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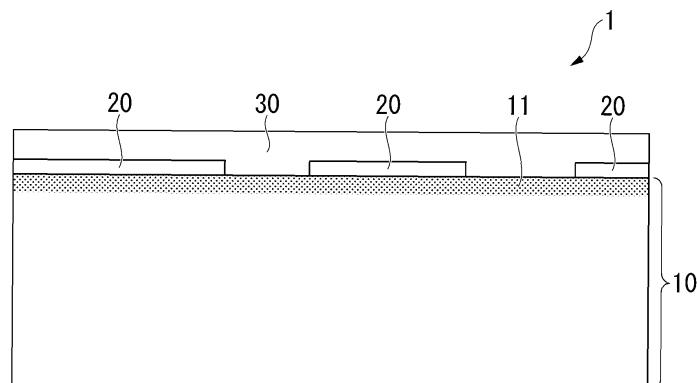
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(54) **GALVANIZED STEEL SHEET AND METHOD FOR PRODUCING SAME**

(57) The zinc-plated steel sheet includes a base steel sheet having a predetermined chemical composition, a Fe-Al alloy layer formed on at least a part of a surface of the base steel sheet, and a zinc-plated layer formed on the base steel sheet surface or a surface of the Fe-Al alloy layer, the base steel sheet has an internal oxide layer of 0.2 μm or more in a sheet thickness direction from the base steel sheet surface, the Fe-Al alloy layer has an

average thickness of 1 nm or more and less than 100 nm, and in a cross section in a thickness direction, the grain boundary coverage by an oxide is 60% or more in the internal oxide layer, a coverage of the base steel sheet surface by the Fe-Al alloy layer is 40% or more, and the tensile strength is 980 MPa or more and 2000 MPa or less.

FIG. 1



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Description

Technical Field of the Invention

5 **[0001]** The present invention relates to a zinc-plated steel sheet and a method for manufacturing the zinc-plated steel sheet.

[0002] The present application claims priority based on Japanese Patent Application No. 2022-027919 filed in Japan on February 25, 2022, the contents of which are incorporated herein by reference.

10 Related Art

[0003] High strength steel sheets are used as a steel sheet for a vehicle in order to reduce the amount of carbon dioxide emission by reducing the weight of the vehicle to improve the fuel consumption, and ensure the safety of passengers. In addition to high strength hot-dip galvanized steel sheets, high strength galvanized steel sheets are recently used as a steel sheet for a vehicle in order to ensure sufficient corrosion resistance of the vehicle body and its component (see, for example, Patent Document 1).

[0004] A high strength steel sheet to be provided for a component for a vehicle is required to have not only strength but also properties, such as uniform elongation, necessary for forming a component (for example, formability, elongation, and bending resistance). Although the strength and the formability are in a trade-off relationship, means for achievement of both the properties are known such as transformation induced plasticity (TRIP) steel sheets, which are high strength steel sheets utilizing transformation induced plasticity of residual austenite, and DP steel sheets, which have a soft phase and a hard phase.

[0005] However, spot welding of zinc-plated steel sheets (hot-dip galvanized steel sheets, electrogalvanized steel sheets, or galvanized steel sheets) or spot welding of a cold-rolled steel sheet and a zinc-plated steel sheet for assembly of a vehicle body and/or a component may cause a crack called a liquid metal embrittlement (LME) crack in the spot-welding portion. The LME crack is caused as follows. Zinc in the zinc-plated layer is melted by heat generated during spot welding, the molten zinc penetrates a grain boundary of the metallographic structure of the weld, and a tensile stress acts on this state causes a crack.

[0006] Such an LME crack is easily caused in high alloys such as TRIP steel sheets and DP steel sheets. In particular, spot welding of a high strength TRIP steel sheet (transformation induced plastic steel sheet) remarkably causes an LME crack. The high strength TRIP steel sheet is a steel sheet having higher concentrations of C, Si, and Mn than normal high strength steel sheets, and containing residual austenite to have excellent energy absorption capacity and press formability.

[0007] Therefore, a zinc-plated steel sheet assumed to be applied to a component for a vehicle is required to have high LME resistance.

[0008] Furthermore, application of a high strength steel sheet to a component for a vehicle enables reduction of the thickness of the steel sheet and reduction of the weight of the vehicle while the collision-resistant performance is maintained. However, there is a problem that the reduction of the sheet thickness of the steel sheet causes deterioration of the bending fatigue strength.

