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(54) [Title of the Invention]

High-Strength Al-Plated Steel Sheet With Excellent Post-Coating Corrosion Resistance, High-Strength Automotive Part, and Manufacturing Method Therefor

(57) [Abstract]

[Problem]

The present invention provides a high-strength Al-plated steel sheet with excellent post-coating corrosion resistance and automotive parts manufactured with this sheet for manufacturing parts requiring high strength, such as reinforcing components in vehicles.

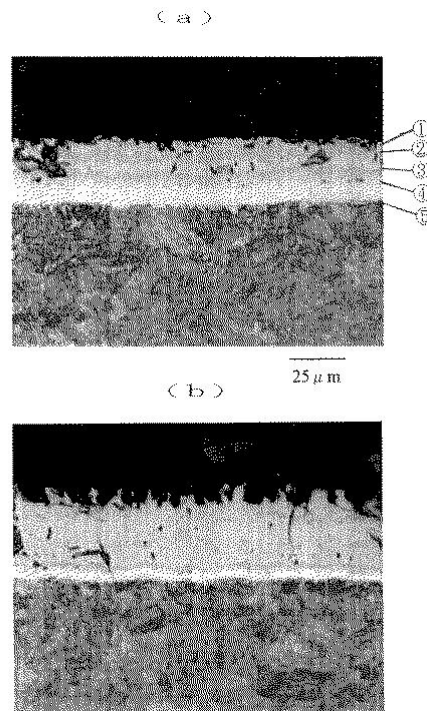
[Solution]

A high-strength Al-plated steel sheet with excellent post-coating corrosion resistance, characterized in that a surface of the steel sheet has an Fe-Al coating, and the Al concentration of the surface phase of the Fe-Al coating is at least 40 mass%. The surface phase can contain up to 5% Si. The steel sheet preferably contains as a steel component from 0.05 to 0.7% C in terms of mass percentage.

[Effect]

The steel sheet of the present invention can contribute to the manufacture of automotive parts with high strength and excellent post-coating corrosion resistance.

[Selected Drawing] Fig. 1



[Claims]

[Claim 1]

A high-strength Al-plated steel sheet with excellent post-coating corrosion resistance, characterized in that a surface of the steel sheet has an Fe-Al coating, and the Al concentration of the surface phase of the Fe-Al coating is at least 40 mass%.

[Claim 2]

The high-strength Al-plated steel sheet with excellent post-coating corrosion resistance according to claim 1, wherein the Fe-Al coating on the outermost surface portion contains no more than 5% Si in terms of mass percentage.

[Claim 3]

The high-strength Al-plated steel sheet with excellent post-coating corrosion resistance according to claim 1 or 2, wherein steel sheet contains as a steel component from 0.05 to 0.7% C in terms of mass percentage.

[Claim 4]

The high-strength Al-plated steel sheet with excellent post-coating corrosion resistance according to any of claims 1 to 3, wherein the total thickness of the Fe-Al coating is at least 20 μm .

[Claim 5]

A high-strength automotive part obtained by press-forming the steel according to claims 1 to 5.

[Claim 6]

The high-strength automotive part according to claim 5, wherein a surface of the automotive part has a 1 to 200 μm coating.

[Claim 7]

A method for manufacturing a high-strength automotive part with excellent post-coating corrosion resistance, characterized in that heating is performed under heating conditions satisfying the following equation, where the amount of plating deposited per side before heating of the Al plating is $X \text{ g/m}^2$ and the average rate of temperature increase from 300°C to 900°C is $Y^\circ\text{C/sec}$.

$$Y > 574 \cdot \exp(-0.033X)$$

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention]

The present invention relates to a steel material used to manufacture parts requiring extremely high strength, such as door impact beams, center pillars, bumper reinforcement, and other types of vehicle reinforcement. It also relates to parts using this steel material, and to a manufacturing method therefor.

[0002]

[Prior Art]

In recent years, there has been strong demand for high-strength steel sheets for automotive applications due to the trend toward reduced fuel consumption triggered by global environmental issues. However, higher strength is generally accompanied by lower workability and formability, and there is demand for steel sheets with both high strength and high formability. One possible solution to this problem is transformation induced plasticity (TRIP) steel, which utilizes martensitic transformation of residual austenite, and applications for this type of steel has expanded in recent years. Although 1,000 MPa-class high-strength steel sheets with excellent formability can be produced using this steel, it is difficult to ensure formability of an ultra-high-strength steel with strength of 1,500 MPa and higher. In particular, higher strength steel has lower dimensional accuracy after pressing, and residual stress after pressing can cause delayed fractures and other problems, limiting the applications for such high-strength steel.

