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

EMAILLIERUNGSFÄHIGES STAHLBLECH UND VERFAHREN ZUR HERSTELLUNG EINES
SOLCHEN BLECHS

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(56) References cited:
**EP-A1- 1 225 241 EP-A1- 1 950 317
JP-A- 2 282 421 JP-A- 6 116 634
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Description**Field of the Invention**

[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.

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 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 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.

[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 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. 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.

Aims of the invention

[0005] The present invention aims to provide a partially decarburized steel sheet suitable for enamelling which do not suffer from the drawbacks of the above cited prior art.

Summary of the invention

[0006] The invention is related to steel sheets and products and to a production method as disclosed in the appended claims. The invention is thus 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 :

- 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%,
 - 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 .

[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%.

[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%.

[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 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.

[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 steel sheet, said slab comprising the following initial composition :

- C between 0.02wt% and 0.08wt%,
- Al between 0.012wt% and 0.07wt%,
- Mn between 0.12wt% and 0.45wt%,
- 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,

- subjecting said cold-rolled sheet to continuous annealing step, wherein said sheet is exposed during a decarburizing time to a decarburizing atmosphere comprising water vapour and hydrogen gas, wherein the H_2 content is between 1vol% and 95vol%, the H_2O content between 0.04vol% and 33vol%, the remainder being mainly nitrogen gas, the ratio $\text{pH}_2\text{O}/\text{pH}_2$ being between 0.04 and 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.

[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%.

[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 $\text{pH}_2\text{O}/\text{pH}_2$ is between 0.04 and 0.25.

[0020] The method of the invention may further 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.

Figure 2 illustrates an example of an annealing step usable in the method of the invention.

Detailed description of the invention

[0022] 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-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 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 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 another embodiment, C_{surface} is between 0 and 0.005wt%.

[0023] 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 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 half-width of the sheet.

[0024] 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 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 special alloying elements such as V are included. Also, N is kept as low as possible.

[0025] 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. 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 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%.

[0026] Mn is present between 0.12wt% and 0.45wt%. This element is added to control the strength properties of the steel and to avoid the formation of free sulphur.

[0027] 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 0.0005wt% to 0.005wt% respectively. These elements improve the enamelling quality.

[0028] The balance of the composition of the steel sheet according to the invention consists of Fe and incidental impurities. The following elements may be present as impurities at levels which are preferably lower than the values (in wt%) given in table 1 :

Table 1 : impurity levels

Si	< 0.1
P	< 0.03
Ti	< 0.01
Cr	< 0.2
Ni	< 0.2
As	< 0.02
Sn	< 0.02
Nb	< 0.01

(continued)

V	< 0.01
Sb	< 0.02
Mo	< 0.03
B	< 0.0005
N	< 0.007

[0029] In a steel sheet of the invention, the depth 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 $200\mu\text{m}$.

[0030] 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).

[0031] 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 $\frac{1}{4}(r_{90} + 2r_{45} + r_0)$, 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).

[0032] 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 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%.

[0033] 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 invention, oxygen is not added deliberately to the composition, but is allowed only at impurity levels.

[0034] 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.

[0035] 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.

[0036] 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).

[0037] According to the invention, the superficial decarburization is done under a decarburizing atmosphere 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 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 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 pressure, or a pressure different from atmospheric but within generally known boundaries applied in this type of annealing process.

[0038] According to one embodiment, the decarburizing atmosphere can be prepared with a mixture of 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 $C + H_2O \rightarrow CO + H_2$. The maximum of said range ensures that 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.

[0039] 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. In the following, the "decarburizing time" refers to the time spent under the conditions of the decarburizing atmosphere.

[0040] 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_{H₂O}/p_{H₂} 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

[0041] 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.

[0042] 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 H₂ and N₂, with H₂O vapour being injected in the first and/or the second soaking area. In the first trial, H₂O vapour was injected only in the second soaking area. In the second trial, H₂O was injected in the first and the second soaking area. Overageing was performed in both trials at 400°C. The overageing time depended on the line speed, e.g. at 180m/min line speed, the overageing 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.