[0009] In order to solve such a problem, for example, Patent Document 2 discloses a steel sheet, a hot-dip galvanized steel sheet, and a galvanized steel sheet excellent in resistance to liquid metal embrittlement cracking, in which the steel sheet has, from a surface of the base metal to a depth of 5.0 μm or more, an internal oxide layer in which at least one part of a grain boundary is covered with an oxide, and in a region from the surface of the base metal to a depth of 5.0 μm , the grain boundary coverage by the oxide is 60% or more.

[0010] Patent Document 2 discloses that generation of LME is suppressed by making a layer in which internal oxidation occurs be present to a predetermined depth and increasing the coverage of the grain boundary by the oxide.

[0011] However, in Patent Document 2, bending fatigue strength and bending resistance are not considered.

Citation List

50 Patent Document

[0012]

55 Patent Document 1: PCT International Publication No. WO 20181043453
Patent Document 2: Japanese Patent No. 6388099

Summary of Invention

Problems to be Solved by the Invention

[0013] As described above, a zinc-plated steel sheet that has high strength and sufficient bending resistance and is excellent in LME resistance and bending fatigue strength has been conventionally unprovided. Therefore, an object of the present invention is to provide a zinc-plated steel sheet having high strength and being excellent in LME resistance and bending fatigue strength without deterioration of the bending resistance. Means for Solving the Problem

[0014] In view of the above problems, the present inventors have studied a method of enhancing LME resistance and bending fatigue strength in a high strength zinc-plated steel sheet.

[0015] As a result of studies by the present inventors, it has been found that in a zinc-plated steel sheet, the LME resistance can be improved, without deterioration of the bending resistance, by providing an Fe-Al alloy layer having a predetermined thickness between a base steel sheet and a zinc-plated layer.

[0016] In addition, it has been found that the bending fatigue strength is improved by forming a predetermined internal oxide layer at the surface of the base steel sheet.

[0017] Furthermore, it has been found that control of the annealing step and the plating step is effective for the formation of such a Fe-Al alloy layer and an internal oxide layer.

[0018] The present invention has been made in view of the above findings. The gist of the present invention is as follows.

[1] A zinc-plated steel sheet according to an aspect of the present invention includes a base steel sheet, a Fe-Al alloy layer formed on at least a part of a surface of the base steel sheet, and a zinc-plated layer formed on the surface of the base steel sheet or a surface of the Fe-Al alloy layer, in which the base steel sheet has a chemical composition including, in mass%, C: 0.10 to 0.40%, Si: 0.10 to 3.00%, Mn: 1.00 to 5.00%, sol.Al: 0.001 to 1.500%, P: 0.0010 to 0.0300%, S: 0.0200% or less, N: 0.0100% or less, O: 0.0100% or less, Ti: 0 to 0.200%, B: 0 to 0.0100%, Cr: 0 to 1.000%, Mo: 0 to 1.000%, Ni: 0 to 1.000%, Cu: 0 to 1.000%, Sn: 0 to 0.500%, Nb: 0 to 0.200%, V: 0 to 0.500%, W: 0 to 0.500%, Ca: 0 to 0.0100%, Mg: 0 to 0.0100%, Bi: 0 to 0.0100%, Sb: 0 to 0.1000%, Zr: 0 to 0.0100%, REM: 0 to 0.1000%, and a remainder: Fe and an impurity, the base steel sheet has an internal oxide layer of 0.2 μm or more in a sheet thickness direction from the surface of the base steel sheet, and the Fe-Al alloy layer has an average thickness of 1 nm or more and less than 100 nm, and in a cross section in a thickness direction, a grain boundary coverage by an oxide is 60% or more in the internal oxide layer, a coverage of the surface of the base steel sheet by the Fe-Al alloy layer is 40% or more, and a tensile strength is 980 MPa or more and 2000 MPa or less.

[2] In the zinc-plated steel sheet described in [1], the chemical composition of the base steel sheet may contain, in mass%, one or more selected from the group consisting of Ti: 0.005 to 0.200%, B: 0.0005 to 0.0100%, Cr: 0.001 to 1.000%, Mo: 0.001 to 1.000%, Ni: 0.001 to 1.000%, Cu: 0.001 to 1.000%, Sn: 0.001 to 0.500%, Nb: 0.001 to 0.200%, V: 0.001 to 0.500%, W: 0.001 to 0.500%, Ca: 0.0001 to 0.0100%, Mg: 0.0001 to 0.0100%, Bi: 0.0001 to 0.0100%, Sb: 0.0001 to 0.1000%, Zr: 0.0001 to 0.0100%, and REM: 0.0001 to 0.1000%.