[0003]

Hot pressing has recently garnered attention as another way to produce steel that combines high strength and high formability. This entails forming steel sheets at a temperature of 800°C or higher to eliminate the formability issues associated with high-strength steel sheets, and then cooling the sheets after formation to obtain the desired material quality. However, because this involves performing heating in air, oxides are formed on the surface, which must be removed in a subsequent step. A technology to improve this steel is disclosed in JP 2000-38640 A (Patent Document 1). Here, Al-plated steel sheets containing 0.15 to 0.5% carbon are used, that is, so-called Al-plated steel sheets, to suppress oxidation during heating.

[0004]

[Cited Documents]

(1) Patent Document 1 (JP 2000-38640 A)

[0005]

[Problem to Be Solved by the Invention]

This invention is effective at efficiently producing high-strength pressed parts, but has the following issue. Al-plated steel sheets are usually plated with an Al alloy containing about 10% Si, and consist of an Al-Si plating layer and an intermetallic compound layer (usually called an alloy layer) that is present at the interface between the plating layer and the steel sheet. The Al-Si plating layer is rapidly alloyed by the heating occurring during hot pressing. Usually, alloying has already occurred on the surface as the heating temperature rises, even if the heating temperature is around 850°C. This alloying process transforms the surface into an intermetallic compound, causing the following two problems to occur.

[0006]

One problem is that the intermetallic compounds formed on the surface are very brittle, so there is concern galling or cracking may occur during processing, in which case the post-coating corrosion resistance may be reduced. The other problem is that the concentration of Al in the intermetallic compounds is at most 50%, which is more corrosion resistant than the steel sheet, but tends to be less corrosion resistant in neutral environments than Al-plated layers (which usually have an Al-10%Si composition). In both cases, post-coating corrosion resistance may be reduced.

[0007]

[Means for Solving the Problem]

In order to overcome these problems, the present inventors conducted extensive research on the alloying behavior of Al-plated steel sheets and their corrosion behavior after alloying. As a result, the conditions for obtaining excellent post-coating corrosion resistance were clarified. The present invention is a product of this research. In sum, the composition of the surface after alloying, especially the phase near the surface, is important, and an Al concentration of 40% or more in terms of mass percentage in the outermost surface portion provides excellent post-coating corrosion resistance.

[0008]

The reason for this is that oxygen reduction reactions (cathodic reactions of corrosion) are reduced significantly on the surface of an alloy layer with at least 40% Al, and the resulting corrosion resistance is excellent. The present inventors were also able to clarify the appropriate steel sheet manufacturing conditions and heating conditions for obtaining such a surface. In other words, it became clear that, in order to obtain the appropriate surface, the amount of plating deposited on the Al-plated steel sheet and the rate of temperature increase during heating should be controlled.

[0009]

[Mode for Carrying Out the Invention]

The alloy layer structure of the Al-plated steel sheet when heated will now be described. Fig. 1 shows a typical cross-sectional microstructure after alloying. After alloying, the Fe-Al coating layer generally has a five-layer structure. These layers are represented by (1) to (5) in Fig. 1. Layers (1) and (3) have a composition of about 50% Al and layers (2) and (4) have a composition of about 30% Al. Also, layer (5) has an Al content of 10 to 20%. The formation of voids may be observed near the interface between layers (4) and (5). The microstructure under layer (5) is the steel matrix, which is a quenched microstructure primarily of martensite.

[0010]

In the present invention, the surface layers have to have more than 40% Al for post-coating corrosion resistance, which correspond to layers (1) and (3) in the optical micrograph shown in Fig. 1. These layers are easy to discern because they appear whiter than layers (2) and (4) under an optical microscope. They can also be identified in, for example, secondary electron images and reflected electron images, and can be more accurately discerned in, for example, an EPMA analysis.

In order to produce layers with about 50% Al on the surface, the present inventors discovered that the equation $X/10 < T < X$ has to be satisfied, where the amount of Al-Si plating deposited per side is $X \text{ g/m}^2$ and the duration of exposure to temperatures above 800°C is T seconds.

[0011]

Fig. 1 shows two micrographs (a) and (b). Two types of microstructures (a) and (b) can be obtained by selecting plating and heating conditions. In (b), layers (4) and (5) can be observed, but the layer (2) in (a) is no longer observed. As a result, the continuous layer corresponding to (2) in (a) is not observed in the image in (b), but is present in fragmented form. From the standpoint of post-coating corrosion resistance, this alloy layer structure is more desirable as it provides even better post-coating corrosion resistance. The present inventors also discovered that, in order to obtain a microstructure such as the one in (b), a large amount of Al-Si plating deposited and a higher rate of temperature increase are preferred, and that a structure with a non-continuous layer (2) such as the one in (b) can be obtained when the rate of temperature increase satisfies the equation $Y > 574 \cdot \exp(-0.033X)$, where the amount of Al-Si plating deposited per side is $X \text{ g/m}^2$ and the average rate of temperature increase from 300°C to 900°C is $Y^\circ\text{C/sec}$.

