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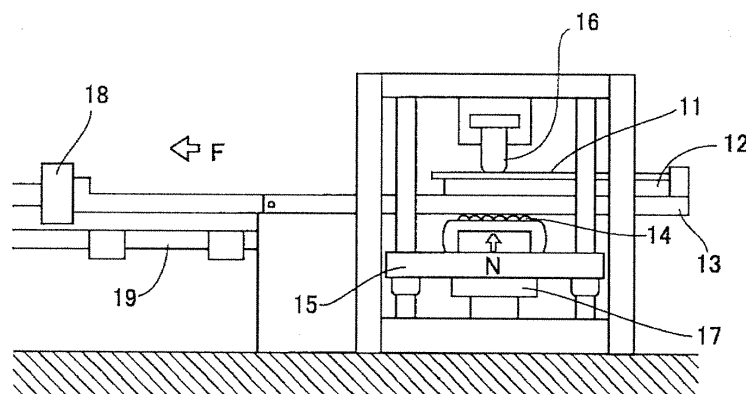
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(74) Representative: **Grünecker, Kinkeldey,****Stockmair & Schwanhäusser****Anwaltssozietät****Leopoldstrasse 4****80802 München (DE)**(54) **GALVANIZED STEEL SHEET AND METHOD FOR MANUFACTURING THE SAME**

(57) A method for manufacturing a galvanized steel sheet, includes: galvanizing a steel sheet; bringing the surface of the steel sheet into contact with an aqueous solution containing zinc ion in the range of 5 to 100 g/l as the zinc ion concentration, having a pH of 4 to 6, and having a liquid temperature of 20 to 70°C, holding the steel sheet for 1 to 60 seconds; and then washing and

drying the steel sheet. The solution containing zinc is preferably one containing zinc sulfate, for example. According to the method described above, a galvanized steel sheet having an oxide layer having an average thickness of 10 nm or more and mainly containing zinc formed on the surface of the steel sheet and having excellent press formability can be stably manufactured in a short time.

FIG2

Description

Technical Field

[0001] The present invention relates to a method for stably manufacturing a galvanized steel sheet having a low sliding resistance during press forming and excellent press formability and a galvanized steel sheet having excellent press formability.

Background Art

[0002] The galvanized steel sheet has been widely utilized in wide ranging fields focusing on the application to automobile bodies. A galvanized steel sheet in such application is press formed for use. However, the galvanized steel sheet has a disadvantage in that the press formability is inferior to that of a cold-rolled steel sheet. This is because the sliding resistance of the galvanized steel sheet in a press die is higher than that of the cold-rolled steel sheet. More specifically, the galvanized steel sheet becomes difficult to flow into a press die in a portion where the sliding resistance between a die and a bead, which easily causes fracture of the steel sheet.

[0003] Here, particularly a galvanized steel sheet that has been subjected to alloying treatment after hot dip galvanizing treatment among galvanized steel sheets has more excellent weldability and coatability than those of a hot-dip zinc-plated steel sheet that has not been subjected to alloying treatment, and thus has been more preferably used as automobile bodies.

[0004] The galvanized steel sheet is one in which an Fe-Zn alloy phase is formed by galvanizing a steel sheet, and heating the same so that Fe in the steel sheet and Zn in a plating layer are dispersed to cause an alloying reaction. The Fe-Zn alloy phase is a coating film generally containing a F phase, a δ_1 phase, and a ξ phase and has a tendency that the hardness and the melting point decrease with a reduction in the Fe concentration, i.e., in the order of F phase $\rightarrow$ δ_1 phase $\rightarrow$ ξ phase. Therefore, a coating film having a high Fe concentration in which the hardness is high, the melting point is high, and adhesion is difficult occur is effective from the viewpoint of slidability. A galvanized steel sheet in which the press formability is emphasized is manufactured in such a manner that the average Fe concentration in the coating film is slightly high.

[0005] However, the coating film having a high Fe concentration has problems in that the F phase that is hard and brittle is easily formed on the plated-steel sheet interface and a phenomenon of separation from the interface during processing, i.e., a so-called powdering, is likely to occur.

[0006] As methods for solving the problems, Patent Document 1 and Patent Document 2 disclose a technique of increasing the weldability and the processability by subjecting the surface of a galvanized steel sheet to electrolysis treatment, immersion treatment, coating oxidation treatment, or heat-treatment to form an oxide film mainly containing ZnO.

[0007] However, when the techniques of Patent Document 1 and Patent Document 2 are applied to a galvanized steel sheet, the surface reactivity becomes poor due to the presence of an Al oxide and an effect of improving the press formability cannot be stably obtained because the surface irregularities are large. More specifically, since the surface reactivity is low, it is difficult to form a given film on the surface even when the electrolysis treatment, immersion treatment, coating oxidation treatment, heat-treatment, or the like is performed and the film thickness is small in a portion where the reactivity is low, i.e., a portion in which the number of Al oxides is large. Since the surface irregularities are large, the surface convex portions directly contact a press die during press forming. The sliding resistance in contact portions of thin portions of the convex portions and the die becomes large, and thus an effect of improving the press formability is not sufficiently obtained.

[0008] Patent Document 3 discloses a technique of forming an oxide layer on a plated surface layer by hot dip galvanizing a steel sheet, alloying the same by heat treatment, subjecting the resultant steel sheet to temper rolling, bringing the same into contact with an acidic solution having pH buffer action, holding the same for 1 to 30 seconds, and then washing with water.

[0009] Similarly, as a method for uniformly forming an oxide layer on a surface flat portion of a hot dip galvanized steel sheet that has not been subjected to alloying treatment, Patent Document 4 discloses a method including bringing a hot dip galvanized steel sheet after temper rolling into contact with an acidic solution having pH buffer action, holding the same for a given period of time in a state where a liquid film of the acidic solution is formed on the surface of the steel sheet, and then washing with water and drying the same.