[0043] In industrial trial 1, the p_{H₂O}/p_{H₂} ratio is below the range of 0.04-0.5 in the first soaking area (due to the fact that no H₂O injection is done). The decarburizing time in this trial is the time spent in the second soaking area, where the p_{H₂O}/p_{H₂} 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.

[0044] In industrial trial 2, H₂O-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_{H₂O}/p_{H₂} values indicated in table 1 are the average values in soaking area 1 in which more H₂O was injected. However, the p_{H₂O}/p_{H₂} in soaking area 2 is estimated to be also within the range of 0.04-0.5. In industrial trial 2, longer decarburizing times could be achieved as compared to the first trial, for similar line velocities, leading to stronger decarburization.

[0045] 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 $\text{pH}_2\text{O}/\text{pH}_2$ in the range [0.04-0.5].

[0046] 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 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 $75\mu\text{m}$ up to $250\mu\text{m}$, as shown in table 1. There is no reason to conclude from the results however that the enamelling quality deteriorates at higher depth values than $250\mu\text{m}$. Such higher depth values are therefore not excluded from the scope of the invention. All tested samples showed a good fish scale resistance.

[0047] Table 2 summarizes the results after 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 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 $\text{pH}_2\text{O}/\text{pH}_2$ ratio too low, or a combination of these factors.

[0048] 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 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 formability characteristics.

Table 2: Overview of experimental conditions and results

sample n°	Trial nr	initial Cl (ppm ₁)	decarburizing 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

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(continued)

sample n°	Trial nr	initial CI (ppm ₁)	decarburizing time (s)	anneal temp. (°C)	pH2O/pH2 (-)	C_surf (ppm)	depth (µm)	enameling aspect	Acc. to invetion ?
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
1 : 1wt% = 10 ⁴ ppm									

[0049] 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.

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

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 4 : mechanical properties

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

Claims

1. 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 :

- 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%,
- 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, wherein said impurities may comprise (in wt%) : 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, and wherein the depth where the C-level reaches $(C_{\text{bulk}} + C_{\text{surface}}) / 2$, is higher than 75µm.

2. Steel sheet according to claim 1, having an r_m value between 1.8 and 2.1.

3. Steel sheet according to claim 1 or 2, wherein C_{surface} is between 0.005wt% and 0.015wt%.

4. Steel sheet according to claim 1 or 2, wherein C_{surface} is between 0 and 0.005wt%.
5. Steel sheet according to any one of claims 1 to 4, wherein C_{bulk} is between 0.02wt% and 0.08wt%.
- 5 6. Steel sheet according to claim 5, wherein C_{bulk} is between 0.025wt% and 0.08wt%.
7. Steel sheet according to claim 5, wherein C_{bulk} is between 0.025wt% and 0.06wt%.
8. Steel sheet according to any one of claims 1 to 7, wherein the Al-level is between 0.02wt% and 0.06wt%.
- 10 9. Steel sheet according to any one of claims 1 to 8, wherein said depth is between 130 μm and 200 μm .
- 10 10. Enamelled steel sheet consisting of a steel sheet according to any one of claims 1 to 9 provided with an enamel layer.
- 15 11. 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 steel sheet, said slab comprising the following initial composition :
 - C between 0.02wt% and 0.08wt%,
 - 20 - Al between 0.012wt% and 0.07wt%,
 - Mn between 0.12wt% and 0.45wt%,
 - O lower than 0.01wt%
 - and optionally :
 - 25 - 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, wherein said impurities may comprise (in wt%) : 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,
 - 30 - subjecting said cold-rolled sheet to continuous annealing step, wherein said sheet is exposed during a decarburizing time to a decarburizing atmosphere comprising water vapour and hydrogen gas, wherein the H_2 content is between 1vol% and 95vol%, the H_2O content between 0.04vol% and 33vol%, the remainder being mainly
 - 35 nitrogen gas, the ratio $\text{pH}_2\text{O}/\text{pH}_2$ being between 0.04 and 0.5.
12. Method according to claim 11, 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.
- 40 13. Method according to claim 12, wherein the anneal temperature is between 800°C and 850°C.
14. Method according to any one of claims 13 to 15, wherein the initial C-level is between 0.025wt% and 0.08wt%.
15. Method according to claim 14, wherein the initial C-level is between 0.025wt% and 0.06wt%.
- 45 16. Method according to any one of claims 11 to 15, wherein the initial Al-level is between 0.02wt% and 0.06wt%.
17. Method according to any one of claims 11 to 16, wherein the ratio $\text{pH}_2\text{O}/\text{pH}_2$ is between 0.04 and 0.25.
- 50 18. Method according to any one of claims 11 to 17, further comprising an over-ageing step at a temperature between 350°C and 450°C during a timespan between 100s and 500s.
19. Method according to claim 18, further comprising a skinpass step with a reduction of between 0.3% and 1.5%.

