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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 A1);
$O \leq 35$;
$S \leq 350$;
$30 \leq N \leq 110$;
$B_{min} < B \leq B_{max}$;

wherein $B_{min} = N \times 0.80 \times 10.8/14$ and $B_{max} = N \times 10.8/14 + 144/6$;
and optionally

$Si \leq 90$;
$50 \leq P \leq 160$; 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.

[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)

$5 \leq C \leq 90$;

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

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

$O \leq 35$;

$30 \leq N \leq 110$;

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

wherein $B_{min} = N \times 0.80 \times 10.8/14$ and $B_{max} = N \times 10.8/14 + 144/6$;

and optionally:

$Si < 190$;

$50 \leq P \leq 160$; 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.

[0005] Herewith is provided an enamelling steel sheet with a minimum content 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 144/6 ppm (i.e. 24 ppm) by weight. 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 and/or free B in the steel matrix.

[0007] In an embodiment, oxygen is not added to extra amounts, since it might form unnecessary precipitates that are unfavourable for the mechanical properties for deep drawing, such as increase in yield strength and lowering of the elongation.

[0008] Oxygen is be present in the steel sheet after oxygen steel making process typically up to an amount of 35 weight-ppm.

[0009] The amount of acid soluble Al (Al_{as}) should be limited to at most 300 weight-ppm. Deep drawing properties may improve as the amount of Al_{as} is kept low as possible, preferably lower than 150 weight-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] Optionally the steel sheet also contains Si ≤ 190 weight-ppm. Addition of Si to amounts above 190 weight-ppm have an effect in increasing the yield strength and lowering the elongation of the resulting cold rolled steel sheet, which is in general a deterioration of the deep drawability. Thus by limiting the amount of Si to a maximum of 190 weight-ppm, some amount of excess B above the atomic ratio B/N of 1.00 can be tolerated.

[0014] Preferably the amount of excess B above the atomic ratio B/N of 1.00 is limited to at most 83/6 ppm by weight. Herewith the mechanical properties are particularly optimised for relatively high Si content, i.e. in the range of 40 weight-ppm to 190 wt.-ppm. The recrystallisation temperature is also lower in that case. The deterioration of the mechanical deep drawing properties with the excess B above the atomic ratio B/N of 1.00 in this is limit is currently thought to be related to the presence of acid soluble B.

[0015] 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.

[0016] 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.

[0017] In an embodiment, the steel sheet comprises:

$45 \le N \le 110$. 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 weight-ppm.

[0018] In an embodiment, the steel sheet comprises less than 89 weight-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.

[0019] In an embodiment wherein the steel sheet comprises less than 89 weight-ppm N, it is preferred that $B_{max} = N \times 1.35 \times 10.8/14$. By keeping the atomic ratio B/N smaller than or equal to 1.35, the mechanical properties are kept closer to their optimum, than by simply limiting the amount of excess B above the atomic ratio B/N of 1.00 to 144/6 ppm by weight.

[0020] In an embodiment wherein the steel sheet comprises less than 89 weight-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.

[0021] When the amount of Si is below 40 weight-ppm, the elongation and thus the deep drawability, of the cold rolled steel sheet is significantly higher than for amounts of 40 weight-ppm and above.

[0022] Preferably, Si is not deliberately added during the steel making process, and only present as an unintentional and/or inevitable impurity, for instance, at a level of approximately 10 weight-ppm. It is found that with such low Si content, a relatively high excess B can be tolerated without noticeable deterioration of the elongation.

[0023] 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 weight-ppm. In a yet more preferred embodiment, the amount of C in the steel sheet is lower than 30 weight-ppm by weight. Herewith, the strengthening of the steel sheet by ageing is maximised.

[0024] 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.

[0025] 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.

[0026] 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.

[0027] 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.

[0028] 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 Ar_3 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.

[0029] The invention will be explained according to some embodiments of the invention.

[0030] 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.

[0031] 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 weight-ppm) can be achieved in most oxygen blowing steel making factories.

[0032] 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.

[0033] 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.

[0034] 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 and/or acid soluble B being present in the steel sheets.

[0035] 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.

[0036] 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

[0037] 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 weight-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.

[0038] 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 MPa	R_m MPa	A_g %	*A*80 %	*r*	*n*
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, particularly in terms of elongation and *r*-value. 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.

[0039] Embodiment of the enamelling steel sheet according to the invention have also been prepared in a production plant. The spectroscopically analysed compositions are 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
4	20	0.30	25	240	200	65	64	1.32	10	250	100	140

The cast melts were hot rolled, and cold rolled to a cold reduction of 80 % and a final thickness of 0.9 mm. The recrystallisation temperatures of these steel sheets were determined to be 650 °C, using the same method as described above. This is slightly higher than in the laboratory melts.

[0040] The cold rolled steel sheets were tight 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 for both types 3 and 4, using the ASTM standard.

[0041] The mechanical properties of these steel sheets 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	*A*80	*r*	*n*
	MPa	MPa	%	%		
3	162	297	24	45	1.97	0.220
4	168	302	23	45	1.92	0.215

It is observed that the elongation is remarkably high compared to the laboratory melts, even though the B/N ratio is relatively high. This is currently thought to be a result of the low Si content in these production plant steel types.