Patent Document 1: Japanese Unexamined Patent Application Publication No. 53-60332
 Patent Document 2: Japanese Unexamined Patent Application Publication No. 2-190483
 Patent Document 3: Japanese Unexamined Patent Application Publication No. 2003-306781
 Patent Document 4: Japanese Unexamined Patent Application Publication No. 2004-3004

[0010] When the techniques disclosed in Patent Document 3 and Patent Document 4 are applied, favorable press formability can be obtained under former manufacturing conditions. However, in recent years, the development of a manufacturing method for generating a thicker oxide film in a shorter period of time has been demanded in order to increase the productivity. When performed under such conditions, a sufficient oxide film is not formed and favorable

press formability is not obtained in some cases in the techniques disclosed in Patent Document 3 and Patent Document 4.

[0011] In view of such circumstance, it is an object of the present invention to provide a method capable of stably manufacturing a galvanized steel sheet having excellent press formability even in a short time and a galvanized steel sheet having excellent press formability.

Disclosure of Invention

[0012] The present inventors have repeatedly conducted extensive research in order to solve the problems. As a result, the following findings have been obtained.

[0013] The acidic solution for use in the techniques of Patent Document 3 and Patent Document 4 has pH buffer action in order to promote the dissolution of zinc. Therefore, it is considered that an increase in the pH is delayed, and thus the formation of an oxide layer is delayed. In order to compensate zinc for forming an oxide layer with zinc eluting from a plated coating film, an elution time of zinc is included in a generation time of the oxide film. As a result, it is considered that generating a thick oxide film in a short time becomes difficult.

[0014] Then, the present inventors have devised a technique of generating an oxide film in a shorter time by omitting an elution time of zinc by blending zinc ion in an aqueous solution for generating an oxide film beforehand. However, the formation of an oxide film has not been promoted merely by blending zinc ion in an aqueous solution beforehand. Particularly in the case where the pH is 2 described in Examples of Patent Document 3 and Patent Document 4, even when zinc is blended in a treatment liquid, the formation of an oxide film has not been promoted.

[0015] This is considered to be because, according to the techniques of Patent Document 3 and Patent Document 4, an environment is established in which a zinc oxide is likely to generate because the pH near the surface increases due to the reduction of hydrogen ion occurring simultaneously with the elution of zinc, but the pH near the surface does not increase merely by blending zinc ion in an aqueous solution, and thus an environment is not established in which a zinc oxide is likely to generate.

[0016] Then, the present inventors have devised a technique of setting the pH of an aqueous solution to 4 to 6, the pH at which a zinc oxide is likely to generate. Then, the present inventors have found that, by setting the pH of a treatment liquid to 4 to 6, zinc is generated as a hydroxide due to a slight increase in the surface pH caused by slight elution of zinc of a plated coating film.

[0017] The present invention has been accomplished based on the findings, and the gist is as follows.

[1] A method for manufacturing a galvanized steel sheet, includes galvanizing a steel sheet, bringing the steel sheet into contact with an aqueous solution, holding the steel sheet for 1 to 60 seconds after the termination of the contact treatment, and then washing with water and drying the steel sheet to thereby form an oxide layer on the surface of the steel sheet, in which the aqueous solution for use in the contact treatment of the steel sheet contains zinc ion in the range of 5 to 100 g/l as the zinc ion concentration, has a pH of 4 to 6, and has a liquid temperature of 20 to 70°C.

[2] The method for manufacturing a galvanized steel sheet according to [1] above, in which the aqueous solution contains zinc sulfate.

[3] The method for manufacturing a galvanized steel sheet according to [1] or [2] above, in which a liquid film to be formed on the surface of the steel sheet after the steel sheet contacts the aqueous solution is 5 to 30 g/m².

[4] A galvanized steel sheet, which is manufactured according to the method for manufacturing a galvanized steel sheet according to any one of [1] to [3] above, in which an oxide layer mainly containing zinc as a metal component is formed on the surface of the steel sheet in such a manner as to have an average thickness of 10 nm or more.

[0018] In the invention, the galvanized steel sheet is a plated steel sheet having a coating film containing zinc as the main component formed on the surface and includes a hot dip galvanized steel sheet (abbreviated as a GI steel sheet), a galvanized Steel Sheet (abbreviated as a GA steel sheet), an electrogalvanized steel sheet (abbreviated as an EG steel sheet), a vapor deposition galvanized steel sheet, an alloy galvanized steel sheet containing an alloy element of Fe, Al, Ni, MgCo, or the like, etc.

Brief Description of Drawings

[0019]

Fig. 1 is a view of a principal part of an oxide layer formation treatment facility used in Examples.

Fig. 2 is a schematic front view showing a friction coefficient measuring device.

Fig. 3 is a schematic perspective view showing the shape and the size of a bead in Fig. 2.

Fig. 4 is a schematic perspective view showing the shape and the size of the bead in Fig. 2.

Fig. 5 is a view showing influence of the zinc ion concentration on the oxide film thickness.

Best Modes for Carrying Out the Invention

[0020] In the invention, when forming an oxide layer on the surface of a steel sheet by galvanizing a steel sheet, bringing the steel sheet into contact with an aqueous solution, holding the steel sheet for 1 to 60 seconds after the termination of the contact treatment, and then washing with water and drying the steel sheet, the aqueous solution contains zinc ion in the range of 5 to 100 g/l as the zinc ion concentration, the pH is 4 to 6, and the liquid temperature is 20 to 70°C. To prepare an aqueous solution containing zinc ion in a given concentration and having a specified pH and a specified liquid temperature as described above as the aqueous solution for use in the contact treatment of the steel sheet is an important requirement and a feature in the invention. Thus, an oxide layer sufficient for securing favorable press formability can be formed in a short time.

[0021] The "after the termination of the contact treatment" refers to "after the termination of an immersion process" in the case of immersion treatment, "after the termination of a spraying process" in the case of spraying treatment, and "after the termination of a coating process" in the case of roll coating.

