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(54) **HIGH TENSION ALLOYED MOLTEN ZINC-PLATED STEEL PLATE HAVING EXCELLENT PLATING CHARACTERISTICS AND METHOD OFF MANUFACTURING THE SAME**

HOCHFESTE FEUERVERZINKTE STAHLPLATTE MIT HERVORRAGENDEN PLATTIERUNGSEIGENSCHAFTEN UND HERSTELLUNGSVERFAHREN

TOLE D'ACIER REVETUE DE ZINC ALLIE FONDU SOUS HAUTE TENSION, A EXCELLENTES CARACTERISTIQUES DE ZINGAGE, ET SON PROCEDE DE FABRICATION

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(56) References cited:
EP-A- 0 434 874
EP-A- 0 574 814
JP-A- 2 011 745
JP-A- 4 041 658
JP-A- 4 154 937
JP-A- 5 339 643
JP-A- 5 345 953

- **PATENT ABSTRACTS OF JAPAN vol. 16 no. 128 (C-924) ,2 April 1992 & JP-A-03 294463 (NIPPON STEEL CORP.) 25 December 1991,**
- **PATENT ABSTRACTS OF JAPAN vol. 18 no. 242 (C-1197) ,10 May 1994 & JP-A-06 025798 (KAWASAKI STEEL CORP.) 1 February 1994,**

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Description

TECHNICAL FIELD

[0001] This invention relates to a high-strength hot dip galvannealed steel sheets mainly usable in bending, press forming, deep drawing or the like for vehicle bodies and a method of producing the same.

BACKGROUND ART

[0002] Recently, it is strongly demanded to reduce the weight of the vehicle body in order to improve the fuel consumption from a viewpoint of regulations for automobile emission gas and the like based on environmental pollution. And also, the improvement of safety in automobiles becomes an important matter. As a countermeasure for these problems, it is required to develop high-strength hot dip galvannealed steel sheets having a tensile strength of not less than about 400 MPa and an excellent press formability.

[0003] In cold rolled steel sheets, however, the press formability or average r-value and balance between strength and ductility (hereinafter referred to as TS-El) are generally degraded as the strength increases, and also it tends to deteriorate surface properties such as plating properties and the like. Therefore, in order to use this steel sheet for the automobile, it is important to improve the plating properties and press formability in addition to the increase of the strength.

[0004] Up to the present, there are proposed various methods for improving the press formability accompanied with the increase of the strength.

[0005] For example, JP-A-63-100158 discloses a high-strength cold rolled steel sheet having an excellent formability in which an extreme-low carbon steel having a reduced amount of C is added with Ti, Nb and the like as a carbonitride forming component to improve the workability and aging property and further added with Si, Mn, P not damaging the workability to mainly increase the strength. Particularly, Si is a component useful for increasing the strength without degrading the workability represented by average r-value, elongation and the like. However, when a great amount of Si is included, the deterioration of surface properties can not be avoided and there is a problem of considerably degrading the plating properties.

[0006] Therefore, in order to increase the strength of the hot dip galvannealed steel sheet, as disclosed in JP-A-5-255807 (high-strength cold rolled steel sheets having an excellent formability and high-strength hot dip galvannealed cold rolled steel sheets as well as a method of producing the same), a method of restricting Si to not more than 0.03% and mainly using P, Mn as a strengthening component is prevalent. However, when a great amount of P is added, there is a problem that the galvannealed alloying is delayed and particularly secondary working embrittlement is apt to be caused in the extreme-low carbon steel. And also, Mn is less in the influence upon the plating properties, but the Mn content of not less than 1% starts the deterioration of the plating properties at a state of restricting Si to not more than 0.1%, and when Mn is included in a great amount, there is a problem that the transformation point is lowered to cause inconveniences bringing about the deterioration of material that the hot rolled sheet is hardened and is not recrystallized in the annealing.

[0007] Thus, there is a limit in the attempt for increasing the strength only by the addition of P, Mn while maintaining the workability and plating properties.

[0008] JP-A-3-2944663 discloses a method for improving the productivity of an alloyed melt- or hot-galvanized steel sheet having high quality and having added P by heat-treating a high strength steel slab of the composition (in weight%) 0.0005-0.005% C, 0.005-1.0% Si, 0.02-2.0% Mn, 0.02-0.15% P, 0.002-0.05% S, 0.01-0.1% Sol Al, 0.001-0.008% N, 0.004-0.05% Ti, 0.004-0.05% Nb, 0.005-0.003% B and the balance Fe and inevitable impurities at a slab surface temperature of 1100 to 1350°C for 1,5 to 5 hours, further ordinary hot-rolling, cold-rolling and annealing the steel and thereafter melt- or hot-galvanizing the steel sheet as obtained and finally performing a successive alloying heat treatment at 400 to 600°C.

[0009] EP-A-0 434 874 discloses a galvannealed steel sheet having a superior spot weldability characteristic in which the steel sheet has a base steel sheet cold-rolled from a material containing 0.005 wt% of less of C, 0.005 to 0.5 wt% of Ti, 0.01 to 0.1 wt% of Al, 0.005 to 0.015 wt% of Nb and 0.0002 to 0.002 wt% of B. In the process for making, the hot-dip plating layer applied after the alloying heat treatment has an Fe content of from 9 wt% to 12 wt%.

