : - Cu between 0.025wt% and 0.1wt%, - S between 0.008wt% and 0.04wt%, - Ca between 0.0005wt% and 0.005wt%, the balance being Fe and incidental impurities, and wherein the depth where the C-level reaches $(C_{\text{bulk}} + C_{\text{surface}})$ 12, is higher than 75μm. The invention is equally related to a method for producing said steel sheet.

WO 2012/136270 A1

5 **A STEEL SHEET SUITABLE FOR ENAMELLING AND METHOD FOR**
 PRODUCING SUCH A SHEET

Field of the Invention

10 **[0001]** The present invention is related to a steel
 sheet suitable for enamelling, and to a method for the
 superficial decarburization of a steel sheet, as a
 preparation for enamelling the steel.

15 **State of the art.**

[0002] The carbon level of a steel sheet has an
 important influence on the results in terms of surface
 quality of an enamel layer applied on the surface of the
 sheet. A high carbon level at the steel surface may give
20 rise to CO-gas bubble formation, which shows up as black
 spots and craters in the enamel surface. On the other
 hand, when a sufficiently high carbon level is present
 initially in the bulk, this carbon forms coarse cementite
 during hot rolling which cracks upon cold rolling. These
25 cracks are capable of capturing hydrogen which enters the
 steel during the enamelling process. When hydrogen is
 insufficiently captured, pressure will rise at the
 steel/enamel surface which gives rise to the so-called
 'fish-scale' deformation of the enamel.

30 **[0003]** It is therefore advantageous to decarburize
 the steel only in a layer at the surface of the steel, i.e.
 to conduct a superficial decarburization. Document JP-A-
 2282421 describes such a method, wherein a continuously
 cast and annealed non-aging steel sheet for enamelling is

2

produced, characterized in that a continuous-cast steel slab containing C between 0.0025 and 0.0050wt%, Si max. 0.03wt%, Mn between 0.1 and 0.6wt%, P between 0.005 and 0.03wt%, S between 0.005 and 0.03wt%, Al max. 0.01wt%, N max. 0.004wt%, Cu between 0.01 and 0.06wt%, O between 0.02 and 0.06wt%, V between 0.01 and 0.06wt%, the balance Fe and inevitable impurities, is hot-rolled with a finishing temperature higher than or equal to 800°C, and a coiling temperature of 600-800°C, cold-rolled with a reduction ratio higher than or equal to 60% and subjected to a decarburization annealing at 700-900°C for 30sec-3min, carried out in a continuous annealing furnace having a decarburizing atmosphere composed of 1-20% water vapour, gaseous hydrogen in an amount higher than or equal to twice the water vapour amount, and the balance being mainly gaseous nitrogen, so as to reduce the C-level to be less than or equal to 0.002wt%. JP-A-6116634 describes a similar method, but wherein the starting material has no vanadium and the initial C level is up to 0.015wt% and B is added instead of V for H-trapping.

[0004] Both prior art methods result in fully or superficially decarburized steel sheets which are suitable for enamelling by Direct White Enamelling (DWE), wherein one white enamel coating is applied on the surface, followed by one firing step. As the initial carbon level is quite low, fish-scale resistance due to cementite formation is not achieved. To compensate for this, a steel with a high oxygen level and a limited Al-level is used in the prior art together with specific alloying elements such as B, V. Thanks to the limited Al-content, oxides of Si and Mn and nitrides of B and V are formed within the bulk of the steel which are beneficial against fish-scaling. However, this alloying involves extra costs and leads to some technical difficulties, e.g. involving casting with V.

75656-18

3

Furthermore, the prior art decarburized sheets have rather low formability as testified by the values of the Lankford coefficient (r_m). These values do not exceed 1.8 which is a concern when deep-drawing is foreseen. In particular, figure 1 of JP6116634 shows that r_m values between 1.6 and 1.8 are only achieved for a very narrow range of carbon level before decarburizing annealing. Below 0.0050wt%C and above 0.0150wt%C, the r_m value is deteriorated.

10

[0005]

15 Summary of the invention

[0006] The invention is related to steel sheets and products and to a production method as disclosed below.

The invention is related to a rolled steel sheet suitable for enamelling, said sheet having a carbon profile, defined by a gradient in the C-level from a level C_{surface} at at least one surface of the sheet, to a level C_{bulk} in the bulk of the sheet, C_{bulk} being higher than C_{surface} , and with :

- 25 - C_{bulk} higher than 0 and lower than or equal to 0.08wt%,
- C_{surface} between 0 and 0.015wt%,
- Al between 0.012wt% and 0.07wt%,
- Mn between 0.12wt% and 0.45wt%,
- 30 - O lower than 0.01wt%

and optionally :

- Cu between 0.025wt% and 0.1wt%,
- S between 0.008wt% and 0.04wt%,

– Ca between 0.0005wt% and 0.005wt%
the balance being Fe and incidental impurities,
and wherein the depth where the C-level reaches
($C_{\text{bulk}} + C_{\text{surface}}$)/2, is higher than 75 μm .

