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(54) **Extra low carbon steel sheets.**

(57) An extra low carbon steel sheet having a good phosphatability is disclosed, which comprises C≤0.01 wt%, N≤0.01 wt%, Si≤0.15 wt%, Mn≤0.6 wt%, Al≤0.10 wt%, Ti≥4.0x([C]+[N]), 1/6x[Ti]≤Nb≤31/4x[C], and the balance being substantially Fe.

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EXTRA LOW CARBON STEEL SHEETS

This invention relates to extra low carbon steel sheets having good chemical conversion characteristics, and more particularly to an improvement of the phosphatability in carbonitride-containing extra low carbon steel sheets.

Extra low carbon steel sheets containing Ti have excellent properties such as low yield point, high ductility and the like in view of their mechanical properties (please refer to Japanese Patent Application Publication No. 44-18,066). However, if it is intended to use the above steel sheet as, for example, an outer panel for automotive vehicles, there is caused a problem that the phosphatability is are poor, so that the use application is considerably restricted.

This results mainly from the fact that the surface of the steel sheet is covered with an oxide film of Ti. That is, Ti abundantly existent in the steel sheet concentrates in the surface of the steel sheet during the retaining at high temperature for a long time after the coiling followed to the hot rolling or during the recrystallization annealing after the cold rolling, which reacts with an oxygen in atmosphere to form an oxide film and has a bad influence of concentration promotion.

As a method for preventing the above drawback, there are known a method wherein Mn, S, P and the like are concentrated on the surface of the steel sheet (as described, for example, in Japanese Patent laid open No. 59-74,259) and so on. However, as the amounts of the above three elements increase, the physical properties of the steel are degraded, so that it is useless to provide good mechanical properties by extremely lowering the carbon content and adding Ti.

It is, therefore, an object of the invention to provide steel sheets having a good phosphatability without causing the material degradation as mentioned above.

According to the invention, there is the provision of an extra low carbon steel sheet having a good phosphatability, which comprises not more than 0.01 wt% of carbon, not more than 0.01 wt% of nitrogen, not more than 0.15 wt% of silicon, not more than 0.6 wt% of manganese, not more than 0.10 wt% of aluminum, titanium being not less than $4.0\times([C]+[N])$, niobium being within a range of $1/6\times[Ti]$ to $31/4\times[C]$, and the balance being iron and inevitable impurities.

For a better understanding of the invention, reference is made to the accompanying drawing, in which:

A single figure is a graph illustrating a relation among amounts of Ti and Nb and pin hole area ratio (PHE).

The invention is based on the phenomenon found during the investigation on the mechanical properties and phosphatability of Nb and/or Ti-containing steel.

Namely, each of steels having a chemical composition shown in the following Table 1, wherein the amount of Nb added is varied to a steel containing an amount of Ti larger than a specified total amount of C and N, was melted in a laboratory and shaped into a slab, which was then hot rolled, cold rolled, electrolytically degreased and continuously annealed at 830°C for 20 seconds. Next, the mechanical properties and phosphatability of the resulting steel sheet were examined.

Table 1

Steel sheet \ Ingredients	C (wt%)	Si (wt%)	Mn (wt%)	P (wt%)	S (wt%)	Aℓ (wt%)	Ti (wt%)	Nb (wt%)	N (wt%)	Ti/Nb (weight ratio)
1	0.0008	0.01	0.08	0.01	0.007	0.023	0.0080	0.0006	0.0011	13.3
2	0.0009	0.01	0.07	0.01	0.006	0.019	0.0081	0.0021	0.0010	3.9
3	0.0007	0.01	0.09	0.01	0.005	0.015	0.0079	0.0035	0.0009	2.6
4	0.0017	0.01	0.15	0.02	0.011	0.033	0.0160	0.0010	0.0020	16.0
5	0.0019	0.01	0.13	0.01	0.013	0.031	0.0160	0.0021	0.0020	7.6
6	0.0015	0.01	0.14	0.03	0.012	0.035	0.0161	0.0035	0.0021	4.6
7	0.0031	0.05	0.25	0.05	0.011	0.042	0.028	0.0021	0.0025	13.3
8	0.0033	0.06	0.28	0.04	0.012	0.041	0.028	0.0035	0.0031	8.0
9	0.0028	0.05	0.24	0.05	0.013	0.038	0.028	0.0054	0.0027	5.2
10	0.0043	0.04	0.53	0.11	0.015	0.045	0.042	0.0054	0.0021	7.8
11	0.0039	0.03	0.54	0.13	0.016	0.039	0.042	0.0066	0.0025	6.4
12	0.0045	0.04	0.55	0.14	0.014	0.033	0.042	0.0078	0.0023	5.4