[0010] JP-A-4-154937 discloses a method for ascertaining a high alloying rate in the manufacture of a high-strength alloyed molten zinc plated steel sheet made of a steel of the composition (in weight%) C: 0.0060% or less, Si: 1.0% or less, Mn: at least 0.5% and no more than 2.0%, P: at least 0.01% and no more than 0.10%, S: no more than 0.1%, A1: at least 0.05% and no more than 0.1%, N: no more than 0.0060%, and 1, 2 or more elements selected from among Nb, Ti, and B, in a range of Nb: at least 0.003% and no more than 0.04%, Ti: at least 0.003% and no more than 0.08%, and B: at least 0.0002% and no more than 0.0040%, and the balance Fe and inevitable impurities by limiting the amounts of Mn and P such that the following condition is met.

$$Mn\ (wt\%) \geq 10 \cdot P\ (wt\%)$$

DISCLOSURE OF INVENTION

[0011] The inventors have made various studies and found that high-strength hot dip galvannealed steel sheets possessing good plating properties and press formability and having a tensile strength of not less than 400 MPa are obtained by utilizing Si as a strengthening component and specifying an interrelation between Si and Mn.
[0012] That is, the essential point of the invention is as follows:
[0013] A high-strength hot dip galvannealed steel sheet having excellent plating properties comprising a steel sheet having a composition of

C: not less than 0.0005 mass% but not more than 0.0050 mass%,
Si: not less than 0.1 mass% but not more than 2.5 mass%,
Mn: not less than 0.1 mass% but not more than 2.5 mass%,
Ti: not less than 0.003 mass% but not more than 0.10 mass%,
Nb: not less than 0.003 mass% but not more than 0.10 mass%,
B: not less than 0.0005 mass% but not more than 0.0080 mass%,
P: not less than 0.040 mass% but not more than 0.18 mass%,
S: not more than 0.008 mass%,
Al: not less than 0.005 mass% but not more than 0.10 mass%, and
N: not more than 0.0060 mass%,

provided that Si and Mn satisfy a relation of the following equation (1), and the remainder being Fe and inevitable impurities, an oxide film mainly composed of $MnSiO_3$ formed on the steel sheet and a hot dip galvannealed layer formed on a surface of the sheet and having a Fe content of 9-12% (first invention),

$$1.5\ (\text{mass\% Mn}) - 2 \leqq (\text{mass\% Si}) \leqq 2(\text{mass\% Mn}) \qquad (1)$$

[0014] A high-strength hot dip galvannealed steel sheet having excellent plating properties according to the first invention, wherein the C content is not less than 0.0005 mass% but not more than 0.004 mass% (second invention).
[0015] A high-strength hot dip galvannealed steel sheet having excellent plating properties according to the first invention, wherein the Si content is not less than 0.2 mass% but not more than 2.5 mass% (third invention).
[0016] A high-strength hot dip galvannealed steel sheet having excellent plating properties according to the first invention, wherein the Mn content is not less than 0.2 mass% but not more than 2.5 mass% (fourth invention).
[0017] A high-strength hot dip galvannealed steel sheet having excellent plating properties according to the first invention, wherein the B content is not less than 0.0005 mass% but not more than 0.0050 mass% (fifth invention).
[0018] A high-strength hot dip galvannealed steel sheet having excellent plating properties according to the first invention, wherein the P content is not less than 0.04 mass% but not more than 0.15 mass% (sixth invention).
[0019] A high-strength hot dip galvannealed steel sheet having excellent plating properties according to the first invention, wherein the Al content is not less than 0.005 mass% but not more than 0.06 mass% (seventh invention).
[0020] A high-strength hot dip galvannealed steel sheet having excellent plating properties according to the first invention, wherein the N content is not more than 0.0040 mass% (eighth invention).
[0021] A method of producing a high-strength hot dip galvannealed steel sheet having excellent plating properties, characterized in that a slab of steel having a composition of

C: not less than 0.0005 mass% but not more than 0.0050 mass%,
Si: not less than 0.1 mass% but not more than 2.5 mass%,
Mn: not less than 0.1 mass% but not more than 2.5 mass%,
Ti: not less than 0.003 mass% but not more than 0.10 mass%,
Nb: not less than 0.003 mass% but not more than 0.10 mass%,
B: not less than 0.0005 mass% but not more than 0.0080 mass%,
P: not less than 0.040 mass% but not more than 0.18 mass%,
S: not more than 0.008 mass%,
Al: not less than 0.005 mass% but not more than 0.10 mass%, and
N: not more than 0.0060 mass%,

provided that Si and Mn satisfy a relation of the following equation (1) for the formation of an oxide film mainly composed of $MnSiO_3$ on the steel sheet, and the remainder being Fe and inevitable impurities is used as a starting material, hot rolled and subjected to a finish rolling within a temperature range of not lower than 750°C but not higher than 1000°C, pickled and subjected to a cold rolling at a draft of not less than 60% but not more than 95%, and the resulting cold rolled sheet is passed through a continuously hot dip galvannealing installation wherein it is recrystallized within a temperature range of not lower than 700°C but not higher than 950°C, quenched to a temperature region of 380-530°C, immersed in a hot dip galvannealing bath of 450-490°C containing 0.12-0.145 mass% of Al in a temperature region of not lower than a bath temperature but not higher than Bath temperature + 10°C and alloyed by heating within a temperature range of 450-550°C for not less than 14 seconds but not more than 28 seconds (tenth invention).

$$1.5\,(\text{mass\% Mn}) - 2 \leqq (\text{mass\% Si}) \leqq 2(\text{mass\% Mn}) \qquad (1)$$

[0022] There will be described experimental results based on the invention below.

[0023] A relation among Si and Mn contents and plating properties was examined with respect to cold rolled steel sheets of 0.75 mm in thickness containing C: 0.002 mass%, Ti: 0.04 mass%, Nb: 0.03 mass%, B: 0.002 mass%, P: 0.10 mass%, S: 0.006 mass%, Al: 0.04 mass% and N: 0.002 mass% and having different Si and Mn contents.

[0024] Moreover, these steel sheets are produced by hot rolling a sheet bar having the above composition at a finish rolling temperature of 820-910°C, pickling, cold rolling at a draft of 75-85% and passing through a hot dip galvannealing line in which it is annealed within a temperature range of 780-890°C, quenched to a temperature region of 450-500°C, immersed in a hot dip galvannealing bath containing 0.13 mass% of Al and alloyed within a temperature range of 450-550°C (Fe content in a plated layer: about 10%). Further, the plating properties are evaluated by visual judgment of appearance (non-plated portion) and judgment of resistance to powdering through 90° bending test.