5 [0007] According to a preferred embodiment, the
steel sheet of the invention has an r_m value between 1.8
and 2.1.

[0008] According to specific embodiments, C_{surface} is
between 0.005wt% and 0.015wt%, or between 0 and 0.005wt%.

10 [0009] According to other specific embodiments, C_{bulk}
is between 0.02wt% and 0.08wt%, or between 0.025wt% and
0.08wt% or between 0.025wt% and 0.06wt%.

[0010] According to another embodiment, the Al-level
is between 0.02wt% and 0.06wt%.

15 [0011] According to a further embodiment, said depth
is between 130 μm and 200 μm .

[0012] The invention is equally related to an
enamelled steel sheet consisting of a steel sheet according
to any of the above paragraphs, provided with an enamel
20 layer.

[0013] The invention is further related to a steel
product produced from a sheet according to the invention,
and to an enamelled steel product consisting of a such a
product, provided with an enamel layer.

25 [0014] The invention is also related to a method for
producing a rolled steel sheet for enamelling, comprising
the steps of :

– subjecting a steel slab to hot rolling followed by
coiling, and cold rolling, so as to obtain a cold-rolled
30 steel sheet, said slab comprising the following initial
composition :

- C between 0.02wt% and 0.08wt%,
- Al between 0.012wt% and 0.07wt%,

5

- Mn between 0.12wt% and 0.45wt%,
 - O lower than 0.01wt%
- and optionally :
- Cu between 0.025wt% and 0.1wt%,
 - 5 - S between 0.008wt% and 0.04wt%,
 - Ca between 0.0005wt% and 0.005wt%,
 - the balance being Fe and incidental impurities,
- subjecting said cold-rolled sheet to continuous annealing step, wherein said sheet is exposed during a
- 10 decarburizing time to a decarburizing atmosphere comprising water vapour and hydrogen gas, wherein the H₂ content is between 1vol% and 95vol%, the H₂O content between 0.04vol% and 33vol%, the remainder being mainly nitrogen gas, the ratio p_{H₂O}/p_{H₂} being between 0.04 and
- 15 0.5.

[0015] According to a preferred embodiment, said continuous annealing takes place at an anneal temperature between 760°C and 850°C, and during a decarburizing time between 45s and 300s.

20 **[0016]** According to a specific embodiment, the anneal temperature is between 800°C and 850°C.

[0017] According to specific embodiments of the method of the invention, the initial C-level is between 0.025wt% and 0.08wt% or between 0.025wt% and 0.06wt%.

25 **[0018]** According to a further embodiment, the initial Al-level is between 0.02wt% and 0.06wt%.

[0019] According to a specific embodiment, the ratio p_{H₂O}/p_{H₂} is between 0.04 and 0.25.

[0020] The method of the invention may further

30 comprise an over-ageing step at a temperature between 350°C and 450°C during a timespan between 100s and 500s. The method may further comprise a skinpass step with a reduction of between 0.3% and 1.5%.

Brief description of the figures

[0021] Figure 1 illustrates the carbon profile in a steel sheet according to the invention.

5 [0022] Figure 2 illustrates an example of an annealing step usable in the method of the invention.

Detailed description of the invention

[0023] The steel sheet of the invention has a C-profile, defined by a gradient in the C-level from a lower value C_{surface} at the surface to a higher value C_{bulk} in the bulk. The sheet is obtainable by a method which includes a continuous decarburization step, as will be described further in this text. Figure 1 illustrates the carbon-
10 distribution across the thickness of two sheets according to the invention, with a thickness of 0.7mm. Curve 10 illustrates a sheet which comprises a bulk portion 11, where the C-level C_{bulk} is substantially constant, and two surface portions 12 (one on each side of the sheet), each
15 surface portion exhibiting the C-profile. The surface level is defined as the minimum value of the C-profile, measured by a suitable measurement technique (e.g. Glow Discharge Optical Emission Spectroscopy (GD-OES), which allows composition measurement as depth analysis). In a
20 steel sheet according to the invention, the C-level at the surface is maximum 0.015wt%, whereas C_{bulk} is higher than zero and lower than or equal to 0.08wt%. At the same time, C_{bulk} is higher than C_{surface} . According to an embodiment, C_{surface} is between 0.005wt% and 0.015wt%. According to
25 another embodiment, C_{surface} is between 0 and 0.005wt%.
30

[0024] Curve 10 is an example of a sheet where the decarburization has not taken place over the entire thickness of the sheet. This means that the level C_{bulk} is equal to the initial C-level applied in the production

method (described further in more detail). According to embodiments which correspond to embodiments of the method of the invention (see further), C_{bulk} is then between 0.02wt% and 0.08wt%, or between 0.025wt% and 0.08wt, or
5 between 0.025wt% and 0.06wt% or between 0.025wt% and 0.05wt%. Curve 13 illustrates the case where decarburization has continued until the middle plane of the sheet. In this case, C_{bulk} is smaller than the initial C-level of the method, and the C-profile extends over each
10 half-width of the sheet.

