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(54) **Cold reduced enamelling steel sheet and an enamelled structure comprising a component of such a steel sheet**

(57) Cold reduced enamelling steel sheet comprising (in weight ppm unless otherwise indicated)

$5 \leq C \leq 90$;

$0.10 \leq Mn \leq 0.50$ (wt. %);

$Al_{as} \leq 300$ (acid soluble Al);

$O \leq 35$;

$S \leq 350$;

$30 \leq N < 110$;

$B_{min} < B \leq B_{max}$;

wherein $B_{min} = N \times 0.80 \times 10.8/14$ and $B_{max} = N \times 10.8/14 + 83/6$; and optionally

$50 \leq P \leq 160$; in combination with

$Cu_{min} \leq Cu \leq Cu_{max}$;

wherein $Cu_{min} = P \times 1.00 \times 63.6/31$ and $Cu_{max} = P \times 2.00 \times 63.6/31$; in each case the balance being Fe and unintentional and/or inevitable impurities.

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Description

[0001] The invention relates to cold reduced enamelling steel sheet. The invention also relates to an enamelled structure comprising a component of such a steel sheet.

[0002] Cold reduced enamelling steel sheet is frequently used to fabricate products such as domestic appliances. During fabrication of such products, the steel sheet material is usually coated with an enamel layer. It is then desirable to obtain an enamel layer with good adhesion to the steel sheet, and with at most only a few visible defects such as fish scale patterns. It is known that the resistance to fish scale formation can be improved by a synergistic effect of boron and nitrogen content in cold reduced steel sheet when boron in an amount of 83 ppm by weight or more and nitrogen in an amount of 89 ppm by weight or more, are present in the steel sheet.

[0003] It is an object of the present invention to provide an alternative enamelling steel sheet. It is another object of the invention to provide a cheap enamelling steel sheet that is suitable for white enamel. It is another object of the invention to provide an enamelling steel sheet with improved balance in enamelling behaviour and mechanical properties, in particular elongation.

[0004] The cold reduced enamelling steel sheet according to the invention comprises (in weight ppm unless otherwise indicated)

$$5 \leq C \leq 90;$$

$$0.10 \leq Mn \leq 0.50 \text{ (wt. \%)};$$

$$Al_{as} \leq 300 \text{ (acid soluble Al)};$$

$$O \leq 35;$$

$$30 \leq N \leq 110;$$

$$B_{min} \leq B \leq B_{max};$$

wherein $B_{min} = N \times 0.80 \times 10.8/14$ and $B_{max} = N \times 10.8/14 + 83/6$; and optionally

$$50 \leq P \leq 160; \text{ in combination with}$$

$$Cu_{min} \leq Cu \leq Cu_{max};$$

wherein $Cu_{min} = P \times 1.00 \times 63.6/31$ and $Cu_{max} = P \times 2.00 \times 63.6/31$; in each case the balance being Fe and unintentional and/or inevitable impurities.

[0005] Herewith is provided an enamelling steel sheet with a minimum of alloying elements that has deep drawing properties which are sufficiently good. After applying and firing white enamel, the steel sheet is essentially free from fish scale defects, and the enamel adhesion is satisfactory.

[0006] The combination of B and N enables formation of precipitates that help suppress the formation of fish scales. In order to sufficiently suppress the formation of fish scale defects, the atomic ratio B/N should be more than 0.80. It is now found that the mechanical properties, in particular deep drawing properties, are better if the amount of excess B above the atomic ratio B/N of 1.00 is limited to at most 83/6 ppm by weight. The recrystallisation temperature is also lower in that case. Thus, when the B-content exceeds B_{max} , the mechanical properties are unnecessarily deteriorating. This deterioration is currently thought to be related to the presence of acid soluble B in the steel matrix.

[0007] Oxygen can be present in the steel sheet after oxygen steel making process typically up to an amount of 35 ppm.

[0008] In an embodiment, oxygen is not added to extra amounts, since it might form unnecessary precipitates that are unfavourable for the mechanical properties.

[0009] The amount of acid soluble Al (Al_{as}) should be limited to at most 300 ppm. Deep drawing properties may improve as the amount of Al_{as} is kept low as possible, preferably lower than 150 ppm. The total amount of Al that may be present in the steel depends primarily on the oxygen content. The total amount of Al is preferably sufficiently high to bind essentially all the oxygen that is present in the steel sheet.