[0025] As to these steel sheets, the results on the relation among Si and Mn contents and plating properties are shown in Table 1.

Table 1

Symbol of steel	Chemical component		1.5(mass% Mn)-2	2(mass% Mn)	Tensile strength (MPa)	Plating properties	
	Mn	Si				non-plated portion	resistance to powdering
A	0.5	0.6	-1.25	1.0	401	◎	◎
B	0.5	0.9	-1.25	1.0	412	◎	◎
C	0.5	1.2	-1.25	1.0	430	○	×
D	1.5	0.2	0.25	3.0	408	○	×
E	1.5	1.0	0.25	3.0	447	◎	◎
F	1.5	1.5	0.25	3.0	477	◎	◎
G	2.0	0.5	1.00	4.0	436	×	×
H	2.0	1.5	1.00	4.0	497	◎	◎
◎ : not occurred ◎ : acceptable ○: slightly occurred ×: unacceptable ×: occurred							

[0026] As seen from the results of Table 1, when the interrelation between Si and Mn is within a range of 1.5 (mass% Mn) - 2 ≦ (mass% Si) ≦ 2(mass% Mn), the appearance and resistance to powdering are good. When at least either of Si and Mn is greater outside the above range, the plating properties are degraded. Although the reason is not clear, it is considered that an oxide film formed on the surface of the steel sheet is SiO_2 in case of adding Si alone or MnO in case of adding Mn alone and is poor in the wettability to molten zinc, while when Si and Mn are included so as to satisfy the above relation, the resulting oxide film is mainly composed of $MnSiO_3$ and improves the wettability to molten zinc.

[0027] The reason why each component in the invention is limited to the above composition range will be described below.

C: not less than 0.0005 mass% but not more than 0.0050 mass%

[0028] The C content is necessary to be not more than 0.0050 mass% in order to provide steel sheets having good workability, particularly good TS-El balance.

It is desirable that steel is an extreme-low carbon steel containing preferably not more than 0.0040 mass%, more particularly not more than 0.0030 mass%. However, when a great amount of P is included together, if C is less than 0.0005 mass%, the resistance to secondary working embrittlement degrades. Therefore, the C content is restricted to not less than 0.0005 mass% but not more than 0.0050 mass%, preferably not less than 0.0005 mass% but not more than 0.0040 mass%, more particularly not less than 0.0005 mass% but not more than 0.0030 mass%.

Si: not less than 0.1 mass% but not more than 2.5 mass%

[0029] Si serves to reduce the deterioration of the workability to strengthen the steel and is required to be not less than 0.1 mass%. However, when the content exceeds 2.5 mass%, the deterioration of the resistance to secondary working embrittlement is caused. Therefore, the Si content is restricted to not less than 0.1 mass% but not more than 2.5 mass%. From the main point of the invention utilizing Si to strengthen the steel while holding the workability, if it is intended to provide the tensile strength of not less than 400 MPa grade, the Si content is preferably not less than 0.2 mass% but not more than 2.5 mass%, more particularly not less than 0.3 mass% but not more than 2.5 mass%. Mn: not less than 0.1 mass% but not more than 2.5 mass%

[0030] The Mn content is desirable to be decreased from a viewpoint of the workability and resistance to secondary working embrittlement, but when it is less than 0.1 mass%, sufficient strengthening effect as a material for automobiles is not obtained. Furthermore, when a great amount of Si raising the transformation point in the hot rolling is included, it is difficult to conduct normal hot rolling in an austenite zone, so that it is desired that the transformation point is adjusted to an adequate temperature region by adding Mn decreasing the transformation point in an amount of not less than 0.2 mass%, more preferably not less than 0.4 mass%. On the other hand, when the content exceeds 2.5 mass%, it is difficult to improve the resistance to secondary working embrittlement and also it is difficult to conduct the cold rolling because the steel is considerably hardened. Therefore, the Mn content is restricted to not less than 0.1 mass% but not more than 2.5 mass%, preferably not less than 0.2 mass% but not more than 2.5 mass%, more particularly not less than 0.4 mass% but not more than 2.5 mass%.

Ti: not less than 0.003 mass% but not more than 0.10 mass%

Nb: not less than 0.003 mass% but not more than 0.10 mass%

[0031] Ti fixes a part or full of N, C, S, and Nb fixes a part or full of C, so that they are effective to ensure the workability and non-aging property of the extreme-low carbon steel. However, when each content is less than 0.003 mass%, the effect is not obtained, so that this value is a lower limit. On the other hand, when it exceeds 0.1 mass%, the workability is inversely degraded, so that this value is an upper limit. Moreover, when the C content is decreased to not more than about 0.0020 mass% from a viewpoint of further improvement of the workability, the total content of Ti and Nb is preferably not less than 0.03 mass% but not more than 0.10 mass%, more particularly not less than 0.03 mass% but not more than 0.08 mass%.

B: not less than 0.0005 mass% but not more than 0.0080 mass%

[0032] B exhibits a remarkable effect of preventing the secondary working embrittlement by segregation into grain boundary. When the content is less than 0.0005 mass%, the effect is less, while when it exceeds 0.0080 mass%, the effect is saturated and the rise of yield strength and decrease of elongation are caused to degrade the workability. Therefore, the content is restricted to not less than 0.0005 mass% but not more than 0.0080 mass%. Since the workability is slightly degraded by the addition of B, except for the case that P of more than 0.15 mass% is included, it is preferably not less than 0.0005 mass% but not more than 0.0050 mass%, more particularly not less than 0.0005 mass% but not more than 0.0030 mass%.