[0025] The decarburized sheet according to the invention further comprises Al, Mn and possibly S, Cu and Ca. Contrary to the prior art references, the oxygen level is to be kept lower than 0.01wt%. According to a preferred
15 embodiment of the steel sheet of the invention, oxygen is not added deliberately to the composition, but is allowed only at impurity levels. Fish scaling resistance is ensured by the higher initial C-level, so no oxide formation is required for this purpose. This means that no
20 special alloying elements such as V are included. Also, N is kept as low as possible.

[0026] The Al-level in the sheet of the invention is between 0.012wt% and 0.07wt%, which is higher than the allowed Al-level in the prior art references cited above.
25 In the cited prior art documents Al needs to be limited to avoid deoxidation, so as to ensure the formation of the oxides that will work against fish-scaling. In the method of the invention (see further), Al is mandatory for deoxidation and binding of free N to avoid the ageing of
30 the mechanical properties. When the Al-level is lower than 0.012wt%, insufficient deoxidation takes place, and binding of N is required through other means. Adding Al at levels higher than 0.07wt% means an increase in cost of the process, and a deterioration of the enamelling quality. A

more preferred range for the Al-level, related to more optimized conditions in terms of deoxidation and cost/enamelling quality is between 0.02wt% and 0.06wt%.

[0027] Mn is present between 0.12wt% and 0.45wt%.

5 This element is added to control the strength properties of the steel and to avoid the formation of free sulphur.

[0028] Copper, Sulphur and Calcium may optionally be added above the impurity level, more precisely in the ranges 0.025wt% to 0.1wt%, 0.008wt% to 0.04wt% and
10 0.0005wt% to 0.005wt% respectively. These elements improve the enamelling quality.

[0029] The balance of the composition of the steel sheet according to the invention consists of Fe and incidental impurities. The following elements may be
15 present as impurities at levels which are preferably lower than the values (in wt%) given in table 1 :

Si	< 0.1
P	< 0.03
Ti	< 0.01
Cr	< 0.2
Ni	< 0.2
As	< 0.02
Sn	< 0.02
Nb	< 0.01
V	< 0.01
Sb	< 0.02
Mo	< 0.03
B	< 0.0005
N	< 0.007

Table 1 : impurity levels

[0030] In a steel sheet of the invention, the depth
20 of the C-profile, being defined as the depth where the C-

level reaches $(C_{\text{bulk}} + C_{\text{surface}})/2$, is higher than $75\mu\text{m}$, to ensure good enamelling capability. According to an embodiment, said depth is between $130\mu\text{m}$ and $200\mu\text{m}$.

[0031] Steel sheets according to the invention, i.e. with a C-level at the surface between 0 and 0.015wt% are suitable for 2C/1F enamelling, i.e. enamelling by applying a ground coat enamel, followed by an outer enamel coating, both coatings being subjected to one firing step, and for 1C/1F enamelling, i.e. enamelling by applying one enamel layer subjected to one firing step. Steel sheets with low C-levels (i.e. 0.005wt% and less) at the surface may be suitable also for Direct White Enamelling (DWE).

[0032] According to a preferred embodiment, the r_m value of a steel sheet according to the invention is between 1.8 and 2.1. This means that the steel sheet has better formability than the prior art steel sheets referred to above. In the present description, the 'r' value refers to the plastic strain ratio (also known as the anisotropy factor), being the ratio of the true strain in the width direction to the true strain in the thickness direction when a sheet material is pulled in uniaxial tension beyond its elastic limit. The ' r_m ' value is defined as $\frac{1}{4}(r_{90} + 2*r_{45} + r_0)$, with r_{90} , r_{45} and r_0 the r-values as defined above, measured on samples oriented respectively at 90° , 45° and 0° with respect to the rolling direction. In a steel sheet according to the invention, fish scaling resistance is ensured by the higher initial C-level applied in the method (see further).

[0033] The steel sheet of the invention can be produced by subjecting a steel slab with a specific initial steel composition to hot rolling, coiling and cold rolling, and by subjecting the cold-rolled sheet to continuous superficial decarburization. The initial composition is

10

mainly characterized by a higher C-level compared to the prior art, and by a higher Al-level and a lower oxygen level. No deliberate addition of elements like V, Nb or B is done, while still allowing to produce enamelled steel sheets with a high fish scale resistance and good enamel surface quality. The initial C-level is between 0.02wt% and 0.08wt%, more preferably between 0.025wt% and 0.08wt%. This is higher than the initial C-levels disclosed in the prior art references referred to above. Despite such higher initial C-levels, the method of the invention allows to obtain steel sheets with improved formability characteristics compared to the prior art. Whereas JP6116634 indicates that above 0.015wt% of initial carbon, it is not possible to obtain acceptable decarburization and good formability, the starting composition of the invention does not encounter these problems. Decarburization is possible down to an acceptable level, while formability is excellent. When the initial C-level is lower than 0.02wt%, insufficient cementite formation occurs which deteriorates fish scale resistance. C-levels above 0.08wt% lead to too high strength levels and thus reduced formability. Specific ranges for the initial C-level, related to more optimized characteristics in terms of fish scale resistance and strength/formability are between 0.025wt% and 0.06wt% and between 0.025wt% and 0.05wt%.