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The phosphatability was estimated by pin hole area ratio (hereinafter abbreviated as PHE) when the steel sheet was degreased, rinsed with water, phosphated and subjected to a pin hole test as mentioned later.

In the pin hole test, a non-covered portion of phosphate crystal coating in the surface of the steel sheet to be tested was detected by sticking a filter paper impregnated with a reagent developing a color through reaction with iron ion to the surface of the steel sheet, which was numeralized as PHE by image analysis.

Separately, it has been confirmed that PHE$\leq$3.0 shows a good phosphatability.

In the single figure is shown a relation of Ti and Nb amounts to PHE, from which there have been found the followings. As the Ti amount increases, PHE becomes higher. While, PHE lowers as the Nb amount increases. In the steel containing any given amount of Ti, when the Nb amount is not less than 1/6 of the amount of Ti, PHE becomes not more than 3, which shows a good phosphatability.

Ti preferentially bonds to S, N and C in the steel to form precipitates, and at the same time concentrates in the surface of the steel to form an oxide film degrading the phosphatability as previously mentioned. Therefore, when the amount of Ti added is sufficiently small, there is no problem on the phosphatability apart from the mechanical properties, but the

phosphatability is degraded as the Ti amount increases. According to the invention, it is necessary that the amount of Ti added is not less than 4 times of the total amount of C and N in order to provide non-aging steel sheets.

On the other hand, the phosphatability is largely improved as the amount of Nb added increases. Because, it is guessed that the surface concentration of Ti is first suppressed with the increase of the Nb amount, so that Ti can not completely fix carbon unless a sufficiently excessive amount of Ti is added to amounts of C, N and S in the steel and hence Nb reacts with C to form NbC series precipitates on the surface of the steel sheet, which provide nuclei for phosphate crystal.

Moreover, it is known that when the amount of solute carbon is not more than 0.005%, even if such solute carbon is existent in the steel, it is included in the crystal grain boundary to provide a complete non-aging steel sheet.

However, when the Nb amount is excessive to the C amount, the phosphatability is degraded. Therefore, the Nb amount must be limited to not more than 31/4 times the C amount.

According to the invention, the reason why the amounts of C and N are limited to not more than 0.01%, respectively, is due to the fact that the press formability is sufficiently ensured as the mechanical

properties of the steel. For the same reason as described above, the amounts of Mn and Si are limited to not more than 0.6% and not more than 0.15%, respectively. Aℓ is accepted to be not more than 0.1% as the deoxidizer in the steel making. Moreover, the inevitable impurities are P and S, which are accepted to be not more than 0.15% and 0.02%, respectively, according to the invention.

The steel sheet according to the invention is manufactured by subjecting a steel of a particular chemical composition to continuous casting, hot rolling, cold rolling and annealing in the usual manner.

The following examples are given in the illustration of the invention and are not intended as limitations thereof.

Each of cold rolled steel sheets having a chemical composition as shown in the following Table 2 was manufactured through box annealing or continuous annealing.