P: not less than 0.040 mass% but not more than 0.18 mass%

[0033] P has an effect of not only strengthening the steel but also improving the workability, particularly average r-value, and is included in accordance with the given strength. The effect becomes remarkable when the content is not less than 0.040 mass%, while when it exceeds 0.18 mass%, the alloying of the plating layer is considerably delayed and also the material is degraded by solidification segregation in the casting. Furthermore, when the C content is decreased for improving the material, the deterioration of the resistance to secondary working embrittlement is started when the content is not less than 0.12 mass%, so that it is required to add a great amount of B at the P content of not less than 0.15 mass%.

[0034] Therefore, the P content is limited to not less than 0.040 mass% but not more than 0.18 mass%, preferably not less than 0.040 mass% but not more than 0.15 mass%, more particularly not less than 0.040 mass% but not more than 0. mass%.

S: not more than 0.008 mass%

[0035] When the S content exceeds 0.008 mass%, a great amount of MnS is precipitated to degrade the workability, so that this is an upper limit. If the S content is not more than 0.008 mass% an improved workability is obtained. The content is desired to be made small, but when it is less than 0.0005 mass%, the production cost considerably rises by the existing technique and it si impractical.

Al: not less than 0.005 mass% but not more than 0.10 mass%

[0036] Al is added for deoxidation and precipitation and fixation of N in steel, if necessary. When the content is less than 0.005 mass%, inclusions increases and a good workability is not obtained. On the other hand, when the content is too large, not only the workability but also the surface properties are deteriorated, so that the Al content is restricted to not less than 0.005 mass% but not more than 0.10 mass%. It is preferably not less than 0.005 mass% but not more than 0.06 mass%, more particularly not less than 0.01 mass% but not more than 0.06 mass% from a viewpoint of the rationalization of the workability through the above mechanism.
N: not more than 0.0060 mass%

[0037] N is a harmful component mainly resulting in strain aging. When the content is too large, it is required to add great amounts of Ti and Al, so that the upper limit is 0.0060 mass%. From a viewpoint of further improvement of the workability, it is preferably not more than 0.0040 mass%, more particularly not more than 0.0030 mass%. Moreover, the content is desirable to become low, but when it is less than 0.0003 mass%, the production cost considerably rises according to the existing technique and it is impractical.

[0038] The reason on the limitations of process conditions will be described below.

[0039] The steel-making and casting conditions are sufficient as conducted according to the usual manner.

[0040] The finish temperature of hot rolling is required to be 750°C at minimum in order to obtain good workability after the cold rolling and annealing. When the temperature is lower than the above value, the rolling structure considerably remains in the hot rolled sheet, which becomes disadvantageous in the formation of texture suitable for the press formability. On the other hand, when the rolling is completed above 1000°C, the coarsening of structure in the hot rolled sheet is caused and hence the texture suitable for the press formability is not obtained. Therefore, the finish temperature of hot rolling is not lower than 750°C but not higher than 1000°C.

[0041] In the cold rolling, if the cold rolling draft is less than 60%, the sufficient workability is not obtained, so that it is restricted to not less than 60%. Preferably, the cold rolling draft of not less than 70% is advantageous. On the other hand, when the cold rolling draft exceeds 95%, the workability is degraded, so that the upper limit is 95%.

[0042] The plating is carried out in a continuous hot dip galvannealing installation. The recrystallization annealing temperature after the cold rolling is sufficient to be not lower than 700°C but not higher than 950°C, but the annealing may desirably be carried out at a temperature of not lower than 800°C. After the annealing, it is quenched to a temperature region of 380-530°C. When the quench stopping temperature is lower than 380°C, non-plated portion is created, while when it exceeds 530°C, unevenness is undesirably be caused on the plated surface. After the quenching, the plating is carried out by immersing in a hot dip galvannealing bath containing 0.12-0.145 mass% of Al. When the Al content in the bath is less than 0.12 mass%, the alloying is too promoted and the plating adhesion property (resistance to powdering) is degraded. On the other hand, when it exceeds 0.145 mass%, the non-plated portion is created. The alloying through heating followed to the plating is carried out so as to render the Fe content in the plated layer into 9-12%. That is, the alloying is carried out by heating within a temperature range of 450-550°C for not less than 14 seconds but not more than 28 seconds. When the heating temperature is lower than 450°C or the heating time is less than 14 seconds, the alloying is not sufficiently conducted and hence the Fe content is less than 9% to degrade the resistance to flaking. On the other hand, when the heating temperature exceeds 550°C or the heating time exceeds 28 seconds, the alloying is excessively promoted and the resistance to powdering is degraded.

[0043] The temperature of the galvannealing bath is within a range of 450-490°C, while the temperature of the sheet to be immersed in the bath is not lower than the bath temperature but not higher than (bath temperature + 10°C). When the bath temperature is lower than 450°C or the temperature of the sheet is lower than the bath temperature, the solidification of zinc is promoted and it is difficult to adjust the plating amount. On the other hand, when the bath temperature exceeds 490°C or the temperature of the sheet exceeds (bath temperature + 10°C), the elusion of iron from the steel sheet into the bath is promoted to form dross and the surface defect is apt to be caused.

[0044] Moreover, even if the steel sheet obtained according to the invention is subjected to a special treatment such as application of lubricant onto the surface or the like to further improve the press formability, weldability or corrosion resistance, the characteristics aiming at the invention are unchangeable. Furthermore, even if the steel sheet according to the invention (or steel sheet according to the invention subjected at its surface to the special treatment) is subjected to temper rolling for the shape correcting or the like, the characteristics aiming at the invention are unchangeable.