[3] A method for manufacturing a zinc-plated steel sheet according to another aspect of the present invention includes an annealing step of holding a steel sheet at an annealing temperature of 700 to 1000°C for 1 second or more to anneal the steel sheet, the steel sheet having a chemical composition including, in mass%, C: 0.10 to 0.40%, Si: 0.10 to 3.00%, Mn: 1.00 to 5.00%, sol.Al: 0.001 to 1.500%, P: 0.0010 to 0.0300%, S: 0.0200% or less, N: 0.0100% or less, O: 0.0100% or less, Ti: 0 to 0.200%, B: 0 to 0.0100%, Cr: 0 to 1.000%, Mo: 0 to 1.000%, Ni: 0 to 1.000%, Cu: a to 1.000%, Sn: 0 to 0.500%, Nb: 0 to 0.200%, V: 0 to 0.500%, W: 0 to 0.500%, Ca: 0 to 0.0100%, Mg: 0 to 0.0100%, Bi: 0 to 0.0100%, Sb: 0 to 0.1000%, Zr: 0 to 0.0100%, REM: 0 to 0.1000%, and a remainder: Fe and an impurity, and a plating step of forming a zinc-plated layer on a surface of the steel sheet after the annealing step, and in the annealing step, in a heating process to the annealing temperature, an average heating rate in a first temperature range of 400 to 650°C is 2.0°C/sec or more, and an average heating rate in a second temperature range of 650°C to the annealing temperature is 0.5 to 5.0°C/sec and an atmosphere having (P(H₂O)/P(H₂)) in the second temperature range is 0.05 to 2.00, in the plating step, the steel sheet is cooled to a temperature of 440 to 550°C at an average cooling rate of 0.5°C/sec or more, is immersed in a plating bath containing Zn as a main component and having an effective Al amount of 0.050 to 0.250 mass%, is pulled up from the plating bath, then is cooled so that a temperature of the steel sheet reaches 400°C within 10 seconds, and subsequently is cooled to 350°C or less so that at an average cooling rate from 400°C to 350°C is 1.0°C/sec or more and 5.0°C/sec or less.

Effects of the Invention

[0019] According to the above-described aspects of the present invention, a zinc-plated steel sheet can be provided that has high strength and sufficient bending resistance and is excellent in LME resistance and bending fatigue strength.

Brief Description of the Drawing

[0020] FIG. 1 is a schematic view showing an example of a cross section of a steel sheet according to the present embodiment.

Embodiments of the Invention

[0021] A zinc-plated steel sheet according to an embodiment of the present invention (sometimes simply referred to as a steel sheet according to the present embodiment) and a method for manufacturing the zinc-plated steel sheet will be described.

[0022] FIG. 1 is a schematic view showing an example of a cross section of a steel sheet according to the present embodiment. A steel sheet 1 according to the present embodiment includes a base steel sheet 10 having a predetermined chemical composition, a Fe-Al alloy layer 20 formed on at least a part of a surface of the base steel sheet, and a zinc-plated layer 30 formed on the surface of the base steel sheet 10 or a surface of the Fe-Al alloy layer 20. Furthermore, the base steel sheet 10 has an internal oxide layer 11 on a surface layer area on the interface side with the Fe-Al alloy layer 20 or the zinc-plated layer 30.

[0023] In a case where the Fe-Al alloy layer 20 is formed only on a part of the base steel sheet 10, the zinc-plated layer 30 is formed on the Fe-Al alloy layer in a portion where the Fe-Al alloy layer 20 is formed on the surface of the base steel sheet 10, and the zinc-plated layer 30 is formed on the base steel sheet 10 in a portion where the Fe-Al alloy layer 20 is not formed.

[0024] In FIG. 1, the Fe-Al alloy layer and the zinc-plated layer are formed only on one surface, but the layers may be also formed on another surface in the same manner.

[0025] Hereinafter, each composition of the steel sheet according to the present embodiment will be described.