Table 2

Steel sheet \ Ingredients	C (wt%)	Si (wt%)	Mn (wt%)	P (wt%)	S (wt%)	Aℓ (wt%)	Ti (wt%)	Nb (wt%)	N (wt%)	Ti/Nb (weight ratio)	
1	0.0012	0.01	0.15	0.01	0.01	0.025	0.025	0.0045	0.0023	5.6	Invention steel
2	0.0045	0.01	0.55	0.11	0.01	0.033	0.042	0.0080	0.0021	5.3	
3	0.0078	0.01	0.35	0.02	0.02	0.045	0.071	0.0120	0.0030	5.9	
4	0.0034	0.01	0.20	0.02	0.01	0.035	0.075	0.0153	0.0083	4.9	
5	0.0036	0.01	0.35	0.02	0.01	0.034	0.031	0.0055	0.0063	5.6	Comparative steel
6	0.0025	0.01	0.15	0.02	0.01	0.029	0.033	0.0051	0.0023	6.5	
7	0.0023	0.01	0.14	0.02	0.01	0.043	0.028	0.0182	0.0015	1.5	

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The phosphatability (PHE) and mechanical properties (AI, aging index, kg/mm^2) were measured with respect to the resulting steel sheets to obtain results as shown in the following Table 3. Moreover, the phosphatic treatment was carried out with BT 3112 made by Japan Perkerizing K.K., adjusting to total acidity of 14.3 and free acidity of 0.5 at 55°C and then spraying to the surface of the steel sheet for 120 seconds. The phosphatability was evaluated by PHE as previously mentioned.

Table 3

Steel sheet	Kind of annealing *1	PHE	AI *2
1	CAL	2.6	0
1	Batch	2.3	0
2	CAL	2.3	0
2	Batch	2.6	0
3	CAL	2.5	0
3	Batch	2.7	0
4	CAL	1.3	0
4	Batch	1.8	0
5	CAL	0.8	1.5
5	Batch	1.2	0.8
6	CAL	3.4	0
6	Batch	3.8	0
7	CAL	3.2	0

Note) *1 ... CAL : : continuous annealing 830°C, 20 seconds soaking

Batch : box annealing 690°C, 5 hours soaking

*2 ... rise of stress (kg/mm^2) in aging treatment at 100°C for 30 minutes after the 7.5% pre-strain

As seen from Table 3, when the Ti amount is less than 4 times the total amount of C and N (Steel sheet No. 5), AI is not zero, so that a so-called non-aging steel sheet can not be obtained. Even when using a high grade, extra low carbon steel containing

not more than 0.01% of each of carbon and nitrogen amounts, if the non-aging property can not be ensured, the application of such steel is restricted considerably. Therefore, the Ti amount is necessary to be not less than 4 times the total amount of C and N.

On the other hand, the phosphatability is degraded with the increase of Ti amount, but it is improved by adding Nb in an amount of not less than 1/6 of the Ti amount. When the Nb amount is less than 1/6 of Ti amount (Steel sheet No. 6) or more than 31/4 of C amount (Steel sheet No. 7), PHE exceeds 3, and the phosphatability is degraded.