[0034] The initial steel composition according to the method of the invention further comprises Al, Mn and possibly O, S, Cu and Ca in the same ranges as the decarburized sheet described above, the balance being Fe and the incidental impurities listed in Table 1. A more preferred range for the initial Al-level, related to more optimized conditions in terms of deoxidation and cost/enamelling quality is between 0.02wt% and 0.06wt%. According to a preferred embodiment of the method of the

11

invention, oxygen is not added deliberately to the composition, but is allowed only at impurity levels.

[0035] The method of the invention comprises standard steps of hot rolling and cold rolling a steel slab of the above composition. According to the preferred embodiment, the slab is (re)heated at a temperature above 1050°C, subjected to hot rolling with a finishing temperature between 850°C and 950°C, and coiling at coiling temperature between 620°C and 770°C. Still according to the preferred embodiment, cold rolling is performed with a reduction of minimum 50%. The final thickness of the cold rolled sheet is preferably between 0.2 and 2mm.

[0036] The decarburization anneal is done in an annealing furnace for continuous annealing (i.e. annealing while the cold-rolled sheet moves through the furnace at a given speed, said speed determining the anneal time, i.e. the time spent at the annealing temperature) as known in the art, possibly provided with a vapour injection device for applying a given annealing atmosphere.

[0037] Figure 2 shows an example of a lay-out of an annealing furnace usable in the method of the invention, starting with heating phase 1 wherein the temperature rises to the annealing temperature. Phase 2 represents the actual annealing (soaking) phase. Phase 3 is an overageing step. Phase 2 can consist of one or more periods with a different (constant or average) annealing temperature and a different annealing atmosphere in each period. Practically speaking, the different periods at different conditions can be obtained by dividing the annealing zone in subsections and by injecting H₂O vapour into an atmosphere comprising H₂, at various points along the annealing line (see example further in this description).

[0038] According to the invention, the superficial decarburization is done under a decarburizing atmosphere

12

comprising water vapour and hydrogen gas, the remainder being essentially nitrogen gas, with the H₂ content between 1vol% and 95vol%, the H₂O content between 0.04vol% and 33vol%, the ratio of partial pressures p_{H₂O}/p_{H₂} being
5 between 0.04 and 0.5, more preferably between 0.04 and 0.25. The above composition describes the atmosphere at the start of the decarburizing time. It is clear that during decarburization, the atmosphere composition will change, primarily due to the decarburization reaction
10 taking place (formation of H₂ and CO). Also at the start of the decarburizing time, small amounts of other gases may already have formed or may be present as impurities in the atmosphere. The total pressure under which the superficial decarburization anneal takes place may be atmospheric
15 pressure, or a pressure different from atmospheric but within generally known boundaries applied in this type of annealing process.

[0039] According to one embodiment, the decarburizing atmosphere can be prepared with a mixture of
20 H₂ and N₂ with between 1,5 and 5% H₂ in which H₂O vapour is injected so that p_{H₂O}/p_{H₂} is between 0.04 and 0.5. The minimum value of this ratio ensures that sufficient H₂O is present to obtain decarburization according to the formula
$$\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$$

The maximum of said range ensures that
25 oxidation of Fe and of the furnace is avoided. A more preferred range for p_{H₂O}/p_{H₂}, related to more optimized conditions in terms of sufficient decarburization and avoiding the occurrence of Fe-oxidation is between 0.04 and 0.25.

30 **[0040]** In the method of the invention, the decarburizing atmosphere is applied during at least one of said periods with a different (constant or average) annealing temperature and a different annealing atmosphere in each period, preferably during the totality of phase 2.

13

In the following, the 'decarburizing time' refers to the time spent under the conditions of the decarburizing atmosphere.

[0041] The decarburizing time and the anneal temperature are chosen so as to obtain a steel sheet according to the invention. It is within the skilled person's knowledge to find suitable combinations of decarburizing time and anneal temperature based on the examples given further in this description. According to a preferred embodiment, the decarburizing time is between 45s and 300s and the anneal temperature between 760°C and 850°C. When the ratio p_{H_2O}/p_{H_2} is lower than about 0.1, the decarburizing time is preferably higher than 70s. A more preferred range of the anneal temperature, applicable in combination with any decarburizing time between 45s and 300s is between 800°C and 850°C. The temperature is not necessarily constant during the decarburizing time. Fluctuations of the temperature may occur due to variations in the line speed for example. An over-ageing step may be applied at a temperature between 350°C and 450°C during a timespan between 100s and 500s. A skinpass may further be applied with a reduction of between 0.3% and 1.5%.