Patentansprüche

1. Emaillierungsfähiges Walzstahlblech, wobei das Blech ein Kohlenstoffprofil aufweist, das durch einen Gradienten

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in der C-Höhe von einer Höhe $C_{\text{Oberfläche}}$ auf zumindest einer Oberfläche des Blechs zu einer Höhe C_{Masse} in der Masse des Blechs definiert ist, wobei C_{Masse} größer als $C_{\text{Oberfläche}}$ ist, und wobei:

- C_{Masse} größer als 0 ist und kleiner als oder gleich 0,08 Gew.-% ist;
 - $C_{\text{Oberfläche}}$ zwischen 0 Gew.-% und 0,015 Gew.-% beträgt;
 - Al zwischen 0,012 Gew.-% und 0,07 Gew.-% beträgt;
 - Mn zwischen 0,12 Gew.-% und 0,45 Gew.-% beträgt;
 - O weniger als 0,01 Gew.-% ist;
- und optional:

- Cu zwischen 0,025 Gew.-% und 0,1 Gew.-% beträgt;
- S zwischen 0,008 Gew.-% und 0,04 Gew.-% beträgt;
- Ca zwischen 0,0005 Gew.-% und 0,005 Gew.-%; beträgt,

wobei der Rest Fe und anfallende Verunreinigungen sind, wobei die Verunreinigungen (in Gew.-%): 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 umfassen können und wobei die Tiefe, bei der die C-Höhe ($C_{\text{Masse}} + C_{\text{Oberfläche}}$) / 2 erreicht, höher als 75 μm ist.

2. Stahlblech nach Anspruch 1, das einen rm-Wert zwischen 1,8 und 2,1 aufweist.
3. Stahlblech nach Anspruch 1 oder 2, wobei $C_{\text{Oberfläche}}$ zwischen 0,005 Gew.-% und 0,015 Gew.-% beträgt.
4. Stahlblech nach Anspruch 1 oder 2, wobei $C_{\text{Oberfläche}}$ zwischen 0 Gew.-% und 0,005 Gew.-% beträgt.
5. Stahlblech nach irgendeinem der Ansprüche 1 bis 4, wobei C_{Masse} zwischen 0,02 Gew.-% und 0,08 Gew.-% beträgt.
6. Stahlblech nach Anspruch 5, wobei C_{Masse} zwischen 0,025 Gew.-% und 0,08 Gew.-% beträgt.
7. Stahlblech nach Anspruch 5, wobei C_{Masse} zwischen 0,025 Gew.-% und 0,06 Gew.-% beträgt.
8. Stahlblech nach irgendeinem der Ansprüche 1 bis 7, wobei die Al-Höhe zwischen 0,02 Gew.-% und 0,06 Gew.-% beträgt.
9. Stahlblech nach irgendeinem der Ansprüche 1 bis 8, wobei die Tiefe zwischen 130 μm und 200 μm beträgt.
10. Emailliertes Stahlblech, das aus einem Stahlblech nach einem der Ansprüche 1 bis 9 besteht, das mit einer Emailleschicht versehen ist.
11. Verfahren zum Herstellen eines Walzstahlblechs zum Emaillieren, das die Schritte umfasst:

- Unterziehen einer Stahlbramme einem Warmwalzen, gefolgt von einer Wicklung und Kaltwalzen, um ein kaltgewalztes Stahlblech zu erhalten, wobei die Bramme die folgende Ausgangszusammensetzung aufweist:
 - C zwischen 0,02 Gew.-% und 0,08 Gew.-%;
 - Al zwischen 0,012 Gew.-% und 0,07 Gew.-%;
 - Mn zwischen 0,12 Gew.-% und 0,45 Gew.-%;
 - O weniger als 0,01 Gew.-% ist;
- und optional:

- Cu zwischen 0,025 Gew.-% und 0,1 Gew.-%;
 - S zwischen 0,008 Gew.-% und 0,04 Gew.-%;
 - Ca zwischen 0,0005 Gew.-% und 0,005 Gew.-%,
- wobei der Rest Fe und anfallende Verunreinigungen sind, wobei die Verunreinigungen (in Gew.-%): 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 umfassen können;

- Unterziehen des kaltgewalzten Blechs einem kontinuierlichen Glühschritt, wobei das Blech während einer Entkohlungszeit einer entkohlenden Atmosphäre ausgesetzt wird, die Wasserdampf und Wasserstoffgas um-

fasst, wobei der H₂-Gehalt zwischen 1 Vol.-% und 95 Vol.-% liegt, der H₂O-Gehalt zwischen 0,04 Vol.-% und 33 Vol.-% liegt, wobei der Rest vorwiegend Stickstoffgas ist, wobei das Verhältnis pH₂O/pH₂ zwischen 0,04 und 0,5 liegt.

- 5 12. Verfahren nach Anspruch 11, wobei das kontinuierliche Glühen bei einer Glüh­temperatur zwischen 760 °C und 850 °C und während einer Entkohlungszeit zwischen 45 s und 300 s erfolgt.
13. Verfahren nach Anspruch 12, wobei die Glüh­temperatur zwischen 800 °C und 850 °C liegt.
- 10 14. Verfahren nach irgendeinem der Ansprüche 13 bis 15, wobei die anfängliche C-Höhe zwischen 0,025 Gew.-% und 0,08 Gew.-% liegt.
15. Verfahren nach Anspruch 14, wobei die anfängliche C-Höhe zwischen 0,025 Gew.-% und 0,06 Gew.-% liegt.
- 15 16. Verfahren nach irgendeinem der Ansprüche 11 bis 15, wobei die anfängliche Al-Höhe zwischen 0,02 Gew.-% und 0,06 Gew.-% liegt.
17. Verfahren nach irgendeinem der Ansprüche 11 bis 16, wobei das Verhältnis pH₂O/pH₂ zwischen 0,04 und 0,25 liegt.
- 20 18. Verfahren nach irgendeinem der Ansprüche 11 bis 17, das darüber hinaus einen Überalterungsschritt bei einer Temperatur zwischen 350 °C und 450 °C innerhalb einer Zeitspanne zwischen 100 s und 500 s umfasst.
19. Verfahren nach Anspruch 18, das darüber hinaus einen Dressierungsschritt mit einer Verringerung von zwischen 0,3 % und 1,5 % umfasst.