[0022] The use of an aqueous solution containing zinc ion as the aqueous solution for use in the contact treatment of the steel sheet allows omission of an elution time of zinc. In this case, the zinc ion is in the range of 5 to 100 g/l as the zinc ion concentration. When the zinc ion concentration is lower than 5 g/l, sufficient zinc is not supplied, resulting in a failure of the formation of an oxide layer. In contrast, when the zinc ion concentration exceeds 100 g/l, the concentration of sulfuric acid contained in the oxide layer to be formed becomes high, resulting in concern about contamination of a treatment liquid when the oxide dissolves in chemical conversion treatment to be carried out thereafter.

[0023] In order to form a stable zinc compound as an oxide layer, it is preferable to add zinc ion as a sulfate. It is considered that when zinc ion is added as a sulfate, sulfuric acid ion is taken into an oxide layer to be formed to thereby produce an effect of stabilizing the oxide layer.

[0024] As described above, the formation of an oxide film is not promoted merely by blending zinc ion in a treatment liquid beforehand. Then, in the invention, the pH needs to be set to 4 to 6, at which a zinc oxide easily generates. When the pH of a treatment liquid is set to 4 to 6, zinc generates as a hydroxide due to a slight increase in the surface pH caused by slight elution of zinc of a plated coating film. As a result thereof, the zinc elution time can be omitted and the generation of a zinc oxide can be achieved. When the pH exceeds 6, zinc ion precipitates in the aqueous solution (formation of a hydroxide) and is not formed as an oxide on the surface of the steel sheet. When the pH is lower than 4, the formation of the oxide layer is hindered due to the delay of an increase in the pH as described above.

[0025] The temperature of the aqueous solution is 20 to 70°C. Since the oxide layer formation reaction occurs when holding the steel sheet in a given period of time after contacting the aqueous solution, it is effective to control the sheet temperature during holding in the range of 20 to 70°C. When the sheet temperature is lower than 20°C, a long period of time is required for the oxide layer generation reaction, resulting in a reduction in the productivity. In contrast, when the sheet temperature exceeds 70°C, a reaction relatively quickly proceeds but treatment unevenness is likely to occur on the surface of the steel sheet.

[0026] The aqueous solution used in Patent Document 3 and Patent Document 4 has a feature in that the aqueous solution is acidic and has pH buffer action. In the invention, however, since an aqueous solution containing zinc ion is used, a sufficient oxide layer can be formed even when the dissolution of zinc is not caused by increasing the pH of the aqueous solution. A prompt increase in the pH is considered to be advantageous for the formation of an oxide. Therefore, the pH buffer action is not necessarily indispensable.

[0027] In the invention, an oxide layer excellent in slidability can be stably formed when zinc is contained in the aqueous solution contacting the surface of the steel sheet. Therefore, even when other metal ions, inorganic compounds, and the like are contained as impurities or intentionally contained in the aqueous solution, the effects of the invention are not impaired. Even when N, P, B, Cl, Na, Mn, Ca, Mg, Ba, Sr, Si, and the like are taken into the oxide layer, it can be applied insofar as the effects of the invention are not impaired.

[0028] Preferably, after bringing a galvanized steel sheet into contact with the aqueous solution containing the above, the aqueous solution is present on the surface of the steel sheet in the form of a thin liquid film. This is because when the amount of the aqueous solution present on the surface of the steel sheet is large, the pH of the aqueous solution is hard to increase even when the dissolution of zinc occurs, and a long period of time is required for the formation of the oxide layer. From this viewpoint, it is preferable and effective to adjust the amount of an aqueous solution film to be formed on the surface of the steel sheet to 30 g/m² or lower. In order to prevent the liquid film from drying, the amount of the liquid film of 5 g/m² or more is suitable. As described above, the liquid film to be formed on the surface of the steel sheet after contacting the aqueous solution is preferably 5 to 30 g/m². The adjustment of the amount of the aqueous

solution film can be performed by a squeeze roll, air wiping, or the like.

[0029] The time (retention time before washing with water) before washing with water after immersion in the aqueous solution is 1 to 60 seconds. When the time before washing with water is lower than 1 second, the aqueous solution is washed away before a sufficient oxide layer is formed, and thus an effect of improving the slidability is not obtained. In contrast, when the time before washing with water exceeds 60 seconds, the productivity decreases. Since the object of the invention is to stably manufacture a galvanized steel sheet even in a short time, the retention time is 60 seconds or lower for sufficiently demonstrating the effects of the invention.

[0030] As described above, on the surface of the plated steel sheet of the invention, an oxide layer mainly containing zinc as a metal component and having an average thickness of 10 nm or more is obtained.

[0031] The "mainly containing zinc" refers to containing zinc in a proportion of 50% by mass or more as a metal component.

[0032] The oxide layer in the invention refers to a layer containing an oxide and/or a hydroxide mainly containing zinc as a metal component. The average thickness of the oxide layer is required to be 10 nm or more. When the average thickness of the oxide layer is small, e.g., lower than 10 nm, an effect of reducing sliding resistance becomes insufficient. In contrast, when the average thickness of the oxide layer containing zinc as an essential ingredient exceeds 100 nm, there is a tendency that the coating film breaks during press processing, the sliding resistance increases, and the weldability decreases. Thus, such a thickness is not preferable.

[0033] Methods for bringing the galvanized steel sheet into contact with the aqueous solution containing zinc are not particularly limited. For example, a method for immersing the plated steel sheet in the aqueous solution, a method for spraying the aqueous solution to the plated steel sheet, a method for applying the aqueous solution to the plated steel sheet with a coating roll, and the like are mentioned. It is preferable for the aqueous solution to be finally present on the surface of the steel sheet in the form of a thin liquid film.

[0034] For manufacturing the galvanized steel sheet according to the invention, Al needs to be added into a plating bath but additional element ingredients other than Al are not particularly limited. More specifically, even when Pb, Sb, Si, Sn, Mg, Mn, Ni, Ti, Li, Cu, and the like other than Al are contained or added, the plating bath can be applied insofar as the effects of the invention are not impaired.

EXAMPLES

[0035] Next, the invention will be described in more detail with reference to Examples.

