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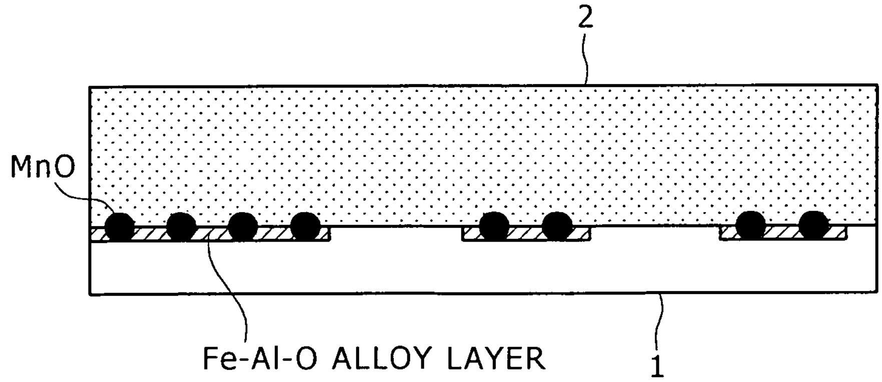
(54) **Alloyed hot-dip galvanized steel sheet and production method thereof**

(57) Disclosed is an alloyed hot-dip galvanized steel sheet containing 2.0 to 3.5 percent by mass of Mn. The steel sheet includes a base steel sheet and a galvanized zinc-coat layer thereon, in which MnO particles are present in an average number of 10 or less per micrometer on a straight line lying in an interface between the galvanized zinc-coat layer and the steel sheet, an Fe-Al-O alloy layer is present at the interface between the MnO particles and the steel sheet, and the length of the Fe-Al-O alloy layer is less than 10% of the overall length of the interface. The alloyed hot-dip galvanized steel sheet, even though having a high Mn content, is resistant to uneven alloying and excels in surface appearance, because the amounts of the MnO particles and the Fe-Al-O alloy layer that cause uneven alloying are controlled.

FIG. 2



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Description

[0001] The present invention relates to an alloyed hot-dip galvanized steel sheet which excels in surface appearance and is used typically in automobiles, home appliances, and building materials; and to a method for producing the alloyed hot-dip galvanized steel sheet.

[0002] Galvanized steel sheets are widely used typically in automobiles, home appliances, and building materials. Among them, alloyed hot-dip galvanized steel sheets excel in corrosion resistance and spot weldability and are thereby widely used as automobile steel sheets. The alloyed hot-dip galvanized steel sheets are more and more demanded to have higher strength and smaller thickness, with recent requirements for automobiles to have higher collision safety and lighter body weight so as to have higher fuel efficiency.

[0003] To meet these requirements and to ensure satisfactory balance between strength and ductility, many of currently used alloyed hot-dip galvanized steel sheets are those further containing easily oxidizable elements such as silicon (Si) and manganese (Mn). These easily oxidizable elements, however, are known to be selectively oxidized upon annealing carried out before galvanization of a steel sheet to thereby significantly impair wettability in galvanization and alloying performance, and it is very difficult to control these elements. Accordingly, stable production of alloyed hot-dip galvanized steel sheets is difficult according to known techniques.

[0004] Under these circumstances, a variety of proposals have been made on alloyed hot-dip galvanized steel sheets.

[0005] Japanese Unexamined Patent Application Publication (JP-A) No. 200711/2005 discloses an alloyed hot-dip galvanized steel sheet and a production method thereof, in which a reaction product between an added element in a steel sheet and a component in an annealing atmosphere is formed during an annealing process. JP-A No. 279410/2001 discloses a galvanized steel sheet and a production method thereof, in which a sulfur-containing ammonium salt is attached to the surface of a high tensile strength steel sheet containing manganese, and the steel sheet is then subjected to a heat treatment and subsequently to a galvanization process.

[0006] JP-A No. No. 88193/1994 discloses a method for producing an alloyed hot-dip galvanized steel sheet, in which the surface layer of a steel sheet is dry-etched before immersing the steel sheet in a plating bath. JP-A No. 328036/2003 discloses a method for improving the plating quality of an alloyed hot-dip galvanized steel sheet, in which a steel sheet after annealing is cooled in a controlled manner in order to reduce grain boundary segregation.

[0007] JP-A No. 263271/2004 discloses a method for producing a high tensile strength galvanized steel sheet, in which 70% or more of a surface enriched layer containing silicon (Si), manganese (Mn), and aluminum (Al) after annealing is removed by acid pickling, and the treated steel sheet is galvanized.

[0008] These methods for producing alloyed hot-dip galvanized steel sheets, however, are all complicated in their steps and are difficult to produce alloyed hot-dip galvanized steel sheets in a simple and easy manner. In addition, they are not intended to produce an alloyed hot-dip galvanized steel sheet that is derived from a steel sheet having a high manganese content and excels in surface appearance.

[0009] Under these circumstances, an object of the present invention is to provide an alloyed hot-dip galvanized steel sheet which is resistant to uneven alloying and excels in surface appearance even when the base steel has a high manganese content, by controlling the amounts of MnO and an Fe-Al-O alloy layer that cause uneven alloying and whereby accelerating the alloying of the galvanized steel sheet. Another object of the present invention is to provide a method for producing the alloyed hot-dip galvanized steel sheet with superior surface appearance.

[0010] According to an embodiment of the present invention, there is provided an alloyed hot-dip galvanized steel sheet which includes a base steel sheet and a galvanized zinc-coat layer on the steel sheet, the galvanized zinc-coat layer and the steel sheet are alloyed, and a steel constituting the base steel sheet contains, on the mass basis, 0.02% to 0.2% of carbon (C), 2.0% to 3.5% of manganese (Mn), 0.03% to 0.5% of chromium (Cr), 0.01% to 0.15% of aluminum (Al), 0.04% or less (including 0%) of silicon (Si), 0.03% or less (including 0%) of phosphorus (P), and 0.03% or less (including 0%) of sulfur (S), with the remainder including iron (Fe) and inevitable impurities, in which MnO particles are present on an arbitrary straight line lying in an interface between the galvanized zinc-coat layer and the steel sheet, which MnO particles are present in an average number of 10 or less per micrometer of the straight line, an Fe-Al-0 alloy layer is present at an interface between the MnO particles and the steel sheet, and the length of the Fe-Al-0 alloy layer is less than 10% of the overall length of the interface, each of the length and the overall length being measured on the arbitrary straight line.