[0012]

Next, the reasons for the restrictions in the present invention will be explained. It is important in the present invention that the Al plating be heated to form an alloy layer, that is, an Fe-Al coating layer, and that the surface phase of this coating (layer (1) in Fig. 1(a)) be at least 40% in terms of mass percentage. The Al concentration of the surface phase of the coating refers to the quantitative analysis value obtained by EPMA $2 \mu\text{m}$ from the surface. The reason for this is the same as that described above, namely, that by increasing the Al concentration on the surface, the cathodic reaction of corrosion is suppressed and extremely good post-coating corrosion resistance is obtained. There are no particular restrictions on the upper limit, but since the Al concentration in the phase formed after alloying is usually no more than 75%, this is effectively the upper limit. The composition of the plating layer on the Al-plated steel sheet before heating is Al-Si, as described above, and the resulting Si can be included in the Fe-Al coating layer. The amount of Si is preferably no more than 5%. In general, a higher amount of Si results in a lower amount of Al in the Fe-Al coating layer after alloying.

[0013]

The total thickness of the Fe-Al coating layer is preferably at least $20 \mu\text{m}$. The Fe-Al coating layer here corresponds to layers (1) to (5) in Fig. 1, and the interface can be easily determined by nital etching. A thickness of $20 \mu\text{m}$ or more is preferred because a thicker layer responsible for corrosion resistance results in greater overall corrosion resistance and a longer material life. Although there are no particular restrictions on the upper limit, the plating thickness is preferably no more than $60 \mu\text{m}$ due to the upper limit on plating thickness that can be stably produced using the hot-dip plating method.

[0014]

Next, the reasons for the steel composition restrictions will be described. The present invention is characterized by the simultaneous performance of pressing and quenching using a die, so the steel sheet must have a composition that is easily quenched. For the purpose

of improving quenchability, the amount of C in the steel is preferably no less than 0.05%. However, if the amount of C is too high, the toughness of the steel sheet decreases significantly, so no more than 0.7% is preferred. There are no particular restrictions on the other steel components, but from the point of view of quenchability, Ti is preferably added to fix N, which traps Mn, Si, Cr, and B.

[0015]

Other elements such as P, S, Al, N, Mo, Nb, Ni, Cu, V, Sn, and Sb may be added. The preferred additive ranges are Mn: 0.5 to 3%, Si: 1% or less, P: 0.1% or less, S: 0.1% or less, Al: 0.1% or less, N: 0.01% or less, Cr: 2% or less, Mo: 0.5% or less, Ti: 0.5% or less, Nb: 0.1% or less, B: 0.05% or less, Ni: 1% or less, Cu: 1% or less, V: 0.1% or less, and Sn, Sb: 0.1% or less.

[0016]

The heating conditions for hot pressing using this steel sheet are preferably $Y > 574 \cdot \exp(-0.033X)$ (where Y is the average rate of temperature increase from 300°C to 900°C and X is the amount of Al-Si plating deposited on both sides). The reason for this is to ensure that there is a thicker layer with an Al concentration of about 50% on the surface, as mentioned above. Such steel sheets can be used to produce high-strength automotive parts, and these parts are usually coated before being put to use. Cationic electrodeposition coating is normally used, and the film thickness is preferably from 1 to 200 μm . A thicker film is more advantageous in terms of corrosion resistance, so an electrodeposition coating thickness of 15 to 25 μm is commonly used.

[0017]

There are no particular restrictions on the method used to apply Al plating to the steel sheet, and hot-dip plating, electroplating, vacuum deposition, or cladding can be used. The most common industrial method at the present time is hot-dip plating, which normally uses Al-10%Si as the plating bath, contaminated with Fe as an unavoidable impurity. Other elements that can be added include Mn, Cr, Mg, Ti, Zn, Sb, Sn, Cu, Ni, Co, In, Bi, and mischmetal, as long as the plating layer is primarily Al. The addition of Zn and Mg is advantageous in terms of making red rust less likely to form, but adding too much of these high vapor pressure elements may cause Zn and Mg fumes and formation of Zn and Mg powdery substances on the surface. Therefore, addition of more than 60% Zn and more than 10% Mg is undesirable.