[0026] In the description, a range indicated by values interposing "to" includes, in principle, values as a lower limit and an upper limit in the range. However, a numerical value indicated with the term "more than" or "less than" is not included in the range.

[Base Steel Sheet]

[0027] First, the base steel sheet 10 included in the steel sheet 1 according to the present embodiment will be described.

<Chemical Composition>

[0028] The base steel sheet 10 included in the steel sheet 1 according to the present embodiment contains the following elements. In the present embodiment, the unit "%" of the amount of each element means % by mass.

C: 0.10 to 0.40%

[0029] C (carbon) is an essential element for high-strengthening of the steel sheet. Sufficient tensile strength cannot be obtained at a C content of less than 0.10%. Therefore, the C content is 0.10% or more. The C content is preferably 0.12% or more. C is also an element that contributes to formation of residual austenite. The residual austenite contributes to an improvement in elongation by the TRIP effect. In the case of obtaining this effect, the C content is preferably 0.16% or more.

[0030] Meanwhile, if the C content is more than 0.40%, the weldability significantly deteriorates. Therefore, the C content is 0.40% or less. From the viewpoint of suppressing deterioration of press formability and weldability, the C content is preferably 0.30% or less.

Si: 0.10 to 3.00%

[0031] Si (silicon) is a solid solution strengthening element and is an element effective for high-strengthening of the steel sheet. Si is also an element that contributes to formation of residual austenite. In order to obtain these effects, the Si content is 0.10% or more. The Si content is preferably 0.30% or more.

[0032] Meanwhile, if Si is excessively contained, the chemical convertibility and the wettability in hot-dip galvanizing of the steel sheet significantly deteriorate. Therefore, the Si content is 3.00% or less. The Si content is preferably 2.00% or less.

Mn: 1.00 to 5.00%

[0033] Mn (manganese) is a strong austenite stabilizing element and is an element effective for improving the

hardenability of the steel sheet. In order to obtain this effect, the Mn content is 1.00% or more. The Mn content is preferably 1.50% or more.

[0034] Meanwhile, if Mn is excessively contained, the weldability and the low temperature toughness deteriorate. Therefore, the Mn content is 5.00% or less. From the viewpoint of suppressing deterioration of the weldability and the low temperature toughness, the Mn content is preferably 3.20% or less.

sol.Al: 0.001 to 1.500%

[0035] Al (aluminum) is an element having an action of deoxidizing steel. Al is also an element that contributes to formation of residual austenite. In order to obtain these effects, the sol.Al content is 0.001% or more. The sol.Al content is preferably 0.005% or more.

[0036] Meanwhile, even if Al is excessively contained, the effect is saturated. As a result, an increase in cost is caused, and in addition, the transformation temperature of the steel is raised to increase the load during hot rolling. Therefore, the sol.Al content is 1.500% or less. The sol.Al content is preferably 1.000% or less.

P: 0.0010 to 0.0300%

[0037] P (phosphorus) is a solid solution strengthening element and is an element effective for high-strengthening of the steel sheet. In order to obtain this effect, the P content is 0.0010% or more. The P content is preferably 0.0050% or more.

[0038] Meanwhile, if the P content is more than 0.0300%, the steel sheet embrittles due to segregation of P at a grain boundary. Furthermore, the weldability and the toughness deteriorate. Therefore, the P content is 0.0300% or less. The P content is preferably 0.0200% or less.

S: 0.0200% or less

[0039] S (sulfur) is an element that causes hot embrittlement and inhibits weldability and corrosion resistance. If the S content is more than 0.0200%, the hot workability, the weldability, and the corrosion resistance significantly deteriorate, and therefore the S content is 0.0200% or less. The S content is preferably 0.0100% or less.

[0040] The S content is preferably low, and may be 0%, but the manufacturing cost is greatly increased by lowering the S content to less than 0.0001%. Therefore, the S content may be 0.0001% or more. The S content may be 0.0010% or more.

N: 0.0100% or less

[0041] N (nitrogen) is an element that forms a coarse nitride in steel and causes deterioration of bending resistance and hole expandability. If the N content is more than 0.0100%, the deterioration is significant, and therefore the N content is 0.0100% or less. The N content is preferably 0.0050% or less.

[0042] The N content is preferably low, and may be 0%, but extreme lowering of the N content increases the denitrogenation cost, and therefore the N content may be 0.0005% or more from the viewpoint of economic efficiency.