[0011] The steel sheet may further contain, on the mass basis, a total of 0.003% to 1.0% of at least one member selected from the group consisting of 0.003% to 0.5% of copper (Cu), 0.003% to 1.0% of nickel (Ni), and 0.003% to 1.0% of titanium (Ti).

[0012] The steel sheet may further contain, on the mass basis, at least one member selected from the group consisting of 0.003% to 1.0% of vanadium (V), 0.003% to 1.0% of niobium (Nb), 0.0002% to 0.1% of boron (B), and 0.003% to 1.0% of molybdenum (Mo).

[0013] The steel sheet may further contain, on the mass basis, at least one member selected from the group consisting of 0.0005% to 0.005% of calcium (Ca) and 0.0005% to 0.001% of magnesium (Mg).

[0014] According to another embodiment of the present invention, there is provided a method for producing any of the above-mentioned alloyed hot-dip galvanized steel sheets, the method includes the steps of carrying out annealing of the steel sheet under such conditions that an oxygen partial pressure PO_2 (in units of atmospheric pressure (atm)) satisfies the following condition: - $\log(PO_2) \geq 20$; galvanizing the annealed steel sheet to form the galvanized zinc-coat layer on the surface of the steel sheet; and alloying the steel sheet bearing the galvanized zinc-coat layer.

[0015] The alloyed hot-dip galvanized steel sheets according to the present invention are alloyed hot-dip galvanized steel sheets that are resistant to uneven alloying and excel in surface appearance, even through they have a high manganese content of 2.0 to 3.5 percent by mass, because the amounts of MnO and an Fe-Al-O alloy layer that cause uneven alloying are controlled.

[0016] Additionally, the method according to the present invention can produce alloyed hot-dip galvanized steel sheets which are resistant to uneven alloying and excel in surface appearance even when their base steels have a high manganese content of 2.0 to 3.5 percent by mass, by controlling the amounts of MnO and an Fe-Al-O alloy layer that cause uneven alloying and thereby accelerating the alloying of the galvanized steel sheet.

[0017] FIGS. 1A, 1B, and 1C are vertical sectional views of a steel sheet illustrating how uneven alloying occurs in the production of an alloyed hot-dip galvanized steel sheet, in which FIG. 1A illustrates the generation of large amounts of MnO particles on the surface of the steel sheet, FIG. 1B illustrates the generation of an Fe-Al-O alloy layer at the interface between the steel sheet and the galvanized zinc-coat layer, and FIG. 1C illustrates that the Fe-Al-O alloy layer acts as a barrier against the diffusion of iron and causes uneven alloying; and

[0018] FIG. 2 is a vertical sectional view showing an alloyed hot-dip galvanized steel sheet according to an embodiment of the present invention.

[0019] In an annealing process conducted in common processes for producing an alloyed hot-dip galvanized steel sheet, iron as a main component of the base steel sheet is not oxidized, but easily oxidizable elements such as silicon and manganese, if added, are selectively oxidized and diffuse to the surface layer of the steel sheet. The surface of the steel sheet thereby bears oxides containing each of these easily oxidizable elements alone (single-component oxide) or in combination (multiple-component oxide).

[0020] Of the easily oxidizable elements, silicon, if enriched on the surface, forms a thin oxide layer in the outermost surface of the steel sheet and/or causes internal oxidation and thereby significantly impairs the plating quality and suitability for alloying. Therefore, of the easily oxidizable elements, manganese is positively added, but silicon is not positively added to the steel in the present invention, although contamination of silicon as an inevitable impurity is accepted.

[0021] On the other hand, manganese is also enriched in the surface layer of the steel sheet but less acts as a barrier than silicon, because manganese grows not as an oxide layer and an internal oxidation layer as with silicon but grows as a granular oxide (MnO) (oxide particles) and less impedes the outward diffusion of iron during alloying. Contrarily, a small amount of manganese rather increases the alloying rate. However, manganese should be added in a large amount because of its low reinforcing efficiency, but such a large amount of manganese may often cause MnO particles in the surface layer of the steel sheet. This complicates the alloying behavior and makes it difficult to control the alloying.

[0022] In consideration of these conditions, the present inventors made investigations while focusing attention on the relationship between the formation mechanism of MnO and alloying and, as a result, succeeded in revealing a detailed formation mechanism of uneven alloying.

[0023] The detailed mechanism will be explained with reference to FIGS. 1A, 1B, and 1C. When a steel sheet 1 containing a large amount of manganese is annealed under a high oxygen partial pressure, a large amount of granular oxide MnO (MnO particles) is initially formed in the outermost surface of the steel sheet 1 (FIG. 1A). When the steel sheet 1 in this state is dipped in a galvanization bath (zinc plating bath) for hot dip galvanization, aluminum contained in the galvanization bath immediately reacts with oxygen of the MnO particles in the surface layer of the steel sheet 1 and with iron diffused from inside of the steel sheet 1 to form an Fe-Al-O alloy layer at the interface between the steel sheet 1 and a galvanized zinc-coat layer 2 (FIG. 1B). The present inventors found that the Fe-Al-O alloy layer acts as a barrier against the diffusion of iron from the steel sheet 1 during alloying and inhibits the alloying of the steel sheet 1 (FIG. 1C). The Fe-Al-O alloy layer causes uneven alloying and impairs the surface appearance of the alloyed hot-dip galvanized steel sheet.

[0024] After detailed investigations on how the alloying behavior varies depending on the state of MnO, the present inventors conceived that uneven alloying can be controlled to thereby give a good appearance of the galvanized zinc-coat surface, by allowing MnO to be dispersed in the steel sheet through internal oxidation and/or by suppressing the oxidation of Mn in the surface layer.