[0018]

In the present invention, there are no particular restrictions on pre-plating and post-plating treatments for the Al plating. Pre-plating with Ni, Cu, Cr, or Fe can be used as a plating pretreatment. Chromate treatment and resin coating can be used as post-plating treatments for primary rust prevention and lubrication, but use of organic resins is undesirable as they disappear when heated. Given the recent regulations imposed on hexavalent chromium, trivalent chromate treatment coatings such as electrolytic chromate are preferred. Post-treatments other than inorganic chromate can also be used. Alumina, silica, or MoS_2 pretreatment can also be applied for lubricity.

[0019]

The following examples are used to explain the present invention in greater detail.

[Examples]

(Example 1)

A cold-rolled steel sheet (1.2 mm thick) of the steel composition shown in Table 1, which had undergone the normal hot-rolling and cold-rolling, was used as a material for hot dip Al plating. A non-oxidation furnace-reduction furnace type line was used for molten Al plating. The amount of plating deposition was adjusted using the gas wiping method after plating, followed by cooling and zero spangle treatment. The composition of the plating bath was Al-10%Si-2%Fe. The unavoidable Fe in the bath was supplied by the plating equipment and strips in the bath. The appearance of the plating was good and there was no non-plating. The steel sheet was heated in air, cooled in air to a temperature of about 700°C, and then quenched with pressure applied on both sides by 50 mm-thick dies. The cooling rate between the dies was about 200°C per second. Samples were prepared by varying the amount of Al plating and the heating conditions for the steel sheets, and the post-coating corrosion resistance of these samples was evaluated. In order to determine the effect of the heating rate, two types of heating method were used, namely, high-frequency induction heating and atmospheric furnace retention.

[0020]

In the evaluation of post-coating corrosion resistance, conversion treatment was performed using Nippon Parkerizing PB-3081M conversion treatment solution, followed by coating with Nippon Paint PERNIX 110 cationic electrodeposition coating to a thickness of about 20 µm. Cross-cuts were then made in the coating film using a cutter, and the combination corrosion test specified by the Society of Automotive Engineers of Japan (JASO-610M) was conducted for 150 cycles (50 groupings) to measure the blistering width from the cross-cuts (maximum blistering on both sides). The criteria for evaluating corrosion are shown below.

(Blistering Width)

O: ≤ 6 mm
 Δ: 6 mm to 9mm
 x: > 9 mm

[0021]

[Table 1]

Table 1

C	Si	Mn	P	S	Al	N	Ti	Cr	Mo	B
0.22	0.12	1.21	0.02	0.009	0.03	0.004	0.02	0.13	-	0.002

[0022]

Table 2 shows the results of evaluating the amount of Al plating deposited, the heating conditions, the Al and Si concentrations on the surface, and post-coating corrosion resistance. The surface Al and Si concentrations were measured by polishing sample cross sections, and performing quantitative analysis about 2 µm from the surface using EPMA. As shown in Table 2, the post-coating corrosion resistance depends on the amount of Al in the surface layer, and the amount of Al in the surface layer depends on the amount of plating

deposited and on the heating conditions. It was revealed that when the amount of plating deposited was low, a higher rate of temperature increase resulted in better post-coating corrosion resistance.

[0023]

[Table 2]

Table 2

No.	Amt. of Plating Deposited (g/m ²)	Temp. Reached (°C)	Heating Rate* ¹ (°C/sec)	Holding Time* ² (min)	Surface Layer Composition (mass%)		Blistering Width	Notes
					Al	Si		
1	80	950	10	1	52	1.2	Δ	Ex.
2	120	950	10	1	48	1.4	Δ	"
3	120	950	20	1	49	1.2	O	"
4	160	900	5	2	53	1.5	O	"
5	160	920	20	2	50	1.0	O	"
6	160	880	5	2.5	51	1.2	O	"
7	80	900	5	3	31	4.5	x	C. Ex.
8	160	950	5	4	29	4.9	x	"

*1 Average rate of temperature increase from 300°C to 900°C

*2 Total time temperature is above 800°C

[0024]

(Example 2)

Cold-rolled steel sheets (1.6 mm thick) with the various steel compositions shown in Table 3 were Al plated by hot dipping in the same manner as in Example 1. The amount of plating deposited was 160 g/m² on both sides. These Al-plated steel sheets were heated and die quenched under the same conditions as in Example 1. The temperature reached was 930°C, the average rate of temperature increase from 300°C to 900°C was 7°C per second, and the holding time above 800°C was two minutes. These steel sheets were evaluated for post-coating corrosion resistance under the same conditions as in Example 1, and good post-coating corrosion resistance (equivalent to "O" in Example 1) was obtained for all samples. The composition of the surface layer was measured under the same conditions as in Example 1, and the amount of Al was confirmed to be in the range of 49 to 54%. At the same time, the hardness (Vickers hardness, 1 kg load) after quenching was also investigated. The hardness ranged from 430 to 520, and the steel structure was confirmed to be martensitic.