Examples

[0042] Results from industrial trials performed by the applicant will be described hereafter, as well as a number of laboratory trials. All tested samples were produced from starting compositions according to the invention. The coiling temperature was 725°C. Two industrial trials were conducted. The thickness of the cold rolled sheet subjected to decarburization annealing in industrial trial 1 was 0.6mm; in the second industrial trial the thickness was 1mm.

14

[0043] The continuous annealing line in which the industrial trials were conducted consists of a heating section, two soaking areas, a cooling and an overaging part. The annealing atmosphere consisted mainly of a mixture of H_2 and N_2 , with H_2O vapour being injected in the first and/or the second soaking area. In the first trial, H_2O vapour was injected only in the second soaking area. In the second trial, H_2O was injected in the first and the second soaking area. Overaging was performed in both trials at $400^\circ C$. The overaging time depended on the line speed, e.g. at 180m/min line speed, the overaging time was 232s. Table 2 shows the annealing conditions for both trials (numbered trial 1 and trial 2). Table 3 shows the composition besides C, for a number of the samples shown in table 1.

[0044] In industrial trial 1, the p_{H_2O}/p_{H_2} ratio is below the range of 0.04-0.5 in the first soaking area (due to the fact that no H_2O injection is done). The decarburizing time in this trial is the time spent in the second soaking area, where the p_{H_2O}/p_{H_2} is within said range. This is an example therefore of a process wherein phase 2 as shown in figure 1 comprises a first period wherein the conditions of the present invention are not met, and a second period wherein these conditions are met. Such a process falls within the scope of the present invention.

[0045] In industrial trial 2, H_2O -injection was performed in both soaking areas. The decarburizing time indicated here is the time spent in soaking areas 1 and 2. The anneal temperature is the average of the temperatures in soaking areas 1 and 2. The p_{H_2O}/p_{H_2} values indicated in table 1 are the average values in soaking area 1 in which more H_2O was injected. However, the p_{H_2O}/p_{H_2} in soaking area 2 is estimated to be also within the range of 0.04-

15

0.5. In industrial trial 2, longer decarburizing times could be achieved as compared to the first trial, for similar line velocities, leading to stronger decarburization.

5 **[0046]** The laboratory trials (marked 'trial 3' in table 2), were conducted on samples which were subjected to a simulation of the continuous annealing step, at the conditions shown in table 2. These trials were conducted in an atmosphere of HN_x with 5% H_2 , with H_2O added to obtain
10 $\text{pH}_2\text{O}/\text{pH}_2$ in the range [0.04-0.5].

[0047] Samples from all three trials were subjected to an enamelling process wherein a ground coat enamel is deposited, this enamel being designed especially to determine the role of C in the enamel characteristics. It
15 was found that the adhesion of the enamelling layer was good for all tested samples. The enamelling aspect was good for C-levels at the surface of maximum 0.015wt%, and for profile depths of 75 μm up to 250 μm , as shown in table 1. There is no reason to conclude from the results however
20 that the enamelling quality deteriorates at higher depth values than 250 μm . Such higher depth values are therefore not excluded from the scope of the invention. All tested samples showed a good fish scale resistance.

[0048] Table 2 summarizes the results after
25 decarburization in terms of the C-level at the surface (i.e. minimum level of the C-profile, measured by GD-OES), the depth of the C-profile, and the quality of an enamel layer produced on the surface of the samples. Samples 25 to 35 yielded a bad enamelling aspect, which can be
30 ascribed to either an insufficient depth of the C-profile (as determined by the depth where the C-level reaches $(C_{\text{surface}} + C_{\text{bulk}})/2$), and/or a C level at the surface which is too high. The reason for these negative results can be

ascribed to the test conditions, either the anneal temperature which is too low, the decarburizing time too short, or the pH_2O/pH_2 ratio too low, or a combination of these factors.

5 **[0049]** Table 4 shows the mechanical properties of a number of samples taken from the sheets of the industrial trials 1 and 2. Importantly, the formability in terms of the r_m value is excellent, despite the initial C-level which is higher than in the prior art : r_m is between 1.8
10 and 2.1. These results prove that the method of the invention allows to produce steel sheets suitable for enamelling, starting from an initial C-level higher than 0.02wt%, the resulting sheets allowing good enamelling quality and fish scale resistance, and having very good
15 formability characteristics.