[0025] The present inventors focused attention on the state of MnO in the surface layer of the steel sheet after annealing; prepared a series of steel sheets having different manganese contents by carrying out annealing under different oxygen partial pressures; observed cross sections of steel sheets suffering from uneven alloying and those of steel sheets without uneven alloying with a scanning electron microscope (SEM) and a transmission electron microscope (TEM); observed cross-sectional structures of these steel sheets after galvanization; and analyzed the iron contents in the galvanized zinc-coat layers. As a result, they succeeded in revealing how the state of uneven alloying varies depending on the state of MnO in the surface layer of the steel sheet after annealing.

[0026] Initially, reasons for specifying contents of components of a base steel (material steel) for use in the present invention will be described. Hereinafter all percentages regarding contents of elements are by mass, unless otherwise specified.

Carbon (C) content: 0.02% to 0.2%

[0027] The carbon (C) element significantly affects the strength of the steel and affects the amounts and shapes of low-temperature transformation products to thereby affect the extensibility (elongation properties) and stretch flange formability of the steel. A steel, if having a carbon content of less than 0.02%, may not give a satisfactory high-strength steel sheet for automobiles. A steel, if having a carbon content of more than 0.2%, may show insufficient weldability. The carbon content is therefore 0.02% and preferably 0.04% in its lower limit and is 0.2% and preferably 0.15% in its upper limit.

Manganese (Mn) content: 2.0% to 3.5%

Manganese (Mn) element acts as a reinforcing element and should be contained in a content of at least 2.0% or more for high strength and for properties as a high-strength steel sheet with very superior workability. In contrast, the manganese content should be 3.5% or less, because manganese, if present in an excessively large content, may impair extensibility (elongation properties) or increase carbon equivalent to thereby adversely affect the weldability. Accordingly, the manganese content should be from 2.0% to 3.5%.

Chromium (Cr) content: 0.03% to 0.5%

Chromium (Cr) element is effective for increasing the hardenability to reinforce the texture. Chromium helps carbon to be enriched and thereby stabilized in austenite and accelerates the formation of martensite. In addition, chromium affects the plating quality by allowing an oxide to form on the surface of the steel sheet. The lower limit of the chromium content should be 0.03%, because chromium, if contained in a content of less than 0.03%, may not effectively improve the hardenability. In contrast, the upper limit of the chromium content should be 0.5%, because if chromium is contained in a content of more than 0.5%, the effect of improving the hardenability may be saturated and the cost may be disadvantageously increased. The upper limit of the chromium content is preferably 0.3%, because chromium, if contained in a content of more than 0.3%, may impair the plating quality.

Aluminum (Al) content: 0.01% to 0.15%

Aluminum (Al) element is effective as a deoxidizer during steel making and should be added in a content of 0.01% or more. However, aluminum, if contained in a content of more than 0.15%, may not only impair the surface appearance but also cause increased production cost. Accordingly, the aluminum content should be 0.01% to 0.15%.

Silicon (Si) content: 0.04% or less (including 0%)

Silicon (Si) element acts to reduce dissolved carbon content in alpha phase to thereby improve the workability such as extensibility (elongation properties); but it forms an oxide film on the surface of steel sheet, significantly impairs the wettability of the galvanized zinc-coat layer, and is not positively added. However, this element may be contained as an inevitable impurity in the steel, and the Si content should be controlled to 0.04% or less so as to avoid adverse effects thereof, and is preferably controlled to 0.03% or less.

Phosphorus (P) content: 0.03% or less (including 0%)

Phosphorus (P) element is effective for obtaining a high-strength steel sheet. However, phosphorus, if contained in a content of more than 0.03%, may often cause uneven plating, may impede alloying, and is not positively added. However, this element may be contained as an inevitable impurity in the steel, and the phosphorus content should be controlled to 0.03% or less.

Sulfur (S) content: 0.03% or less (including 0%)

Sulfur (S) element causes hot crack during hot rolling and significantly impairs spot crack resistance. Sulfur is fixed as a precipitate in the steel, but, if contained in a large content, may impair the extensibility (elongation properties) and stretch flange formability, and is not positively added. However, this element may be contained as an inevitable impurity in the steel, and the sulfur content should be controlled to 0.03% or less.

[0028] The material steel for use herein contains the above elements with the remainder being iron (Fe) and inevitable impurities. Where necessary, the steel may further contain elements mentioned below.

Copper (Cu): 0.003% to 0.5%, Nickel (Ni): 0.003% to 1.0%

Copper (Cu) and nickel (Ni) elements are effective to increase the strength of the material steel itself and to improve the plating quality. Copper and nickel, if enriched in the surface layer of the steel sheet, serve to change the shapes (states) of oxides of silicon (Si) and manganese (Mn) to thereby prevent deterioration in plating quality, because copper and nickel are less oxidizable than iron mainly constituting the material steel. For sufficiently exhibiting these advantages, they are preferably contained in contents of 0.003% or more. However, these elements, if contained in excessively large contents, may impair the workability and cause the cost to increase, and the upper limits of the copper and nickel contents are preferably 0.5% and 1.0%, respectively.

Titanium (Ti): 0.003% to 1.0%

Titanium (Ti) element forms a carbide and is thereby effective for strengthening the steel. This element also fixes carbon and nitrogen to thereby increase the gamma value of the steel sheet. For satisfactorily exhibiting these advantages, the titanium content is preferably 0.003% or more. However, this element, if present in an excessively large content, may impair the workability and cause the production cost to increase, and the upper limit of its content is preferably 1.0%.

[0029] Copper, nickel, and titanium, if contained in combination, improve the surface cleanliness of the steel sheet and form multiple oxides with iron upon melting of iron so as to improve the plating quality. The total content of these elements, if two or more of them are contained in combination, is preferably 0.003% to 1.0% in consideration of the upper and lower limits of their contents in the case of single use.