BEST MODE FOR CARRYING OUT THE INVENTION

Example

[0045] Slabs of steel prepared in a convertor and having a chemical component shown in Table 2 is used as a starting material and subjected to hot rolling, pickling and cold rolling to a sheet thickness of 0.8 mm, which is subjected to a plating in a continuous hot dip galvannealing line. The tensile properties and plating properties are measured with respect to the thus obtained steel sheets. Moreover, the plating bath temperature is within a range of 460-480°C, and the temperature of sheet to be immersed is within a range of plating bath temperature to (plating bath temperature +

10°C), and the alloying condition is a heating within a temperature range of 480-540°C for 15-28 seconds.

Table 2

Steel No.	Chemical components (mass%)										1.5(mass%Mn)-2	2(mass%Mn)
	C	Si	Mn	Ti	Nb	B	P	S	Al	N		
1	0.0042	0.30	0.16	0.047	0.016	0.0025	0.112	0.006	0.045	0.0026	-1.76	0.32
2	0.0040	0.35	0.42	0.062	0.018	0.0029	0.125	0.008	0.036	0.0031	-1.37	0.84
3	0.0031	0.78	0.44	0.058	0.008	0.0028	0.087	0.006	0.032	0.0025	-1.34	0.88
4	0.0031	0.78	0.44	0.058	0.005	0.0016	0.087	0.005	0.032	0.0026	-1.34	0.88
**5	0.0031	0.78	0.44	0.058	0.006	0.0034	0.087	0.010	0.032	0.0029	-1.34	0.88
6	0.0031	0.78	0.44	0.058	0.014	0.0022	0.087	0.008	0.032	0.0032	-1.34	0.88
7	0.0031	0.78	0.44	0.058	0.014	0.0024	0.087	0.005	0.032	0.0022	-1.34	0.88
8	0.0008	0.52	1.01	0.014	0.021	0.0050	0.152	0.006	0.016	0.0020	-0.49	2.02
9	0.0016	1.50	0.98	0.008	0.028	0.0032	0.065	0.005	0.025	0.0041	-0.53	1.96
10	0.0020	1.86	1.14	0.030	0.018	0.0042	0.042	0.004	0.027	0.0035	-0.29	2.28
11	0.0024	0.51	1.56	0.011	0.033	0.0012	0.082	0.007	0.042	0.0026	0.34	3.12
12	0.0025	1.55	1.65	0.005	0.052	0.0025	0.062	0.006	0.046	0.0027	0.48	3.30
13	0.0021	1.95	1.66	0.007	0.044	0.0021	0.052	0.006	0.045	0.0032	0.49	3.32
14	0.0040	*0.52	0.18	0.042	0.026	0.0026	0.108	0.006	0.046	0.0040	-1.73	0.36
15	0.0038	*1.21	0.45	0.048	0.009	0.0027	0.062	0.008	0.050	0.0038	-1.33	0.90
16	0.0026	*2.25	1.02	0.035	0.008	0.0026	0.042	0.008	0.043	0.0026	-0.47	2.04
17	0.0028	*0.16	1.54	0.039	0.016	0.0028	0.143	0.006	0.055	0.0028	0.31	3.08
18	0.0026	*0.89	2.10	0.037	0.011	0.0026	0.104	0.007	0.042	0.0026	1.15	4.20

Note: * means that Si does not satisfy a relation of 1.5(mass%Mn)-2≦(mass%Si)≦2(mass%Mn)

**: the S content is outside the range defined in the invention

[0046] As the above production conditions, the finisher delivery temperature of hot rolling (FDT), cold rolling draft, annealing temperature, quench stopping temperature, Al content in the plating bath, Fe content in plated layer after the alloying and the like are measured to obtain results as shown in Table 3.

Table 3

Steel No.	FDT (°C)	Draft of cold rolling (%)	Plating conditions				TS (MPa)	El (%)	TS×El (MPa·%)	Plating properties		Remarks
			annealing temperature (°C)	quench stopping temperature (°C)	Al content in bath (mass%)	Fe content in plated layer (%)				non-plated portion	Resistance to powdering	
1	850	82	830	420	0.130	10.5	388	42.5	16503	◎	◎	Acceptable Example
2	840	85	850	400	0.141	10.2	415	40.2	16699	◎	◎	"
3	850	83	820	460	0.135	10.8	417	39.6	16523	◎	◎	"
4	860	80	820	*350	0.135	10.8	416	39.6	16492	×	◎	Comparative Example
5	850	82	820	*560	0.135	10.8	418	39.6	16539	◎ (unevenness)	◎	"
6	870	78	820	460	*0.112	12.8	417	39.6	16508	◎	×	"
7	880	80	820	460	*0.148	9.2	417	39.6	16513	×	◎	"
8	860	79	870	480	0.124	9.8	431	37.4	16105	◎	◎	Acceptable Example
9	880	78	840	500	0.128	11.2	441	35.2	15538	◎	◎	"
10	870	74	820	430	0.127	10.5	470	35.1	16501	◎	◎	"
11	830	81	800	450	0.132	10.6	410	40.1	16457	◎	◎	"
12	860	76	820	470	0.143	10.3	468	35.6	16650	◎	◎	"
13	880	75	830	510	0.134	10.0	486	28.5	13838	◎	◎	"
14	890	81	850	440	0.124	11.2	397	36.2	14383	×	×	Comparative Example
15	900	78	820	460	0.133	11.1	428	34.3	14675	×	×	"
16	900	73	840	460	0.138	10.5	492	27.2	13395	×	×	"
17	850	77	860	480	0.131	10.8	442	36.7	16223	○	×	"
18	800	73	820	480	0.137	10.4	486	33.3	16183	×	×	"

Note: * is outside the range defined in the invention

◎: not occurred
○: slightly occurred
×: occurred

◎: acceptable
×: unacceptable

[0047] Moreover, the tensile properties are measured by using a test piece of JIS No. 5, and the plating properties are evaluated by the same method as in the aforementioned experiment.
[0048] As seen from Tables 2 and 3, all of acceptable examples according to the invention are excellent in TS-El balance shown by TS x El and have excellent plating properties.