[0036] A GI steel sheet was produced by performing hot dip galvanizing in which the deposit amount per surface was 45 g/m² and the Al concentration was 0.20% by mass on a cold-rolled steel sheet having a sheet thickness of 0.8 mm, and then performing temper rolling. A GA steel sheet was obtained by forming a plated coating film in which the deposit amount per surface was 45 g/m², the Fe concentration was 10% by mass, and the Al concentration was 0.20% by mass on a cold-rolled steel sheet having a sheet thickness of 0.8 mm by a standard galvannealing method, and further performing temper rolling. An EG steel sheet was produced by having a plated coating film having a deposit amount per surface of 30 g/m² on a cold-rolled steel sheet having a sheet thickness of 0.8 mm by a standard electrogalvanizing method.

[0037] Subsequently, an oxide layer was formed using a treatment facility having a structure shown in Fig. 1. First, steel sheets S, such as the GI steel sheet, the GA steel sheet, and the EG steel sheet obtained above were immersed in aqueous solutions in which the treatment liquid composition, the temperature, and the pH were different from each other as shown in Tables 1-1 and 1-2 in a solution bath 2. Subsequently, the amount of liquid films on the surface of the steel sheets was adjusted with a squeeze roll 3. The adjustment of the amount of liquid films was performed by changing the pressure of the squeeze roll. Subsequently, the steel sheets were made to pass through a washing bath 5 and a washing bath 6 without being treated, hot water of 50°C was sprayed to the steel sheets in a washing bath 7 for washing, and the steel sheets were dried with a drier 8, so that an oxide layer is formed on the plated surface. A washing bath 1 can be provided before the solution bath 2.

[0038] As the aqueous solution for use in the immersion treatment in the solution bath 2, an aqueous solution was used to which a given amount of zinc sulfate heptahydrate was added in order to add zinc ion. For comparison, a solution containing 20 g/L of sodium acetate whose pH was adjusted with sulfuric acid was also used in some cases.

[0039] The retention time before washing with water was the time before washing in the washing bath 7 was started after adjusting the amount of liquid films with the squeeze roll 3 and was adjusted by changing the line speed. Some of the steel sheets were produced by washing immediately after squeezing using a shower washing device 4 at the exit side of the squeeze roll 3.

[0040] Next, the steel sheets produced as described above were judged whether or not they have an appearance sufficient as an exterior panel for automobiles, and also the measurement of a friction coefficient as a method for simply evaluating the press formability and a spherical head bulging test was carried out in order to simulate the actual formability in detail were carried out. The measurement methods are as follows.

(1) Press formability evaluation test (Friction coefficient measurement test)

[0041] In order to evaluate the press formability, the friction coefficient of each test piece was measured as follows.

[0042] Fig. 2 is a schematic front view showing a friction coefficient measuring device. As shown in Fig. 2, a friction coefficient measuring sample 11 extracted from the test piece is fixed to a sample stand 12. The sample stand 12 is fixed to the upper surface of a horizontally movable slide table 13. On the lower surface of the slide table 13, a vertically movable slide table support stand 15 having a roller 14 contacting the lower surface of the slide table 13. By pressing up the same, a first load cell 17 for measuring a pressing load N to the friction coefficient measuring sample 11 by a bead 16 is attached to the slide table support stand 15. In order to measure a sliding resistance F for horizontally moving the slide table 13 along a rail 19 in the state where the pressing force was made to act, a second load cell 18 is attached to one end of the slide table 13. As a lubricant, a cleaning oil for pressing, Preton R352L manufactured by Sugimura Chemical Industrial Co., Ltd., was applied onto the surface of the friction coefficient measuring sample 11, and thus a test was carried out.

[0043] Figs. 3 and 4 are schematic perspective view showing the shape and the size of the used bead. The bead 16 slides while the lower surface of the bead 16 being pressed against the surface of the sample 11. In the bead 16 shown in FIG. 3, the width is 10 mm, the length in the sliding direction of the sample is 12 mm, and each end in the sliding direction of the lower surface of the bead 16 is curved with a curvature of 4.5 mmR. The lower surface of the bead 16 against which the sample is pressed has a plane with a width of 10 mm and a length in the sliding direction of 3 mm. In the bead 16 shown in FIG. 4, the width is 10 mm, the length in the sliding direction of the sample is 69 mm, and each end in the sliding direction of the lower surface of the bead 16 is curved with a curvature of 4.5 mmR. The lower surface of the bead 16 against which the sample is pressed has a plane with a width of 10 mm and a length in the sliding direction of 60 mm.

[0044] The friction coefficient measurement test was carried out under two conditions shown below.

[Condition 1]

[0045] The bead shown in Fig. 3 was used, the pressing load N was 400 kgf, and the sample drawing rate (horizontal movement rate of the slide table 13) was 100 cm/min.

[Condition 2]

[0046] The bead shown in Fig. 4 was used, the pressing load N was 400 kgf, and the sample drawing rate (horizontal movement rate of the slide table 13) was 20 cm/min.

[0047] The friction coefficient between the test piece and the bead was calculated based on Equation: $\mu = F/N$.

(2) Spherical head bulging test

[0048] A test piece having a size of 200 × 200 mm was subjected to bulge forming using a 150 mmφ punch by a liquid pressure bulge testing machine. Then, the maximum forming height when the test piece was broken was measured. During the test, a wrinkle pressing force of 100 Ton was applied in order to prevent inflow of materials, and a lubricating oil was applied only to the surface which the punch contacted. The used lubricating oil is the same as that of the friction coefficient measurement test described above.

(3) Measurement of thickness of oxide layer (oxide film thickness)

[0049] An Si wafer on which a thermal oxidation SiO₂ film having a film thickness of 96 nm was formed was used as a reference substance, and the average thickness of the oxide layer in terms of SiO₂ was determined by measuring the O-KαX rays by an x-ray fluorescence spectrometer. The analysis area is 30 mmφ.

[0050] The test results obtained in the above are shown in Tables 1-1 and 1-2.