Sam- ple N°	Trial nr	initial C (ppm ¹)	decarb urizing time (s)	anneal temp. (°C)	pH ₂ O/ pH ₂ (-)	C_surf (ppm)	depth (µm)	enameling aspect	Acc. to invention ?
1	1	362	45	807	0,12	126	90	good	y
2	3	330	70	770	0,05	123	92	good	y
3	3	330	70	770	0,12	108	100	good	y
4	3	330	70	770	0,24	47	94*	good	y
5	1	367	90	782	0,16	132	123	good	y
6	1	367	90	785	0,16	133	130	good	y
7	2	330	90	810	0,13	87	130*	good	y
8	2	346	90	817	0,09	89	116*	good	y
9	2	386	105	801	0,12	106	130	good	y
10	2	348	105	809	0,11	88	145*	good	y
11	2	316	105	817	0,12	78	180	good	y
12	2	346	105	824	0,09	81	142*	good	y
13	2	360	126	799	0,09	106	138*	good	y
14	2	348	126	814	0,09	78	124*	good	y
15	2	375	126	824	0,09	76	140*	good	y
16	3	330	155	840	0,05	51	94*	good	y
17	3	330	155	840	0,12	61	94*	good	y
18	3	330	155	840	0,24	35	94*	good	y
19	2	391	209	815	0,08	68	121*	good	y
20	2	437	209	817	0,08	70	145*	good	y
21	2	340	209	821	0,07	71	222	good	y
22	1	500	45	795	0,08	211	40	bad	n
23	1	491	45	796	0,09	164	75	bad	n
24	1	490	45	800	0,09	177	49	bad	n
25	1	360	45	793	0,09	150	70	bad	n
26	1	360	45	794	0,09	167	75	bad	n
27	1	360	45	795	0,09	176	68	bad	n
28	3	330	70	770	0,01	198	57	bad	n
29	2	363	105	743	0,17	187	135	bad	n
30	2	370	105	752	0,16	165	120	bad	n
31	3	330	155	840	0,01	192	89	bad	n

Table 2 : Overview of experimental conditions and results

¹ : 1wt% = 10⁴ ppm

The depth-values given in table 1 are values of the depth where the C-level reaches $(C_{\text{surface}} + C_{\text{bulk}})/2$. The depth measurements indicated with '*' show the maximum depth which could be measured with the applied equipment. The real value is thus higher than this value.

Sample n°	Al(wt%)	Mn(wt%)	Cu (wt%)	S (wt%)
1	0.024	0.18	0.022	0.0049
5	0.03	0.18	0.028	0.0046
6	0.028	0.19	0.041	0.0052
9	0.035	0.18	0.029	0.0088
11	0.034	0.17	0.028	0.0077

Table 3 : composition of samples (C-level in table 1, remaining elements are beneath impurity level, the remainder is Fe)

sample n°	initial C-level (ppm)	Anneal Temp (°C)	Anneal time (s)	pH₂O/pH₂ (-)	Rp0.2 (MPa)	Rm (MPa)	r_m	Thickness (mm)
23	490	796	209	0,09	189	318	1,8	0,6
1	362	807	126	0,12	182	318	1,9	0,6
5	367	782	105	0,16	189	319	1,8	0,6
19	391	821	105	0,08	185	320	1,8	1
15	375	824	45	0,09	187	331	2,0	1
11	316	817	45	0,12	188	329	1,8	1
9	386	801	90	0,12	183	319	1,9	1

5 Table 4 : mechanical properties

75656-18

19

CLAIMS:

1. A rolled steel sheet for enamelling, said sheet having a carbon profile, defined by a gradient in the C-level from a level C_{surface} at at least one surface of the sheet, to a
5 level C_{bulk} in the bulk of the sheet, C_{bulk} being higher than C_{surface} , and comprising:
 - C_{bulk} higher than 0 and lower than or equal to 0.08wt%;
 - C_{surface} between 0 and 0.015wt%;
 - 10 Al between 0.012wt% and 0.07wt%;
 - Mn between 0.12wt% and 0.45wt%; and
 - O lower than 0.01wt%,
 - the balance being Fe and incidental impurities,
 - and wherein the depth where the C-level reaches
15 $(C_{\text{bulk}} + C_{\text{surface}})/2$, is higher than 75 μm .
2. The steel sheet according to claim 1, having an r_m value between 1.8 and 2.1.
3. The steel sheet according to claim 1 or 2, wherein C_{surface} is between 0.005wt% and 0.015wt%.
- 20 4. The steel sheet according to claim 1 or 2, wherein C_{surface} is between 0 and 0.005wt%.
5. The steel sheet according to any one of claims 1 to 4, wherein C_{bulk} is between 0.02wt% and 0.08wt%.

75656-18

20

6. The steel sheet according to claim 5, wherein C_{bulk} is between 0.025wt% and 0.08wt%.

7. The steel sheet according to claim 6, wherein C_{bulk} is between 0.025wt% and 0.06wt%.

5 8. The steel sheet according to any one of claims 1 to 7, wherein the Al-level is between 0.02wt% and 0.06wt%.

9. The steel sheet according to any one of claims 1 to 8, wherein said depth is between 130 μm and 200 μm .

10 10. The steel sheet according to any one of claims 1 to 9, further comprising one or more of the following:

Cu between 0.025wt% and 0.1wt%;

S between 0.008wt% and 0.04wt%; and

Ca between 0.0005wt% and 0.005wt%.

15 11. An enamelled steel sheet consisting of the steel sheet according to any one of claims 1 to 10, provided with an enamel layer.