Vanadium (V): 0.003% to 1.0%, Niobium (Nb): 0.003% to 1.0%

Vanadium (V) and niobium (Nb) elements form carbides and are thereby effective for increasing the strength of the steel. For satisfactorily exhibiting these advantages, their contents are preferably 0.003% or more, respectively. However, these elements, if contained in excessively large contents, may impair the workability and cause the production cost to increase, and the upper limits of their contents are preferably 1.0%, respectively.

Boron (B): 0.0002% to 0.1%

Boron (B) element serves to improve the weldability and to increase the hardenability. For effectively exhibiting these advantages, the boron content is preferably 0.0002% or more. However, if this element is present in an excessively large content, the effects thereof may be saturated and, in addition, the element may impair the ductility and the workability. Accordingly, the upper limit of its content is preferably 0.1%.

Molybdenum (Mo): 0.003% to 1.0%

Molybdenum (Mo) element is effective for solid-solution strengthening without impairing the plating quality. For satisfactorily exhibiting these advantages, the molybdenum content is preferably 0.003% or more. However, this element, if present in an excessively large content, may cause the production cost to increase, and the upper limit of its content is preferably 1.0%.

Calcium (Ca): 0.0005% to 0.005%, Magnesium (Mg): 0.0005% to 0.001%

Calcium (Ca) element acts to control the shapes of inclusions to thereby increase the ductility and to increase the workability. For effectively exhibiting these advantages, the calcium content is preferably 0.0005% or more. However, this element, if present in an excessively large content, may increase the amounts of inclusions in the steel to thereby reduce the ductility and to impair the workability. The upper limit of its content is therefore preferably 0.005%. Magnesium (Mg) acts in the steel in the same manner as with calcium. The magnesium content is therefore preferably from 0.0005% to 0.001% for the same reasons as with calcium.

[0030] Based on the investigations on how the generation of uneven alloying varies depending on the state of MnO in the surface layer of the steel sheet after annealing, as used herein the term "alloyed hot-dip galvanized steel sheet having good surface appearance with less uneven alloying" refers to an alloyed hot dip galvanized steel sheet, in which MnO particles are present on an arbitrary straight line lying in an interface between the galvanized zinc-coat layer 2 and the steel sheet 1 in an average number of 10 or less per micrometer of the straight line, an Fe-Al-O alloy layer is present at an interface between the MnO particles and the steel sheet 1, and the length of the Fe-Al-O alloy layer is less than 10% of the overall length of the interface, in which each of the length and the overall length are measured on the arbitrary straight line, as illustrated typically in FIG. 2.

[0031] In this connection, it requires much efforts and time and is practically difficult to observe the entire interface between the galvanized zinc-coat layer and the steel sheet typically with a scanning electron microscope (SEM). Accordingly, it is enough to observe only part of the interface. However, if the area to be observed is excessively narrow, the obtained data may significantly differ from actual data, and the interface should be observed in a length of at least 500 μm. As used herein the "overall length of an interface" refers to the length of the interface in an area to be observed.

[0032] The length of the Fe-Al-O alloy layer in FIG. 2 is not illustrated as being less than 10% of the overall length of the interface on an arbitrary straight line. FIG. 2 is, however, an exemplary diagram in order to illustrate the present invention, and, in actual, the length of the Fe-Al-O alloy layer on the arbitrary straight line is less than 10% of the overall length of the interface. Typically, the area shown in FIG. 2 is the area to be observed; the overall longitudinal width of FIG. 2 is the overall length of the interface; the total length of three parts of the Fe-Al-O alloy layer is the length of the Fe-Al-O alloy layer; and the percentage of the length of the Fe-Al-O alloy layer is calculated according to the formula: (Length of the Fe-Al-O alloy layer)/(Overall length of the interface) $\times$ 100.

[0033] When MnO particles are generated in the surface layer of the steel sheet and the steel sheet is dipped in a galvanization bath, aluminum contained in the galvanization bath immediately reacts with oxygen of the MnO on the surface of the steel sheet and with iron diffused from inside of the steel sheet to form an Fe-Al-O alloy layer at the interface between the steel sheet and a galvanized zinc-coat layer. The Fe-Al-O alloy layer acts as a barrier to inhibit the diffusion of iron during alloying, thus causing uneven alloying.

[0034] The average number of MnO particles on an arbitrary straight line lying in the interface between the galvanized zinc-coat layer 2 and the steel sheet 1 is preferably 10 or less per micrometer of the straight line. MnO particles, if present in an average number of more than 10 per micrometer, may accelerate uneven alloying of the alloyed hot-dip galvanized steel sheet, and MnO particles, if present in an average number of more than 20 per micrometer, may further impair the wettability in galvanization, cause bare spots when the steel sheet is dipped in a galvanization bath, and this impedes the production of a galvanized steel sheet. The average number of MnO particles is more preferably 5 or less per micrometer.

[0035] The length of the Fe-Al-O alloy layer generated at an interface between the MnO particle and the steel sheet 1 is preferably less than 10% of the overall length of the interface. An Fe-Al-O alloy layer, if present in a length of 10% or more of the overall length of the interface, may accelerate uneven alloying of the alloyed hot-dip galvanized steel sheet and significantly impair the surface appearance thereof. The resulting alloyed hot dip galvanized steel sheet is not suitable for use typically as an automotive outside sheathing. The length of the Fe-Al-O alloy layer is more preferably less than 5% of the overall length of the interface.

[0036] Such an alloyed hot dip galvanized steel sheet according to the present invention may be prepared in the following manner. In the alloyed hot dip galvanized steel sheet, MnO particles are present on an arbitrary straight line lying in the interface between the galvanized zinc-coat layer 2 and the steel sheet 1 in an average number of 10 or less per micrometer, and the length of an Fe-Al-O alloy layer present at an interface between the MnO particle and the steel sheet 1 on the arbitrary straight line is less than 10% of the overall length of the interface. Specifically, an annealing process is preferably carried out under such conditions that an oxygen partial pressure PO_2 (in units of atmospheric pressure (atm)) satisfies the following condition: $-\log(PO_2) \geq 20$. This annealing process is carried out prior to a galvanizing process to form a galvanized zinc-coat layer 2 on the surface of the annealed steel sheet 1. For further reducing the average number of the MnO particles to 5 or less per micrometer, the annealing process is more preferably carried out under such conditions that the oxygen partial pressure PO_2 (in units of atmospheric pressure (atm)) satisfies the following condition: $-\log(PO_2) \geq 23$.