Table 1-1

No .	Test piece	Used solution		pH	Solution Temperature	Liquid film amount (g/m ²)	Time beforewater Washing (second)	Oxide film thickness (nm)	Friction coefficient		Maxium forming height (mm)	Steel sheet appearance	Remarks
		pH buffer	Zn concentratio						Condition 1	Condition 2			
1	GA	-	-	-	35°C	-	-	8	0.180	0.223	35.0	○	Comparative example 1
2		Sodium acetate (20g/L)	-	2.0 sulfuric acid added		10	10	15	0.149	0.190	36.5	○	Comparative example 2
3			10	30		30	0.128	0.165	38.1	○	Comparative example 3		
4			10	60		42	0.120	0.163	39.3	○	Comparative example 4		
5		-	5.0 sulfuric acid added	35°C	10	10	8	0.183	0.219	35.6	○	Comparative example 5	
6					10	30	8	0.179	0.221	35.9	○	Comparative example 6	
7					10	60	8	0.180	0.217	35.9	○	Comparative example 7	
8		-	2.5g/l	5.6	35°C	10	10	12	0.148	0.200	36.5	○	Comparative example 8
9						10	30	25	0.140	0.174	37.9	○	Comparative example 9
10						10	60	32	0.132	0.163	38.9	○	Comparative example 10

(continued)

No	Test piece	Used solution		pH	Solution Temperature	Liquid film amount (g/m ²)	Time beforewater Washing (second)	Oxide film thickness (nm)	Friction coefficient		Maximum forming height (mm)	Steel sheet appearance	Remarks
		pH buffer	Zn concentration						Condition 1	Condition 2			
11			5g/l	5.5	35°C	10	10	18	0.138	0.187	37.6	○	Example of present invention 1
12						10	30	32	0.123	0.166	39.1	○	Example of present invention 2
13						10	60	43	0.122	0.163	39.5	○	Example of present invention 3
14			10g/l	5.2	35°C	10	10	25	0.134	0.174	39.0	○	Example of present invention 4
15						10	30	35	0.128	0.164	39.4	○	Example of present invention 5
16						10	60	45	0.124	0.163	40.1	○	Example of present invention 6

(continued)

No	Test piece	Used solution		pH	Solution Temperature	Liquid film amount (g/m ²)	Time beforewater Washing (second)	Oxide film thickness (nm)	Friction coefficient		Maximum forming height (mm)	Steel sheet appearance	Remarks
		pH buffer	Zn concentration						Condition 1	Condition 2			
17			50g/l	5.0	35°C	10	0	12	0.160	0.205	37.2	○	Comparative example 11
18						10	1	15	0.145	0.200	38.1	○	Example of present invention 7
19						10	5	24	0.137	0.173	39.0	○	Example of present invention 8
20						10	10	32	0.127	0.165	38.9	○	Example of present invention 9
21						10	30	40	0.127	0.159	39.9	○	Example of present invention 10
22						10	60	50	0.125	0.160	40.8	○	Example of present invention 11
23					15°C	10	10	14	0.145	0.198	37.1	○	Comparative example 12
24						10	30	27	0.134	0.169	38.1	○	Comparative example 13
25						10	60	37	0.125	0.166	39.2	○	Comparative example 14

(continued)

No	Test piece	Used solution		pH	Solution Temperature	Liquid film amount (g/m ²)	Time beforewater Washing (second)	Oxide film thickness (nm)	Friction coefficient		Maximum forming height (mm)	Steel sheet appearance	Remarks
		pH buffer	Zn concentration						Condition 1	Condition 2			
26					25°C	10	10	19	0.138	0.189	38.5	○	Example of present invention 12
27						10	30	32	0.129	0.166	40.3	○	Example of present invention 13
28						10	60	43	0.127	0.162	40.0	○	Example of present invention 14
29					65°C	10	10	35	0.128	0.164	40.5	○	Example of present invention 15
30						10	30	44	0.125	0.162	41.6	○	Example of present invention 16
31						10	60	51	0.123	0.160	41.8	○	Example of present invention 17
32					75°C	10	10	35	0.124	0.161	40.6	×	Comparative example 15
33						10	30	45	0.120	0.163	40.5	×	Comparative example 16
34						10	60	52	0.121	0.158	41.0	×	Comparative example 17

(continued)

No	Test piece	Used solution		pH	Solution Temperature	Liquid film amount (g/m ²)	Time beforewater Washing (second)	Oxide film thickness (nm)	Friction coefficient		Maximum forming height (mm)	Steel sheet appearance	Remarks
		pH buffer	Zn concentration						Condition 1	Condition 2			
35					35°C	30	10	20	0.143	0.185	38.5	○	Example of present invention 18
36						30	30	34	0.128	0.163	39.1	○	Example of present invention 19
37						30	60	49	0.127	0.161	40.4	○	Example of present invention 20
38					35°C	40	10	13	0.155	0.202	37.4	○	Example of present invention 21
39						40	30	28	0.132	0.167	39.0	○	Example of present invention 22
40						40	60	42	0.127	0.163	39.7	○	Example of present invention 23
41				3.5 sulfuric acid added	35°C	10	10	14	0.149	0.201	36.0	○	Comparative example 18
42						10	30	27	0.130	0.165	39.2	○	Comparative example 19
43						10	60	40	0.124	0.162	41.0	○	Comparative example 20

(continued)

No	Test piece	Used solution		pH	Solution Temperature	Liquid film amount (g/m ²)	Time beforewater Washing (second)	Oxide film thickness (nm)	Friction coefficient		Maximum forming height (mm)	Steel sheet appearance	Remarks
		pH buffer	Zn concentration						Condition 1	Condition 2			
44			100g/l	4.9	35°C	10	10	34	0.125	0.166	40.5	○	Example of present invention 24
45						10	30	41	0.123	0.164	40.9	○	Example of present invention 25
46						10	60	50	0.121	0.163	40.8	○	Example of present invention 26