INDUSTRIAL APPLICABILITY

[0049] The invention provides high-strength hot dip galvannealed steel sheets having excellent plating properties and good properties suitable for press forming by utilizing Si as a strengthening component in extreme-low carbon steels and specifying an interrelation between Si and Mn contents. The steel sheets according to the invention largely contribute to reduce the weight of automobile and improve the safety.

Claims

1. A high-strength hot dip galvannealed steel sheet having excellent plating properties comprising a steel sheet having a composition of

   C: not less than 0.0005 mass% but not more than 0.0050 mass%,
   Si: not less than 0.1 mass% but not more than 2.5 mass%,
   Mn: not less than 0.1 mass% but not more than 2.5 mass%,
   Ti: not less than 0.003 mass% but not more than 0.10 mass%,
   Nb: not less than 0.003 mass% but not more than 0.10 mass%,
   B: not less than 0.0005 mass% but not more than 0.0080 mass%,
   P: not less than 0.040 mass% but not more than 0.18 mass%,
   S: not more than 0.008 mass%,
   Al: not less than 0.005 mass% but not more than 0.10 mass%, and
   N: not_more than 0.0060 mass%,

   provided that Si and Mn satisfy a relation of the following equation (1), and the remainder being Fe and inevitable impurities, an oxide film mainly composed of $MnSiO_3$ formed on the steel sheet and a hot dip galvannealed layer formed on the surface of the steel sheet and having Fe content of 9-12%,

   $$1.5\,(\text{mass\% Mn}) - 2 \leqq (\text{mass\% Si}) \leqq 2(\text{mass\% Mn}) \qquad (1)$$

2. A high-strength hot dip galvannealed steel sheet having excellent plating properties according to claim 1, wherein the C content is not less than 0.0005 mass% but not more than 0.004 mass%.

3. A high-strength hot dip galvannealed steel sheet having excellent plating properties according to claim 1, wherein the Si content is not less than 0.2 mass% but not more than 2.5 mass%.

4. A high-strength hot dip galvannealed steel sheet having excellent plating properties according to claim 1, wherein the Mn content is not less than 0.2 mass% but not more than 2.5 mass%.

5. A high-strength hot dip calvannealed steel sheet having excellent plating properties according to claim 1, wherein the B content is not less than 0.0005 mass% but not more than 0.0050 mass%.

6. A high-strength hot dip galvannealed steel sheet having excellent plating properties according to claim 1, wherein the P content is not less than 0.04 mass% but not more than 0.15 mass%.

7. A high-strength hot dip galvannealed steel sheet having excellent plating properties according to claim 1, wherein the Al content is not less than 0.005 mass% but not more than 0.06 mass%.

8. A high-strength hot dip calvannealed steel sheet having excellent plating properties according to claim 1, wherein the N content is not more than 0.0040 mass%.

9. A method of producing a high-strength hot dip calvannealed steel sheet having excellent plating properties, **char-**

acterized in that a slab of steel having a composition of

C: not less than 0.0005 mass% but not more than 0.0050 mass%,
Si: not less than 0.1 mass% but not more than 2.5 mass%,
Mn: not less than 0.1 mass% but not more than 2.5 mass%,
Ti: not less than 0.003 mass% but not more than 0.10 mass%,
Nb: not less than 0.003 mass% but not more than 0.10 mass%,
B: not less than 0.0005 mass% but not more than 0.0080 mass%,
P: not less than 0.040 mass% but not more than 0.18 mass%,
S: not more than 0.008 mass%,
Al: not less than 0.005 mass% but not more than 0.10 mass%, and
N: not more than 0.0060 mass%,

provided that Si and Mn satisfy a relation of the following equation (1) for the formation of an oxide film mainly composed of $MnSiO_3$ on the steel sheet, and the remainder being Fe and inevitable impurities is used as a starting material, hot rolled and subjected to a finish rolling within a temperature range of not lower than 750°C but not higher than 1000°C, pickled and subjected to a cold rolling at a draft of not less than 60% but not more than 95%, and the resulting cold rolled sheet is passed through a continuously hot dip calvannealing installation wherein it is recrystallized within a temperature rance of not lower than 700°C but not higher than 950°C, quenched to a temperature region of 380-530°C, immersed in a hot dip galvannealing bath of 450-490°C containing 0.12-0.145 mass% of Al in a temperature region of not lower than a bath temperature but not higher than Bath temperature + 10°C and alloyed by heating within a temperature range of 450-550°C for not less than 14 seconds but not more than 28 seconds,

$$1.5\,(\text{mass\% Mn}) - 2 \leqq (\text{mass\% Si}) \leqq 2(\text{mass\% Mn}) \qquad (1)$$

Patentansprüche

1. Nach dem Feuerverzinken wärmebehandeltes hochfestes Stahlblech hervorragender Plattierungseigenschaften, umfassend ein Stahlblech der folgenden Zusammensetzung:

C: nicht weniger als 0,0005 Massen-%, jedoch nicht mehr als 0,0050 Massen-%;
Si: nicht weniger als 0,1 Massen-%, jedoch nicht mehr als 2,5 Massen-%;
Mn: nicht weniger als 0,1 Massen-%, jedoch nicht mehr als 2,5 Massen-%;
Ti: nicht weniger als 0,003 Massen-%, jedoch nicht mehr als 0,10 Massen-%;
Nb nicht weniger als 0,003 Massen-%, jedoch nicht mehr als 0,10 Massen-%;
B: nicht weniger als 0,0005 Massen-%, jedoch nicht mehr als 0,0080 Massen-%;
P: nicht weniger als 0,040 Massen-%, jedoch nicht mehr als 0,18 Massen-%;
S: nicht mehr als 0,008 Massen-%;
Al: nicht weniger als 0,005 Massen-%, jedoch nicht mehr als 0,10 Massen-%, und
N: nicht mehr als 0,0060 Massen-%,

wobei Si und Mn in einer Beziehung entsprechend der folgenden Gleichung (1)

$$1{,}5\,(\text{Massen-\% Mn}) - 2 \leq (\text{Massen-\% Si}) \leq 2(\text{Massen-\% Mn}) \qquad (1)$$

stehen,
sowie zum Rest Eisen und beiläufige Verunreinigungen, wobei auf dem Stahlblech ein hauptsächlich aus $MnSiO_3$ bestehender Oxidfilm und auf der Oberfläche des Stahlblechs eine nach dem Feuerverzinken wärmebehandelte und einen Fe-Gehalt von 9 bis 12 % aufweisende Schicht gebildet sind.