[0037] As has been described above, by suppressing the generation of MnO particles, aluminum in the galvanization bath less reacts with oxygen in the MnO particles, this suppresses the generation of an Fe-Al-O alloy layer at an interface between the galvanized zinc-coat layer 2 and the steel sheet 1, and the resulting Fe-Al-O alloy layer, even if generated, less works as a barrier against the diffusion of iron. Thus, the diffusion of iron smoothly proceeds during alloying to thereby give an alloyed hot-dip galvanized steel sheet with superior surface appearance and with less uneven alloying.

[0038] Next, a method according to an embodiment of the present invention for producing an alloyed hot-dip galvanized steel sheet will be illustrated below with production conditions.

[0039] Initially, a slab of steel containing the components is hotrolled, wound as a coil, subjected to acid pickling of the surface according to necessity, cold-rolled, and thereby yields a base steel sheet (steel sheet).

[0040] Next, annealing of the base steel sheet is conducted in a continuous hot-dip galvanizing line. For example, the annealing in the annealing process may be conducted at a temperature of from 750°C to 900°C for a duration of 200 seconds or less. The annealing process is conducted under such conditions that an oxygen partial pressure PO_2 (in units of atmospheric pressure (atm)) in the atmosphere satisfies the following condition: $-\log(PO_2) \geq 20$.

[0041] After the completion of the annealing process, galvanization (hot-dip zinc plating) is conducted as a galvanizing process. A plating bath for use herein may be a galvanization bath containing 0.05 to 0.20 percent by mass of aluminum. The temperature of the steel sheet upon dipping in the galvanization bath herein is 440°C or higher and lower than 480°C, as being substantially equal to the temperature of the hot-dip galvanization bath. The dipping duration of the steel sheet in the galvanization bath is, for example, 5 seconds or less.

[0042] The steel sheet after dipping is retrieved from the galvanization bath, and the amount of the zinc coat deposited on the surface of the steel sheet is adjusted. Typically, the amount of the zinc coat is adjusted to a suitable amount of 60 ± 5 g/m^2 typically with a gas wiper.

[0043] After the completion of the galvanizing process, alloying of the galvanized steel sheet is conducted as an alloying process to give an alloyed hot-dip galvanized steel sheet. Typically, the alloying process is conducted at a temperature of from 450°C to 600°C for a duration of 60 seconds or less. Through these processes (steps), an alloyed hot-dip galvanized steel sheet with superior surface appearance and with less uneven alloying can be produced.

Examples

[0044] The present invention will be illustrated in further detail with reference to several examples below. It should be noted, however, the following examples are never intended to limit the scope of the present invention, and appropriate modifications and variations without departing from the spirit and scope of the present invention set forth above and below are possible and fall within the technical scope of the present invention.

[0045] In the following tests, test pieces of alloyed hot-dip galvanized steel sheets were prepared by working cold-rolled steel sheets having component compositions given in Table 1 to a size of 100 mm wide and 250 mm long, and sequentially subjecting the same to annealing, galvanizing, and alloying with a hot-dip galvanization simulator.

TABLE 1

Steel type	C	Si	Mn	P	S	Al	Cr	Cu	Ni	Ti	V	Nb	Mo	B	Ca	Mg
A	0.070	0.02	2.1	0.011	0.002	0.043	0.18									
B	0.110	0.02	2.70	0.011	0.002	0.045	0.18									
C	0.093	0.02	3.50	0.012	0.002	0.043	0.17									
D	0.095	0.02	2.56	0.011	0.002	0.043	0.18	0.2								
E	0.080	0.02	2.64	0.013	0.002	0.045	0.18		0.3							
F	0.120	0.02	2.12	0.011	0.002	0.043	0.23	0.4		0.02						
G	0.093	0.02	2.30	0.011	0.002	0.043	0.18	0.5	0.2	0.07						
H	0.094	0.02	3.21	0.013	0.002	0.043	0.18				0.1					
I	0.120	0.02	2.31	0.011	0.002	0.043	0.18					0.1				
J	0.093	0.02	2.98	0.011	0.002	0.043	0.20						0.07			
K	0.095	0.02	2.32	0.011	0.002	0.045	0.18							0.0009		
L	0.130	0.02	2.30	0.011	0.002	0.043	0.17				0.1		0.15			
M	0.094	0.02	2.45	0.011	0.002	0.043	0.18	0.3		0.05			0.31	0.0004		
N	0.093	0.02	2.31	0.011	0.002	0.043	0.18								0.0012	

[0046] Initially, the surfaces of the cold-rolled steel sheets having component compositions given in Table 1 were cleaned by acid pickling, and annealing was conducted in an atmosphere of N_2-3% H_2. The annealing conditions are shown in Table 2. The annealing was conducted at temperatures of from 750°C to 900°C for a duration of 120 seconds. The parameter -log(PO_2) was controlled by setting the annealing temperature within a range of from 750°C to 900°C and varying the dew point within a range of from -75°C to 0°C, as shown in Table 2.

Table 2

Type	Annealing conditions				
	Annealing temperature (°C)	Dew point (°C)	H_2 concentration (% by volume)	log(H_2O/H_2)	-log(PO_2)
a	750	-75	3	-4.399	28.5
b	750	-50	3	-2.887	25.5
c	750	-25	3	-1.68	23.1
d	750	0	3	-0.697	21.1
e	800	-75	3	-4.399	27.3
f	800	-50	3	-2.887	24.3
g	800	-25	3	-1.68	21.9
h	800	0	3	-0.697	19.9
i	850	-50	3	-2.887	24.3
j	850	-25	3	-1.68	20.8
k	850	0	3	-0.697	18.8
l	900	-75	3	-4.399	25.2
m	900	-50	3	-2.887	22.2
n	900	-25	3	-1.68	19.8
o	900	0	3	-0.697	17.8

[0047] The annealed steel sheets were dipped in a hot-dip galvanization bath containing 0.13 percent by mass of aluminum to thereby form a galvanized zinc-coat layer on the surface of the steel sheets. The dipping was conducted at a temperature of the steel sheet of 460°C for a duration of 2 seconds. After the formation of the galvanized zinc-coat layer, the amount of zinc coat was adjusted to 60 g/m^2 with a gas wiper, and thereby yielded galvanized steel sheets. The temperature of the galvanization bath was set to the same temperature as that of the steel sheet.