12. A steel product produced from the sheet according to any one of claims 1 to 10.

20 13. An enamelled steel product consisting of the steel product according to claim 12, provided with an enamel layer.

14. A method for producing a rolled steel sheet for enamelling, comprising the steps of:

75656-18

21

subjecting a steel slab to hot rolling followed by coiling, and cold rolling, so as to obtain a cold-rolled steel sheet, said slab comprising the following initial composition:

C between 0.02wt% and 0.08wt%;

5 Al between 0.012wt% and 0.07wt%;

Mn between 0.12wt% and 0.45wt%; and

O lower than 0.01wt%,

the balance being Fe and incidental impurities; and

10 subjecting said cold-rolled sheet to a continuous annealing step, wherein said sheet is exposed during a decarburizing time to a decarburizing atmosphere comprising water vapour and hydrogen gas, wherein the H₂ content is between 1vol% and 95vol%, the H₂O content between 0.04vol% and 33vol%, the remainder being mainly nitrogen gas, the ratio
15 p_{H₂O}/p_{H₂} being between 0.04 and 0.5.

15. The method according to claim 14, wherein said continuous annealing takes place at an anneal temperature between 760°C and 850°C, and during a decarburizing time between 45s and 300s.

20 16. The method according to claim 15, wherein the anneal temperature is between 800°C and 850°C.

17. The method according to any one of claims 14 to 16, wherein the C-level is between 0.025wt% and 0.08wt%.

18. The method according to claim 17, wherein the C-level
25 is between 0.025wt% and 0.06wt%.

75656-18

22

19. The method according to any one of claims 14 to 18, wherein the Al-level is between 0.02wt% and 0.06wt%.

20. The method according to any one of claims 14 to 19, wherein the ratio pH_2O/pH_2 is between 0.04 and 0.25.

5 21. The method according to any one of claims 14 to 20, further comprising an over-ageing step at a temperature between 350°C and 450°C during a time span between 100s and 500s.

22. The method according to claim 21, further comprising a skinpass step with a reduction of between 0.3% and 1.5%.

10 23. The method according to any one of claims 14 to 22, wherein the slab further comprises one or more of the following:

Cu between 0.025wt% and 0.1wt%;