O: 0.0100% or less

[0043] O (oxygen) is an element that forms a coarse oxide in steel and causes deterioration of bending resistance and hole expandability. If the O content is more than 0.0100%, the property deterioration is significant, and therefore the O content is 0.0100% or less. The O content is preferably 0.0070% or less.

[0044] The O content is preferably low, and may be 0%, but from the viewpoint of manufacturing cost, the O content may be 0.0001% or more. The O content may be 0.0010% or more.

[0045] The steel sheet according to the present embodiment may contain the above-described elements and a remainder of Fe and an impurity. However, one or more elements (optional elements) selected from Ti, B, Cr, Mo, Ni, Cu, Sn, Nb, V, W, Ca, Mg, Bi, Sb, Zr, and REM shown below may be further contained for the purpose of improving various properties. Optional elements may be not contained, and therefore the lower limit is 0%.

Ti: 0 to 0.200%

[0046] Ti (titanium) is an element that suppresses formation of BN, which is a factor of hardenability deterioration, by fixing N in a form of TiN in steel. Ti is also an element that refines the austenite grain size at the time of heating and thus improves the toughness. In the case of obtaining this effect, the Ti content is preferably 0.005% or more. The Ti content is more preferably 0.010% or more.

[0047] Meanwhile, if the Ti content is excessive, the ductility of the steel sheet deteriorates. Therefore, in a case where Ti

is contained, the Ti content is 0.200% or less. The Ti content is preferably 0.050% or less.

B: 0 to 0.0100%

[0048] B (boron) is an element that segregates at an austenite grain boundary during welding, strengthens the grain boundary, and contributes to improvement of resistance to liquid metal embrittlement cracking (LME resistance). In the case of obtaining this effect, the B content is preferably 0.0005% or more. The B content is more preferably 0.0008% or more.

[0049] Meanwhile, if the B content is more than 0.0100%, a carbide and a nitride are generated, the above-described effect is saturated, and the hot workability deteriorates. Therefore, the B content is 0.0100% or less. The B content is preferably 0.0050% or less.

[0050]

Cr: 0 to 1.000%

Mo: 0 to 1.000%

Ni: 0 to 1.000%

Cu: 0 to 1.000%

Sn: 0 to 0.500%

[0051] All of Cr (chromium), Mo (molybdenum), Ni (nickel), Cu (copper), and Sn (tin) are an element effective for high-strengthening of the steel sheet. In order to obtain the above-described effect, one or more selected from Cr, Mo, Ni, Cu, and Sn are each preferably contained at a content of 0.001% or more, more preferably 0.010% or more, and still more preferably 0.050% or more.

[0052] Meanwhile, if these elements are excessively contained, the effect is saturated, and the cost is increased. Therefore, in a case where these elements are contained, all of the contents of Cr, Mo, Ni, and Cu are 1.000% or less, and the Sn content is 0.500% or less. All of the contents of Cr, Mo, Ni, and Cu are preferably 0.600% or less, and the Sn content is preferably 0.300% or less.

[0053]

Nb: 0 to 0.200%

V: 0 to 0.500%

W: 0 to 0.500%

Nb (niobium), V (vanadium), and W (tungsten) are a carbide forming element, and are an element effective for high-strengthening of the steel sheet. In order to obtain the above-described effect, one or more selected from Nb, V, and W are each preferably contained at a content of 0.001 % or more, more preferably 0.005% or more, and still more preferably 0.010% or more.

[0054] Meanwhile, even if these elements are excessively contained, the effect is saturated, resulting in an increase in the cost. Therefore, in a case where these elements are contained, the Nb content is 0.200% or less, and both of the V content and the W content are 0.500% or less. The Nb content is preferably 0.100% or less, and both of the V content and the W content are preferably 0.300% or less.

[0055]

Ca: 0 to 0.0100%

Mg: 0 to 0.0100%

Bi: 0 to 0.0100%

Sb: 0 to 0.1000%

Zr: 0 to 0.0100%

REM: 0 to 0.1000%

Ca (calcium), Mg (magnesium), Sb (antimony), Zr (zirconium), and REM (rare earth elements) are an element that contributes to fine dispersion of an inclusion in steel, and Bi (bismuth) is an element that reduces microsegregation of a substitutional alloying element such as Mn or Si in steel. These elements each contribute to improvement in bending resistance of the steel sheet. Therefore, these elements may be contained as necessary.