[0048] The alloying was conducted with an infrared heating furnace in the galvanizing simulator immediately after the galvanization. The alloying was conducted at a temperature of 550°C for a duration of 10 seconds. In the tests, the test pieces of the alloyed hot-dip galvanized steel sheets were examined on properties and alloying performance of the steel sheets after alloying. The results are shown in Table 3.

TABLE 3

Sample number	Steel type	Annealing condition	Properties and alloying performance of steel sheet after annealing				Remarks
			Length of Fe-Al-O alloy layer (%)	Number of MnO particles at interface between galvanized zinc-coat layer and steel (per micrometer)	Fe (percent by mass)	Surface appearance (uneven alloying, bare spots)	
1	A	b	1	0.2	11.5	Excellent	Example
2	A	e	0.8	0.1	9.9	Excellent	Example
3	A	h	15	19	4.1	Poor	Com. Ex.
4	A	i	1.2	0.9	10.6	Excellent	Example
5	A	j	7.2	8.8	9.1	Good	Example
6	A	k	19	13.3	7.2	Fair	Com. Ex.
7	A	n	25	12	3.3	Poor	Com. Ex.
8	A	o	23	15	4.5	Poor	Com. Ex.
9	B	c	1.9	2.5	10.9	Excellent	Example
10	B	d	8.6	5.7	9.3	Good	Example
11	B	f	2.2	3.2	10.5	Excellent	Example
12	B	g	7.3	6.9	9.0	Good	Example
13	B	h	14	15	4.5	Poor	Com. Ex.
14	B	i	2.4	1.6	10.7	Excellent	Example
15	B	j	8.2	7.9	8.8	Good	Example
16	B	k	22	18	2.6	Poor	Com. Ex.
17	B	m	6.4	7.7	9.4	Good	Example
18	B	n	21	13	2.9	Poor	Com. Ex.
19	B	o	18	16	2.1	Poor	Com. Ex.
20	C	a	4.2	3.8	10.4	Excellent	Example
21	C	b	4.6	4.2	10.7	Excellent	Example
22	C	d	7.9	8.7	8.9	Good	Example
23	C	e	4.7	4.1	9.9	Excellent	Example
24	C	g	7.2	6.9	9.2	Good	Example
25	C	i	4.5	3.3	10.6	Excellent	Example
26	C	k	26	16.8	1.8	Poor	Com. Ex.
27	C	l	4.8	3.7	9.2	Excellent	Example
28	C	n	53	29	-	Bare spot	Com. Ex.
29	C	o	65	32	-	Bare spot	Com. Ex.
30	D	a	4.3	4.2	8.9	Excellent	Example

(continued)

Sample number	Steel type	Annealing condition	Properties and alloying performance of steel sheet after annealing				Remarks
			Length of Fe-Al-O alloy layer (%)	Number of MnO particles at interface between galvanized zinc-coat layer and steel (per micrometer)	Fe (percent by mass)	Surface appearance (uneven alloying, bare spots)	
31	E	a	3.6	4.1	9.2	Excellent	Example
32	F	a	3.1	3.8	9.3	Excellent	Example
33	G	a	3.8	3.1	9.6	Excellent	Example
34	H	a	2.2	2.9	8.8	Excellent	Example
35	I	a	2.6	4.3	8.7	Excellent	Example
36	J	a	2.9	3.2	9.1	Excellent	Example
37	K	a	3.7	4.4	9.5	Excellent	Example
38	L	a	1.5	1.1	9	Excellent	Example
39	M	a	0.8	1	10.6	Excellent	Example
40	N	a	1.2	1.6	9.7	Excellent	Example

[0049] Initially, cross-sectional specimens were prepared by cutting out 10-mm square pieces from the center of the test pieces after alloying. Iron (Fe) contents (percent by mass) of the galvanized zinc-coat layers were analyzed by scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX). The iron contents indicate to which extent the alloying proceeds, and whether uneven alloying occurs or not may be supposed based on the magnitude of the iron content. Specifically, a small iron content indicates insufficient alloying; and a large iron content indicates delamination of the zinc coat due to excessive alloying.

[0050] To which extent uneven alloying occurs was evaluated according to the following criteria:

Excellent: no uneven alloying occurs,
Good: uneven alloying occurs in an area ratio of less than 10%,
Fair: uneven alloying occurs in an area ratio of 10% or more and less than 30%, and
Poor: uneven alloying occurs in an area ratio of 30% or more.

[0051] When no galvanized zinc-coat layer was formed, the sample was indicated as "Bare spot". Samples evaluated as "Excellent" or "Good" are accepted herein.

[0052] Next, enrichment of manganese (Mn) and aluminum (Al) were determined and the lengths of manganese- and aluminum-enriched portions were measured through electron prove microanalysis (EPMA), so as to identify or detect MnO particles at the interface between the galvanized zinc-coat layer and the steel sheet and to detect an Fe-Al-O alloy layer. After identifying the enrichment of manganese and aluminum, the number of the MnO particles was measured, and an area where the Fe-Al-O alloy layer is present was identified. For these measurements, a 5-μm square cross section sample was sampled at random from an area of 500 μm length including the interface between the galvanized zinc-coat layer and the steel sheet of each alloyed hot-dip galvanized steel sheet, according to a focused ion beam (FIB) microsampling process. The sample was machined to a thickness of about 0.1 μm through focused ion beam micromachining and used as a test specimen to be observed in the tests.