Table 1-2

No	Test piece	Used solution		pH	Solution Temperature	Liquid film amount (g/m ²)	Time before water washing (second)	Oxide film thickness (nm)	Friction coefficient		Maximum forming height (mm)	Steel sheet appearance	Remarks
		pH buffer	Zn concentration						Condition 1	Condition 2			
47	GI	-	-	-	-	-	-	7	0.175	0.215	35.7	○	Comparative example 21
48		Sodium acetate (20 g/L)	-	2.0 sulfuric acid added	35°C	10	10	13	0.147	0.187	36.7	○	Comparative example 22
49						10	30	27	0.125	0.164	38.6	○	Comparative example 23
50						10	60	39	0.119	0.160	39.6	○	Comparative example 24

(continued)

No	Test piece	Used solution		pH	Solution Temperature	Liquid film amount (g/m ²)	Time before water washing (second)	Oxide film thickness (nm)	Friction coefficient		Maximum forming height (mm)	Steel sheet appearance	Remarks
		pH buffer	Zn concentration						Condition 1	Condition 2			
51		-	2.5g/l	5.6	35°C	10	10	11	0.161	0.198	36.3	○	Comparative example 25
52						10	30	24	0.13	0.168	38	○	Comparative example 26
53						10	60	34	0.121	0.163	39.1	○	Comparative example 27
54						10	10	19	0.138	0.177	37.1	○	Example of present invention 27
55		-	10g/l	5.2	35°C	10	30	32	0.124	0.161	38.5	○	Example of present invention 28
56						10	60	42	0.121	0.161	39.5	○	Example of present invention 29
57						10	10	26	0.127	0.166	38.4	○	Example of present invention 30
58						10	30	36	0.122	0.163	39	○	Example of present invention 31
59						10	60	45	0.12	0.159	39.7	○	Example of present invention 32
60						-	-	9	0.146	0.289	33.7	○	Comparative example 28

(continued)

No	Test piece	Used solution		pH	Solution Temperature	Liquid film amount (g/m ²)	Time before water washing (second)	Oxide film thickness (nm)	Friction coefficient		Maximum forming height (mm)	Steel sheet appearance	Remarks
		pH buffer	Zn concentration						Condition 1	Condition 2			
61		Sodium acetate (20g/L)	-	2.0 sulfuric acid added	35°C	10	10	11	0.136	0.241	34.0	○	Comparative example 29
62						10	30	23	0.135	0.195	36.6	○	Comparative example 30
63						10	60	36	0.128	0.173	37.9	○	Comparative example 31

(continued)

No	Test piece	Used solution		pH	Solution Temperature	Liquid film amount (g/m ²)	Time before water washing (second)	Oxide film thickness (nm)	Friction coefficient		Maximum forming height (mm)	Steel sheet appearance	Remarks
		pH buffer	Zn concentration						Condition 1	Condition 2			
64		-	2.5g/l	5.6	35°C	10	10	12	0.140	0.199	37.0	○	Comparative example 32
65						10	30	23	0.131	0.181	37.2	○	Comparative example 33
66						10	60	31	0.131	0.159	37.5	○	Comparative example 34
67			10g/l	5.2	35°C	10	10	20	0.139	0.221	35.4	○	Example of present invention 33
68						10	30	35	0.132	0.195	36.9	○	Example of present invention 34
69						10	60	45	0.129	0.160	37.6	○	Example of present invention 35
70			50g/l	5.0	35°C	10	10	22	0.136	0.192	37.6	○	Example of present invention 36
71						10	30	37	0.131	0.153	39.3	○	Example of present invention 37
72						10	60	46	0.125	0.156	38.9	○	Example of present invention 38

[0051] The following items were clarified from the test results shown in Tables 1-1 and 1-2.

(1) Since Nos. 1, 47, and 60 were not treated with a solution, an oxide film sufficient for increasing the slidability was not formed on the flat portion. Thus, the friction coefficient is high.

(2) Nos. 2 to 4, Nos. 48 to 50, and Nos. 61 to 63 are comparative examples using an acidic solution having pH buffer action. In the case of the treatment of 30 seconds or more, the friction coefficient is low and the maximum forming height is large but in the case of the treatment of 10 seconds, a sufficient reduction in the friction coefficient and an increase in the maximum forming height are not satisfied.

(3) Nos. 5 to 7 are comparative examples using an acidic solution having pH buffer action. High friction coefficients are exhibited.

(4) Nos. 8 to 10, Nos. 51 to 53, and Nos. 64 to 66 are comparative examples in which zinc ion is contained but the amount is smaller than the range of the invention. In the case of the treatment of 30 seconds or more, the friction coefficient is low and the maximum forming height is large but in the case of the treatment of 10 seconds, a sufficient reduction in the friction coefficient and an increase in the maximum forming height are not satisfied.

(5) Nos. 11 to 13, Nos. 54 to 56, and Nos. 67 to 69 are examples of the invention that were treated with a solution containing zinc ion, in which the friction coefficient decreases and also the maximum forming height increases. Nos. 14 to 16 and Nos. 44 to 46 are examples of the invention in which the treatment conditions were the same as those of Nos. 11 to 13 and the zinc ion concentration in the liquid was increased. The friction coefficient becomes stable at lower levels and also the maximum forming height further increases. Similarly, Nos. 57 to 59 and Nos. 70 to 72 are examples of the invention in which the treatment conditions were the same as those of Nos. 54 to 56 and the zinc ion concentration in the liquid was increased. The friction coefficient becomes stable at lower levels and also the maximum forming height further increases.

(6) Nos. 17 to 22 are examples in which a solution film was formed on the surface of the steel sheets and the time until washing with water was carried out was changed. In No. 17 which was washed with water without being held, the friction coefficient merely slightly decreases. In contrast, in Nos. 18 to 22 in which the retention time was 1 second or more, the friction coefficient decreases and also the bulging properties stably increase.

(7) Nos. 23 to 40 are examples in which the treatment liquid temperature was changed. In Nos. 23 to 25 having a low treatment liquid temperature, effects of improving the friction coefficient and the maximum forming height are not sufficient as compared with the other examples. In contrast, Nos. 32 to 34 are examples having a high treatment liquid temperature and effects of improving the friction coefficient or the maximum forming height were sufficient but treatment unevenness was observed in many portions and thus the appearance was not favorable as an exterior panel for automobiles.