[0010] Mn is important for forming MnS precipitates, and MnO precipitates in the case that not all oxygen is already

bound by Al. S may be, and in practice often is present in the steel sheet as unintentional element. A significant effect is obtained when at least 0.10 wt. % of Mn is present in the steel sheet. Preferably, the amount of Mn is at least 0.23 wt. % to gain full advantage of this alloying element. However, for maintaining sufficient deep drawing capability of the steel sheet, the Mn content should be kept to a maximum of 0.50 wt. %.

[0011] Optionally the steel sheet also contains:

$$50 \leq P \leq 160;$$

in combination with

$$Cu_{min} \leq Cu \leq Cu_{max};$$

wherein $Cu_{min} = P \times 1.00 \times 63.6/31$ and $Cu_{max} = P \times 2.00 \times 63.6/31$. Herewith, the quality of the steel sheet is preserved during a pickling operation. The optimal atomic ratio Cu/P will depend on the sheet velocity in a pickling unit. When the atomic ratio Cu/P can lie anywhere between 1.00 and 2.00, the atomic ratio can be freely optimised to the particular pickling conditions of an existing pickling line.

[0012] However, an atomic ratio Cu/P of between 1.00 and 1.50 is preferred, since under this condition in most cases the pickling behaviour is sufficiently good, with less Cu added to the alloy.

[0013] It is preferred that $B_{min} = N \times 0.90 \times 10.8/14$. Herewith the atomic ratio B/N is higher than 0.90. Herewith it is better assured that all nitrogen is indeed precipitated with B.

[0014] It is more preferred that $B_{min} = N \times 1.00 \times 10.8/14$. Herewith the atomic ratio B/N is higher than 1.00. It has been found that a small excess of B can be tolerated regarding the mechanical properties, with the advantage that it ensures that all N is indeed precipitated. Herewith the formation of fish scales is essentially fully suppressed.

[0015] In an embodiment, the steel sheet comprises:

[0016] $45 \leq N \leq 110$. The formation of fish scale defects has been found to be suppressed better if the amount of N present in the steel sheet is at least 45 ppm.

[0017] In an embodiment, the steel sheet comprises less than 89 ppm N. It has been found that the amount of added B can then be reduced while the formation of fish scale defects is nevertheless sufficiently reduced.

[0018] In an embodiment wherein the steel sheet comprises less than 89 ppm N, it is preferred that $B_{max} = N \times 1.20 \times 10.8/14$. By keeping the atomic ratio B/N smaller than or equal to 1.20, the mechanical properties are kept close to their optimum. It is more preferred to keep the atomic ratio B/N smaller than or equal to 1.10. Herewith it is even better assured that no deteriorating effect on the mechanical properties results from the B addition.

[0019] In a preferred embodiment, the maximum amount of C in the steel sheet is 50 ppm by weight. Herewith the ageing properties are better suited. In a more preferred embodiment, the maximum amount of C is 40 ppm. In a yet more preferred embodiment, the amount of C in the steel sheet is lower than 30 ppm by weight. Herewith, the strengthening of the steel sheet by ageing is maximised.

[0020] In an embodiment of the invention the cold reduced enamelling steel sheet has a composition of C, Mn, Al, S, N, B, Cu, P in the amounts as specified above, the balance being Fe and unintentional and/or inevitable impurities such as O, Si.

[0021] In an embodiment of the invention, the steel sheet as described above has a grain size according to ASTM of 9.5 units or less. Herewith the desired mechanical properties and the pickling properties are achieved.

[0022] In an embodiment, the yield strength is between 140 MPa and 190 MPa, the tensile strength is between 270 MPa and 350 MPa, and the elongation to fracture is at least 35 %, all numbers measured in cross sectional direction to rolling in annealed, unaged and 1 % temper rolled condition. With these mechanical properties, the enamelling steel is sufficiently suited for most deep drawing applications. The steel sheet can have an *r*-value (at 90° to rolling direction) of higher than 1.85, and/or an *n*-value exceeding 0.233.

[0023] In another aspect, the invention relates to an enamelled structure comprising at least one component made of the above described steel sheet, provided with an enamel layer.

[0024] The invention will be explained according to some embodiments of the invention.