[0053] The test specimen was observed with a TEM (JEM-2010F) equipped with a high angle annular dark field detector (HAADF) (EM-24015BU) at an accelerating voltage of 200 kV, to determine the number of the MnO particles, and the percentage of the length of the Fe-Al-O alloy layer to the overall length of the interface.

[0054] Samples Nos. 1, 2, 4, 5, 9-12, 14, 15, 17, 20-25, 27, and 30-40 each had an average number of MnO particles present on an arbitrary straight line lying in the interface between the galvanized zinc-coat layer and the steel sheet of 10 or less per micrometer and each had a length of the Fe-Al-O alloy layer present at the interface between the series of the MnO particles and the steel sheet of less than 10% of the overall length of the interface. These samples are therefore examples according to the present invention. These examples, in which uneven alloying occurs in a quantity of less than 10%, are resistant to uneven alloying and excel in surface appearance.

[0055] In contrast, Samples Nos. 3, 6-8, 13, 16, 18, 19, and 26 each had an average number of MnO particles present on an arbitrary straight line lying in the interface between the galvanized zinc-coat layer and the steel sheet of more than 10 and equal to or less than 20 per micrometer and each had a length of an Fe-Al-O alloy layer present at the interface between the series of the MnO particles and the steel sheet of 10% or more of the overall length of the interface (Comparative Examples). These comparative examples are poor in surface appearance. This is probably because, when the sample was dipped in the galvanization bath, aluminum contained in the galvanization bath immediately reacted with oxygen in the MnO particles on the surface of the sample and with iron diffused from inside of the sample to form an Fe-Al-O alloy layer in a wide region at the interface, and the Fe-Al-O alloy layer inhibited the diffusion of iron during alloying to thereby cause uneven alloying.

[0056] Samples Nos. 28 and 29 each had an average number of MnO particles present on an arbitrary straight line lying in the interface between the galvanized zinc-coat layer and the steel sheet of more than 20 per micrometer (Comparative Examples). These comparative examples had further deteriorated wettability in galvanization and suffered from bare spots when they were dipped in the galvanization bath. Thus, galvanized steel sheets were not produced from these samples.

Claims

1. An alloyed hot-dip galvanized steel sheet, including a base steel sheet and a galvanized zinc-coat layer on the steel sheet, the galvanized zinc-coat layer and the steel sheet being alloyed, a steel constituting the base steel sheet comprising, on the mass basis, 0.02% to 0.2% of carbon (C), 2.0% to 3.5% of manganese (Mn), 0.03% to 0.5% of chromium (Cr), 0.01% to 0.15% of aluminum (Al), 0.04% or less (including 0%) of silicon (Si), 0.03% or less (including 0%) of phosphorus (P), and 0.03% or less (including 0%) of sulfur (S), with the remainder including iron (Fe) and inevitable impurities,
wherein MnO particles are present on an arbitrary straight line lying in an interface between the galvanized zinc-coat layer and the steel sheet in an average number of 10 or less per micrometer of the straight line,
wherein an Fe-Al-O alloy layer is present at an interface between the MnO particles and the steel sheet, and
wherein the length of the Fe-Al-O alloy layer is less than 10% of the overall length of the interface, each of the length and the overall length being measured on the arbitrary straight line.

2. The alloyed hot-dip galvanized steel sheet according to claim 1, wherein the steel further comprises, on the mass basis, a total of 0.003% to 1.0% of at least one member selected from the group consisting of 0.003% to 0.5% of copper (Cu), 0.003% to 1.0% of nickel (Ni), and 0.003% to 1.0% of titanium (Ti).

3. The alloyed hot-dip galvanized steel sheet according to claim 1, wherein the steel further comprises, on the mass basis, at least one member selected from the group consisting of 0.003% to 1.0% of vanadium (V), 0.003% to 1.0% of niobium (Nb), 0.0002% to 0.1% of boron (B), and 0.003% to 1.0% of molybdenum (Mo).

4. The alloyed hot-dip galvanized steel sheet according to claim 2, wherein the steel further comprises, on the mass basis, at least one member selected from the group consisting of 0.003% to 1.0% of vanadium (V), 0.003% to 1.0% of niobium (Nb), 0.0002% to 0.1% of boron (B), and 0.003% to 1.0% of molybdenum (Mo).

5. The alloyed hot-dip galvanized steel sheet according to claim 1, wherein the steel further comprises, on the mass basis, at least one member selected from the group consisting of 0.0005% to 0.005% of calcium (Ca) and 0.0005% to 0.001% of magnesium (Mg).

6. The alloyed hot-dip galvanized steel sheet according to claim 2, wherein the steel further comprises, on the mass basis, at least one member selected from the group consisting of 0.0005% to 0.005% of calcium (Ca) and 0.0005% to 0.001% of magnesium (Mg).

7. The alloyed hot-dip galvanized steel sheet according to claim 3, wherein the steel further comprises, on the mass basis, at least one member selected from the group consisting of 0.0005% to 0.005% of calcium (Ca) and 0.0005% to 0.001% of magnesium (Mg).

8. The alloyed hot-dip galvanized steel sheet according to claim 4, wherein the steel further comprises, on the mass basis, at least one member selected from the group consisting of 0.0005% to 0.005% of calcium (Ca) and 0.0005% to 0.001% of magnesium (Mg).

9. A method for producing the alloyed hot-dip galvanized steel sheet of any one of claims 1 to 8, the method comprising the steps of:

carrying out annealing of the steel sheet under such conditions that an oxygen partial pressure PO_2 (in units of atmospheric pressure (atm)) satisfies the following condition: $-\log(PO_2) \geq 20$;
galvanizing the annealed steel sheet to form the galvanized zinc-coat layer on the surface of the steel sheet; and
alloying the steel sheet bearing the galvanized zinc-coat layer.