[0025]

[Table 3]

Table 3

No.	C	Si	Mn	P	S	Al	N	Ti	Cr	Mo	B
1	0.23	0.12	1.21	0.02	0.009	0.03	0.004	0.02	0.13	-	0.002
2	0.21	0.20	0.81	0.02	0.007	0.05	0.004	0.22	0.20	-	-
3	0.17	0.15	1.24	0.01	0.008	0.03	0.003	0.01	1.10	-	0.0008
4	0.23	0.31	1.54	0.02	0.007	0.05	0.003	0.02	0.44	-	0.002
5	0.25	0.18	1.22	0.01	0.01	0.04	0.003	0.02	0.66	0.20	0.005
6	0.24	0.2	0.95	0.01	0.02	0.05	0.004	0.09	0.5	0.15	0.01
7	0.2	0.2	2.43	0.01	0.01	0.04	0.003	0.09	0.21	-	0.0008
8	0.04	0.1	1.4	0.02	0.01	0.03	0.004	0.25	0.15	-	0.0003

[0026]

(Example 3)

A cold-rolled steel sheet with the composition of Example 1 was plated using Galvalume plating, that is, in a plating bath of 55% Al and 1.5% Si, with the balance being Zn. The same evaluations as in Example 1 were performed on this. As a result, the Al concentration of the surface layer was 42%, and the post-coating corrosion resistance was equivalent to Δ in Example 1. However, fuming occurred in the furnace, possibly caused by Zn.

[0027]

[Effect of the Invention]

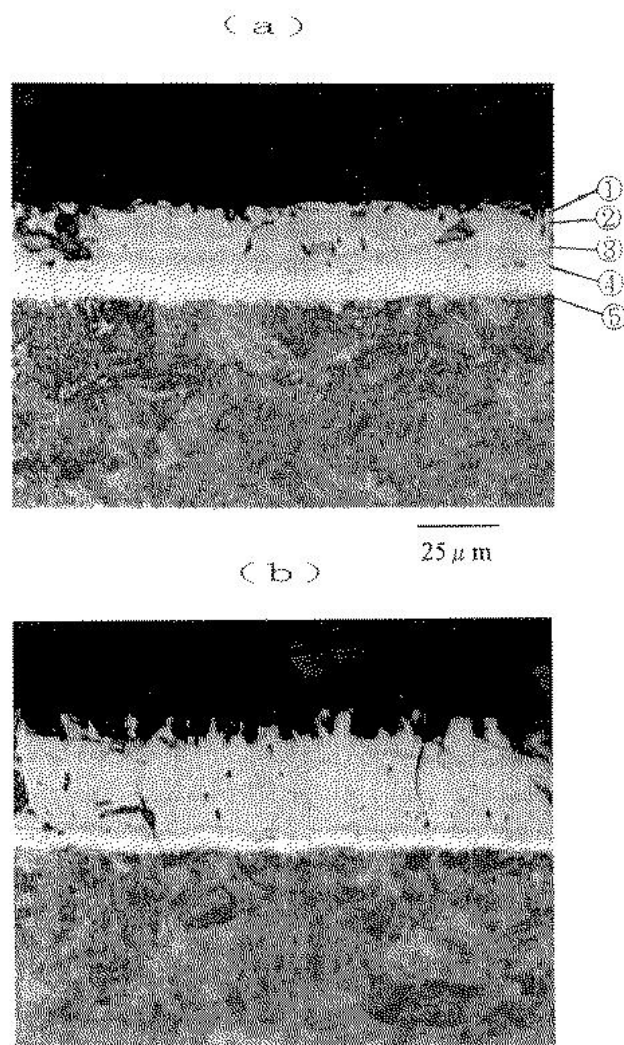
The present invention provides a high-strength Al-plated steel sheet with excellent post-coating corrosion resistance. The present invention can be expected to make a significant contribution to vehicle weight reduction, and will make an extremely large contribution to the industry.

[Brief Description of the Drawings]

[Fig. 1]

Fig. 1 shows cross-sectional microstructure under an optical microscope of the Al-plating layer of the present invention after alloying.

[Fig. 1]



(12) JP 2004-244704 A (P2004-244704A)

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