[0025] Cold reduced enamelling steel sheet can be produced by preparing a suitable steel melt and casting the melt into a slab. The production process can include operations of hot rolling the slab, pickling the rolled product, cold rolling, annealing, temper rolling. In particular, cold rolling can be applied to a reduction exceeding 50 %, or exceeding 70 %, and in an embodiment not exceeding 90 %. In particular, annealing can be performed to a temperature between the recrystallisation temperature of the rolled sheet and the A_{r3} temperature. Annealing may be performed as coil annealing, continuous annealing, or any suitable type of annealing. In particular, temper rolling may be performed to a reduction between 0.5 % and 2 %. The embodiments of the invention are, however, not limited to these operations and conditions.

[0026] Laboratory melts were provided with various compositions as determined using spectrometric analysis and shown in Table I, in wt. ppm except for Mn in which case wt. % is used.

Table I

Type	C	Mn	O	Al	Al _{as}	B	N	B/N	Si	Cu	P	S
Ref.	35	0.44	19	180	150	0	32	0	70	220	70	350
1	26	0.45	20	140	100	64	92	0.90	80	230	70	80
2	26	0.42	33	40	0	73	83	1.14	40	260	70	90

For reference, the atomic ratio B/N is also included in Table I.

[0027] B was added to the melt in the form of FeB after Al and Mn had been added. The composition of the melts were determined using spectrometric analysis of the melts. The amount of C in these steel types (between 20 and 30 ppm) can be achieved in most oxygen blowing steel making factories.

[0028] The melts were cast and hot rolled, with a finishing temperature of 930 °C. Then the sheets were cooled at a velocity of 20 °C/s, and coiled at a temperature of 690 °C.

[0029] After coil cooling, the sheets were pickled at a temperature of 70 °C, and cold rolled to three reductions of 75 %, 80 %, and 85 % (corresponding to respective final thicknesses of 1.0 mm, 0.8 mm, and 0.6 mm) for each type.

[0030] The recrystallisation temperature for tight coil annealing was determined for each type for various reductions using a heating rate of 2.4×10^{-5} /sec in HN_x . Each sample was heated to a certain temperature, and cooled, and successively heated to a temperature 10° above the previous temperature. After each cooling step, a microscopic study of the microstructure of the sample was performed to determine whether recrystallisation had occurred. The thus found recrystallisation temperatures are given in °C in the following Table II.

Table II

Type	Cold reduced by:		
	75%	80%	85%
Ref.	640	640	640
1	640	640	640
2	610	620	620

It has been found that the presence of B does not result in an increase of the recrystallisation temperature. This is believed to be a result of no free B being present in the steel sheets.

[0031] After cold reduction, each type of thus obtained and rolled steel sheet was tight-coil annealed at 640 °C using a heating rate of 2.4×10^{-5} /sec, and after cooling down to room temperature subsequently temper rolled to a 1 % reduction.

[0032] The final grain structure in cross section of the rolling direction was determined after cold rolling, annealing, and temper rolling to a 1 % reduction according to the ASTM standard. The results are given in the following Table III in ASTM units.

Table III

Type	Cold reduced by		
	75 %	80 %	85 %
Ref.	9.5	9.5	10
1	9.0	9.5	9.5
2	9.0	9.0	9.0

[0033] White enamel was applied to these steel sheets, using various firing temperatures between 780 and 860°C. The reference steel sheet showed a high abundance of fish scales after application of white enamel, while none of the steel sheets of types 1 or 2 suffered from visible fish scale defects. This shows that in cold rolled sheet even a low B content of 64 ppm can be sufficient to suppress fish scale formation, as long as the amount of B is carefully adapted to the amount of N that is present in the steel sheet. Also, the adhesion of the white enamel was excellent.

[0034] The following Table IV shows results of mechanical tests of temper rolled (1 %) non-aged sheet sheets. The results are average results obtained on 75, 80, and 85 % cold reduced sheets, measured in the transverse direction,

according to the small Euronorm using a small rod from the sheet. R_p denotes yield strength, R_m is the tensile strength, A_g is the uniform elongation, and A80 the elongation to fracture. Also given are transverse r -value (90°) and n -value.