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Revendications

- 30 1. Feuille d'acier laminée appropriée pour un émaillage, ladite feuille présentant un profil de carbone, défini par un gradient du niveau de C d'un niveau C_{surface} au niveau d'au moins une surface de la feuille, à un niveau C_{masse} dans la masse de la feuille, C_{masse} étant supérieur à C_{surface}, et avec :
 - C_{masse} supérieur à 0 et inférieur ou égal à 0,08 % en poids,
 - C_{surface} entre 0 et 0,015 % en poids,
 - 35 - Al entre 0,012 % en poids et 0,07 % en poids,
 - Mn entre 0,12 % en poids et 0,45 % en poids,
 - O inférieur à 0,01 % en poidset optionnellement :
 - 40 - Cu entre 0,025 % en poids et 0,1 % en poids,
 - S entre 0,008 % en poids et 0,04 % en poids,
 - Ca entre 0,0005 % en poids et 0,005 % en poids,
- 45 le reste étant du Fe et des impuretés accidentelles, dans laquelle lesdites impuretés peuvent comprendre (en % en poids) : 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, et dans laquelle la profondeur à laquelle le niveau de C atteint (C_{masse} + C_{surface})/2, est supérieure à 75 µm.
- 50 2. Feuille d'acier selon la revendication 1, ayant une valeur r_m entre 1,8 et 2,1.
3. Feuille d'acier selon la revendication 1 ou 2, dans laquelle C_{surface} est entre 0,005 % en poids et 0,015 % en poids.
4. Feuille d'acier selon la revendication 1 ou 2, dans laquelle C_{surface} est entre 0 et 0,005 % en poids.
- 55 5. Feuille d'acier selon l'une quelconque des revendications 1 à 4, dans laquelle C_{masse} est entre 0,02 % en poids et 0,08 % en poids.
6. Feuille d'acier selon la revendication 5, dans laquelle C_{masse} est entre 0,025 % en poids et 0,08 % en poids.

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7. Feuille d'acier selon la revendication 5, dans laquelle C_{masse} est entre 0,025 % en poids et 0,06 % en poids.
8. Feuille d'acier selon l'une quelconque des revendications 1 à 7, dans laquelle le niveau d'Al est entre 0,02 % en poids et 0,06 % en poids.
9. Feuille d'acier selon l'une quelconque des revendications 1 à 8, dans laquelle ladite profondeur est entre 130 μm et 200 μm .
10. Feuille d'acier émaillée constituée d'une feuille d'acier selon l'une quelconque des revendications 1 à 9 présentant une couche d'émail.
11. Procédé de production d'une feuille d'acier laminée pour émaillage, comprenant les étapes consistant à :
- soumettre une brame d'acier à un laminage à chaud suivi d'un bobinage et d'un laminage à froid, de manière à obtenir une feuille d'acier laminée à froid, ladite brame comprenant la composition initiale suivante :
 - C entre 0,02 % en poids et 0,08 % en poids,
 - Al entre 0,012 % en poids et 0,07 % en poids,
 - Mn entre 0,12 % en poids et 0,45 % en poids,
 - O inférieur à 0,01 % en poids
 - et optionnellement :
 - Cu entre 0,025 % en poids et 0,1 % en poids,
 - S entre 0,008 % en poids et 0,04 % en poids,
 - Ca entre 0,0005 % en poids et 0,005 % en poids,
 - le reste étant du Fe et des impuretés accidentelles, dans lequel lesdites impuretés peuvent comprendre (en % en poids) : 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,
 - soumettre ladite feuille laminée à froid à une étape de recuit continu, dans lequel ladite feuille est exposée pendant une durée de décarburation à une atmosphère décarburente comprenant de la vapeur d'eau et un gaz d'hydrogène, dans lequel la teneur en H_2 est entre 1 % en vol et 95 % en vol, la teneur en H_2O entre 0,04 % en vol et 33 % en vol, le reste étant principalement du gaz d'azote, le rapport $\text{pH}_2\text{O}/\text{pH}_2$ étant entre 0,04 et 0,5.
12. Procédé selon la revendication 11, dans lequel ledit recuit continu a lieu à une température de recuit entre 760 °C et 850 °C, et pendant une durée de décarburation entre 45 s et 300 s.
13. Procédé selon la revendication 12, dans lequel la température de recuit est entre 800 °C et 850 °C.
14. Procédé selon l'une quelconque des revendications 13 à 15, dans lequel le niveau de C initial est entre 0,025 % en poids et 0,08 % en poids.
15. Procédé selon la revendication 14, dans lequel le niveau de C initial est entre 0,025 % en poids et 0,06 % en poids.
16. Procédé selon l'une quelconque des revendications 11 à 15, dans lequel le niveau d'Al initial est entre 0,02 % en poids et 0,06 % en poids.
17. Procédé selon l'une quelconque des revendications 11 à 16, dans lequel le rapport $\text{pH}_2\text{O}/\text{pH}_2$ est entre 0,04 et 0,25.
18. Procédé selon l'une quelconque des revendications 11 à 17, comprenant en outre une étape de surveillance à une température entre 350 °C et 450 °C pendant un laps de temps entre 100 s et 500 s.
19. Procédé selon la revendication 18, comprenant en outre une étape d'écrouissage avec une réduction située entre 0,3 % et 1,5 %.