[0056] In order to obtain the above-described effect, one or more selected from Ca, Mg, Bi, Sb, Zr, and REM are each

preferably contained at a content of 0.0001% or more, and more preferably 0.0010% or more.

[0057] Meanwhile, if these elements are excessively contained, the ductility deteriorates. Therefore, all of the Ca content, the Mg content, the Bi content, and the Zr content are 0.0100% or less. The Sb content and the REM content are 0.1000% or less. All of the Ca content, the Mg content, the Bi content, and the Zr content are preferably 0.0080% or less, and more preferably 0.0060% or less. The Sb content and the REM content are preferably 0.0800% or less, more preferably 0.0600% or less, and still more preferably 0.0200% or less.

[0058] Here, REM refers to 17 elements including Sc, Y, and lanthanoids in total, and the REM content means the total amount of these elements. A lanthanoid is industrially added in the form of a misch metal.

[0059] The chemical composition of the base steel sheet of the steel sheet according to the present embodiment can be determined with the following method.

[0060] The chemical composition of the base steel sheet is to be measured as a general method. The measurement is to be performed by, for example, inductively coupled plasma-atomic emission spectrometry (ICP-AES). The sol.Al is to be measured by ICP-AES using a filtrate after thermal decomposition of a sample with an acid. C and S are to be measured with a combustion-infrared absorption method, N is to be measured with an inert gas fusion-thermal conductivity method, and O is to be measured with an inert gas fusion-non-dispersive infrared absorption method. In a case where the steel sheet includes a plated layer on the surface, the chemical composition is to be analyzed after removing the plated layer by mechanical grinding.

[0061] As described above, the chemical composition of the base steel sheet of the steel sheet according to the present embodiment contains C, Si, Mn, sol.Al, P, S, O, and N, and the remainder of Fe and an impurity. Alternatively, the chemical composition contains C, Si, Mn, sol.Al, P, S, O, and N, and further contains one or more elements selected from Ti, B, Cr, Mo, Ni, Cu, Sn, Nb, V, W, Ca, Mg, Bi, Sb, Zr, and REM, and the remainder of Fe and an impurity. The impurity is an element mixed in a raw material or mixed during the manufacturing process. The amount of the impurity is preferably 0.5% or less in total, and more preferably 0.1% or less in total.

<Metallographic Structure (Microstructure)>

[0062] The base steel sheet of the steel sheet according to the present embodiment is not limited in terms of the metallographic structure, but in the case of obtaining a tensile strength of 980 MPa or more, the total volume percentage of fresh martensite and tempered martensite is preferably 40% or more in the metallographic structure at the 1/4 thickness position, which is a range of 118 to 318 of the sheet thickness from the surface and has a center on the position of 1/4 of the sheet thickness in the sheet thickness direction from the surface of the base steel sheet. The total volume percentage is more preferably more than 50%, and still more preferably 55% or more. In a case where a higher tensile strength is desired, the total volume percentage of fresh martensite and tempered martensite is preferably 80% or more.

[0063] The metallographic structure other than fresh martensite and tempered martensite is, for example, one or more of ferrite, bainite, pearlite, cementite, and residual austenite.

[0064] The volume percentage of ferrite, bainite, martensite (tempered martensite and fresh martensite), pearlite, cementite, and residual austenite contained in the metallographic structure at the 1/4 thickness position can be measured using the following method.

[0065] A sample is collected to have an observed section that is a cross section parallel to the rolling direction and the sheet thickness direction of the steel sheet, and the observed section is polished and etched with nital.

[0066] Next, in the case of observing the microstructure at the 1/4 thickness position, a visual field is set to have an area of 250 μm^2 or more, and 5 visual fields in total are observed with a field emission scanning electron microscope (FE-SEM) at a magnification of 5000 times in the range of 118 to 318 of the thickness having a center on the position of 1/4 of the thickness from the surface. Then, the area fraction of each of ferrite, bainite, tempered martensite, fresh martensite, pearlite, cementite, and residual austenite is measured and regarded as the volume percentage.

[0067] Here, in identification of each phase, a region having a substructure in the grains and including a carbide precipitated with a plurality of variants is determined as tempered martensite. A region including cementite precipitated in a lamellar shape is determined as pearlite or cementite. A region having a low brightness with no substructure recognized is determined as ferrite. A region having a high brightness and a substructure that is not exposed by etching is determined as fresh martensite or residual austenite. The remainder is determined as bainite. Each volume percentage is calculated with a point counting method to determine the volume percentage of each microstructure.