FIG.1A FIG.1B FIG.1C

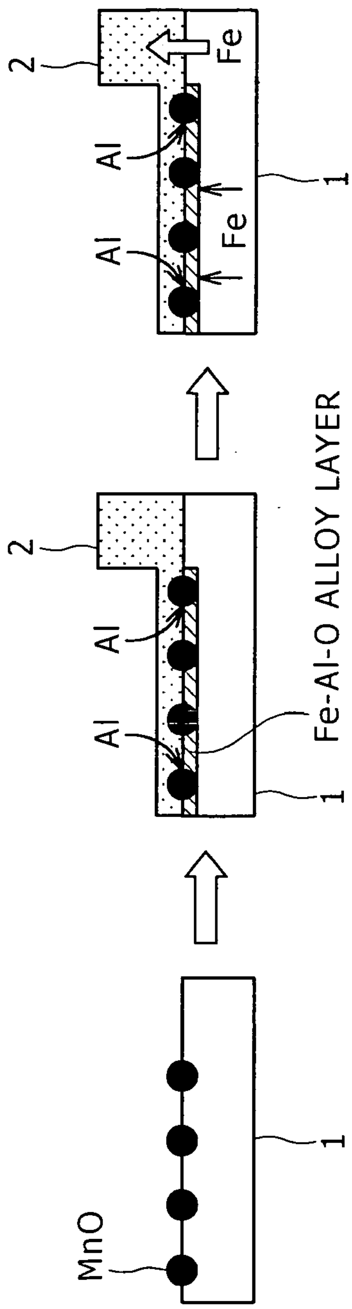
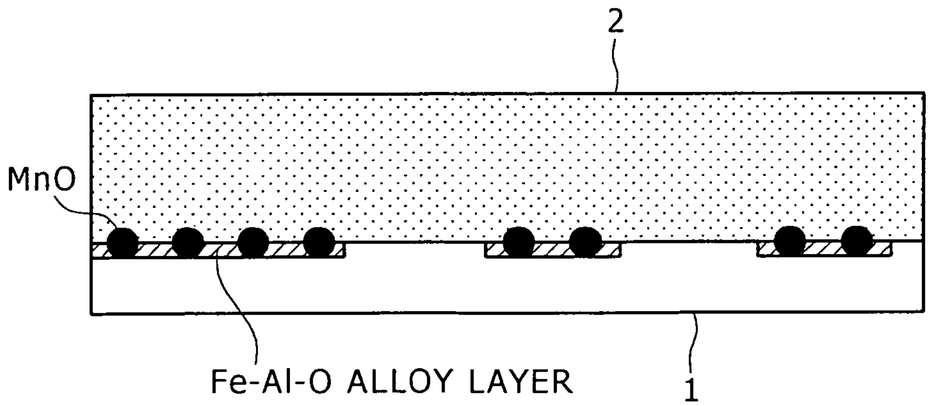


FIG. 2



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EUROPEAN SEARCH REPORT

Application Number
EP 09 00 8686

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	EP 1 041 167 A (KAWASAKI STEEL CO [JP]) 4 October 2000 (2000-10-04) * page 3, paragraph 27 - paragraph 28 * * page 4, paragraph 31 - page 8 * * page 12, paragraph 87 - page 13, paragraph 96 * * page 16, paragraph 143 - page 17, paragraph 172 * * claims 1,3,4; tables 1-5,8 * -----	1-8	INV. C23C2/02 C23C2/06 C21D1/74 C21D6/00 C21D9/46
X	US 2003/091857 A1 (PRADHAN RAJENDRA [US] ET AL) 15 May 2003 (2003-05-15) * the whole document * -----	1-8	
X	WO 2004/063410 A (NIPPON STEEL CORP [JP]; TAKADA YOSHIHISA [JP]; SUEHIRO MASAYOSHI [JP];) 29 July 2004 (2004-07-29) * page 8, line 30 - page 9, line 22 * * page 11, line 25 - page 13, line 4 * * page 15, line 24 - line 36 * * page 22, line 19 - line 33 * * page 24, line 5 - page 25, line 15 * * example 1; table 1 * * claims 1,9,13 * -----	1-8	TECHNICAL FIELDS SEARCHED (IPC) C23C C21D
X	WO 2007/109865 A (CT DE RECH S METALLURG ASBL CT [BE]; BORDIGNON MICHEL [BE]; VANDEN EYN) 4 October 2007 (2007-10-04) * page 1, paragraph 1 - page 4, paragraph 6 * * page 5, paragraph 13 - page 6, paragraph 15 * * page 8, paragraph 29 * * claims 1,2,9-11 * * figures 1,3-5 * ----- -/--	1-8	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	18 September 2009	Ovejero, Elena

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EUROPEAN SEARCH REPORT

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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 (IPC)
A	R. KHONDKER ET AL: "Effect of annealing atmosphere on the galvanizing behaviour of a dua-phase steel" MATERIALS SCIENCE AND ENGINEERING A, vol. 463, 2007, pages 157-165, XP002546226 * abstract * * the whole document * -----	1-8	
			TECHNICAL FIELDS SEARCHED (IPC)

The present search report has been drawn up for all claims

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The Hague	18 September 2009	Ovejero, Elena

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18-09-2009

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 1041167 A	04-10-2000	CA 2310335 A1	06-04-2000
		CN 1286730 A	07-03-2001
		WO 0018976 A1	06-04-2000
		US 6410163 B1	25-06-2002
US 2003091857 A1	15-05-2003	US 2004033386 A1	19-02-2004
WO 2004063410 A	29-07-2004	CA 2513298 A1	29-07-2004
		EP 1587966 A1	26-10-2005
		JP 2006517257 T	20-07-2006
		KR 20050092113 A	20-09-2005
		US 2006124907 A1	15-06-2006
		US 2008053576 A1	06-03-2008
WO 2007109865 A	04-10-2007	AT 440156 T	15-09-2009
		AU 2007231473 A1	04-10-2007
		BE 1017086 A3	05-02-2008
		CA 2644459 A1	04-10-2007
		CN 101466860 A	24-06-2009
		EP 1999287 A1	10-12-2008
		KR 20080111507 A	23-12-2008

EPO FORM P0459

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Patent documents cited in the description

- JP 2005200711 A **[0005]**
- JP 2001279410 A **[0005]**
- JP 6088193 A **[0006]**
- JP 2003328036 A **[0006]**
- JP 2004263271 A **[0007]**