2. Nach dem Feuerverzinken wärmebehandeltes hochfestes Stahlblech hervorragender Plattierungseigenschaften nach Anspruch 1, wobei der C-Gehalt nicht weniger als 0,0005 Massen-%, jedoch nicht mehr als 0,004 Massen-% beträgt.

3. Nach dem Feuerverzinken wärmebehandeltes hochfestes Stahlblech hervorragender Plattierungseigenschaften nach Anspruch 1, wobei der Si-Gehalt nicht weniger als 0,2 Massen-%, jedoch nicht mehr als 2,5 Massen-% beträgt.

4. Nach dem Feuerverzinken wärmebehandeltes hochfestes Stahlblech hervorragender Plattierungseigenschaften nach Anspruch 1, wobei der Mn-Gehalt nicht weniger als 0,2 Massen-%, jedoch nicht mehr als 2,5 Massen-% beträgt.

5. Nach dem Feuerverzinken wärmebehandeltes hochfestes Stahlblech hervorragender Plattierungseigenschaften nach Anspruch 1, wobei der B-Gehalt nicht weniger als 0,0005 Massen-%, jedoch nicht mehr als 0,0050 Massen-% beträgt.

6. Nach dem Feuerverzinken wärmebehandeltes hochfestes Stahlblech hervorragender Plattierungseigenschaften nach Anspruch 1, wobei der P-Gehalt nicht weniger als 0,04 Massen-%, jedoch nicht mehr als 0,15 Massen-% beträgt.

7. Nach dem Feuerverzinken wärmebehandeltes hochfestes Stahlblech hervorragender Plattierungseigenschaften nach Anspruch 1, wobei der Al-Gehalt nicht weniger als 0,005 Massen-%, jedoch nicht mehr als 0,06 Massen-% beträgt.

8. Nach dem Feuerverzinken wärmebehandeltes hochfestes Stahlblech hervorragender Plattiereigenschaften nach Anspruch 1, wobei der N-Gehalt nicht mehr als 0,0040 Massen-% beträgt.

9. Verfahren zur Herstellung eines nach dem Feuerverzinken wärmbehandelten hochfesten Stahlblechs hervorragender Plattierungseigenschaften, **dadurch gekennzeichnet, dass** eine als Ausgangsmaterial verwendete Stahlbramme der folgenden Zusammensetzung:

C: nicht weniger als 0,0005 Massen-%, jedoch nicht mehr als 0,0050 Massen-%;
Si: nicht weniger als 0,1 Massen-%, jedoch nicht mehr als 2,5 Massen-%;
Mn: nicht weniger als 0,1 Massen-%, jedoch nicht mehr als 2,5 Massen-%;
Ti: nicht weniger als 0,003 Massen-%, jedoch nicht mehr als 0,10 Massen-%;
Nb nicht weniger als 0,003 Massen-%, jedoch nicht mehr als 0,10 Massen-%;
B: nicht weniger als 0,0005 Massen-%, jedoch nicht mehr als 0,0080 Massen-%;
P: nicht weniger als 0,040 Massen-%, jedoch nicht mehr als 0,18 Massen-%;
S: nicht mehr als 0,008 Massen-%;
Al: nicht weniger als 0,005 Massen-%, jedoch nicht mehr als 0,10 Massen-%, und
N: nicht mehr als 0,0060 Massen-%,

wobei Si und Mn in einer Beziehung entsprechend der folgenden Gleichung (1)

$$1{,}5\,(\text{Massen-\% Mn}) - 2 \leq (\text{Massen-\% Si}) \leq 2(\text{Massen-\% Mn}) \qquad (1)$$

stehen, um einen hauptsächlich aus $MnSiO_3$ bestehenden Oxidfilm auf dem Stahlblech auszubilden,
sowie zum Rest Eisen und beiläufige Verunreinigungen, warmgewalzt und einer Walzendtemperatur innerhalb eines Temperaturbereichs von nicht unter 750 °C und nicht über 1000 °C ausgesetzt, gebeizt und zu einer Durchschnittsverminderung von nicht weniger als 60 %, jedoch nicht mehr als 95 % kaltgewalzt wird und das erhaltene kaltgewalzte Blech durch eine kontinuierlich arbeitende Feuerverzinkungs-/Wärmebehandlungs-Einrichtung, in welcher es innerhalb eines Temperaturbereichs von nicht unter 700 °C, jedoch nicht über 950 °C rekristallisiert, auf einen Temperaturbereich von 380 bis 530 °C abgeschreckt, in ein Feuerverzinkungs/Wärmebehandlungsbad von 450 bis 490 °C mit 0,12 bis 0,145 Massen-% Al innerhalb eines Temperaturbereichs von nicht unter Badtemperatur, jedoch nicht höher als Badtemperatur plus 10 °C getaucht und durch nicht weniger als 14 s, jedoch nicht mehr als 28 s dauerndes Erwärmen innerhalb eines Temperaturbereichs von 450 bis 550 °C legiert wird, hindurchgeführt wird.