[0042] The resistance against fish scale formation is in both types 3 and 4 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)
$5 \leq C \leq 90$;
$0.10 \leq Mn \leq 0.50$ (wt. %);
$Al_{as} \leq 300$ (acid soluble Al);
$O \leq 35$;
$S \leq 350$;
$30 \leq N \leq 110$;
$B_{min} < B \leq B_{max}$;
wherein $B_{min} = N \times 0.80 \times 10.8/14$ and $B_{max} = N \times 10.8/14 + 144/6$;

and optionally: Si ≤ 190;
50 ≤ P ≤ 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 $B_{max} = N \times 10.8/14 + 83/6$.

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

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

5. Steel sheet according to any one of the preceding claims, wherein $45 \leq N \leq 110$.

6. Steel sheet according to any one of the preceding claims, wherein $30 \leq N < 89$.

7. Steel sheet according to claim 6, wherein $B_{max} = N \times 1.35 \times 10.8/14$.

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

9. Steel sheet according to any one of the preceding claims, wherein Si < 40.

10. Steel sheet according to any one of the preceding claims, wherein Si is present as an unintentional and/or inevitable impurity.

11. Steel sheet according to any one of the claims 1 to 10, wherein $Cu_{max} = P \times 1.50 \times 63.6/31$.

12. Steel sheet according to any one of the claims 1 to 11, wherein the maximum amount of C is 30 ppm by weight.

13. 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 12, the balance being Fe and unintentional and/or inevitable impurities such as O, Si.

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

15. 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 %.

16. Enamelled structure comprising at least one component made of the steel sheet according to any one of the claims 1 to 15 inclusive, provided with an enamel layer.

17. Enamelled structure according to claim 16, wherein the enamel is white enamel.

18. Enamelled structure according to claim 16 or 17, wherein the at least one component has been deep drawn.

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EUROPEAN SEARCH REPORT

Application Number
EP 02 07 5654

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	EP 0 769 565 A (NIPPON STEEL CORP) 23 April 1997 (1997-04-23)	1-8,12, 13,15	C22C38/00 C22C38/16 C21D8/04
A	* claims 1-20 * * examples 1-4 * * page 4, line 35 - page 10, line 20 *	9-11,14, 16-18	
X	US 4 576 657 A (SATOH SUSUMU ET AL) 18 March 1986 (1986-03-18)	1-8,12, 13,15	
A	* table 2 * * claims 1-4 * * column 2, line 60 - column 7, line 6 *	9-11,14, 16-18	
X	PATENT ABSTRACTS OF JAPAN vol. 006, no. 191 (C-127), 30 September 1982 (1982-09-30) -& JP 57 104627 A (NIPPON KOKAN KK), 29 June 1982 (1982-06-29)	1-8,12, 13,15	
A	* abstract *	9-11,14, 16-18	TECHNICAL FIELDS SEARCHED (Int.Cl.7)
X	EP 0 672 758 A (KAWASAKI STEEL CO) 20 September 1995 (1995-09-20)	1,5,6,9, 12,13,15	C22C C21D
A	* claims 1-23 * * examples 1,2 * * page 4, line 45 - page 8, line 15 *	2-4, 7-11,14, 16-18	
X	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 01, 30 January 1998 (1998-01-30) -& JP 09 227947 A (NKK CORP), 2 September 1997 (1997-09-02)	1,6,12, 13	
A	* abstract *	2-5, 7-11, 14-18	
	-/--		

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	9 April 2002	Vlassi, E

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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	PATENT ABSTRACTS OF JAPAN vol. 1996, no. 12, 26 December 1996 (1996-12-26) -& JP 08 199299 A (NKK CORP), 6 August 1996 (1996-08-06) * abstract *	1-18	
A	PATENT ABSTRACTS OF JAPAN vol. 014, no. 184 (C-0709), 13 April 1990 (1990-04-13) -& JP 02 030738 A (KAWASAKI STEEL CORP), 1 February 1990 (1990-02-01) * abstract *	1-18	
A	PATENT ABSTRACTS OF JAPAN vol. 1997, no. 07, 31 July 1997 (1997-07-31) -& JP 09 087748 A (NKK CORP), 31 March 1997 (1997-03-31) * abstract *	1-18	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	9 April 2002	Vlassi, E

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09-04-2002

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
EP 0769565	A	23-04-1997	JP	8283908	A	29-10-1996
			EP	0769565	A1	23-04-1997
			US	5855696	A	05-01-1999
			CN	1152340	A	18-06-1997
			WO	9630555	A1	03-10-1996
			JP	8325634	A	10-12-1996
US 4576657	A	18-03-1986	JP	1318402	C	29-05-1986
			JP	58144430	A	27-08-1983
			JP	60045689	B	11-10-1985
			DE	3371793	D1	02-07-1987
			EP	0101740	A1	07-03-1984
			WO	8302957	A1	01-09-1983
JP 57104627	A	29-06-1982	JP	1499816	C	29-05-1989
			JP	61006133	B	24-02-1986
EP 0672758	A	20-09-1995	CN	1118814	A ,B	20-03-1996
			DE	69518451	D1	28-09-2000
			DE	69518451	T2	04-01-2001
			EP	0672758	A1	20-09-1995
			JP	7278678	A	24-10-1995
			KR	221349	B1	15-09-1999
			US	5587027	A	24-12-1996
JP 09227947	A	02-09-1997	NONE			
JP 08199299	A	06-08-1996	JP	3067569	B2	17-07-2000
JP 02030738	A	01-02-1990	JP	2020931	C	19-02-1996
			JP	7059735	B	28-06-1995
JP 09087748	A	31-03-1997	NONE			

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82