S between 0.008wt% and 0.04wt%; and

15 Ca between 0.0005wt% and 0.005wt%.

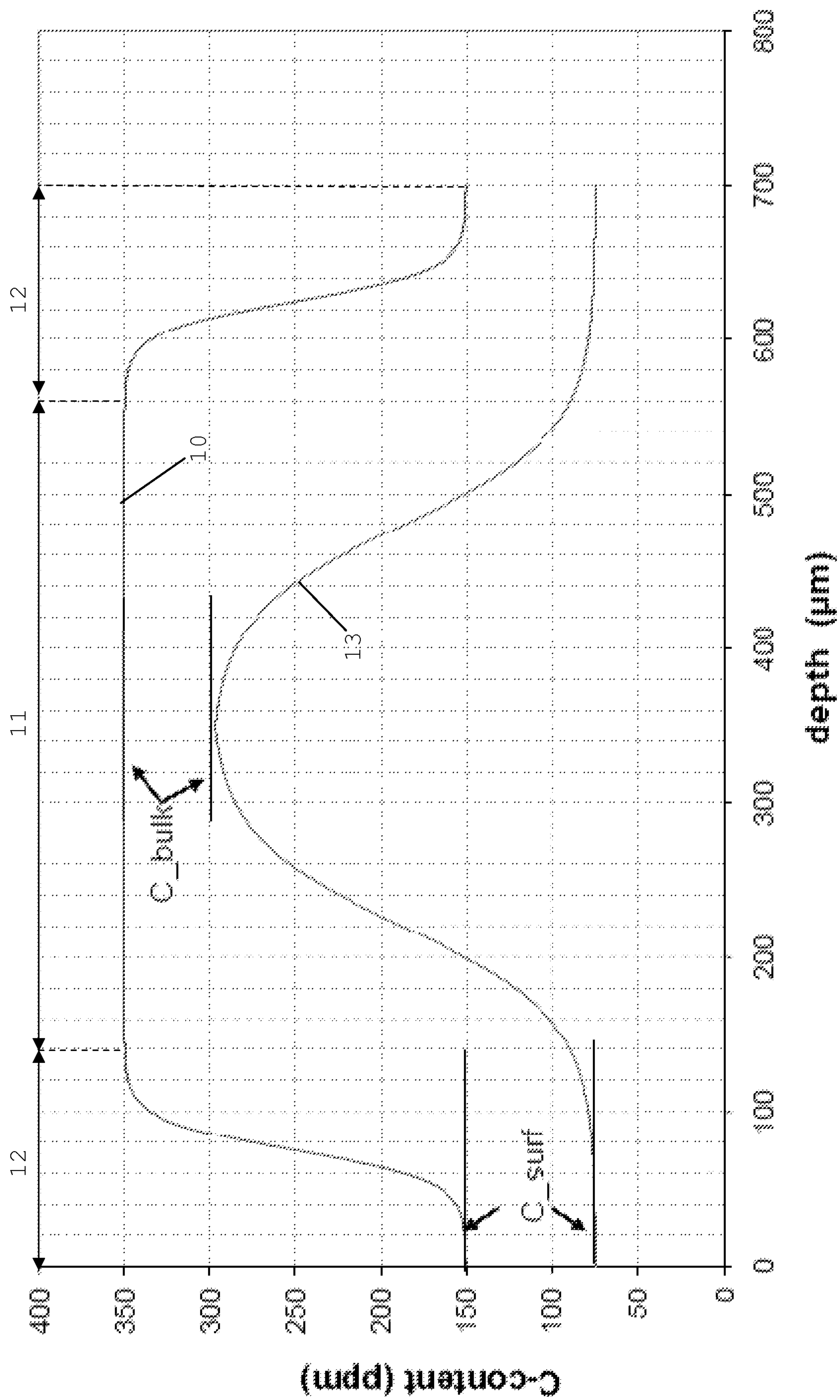
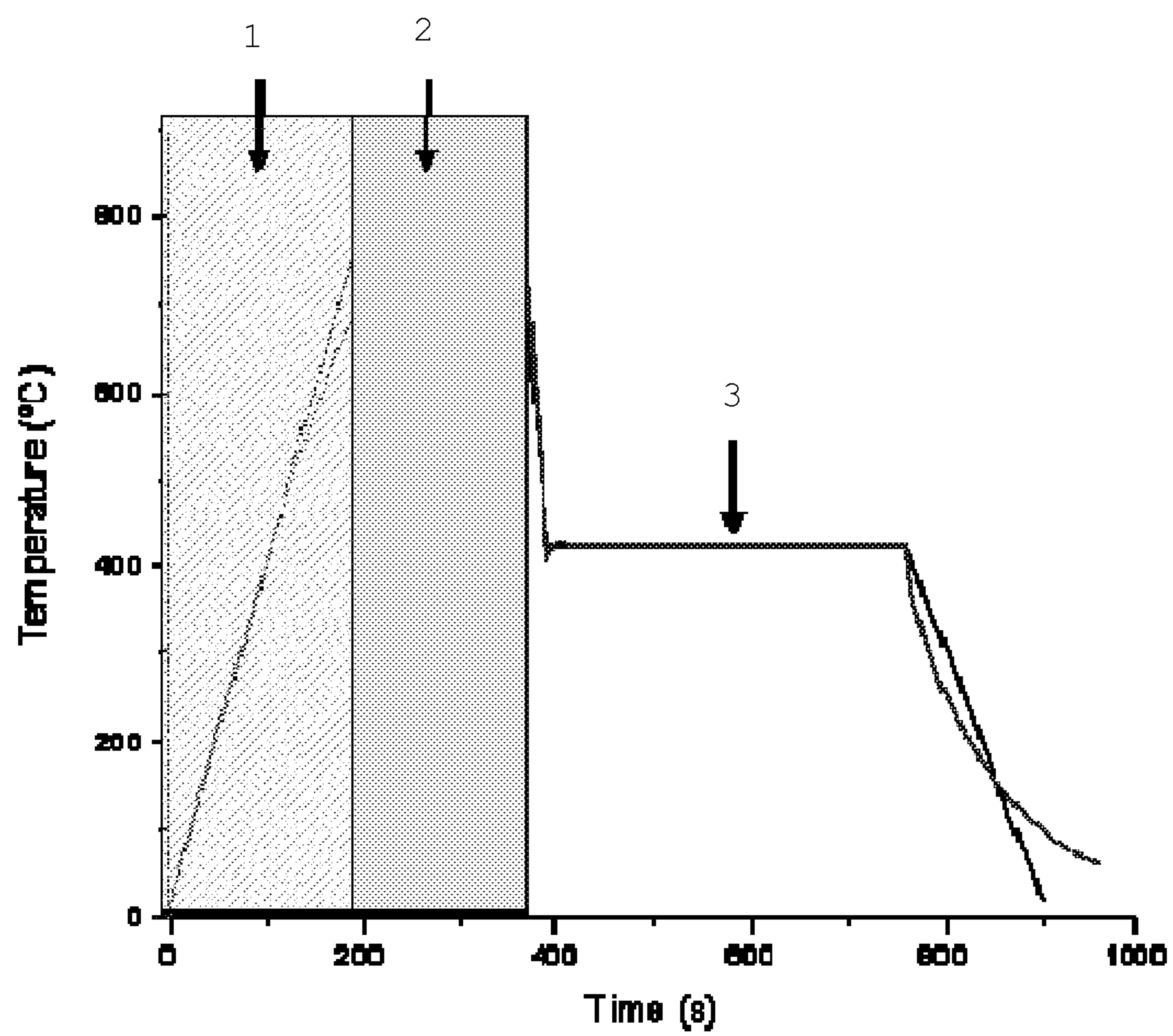


FIG. 1

FIG. 2