Revendications

1. Tôle d'acier à haute résistance galvanisée et recuite par immersion à chaud, ayant d'excellentes propriétés de placage, comprenant une tôle d'acier ayant une composition de :

   C : pas moins de 0,0005 % en masse, mais pas plus de 0,0050 % en masse,
   Si : pas moins de 0,1 % en masse, mais pas plus de 2,5 % en masse,
   Mn : pas moins de 0,1 % en masse, mais pas plus de 2,5 % en masse,
   Ti : pas moins de 0,003 % en masse, mais pas plus de 0,10 % en masse,
   Nb : pas moins de 0,003 % en masse, mais pas plus de 0,10 % en masse,
   B : pas moins de 0,0005 % en masse, mais pas plus de 0,0080 % en masse,
   P : pas moins de 0,040 % en masse, mais pas plus de 0,18 % en masse,
   S : pas plus de 0,008 % en masse,
   Al : pas moins de 0,005 % en masse, mais pas plus de 0,10 % en masse, et
   N : pas plus de 0,0060 % en masse,

   à condition que Si et Mn satisfassent à la relation correspondant à l'équation (1) suivante, et le reste étant Fe et des impuretés inévitables, un film d'oxyde principalement composé de $MnSiO_3$ formé sur la tôle d'acier et une couche de recuit et de galvanisation par immersion à chaud formée sur la surface de la tôle d'acier et ayant une teneur en Fe de 9 à 12 %,

   $$1{,}5(\text{Mn \% en masse}) - 2 \leq (\text{Si \% en masse}) \leq 2(\text{Mn \% en masse}) \qquad (1)$$

2. Tôle d'acier à haute résistance galvanisée et recuite par immersion à chaud ayant d'excellentes propriétés de placage selon la revendication 1, dans laquelle la teneur en C n'est pas inférieure à 0,0005 % en masse, mais non supérieure à 0,004 % en masse.

3. Tôle d'acier à haute résistance recuite et galvanisée par immersion à chaud ayant d'excellentes propriétés de placage selon la revendication 1, dans laquelle la teneur en Si n'est pas inférieure à 0,2 % en masse, mais non supérieure à 2,5 % en masse.

4. Tôle d'acier à haute résistance recuite et galvanisée par immersion à chaud ayant d'excellentes propriétés de placage selon la revendication 1, dans laquelle la teneur en Mn n'est pas inférieure à 0,2 % en masse, mais non supérieure à 2,5 % en masse.

5. Tôle d'acier à haute résistance recuite et galvanisée par immersion à chaud ayant d'excellentes propriétés de placage selon la revendication 1, dans laquelle la teneur en B n'est pas inférieure à 0,0005 % en masse, mais non supérieure à 0,0050 % en masse.

6. Tôle d'acier à haute résistance recuite et galvanisée par immersion à chaud ayant d'excellentes propriétés de placage selon la revendication 1, dans laquelle la teneur en P n'est pas inférieure à 0,04 % en masse, mais non supérieure à 0,15 % en masse.

7. Tôle d'acier à haute résistance galvanisée et recuite par immersion à chaud ayant d'excellentes propriétés de placage selon la revendication 1, dans laquelle la teneur en A1 n'est pas supérieure à 0,005 % en masse, mais non supérieure à 0,06 % en masse.

8. Tôle d'acier à haute résistance recuite et galvanisée par immersion à chaud ayant d'excellentes propriétés de placage selon la revendication 1, dans laquelle la teneur en N n'est pas supérieure à 0,0040 % en masse.

9. Procédé de production d'une tôle d'acier à haute résistance recuite et galvanisée par immersion à chaud, ayant d'excellentes propriétés de placage, **caractérisé en ce qu'**une brame d'acier ayant une composition de :

   C : pas moins de 0,0005 % en masse, mais pas plus de 0,0050 % en masse,
   Si : pas moins de 0,1 % en masse, mais pas plus de 2,5 % en masse,
   Mn : pas moins de 0,1 % en masse, mais pas plus de 2,5 % en masse,
   Ti : pas moins de 0,003 % en masse, mais pas plus de 0,10 % en masse,

Nb : pas moins de 0,003 % en masse, mais pas plus de 0,10 % en masse,
B : pas moins de 0,0005 % en masse, mais pas plus de 0,0080 % en masse,
P : pas moins de 0,040 % en masse, mais pas plus de 0,18 % en masse,
S : pas plus de 0,008 % en masse,
Al : pas moins de 0,005 % en masse, mais pas plus de 0,10 % en masse, et
N : pas plus de 0,0060 % en masse,

à condition que Si et Mn satisfassent à la relation correspondant à l'équation (1) suivante pour la formation d'un film d'oxyde principalement composé de $MnSiO_3$ sur la tôle d'acier, et le reste consistant en Fe et en impuretés inévitables, est employée comme matériau de départ, et est laminée à chaud et soumise à un laminage de finition dans une plage de température non inférieure à 750 °C mais non supérieure à 1 000 °C, décapée et soumise à un laminage à froid selon un taux d'étirage non inférieur à 60 % mais non supérieur à 95 %, et on fait passer la tôle laminée à froid résultante à travers une installation de galvanisation et de recuit par immersion à chaud continue dans laquelle elle est recristallisée dans une plage de température non inférieure à 700°C mais non supérieure à 950°C, brusquement refroidie jusqu'à une plage de température de 380 à 530°C, immergée dans un bain de recuit et de galvanisation par immersion à chaud à 450-490°C contenant de 0,12 à 0,145 % en masse de Al dans une région de température non inférieure à la température du bain mais non supérieure à la température du bain + 10°C, et alliée par chauffage dans une plage de température de 450 à 550°C pendant pas moins de 14 s mais pas plus de 28 s,

$$1{,}5(\text{Mn \% en masse}) - 2 \leq (\text{Si \% en masse}) \leq 2(\text{Mn \% en masse}) \qquad (1)$$