(8) Nos. 35 to 40 are examples of the invention in which the liquid film formation amount was changed relative to Nos. 20 to 22. A comparison between the samples in which the retention time until washing with water was carried out is the same shows that when the liquid film amount was large, a sufficient reduction in the friction coefficient and an increase in the maximum forming height are achieved but the friction coefficient was slightly high and also the maximum forming height was small as compared with the samples in which the liquid film amount was small.

(9) Nos. 41 to 43 are comparative examples using a treatment liquid in which pH is lower than the range of the invention. The effect of reducing the friction coefficient is not observed and also an increase in the maximum forming height is not observed as compared with Nos. 20 to 22.

[0052] Fig. 5 is a view showing the influence of the zinc ion concentration on the oxide film thickness using Nos. 8 to 22 and Nos. 44 to 46 of Tables 1-1 and 1-2. Fig. 5 shows that the oxide film has a sufficient thickness even when the retention time is short (e.g., 10 seconds) in the case where the zinc concentration is 5 g/l or more, and the problem of the invention that the oxide film thickness becomes small when the retention time is short is solved.

Industrial Applicability

[0053] According to the present invention, a galvanized steel sheet having a low sliding resistance during press forming and excellent press formability can be stably manufactured at a saved space even under short-time manufacturing conditions. For example, even when a high strength galvanized steel sheet which has a high forming load and is likely to cause die galling, the sliding resistance during press forming is low and excellent press formability can be achieved. Since the press formability is excellent, the invention can be applied to wide ranging fields focusing on the application to automobile bodies.

Claims

1. A method for manufacturing a galvanized steel sheet, comprising:

galvanizing a steel sheet;
bringing the steel sheet into contact with an aqueous solution;
holding the steel sheet for 1 to 60 seconds after the termination of the contact treatment; and
washing with water and drying the steel sheet to thereby form an oxide layer on the surface of the steel sheet,
the aqueous solution for use in the contact treatment of the steel sheet containing zinc ion in the range of 5 to
100 g/l as the zinc ion concentration, having a pH of 4 to 6, and having a liquid temperature of 20 to 70°C.

2. The method for manufacturing a galvanized steel sheet according to Claim 1, wherein the aqueous solution contains zinc sulfate.

3. The method for manufacturing a galvanized steel sheet according to Claim 1 or 2, wherein a liquid film to be formed on the surface of the steel sheet after the steel sheet contacts the aqueous solution is 5 to 30 g/m².

4. A galvanized steel sheet, which is manufactured according to the method for manufacturing a galvanized steel sheet according to any one of Claims 1 to 3,
an oxide layer mainly containing zinc as a metal component being formed on the surface of the steel sheet in such a manner as to have an average thickness of 10 nm or more.