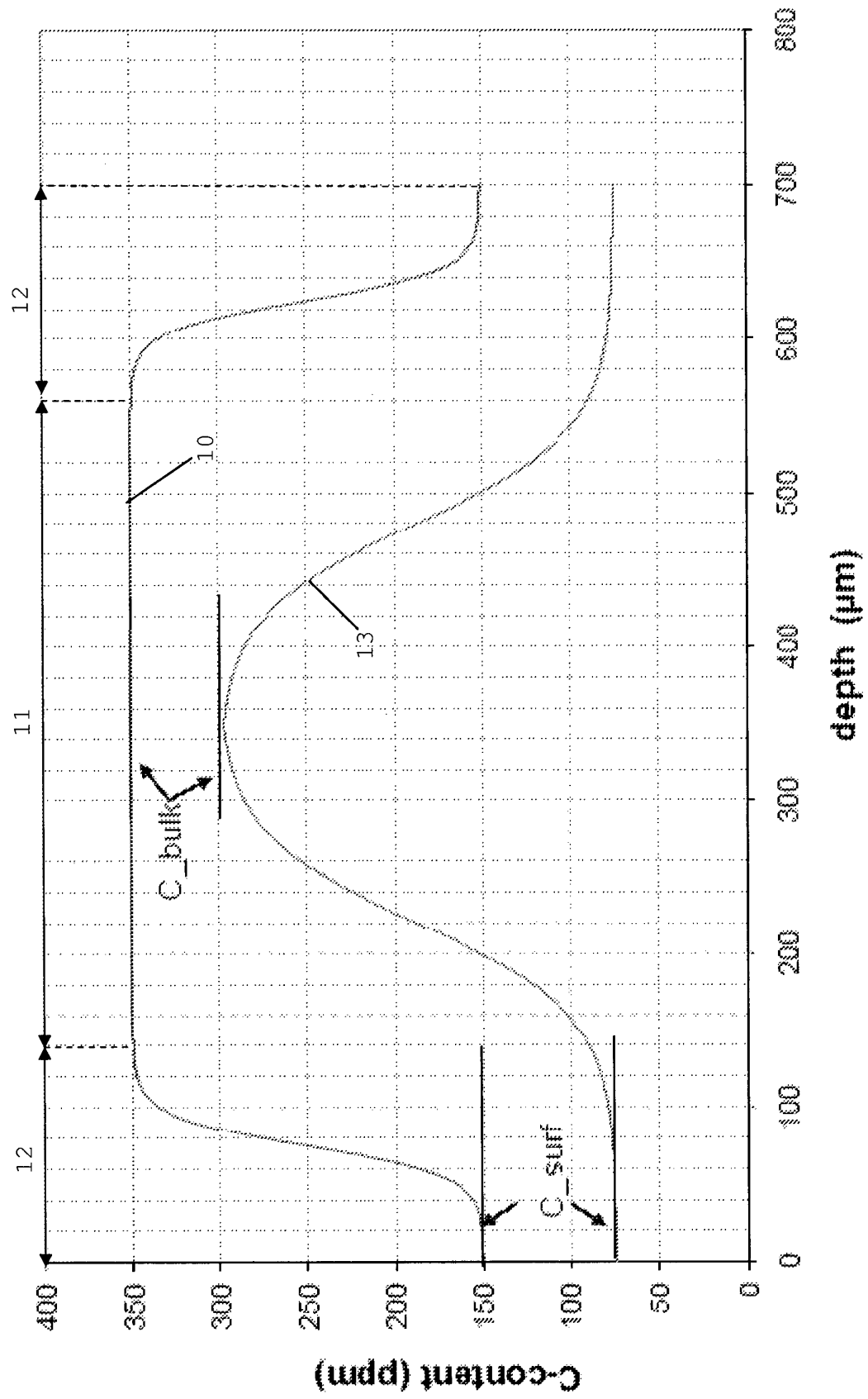


FIG. 1

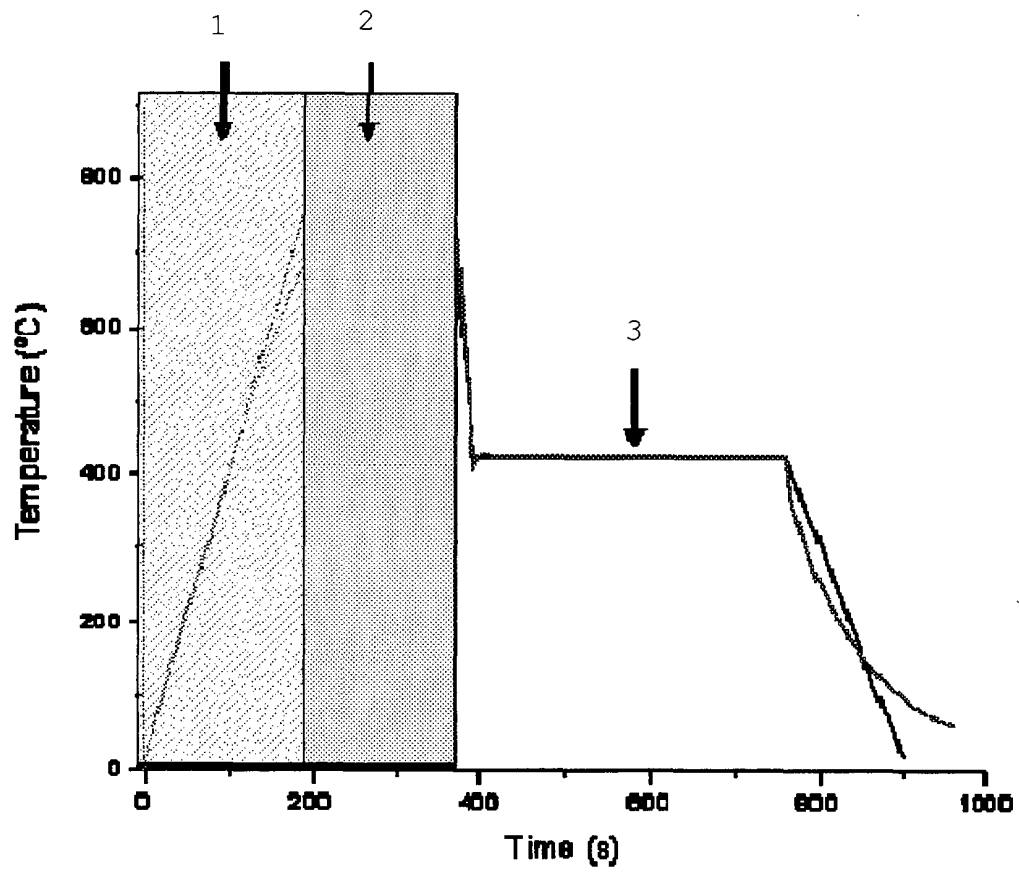


FIG. 2

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2282421 A [0003]
- JP 6116634 A [0003]
- JP 6116634 B [0004] [0032]