Table IV

Type	R_p	R_m	A_g	A80	r	n
	MPa	MPa	%	%		
Ref.	195	320	22	31	1.48	0.214
1	162	301	26	38	1.94	0.241
2	160	296	26	37	2.07	0.243

Both types 1 and 2 being embodiments of the invention have better mechanical properties than the reference steel sheet. The elongation percentages of steel type 1 slightly exceed those of type 2. Type 1 contains more Al_{as} than type 2, yet type 1 has slightly better mechanical properties. The present understanding is that this shows the onset of the adverse effect of excess B, since in type 2 both the absolute amount of B as well as the atomic ratio B/N are higher than those of type 1.

[0035] An embodiment of the enamelling steel sheet according to the invention has also been prepared in a production plant. The spectroscopically analysed composition is given in Table V.

Table V

Type	C	Mn	O	Al	Al_{as}	B	N	B/N	Si	Cu	P	S
3	50	0.29	20	260	230	59	60	1.27	10	250	100	130

The cast melt was hot rolled, and cold rolled to a cold reduction of 80 % and a final thickness of 0.9 mm. The cold rolled steel sheet was coil annealed to a temperature of 650°C, and subsequently cooled down to room temperature and temper rolled by 0.8 %. The grain size in cross section to rolling direction was determined to be 9.0 ASTM units using the ASTM standard.

[0036] The mechanical properties of this steel sheet were determined in cross section to the rolling direction as was done with the laboratory melts above. The results are shown in Table VI.

Table VI

Type	R_p	R_m	A_g	A80	r	n
	MPa	MPa	%	%		
3	162	297	24	45	1.97	0.220

The resistance against fish scale formation is as good as the laboratory melts, and the adhesion of enamel is good.

Claims

1. Cold reduced enamelling steel sheet comprising (in weight ppm unless otherwise indicated)

$$5 \leq C \leq 90;$$

$$0.10 \leq Mn \leq 0.50 \text{ (wt. \%)};$$

$$Al_{as} \leq 300 \text{ (acid soluble Al)};$$

$$O \leq 35;$$

$$S \leq 350;$$

$$30 \leq N \leq 110;$$

$$B_{min} < B \leq B_{max};$$

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wherein $B_{\min} = N \times 0.80 \times 10.8/14$ and $B_{\max} = N \times 10.8/14 + 83/6$; and optionally

$50 \leq P \leq 160$; in combination with

$Cu_{\min} \leq Cu \leq Cu_{\max}$;

wherein $Cu_{\min} = P \times 1.00 \times 63.6/31$ and $Cu_{\max} = P \times 2.00 \times 63.6/31$; in each case the balance being Fe and unintentional and/or inevitable impurities.

2. Steel sheet according to claim 1, wherein $B_{\min} = N \times 0.90 \times 10.8/14$.

3. Steel sheet according to claim 1 or 2, wherein $B_{\min} = N \times 1.00 \times 10.8/14$.

4. Steel sheet according to claim 1, 2, or 3, wherein

$45 \leq N \leq 110$.

5. Steel sheet according to claim 1, 2, or 3, wherein

$30 \leq N < 89$.

6. Steel sheet according to claim 5, wherein $B_{\max} = N \times 1.20 \times 10.8/14$.

7. Steel sheet according to any one of the claims 1 to 6, wherein $Cu_{\max} = P \times 1.50 \times 63.6/31$.

8. Steel sheet according to any one of the claims 1 to 7, wherein the maximum amount of C is 30 ppm by weight.

9. Cold reduced enamelling steel sheet having a composition of C, Mn, Al, S, N, B, Cu, P in the amounts as specified in any one of the claims 1 to 8, the balance being Fe and unintentional an/or inevitable impurities such as O, Si.

10. Steel sheet according to any one of the preceding claims, wherein the grain size according to ASTM is 9.5 units or less.

11. Steel sheet according to any one of the preceding claims, wherein the yield strength is between 140 MPa and 190 MPa, the tensile strength is between 270 MPa and 350 MPa, and the elongation to fracture is at least 35 %.

12. Enamelled structure comprising at least one component made of the steel sheet according to any one of the claims 1 to 11 inclusive, provided with an enamel layer.

13. Enamelled structure according to claim 12, wherein the enamel is white enamel.

14. Enamelled structure according to claim 12 or 13, wherein the at least one component has been deep drawn.



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EUROPEAN SEARCH REPORT

Application Number
EP 01 20 0567

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The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 12 June 2001	Examiner Vlassi, E
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The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 12 June 2001	Examiner Vlassi, E
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