FIG1

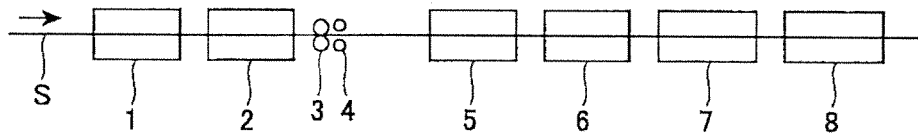


FIG2

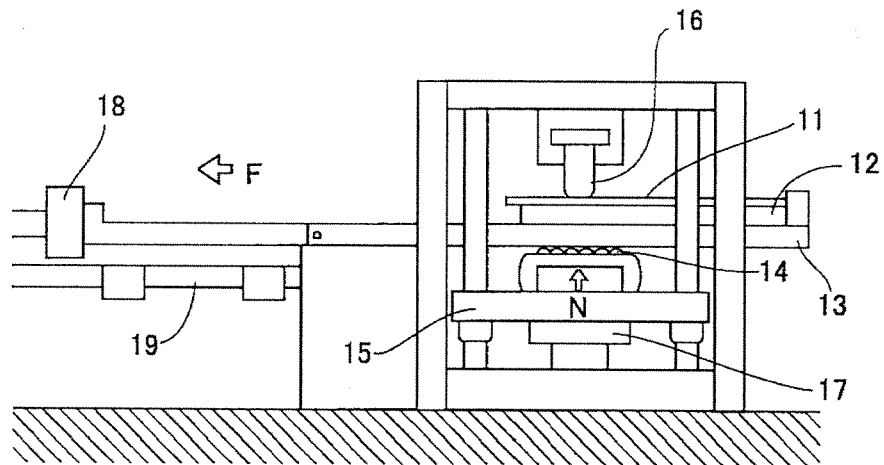


FIG3

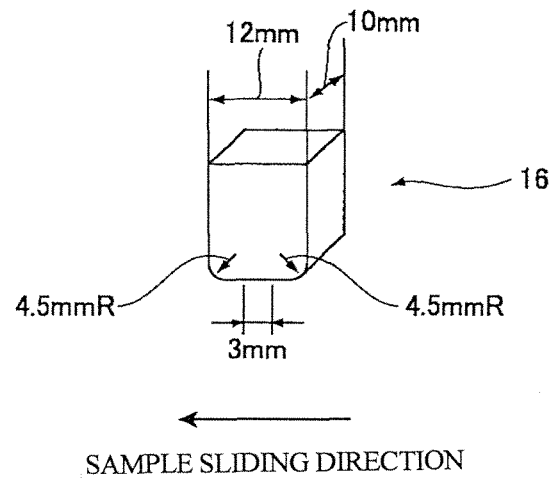


FIG4

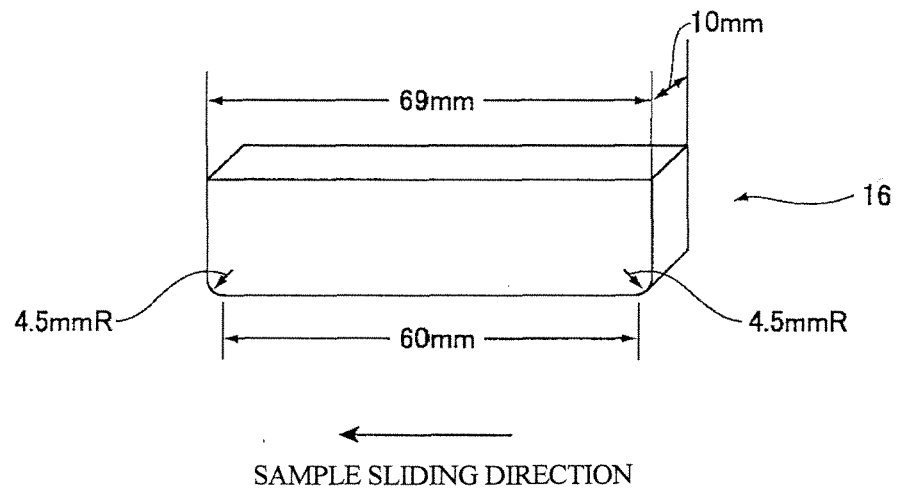
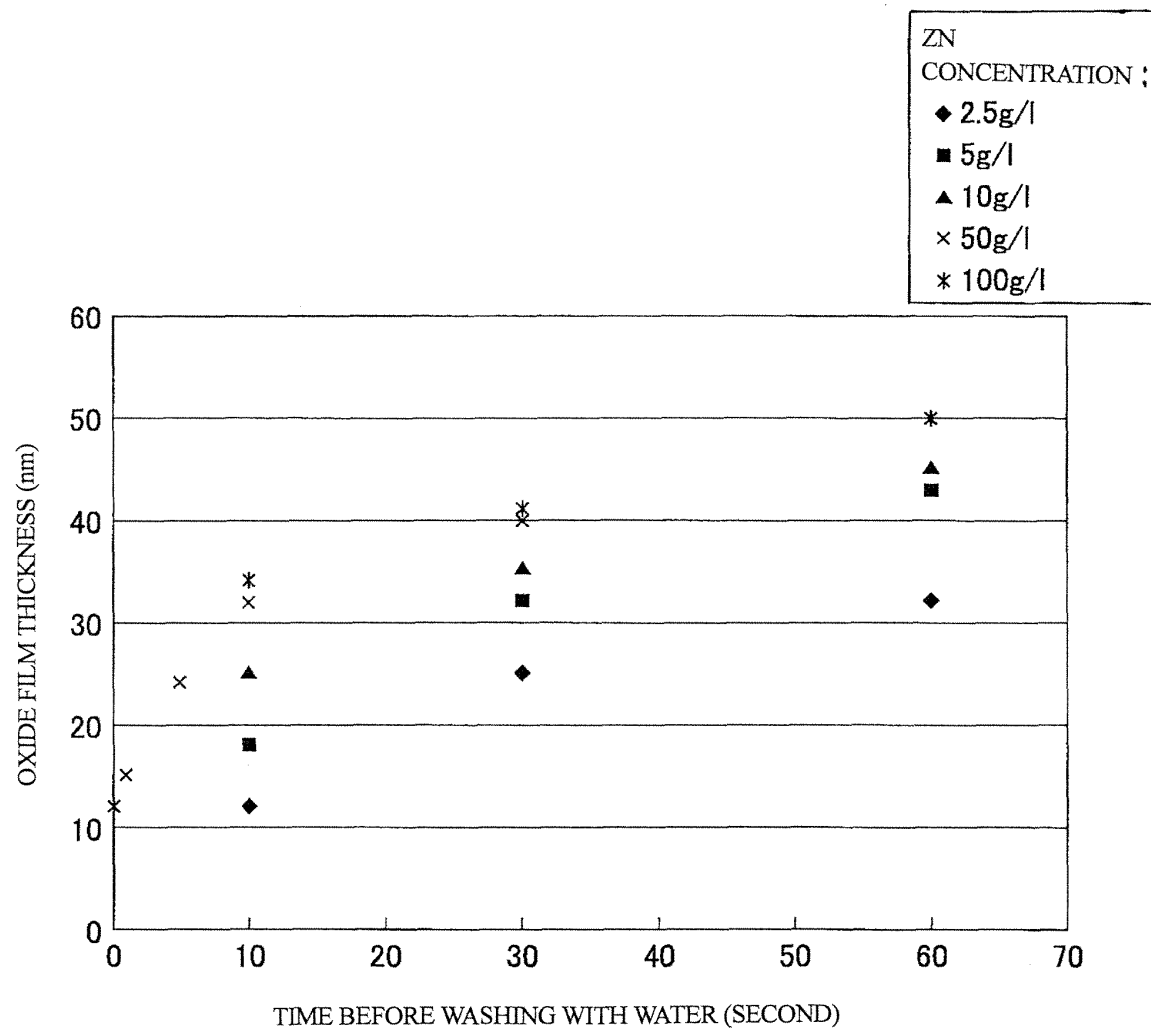


FIG5



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2009/058426

A. CLASSIFICATION OF SUBJECT MATTER

C23C28/00 (2006.01) i, C23C22/53 (2006.01) i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C23C24/00-30/00, C23C22/00-22/86

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2009
Kokai Jitsuyo Shinan Koho	1971-2009	Toroku Jitsuyo Shinan Koho	1994-2009

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JP 2003-306781 A (JFE Steel Corp.), 31 October, 2003 (31.10.03), Claims; Par. Nos. [0011] to [0046] (Family: none)	4 1-3
Y	JP 2000-328220 A (Sumitomo Metal Industries, Ltd.), 28 November, 2000 (28.11.00), Claims; Par. Nos. [0015] to [0018], [0032] to [0033], [0035], [0043] to [0044] (Family: none)	1-3

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

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Date of the actual completion of the international search
21 May, 2009 (21.05.09)Date of mailing of the international search report
02 June, 2009 (02.06.09)Name and mailing address of the ISA/
Japanese Patent Office

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