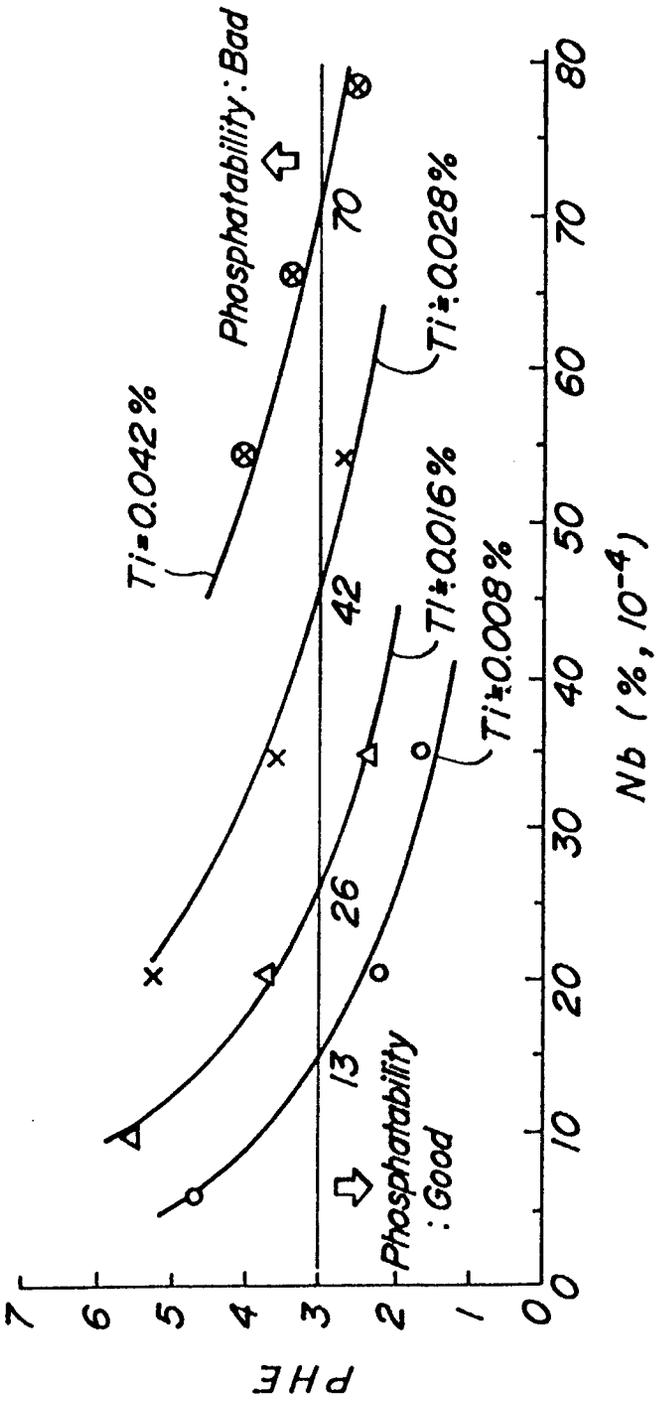
Even in case of steels containing more than 0.01% of C or N amount, the non-aging property can be obtained by the sufficient addition of Ti. In this case, the yield strength becomes high and the elongation or ductility becomes poor, so that there is no meaning on the addition of the large amount of Ti. For this reason, a large amount of Nb is also required to be added to improve the phosphatability. As a result, the mechanical properties of the steel are largely deteriorated (rise of yield point, reduction of elongation and the like). Therefore, the Nb amount is limited up to 31/4 of C amount.

According to the invention, the remarkable improvement of phosphatability can be realized without causing the deterioration of excellent properties as the material of Ti-containing extra low carbon steel sheets.

CLAIMS

1. An extra low carbon steel sheet having a good phosphatability, which comprises not more than 0.01 wt% of carbon, not more than 0.01 wt% of nitrogen, not more than 0.15 wt% of silicon, not more than 0.6 wt% of manganese, not more than 0.10 wt% of aluminum, titanium being not less than $4.0\times([C]+[N])$, niobium being within a range of $1/6\times[Ti]$ to $31/4\times[C]$, and the balance being iron and inevitable impurities.

2. The extra low carbon steel sheet according to claim 1, wherein said inevitable impurities are not more than 0.15 wt% of phosphorus and not more than 0.02 wt% of sulfur.


Phosphatability : Bad
Ti=0.042%
Ti=0.028%
Ti=0.016%
Ti=0.008%
42
26
13
Phosphatability
: Good
PHE
Nb (%, 10^{-4})
0
10
20
30
40
50
60
70
80
1
2
3
4
5
6
7

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EUROPEAN SEARCH REPORT

Application number 0228756

EP 86 30 0108

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 4)
Y	US-A-3 765 874 (ELIAS et al.) * Claims 1-3,5-8,10,11,13; table I * & GB - A - 1 402 492, & FR - A - 2 185 690, & DE - A - 2 324 788, & BE - A - 799 357	1,2	C 22 C 38/14 C 22 C 38/12
Y	DE-A-2 362 658 (NIPPON STEEL CORP.) * Claims 1,2; page 11, table III, Erfindungemässer Stahl K * & US - A - 3 897 280, & GB - A - 1 450 131	1,2	
E	JAPANESE PATENT ABSTRACTS, vol. J6-M, Week 8612, page 17, no. JP 86 078 320 (KAWASAKI STEEL K.K.) 06-02-1986	1,2	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

C 22 C 38

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	10-09-1986	LIPPENS M.H.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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