[0068] The volume percentage of fresh martensite can be determined by subtracting the volume percentage of residual austenite determined with an EBSD method described below from the volume percentage of fresh martensite or residual austenite.

[0069] In the steel sheet according to the present embodiment, the volume percentage of residual austenite at the 1/4 thickness position is evaluated by high-resolution crystal structural analysis using an EBSD method (electron backscatter diffraction method). Specifically, a sample is collected to have an observed section that is a cross section parallel to the rolling direction and the sheet thickness direction of the steel sheet, and the observed section is polished and finished into a

mirror surface. Furthermore, electrolytic polishing or mechanical polishing using colloidal silica is performed to remove the machined layer on the surface layer.

[0070] Next, at the 1/4 thickness position of the steel sheet, 5 visual fields are subjected to crystal structural analysis with the EBSD method while the magnification is set to 5000 times and the size of a visual field is set to 250 μm^2 or more. The distance between evaluation points (step) is 0.01 to 0.20 μm .

[0071] The data obtained by the EBSD method is analyzed using "OIM Analysis 6.0" manufactured by TSL Solutions K.K. From the observation result at each position, a region determined as FCC iron is determined as residual austenite, and the volume percentage of each residual austenite at the 1/4 thickness position is calculated.

<Internal Oxide Layer>

[0072] The base steel sheet 10 included in the steel sheet 1 according to the present embodiment has an internal oxide layer of 0.2 μm or more from the surface (interface with the Fe-Al alloy layer 20, or interface with the zinc-plated layer 30 in a portion where the Fe-Al alloy layer 20 is not formed) in the sheet thickness direction (internal oxide layer having a thickness of 0.2 μm or more). In the present embodiment, the internal oxide layer is a layer in which at least a part of the grain boundary of the base metal is covered with an oxide of an easily oxidizable element such as Si or Mn (an oxide is observed on the grain boundary during observation of a cross section).

[0073] In the base steel sheet 10 included in the steel sheet 1 according to the present embodiment, the grain boundary coverage by the oxide in the internal oxide layer 11 is 60% or more. The grain boundary coverage is the percentage (%) of the length of the grain boundary covered with the oxide in the total length of the grain boundary in the internal oxide layer 11.

[0074] If the grain boundary is covered with the oxide, dislocation motion is hindered, and the fatigue strength is improved.

[0075] If the thickness of the internal oxide layer 11 is less than 0.2 μm or the grain boundary coverage is less than 60%, the effect of improving the fatigue strength is not sufficiently obtained.

[0076] The thickness of the internal oxide layer 11 does not have a particular upper limit, but if the thickness is more than 3.0 μm , the effect of improving the fatigue strength is saturated, and deterioration of the deformability may cause deterioration of the bendability, and therefore the thickness of the internal oxide layer 11 is preferably 3.0 μm or less.

[0077] If an easily oxidizable element such as Si or Mn is present as an oxide at the grain boundary, concentration of the oxide on the surface of the base metal is suppressed. The oxide formed on the base metal surface deteriorates the wettability of the hot-dip plated metal, and also causes bare spots. Therefore, formation of the internal oxide layer can prevent occurrence of bare spots and improve the plating property.

[0078] In the steel sheet according to the present embodiment, the oxide is mainly formed on the grain boundary in the internal oxide layer 11, and therefore the oxide is often present in a network shape.

[0079] The thickness of the internal oxide layer (the depth at which the internal oxide layer is present) and the grain boundary coverage of the internal oxide layer are determined with the following method.

[0080] A sample for microstructure observation is collected from the steel sheet so that the microstructure of a cross section in the sheet thickness direction can be observed.

[0081] In the collected sample, a surface parallel to the rolling direction and the sheet thickness direction is subjected to wet polishing with emery paper, and further subjected to buffing using diamond abrasive grains having an average size of 1 μm to finish the observed section into a mirror surface.

[0082] Subsequently, in order to remove the strain introduced into the polished surface by the above-described mechanical polishing, polishing using colloidal silica is performed using a suspension containing an alcohol as a solvent.

[0083] In the polishing using colloidal silica, an increase in the load during polishing may further introduce strain, and therefore the load is suppressed during polishing. Therefore, for example, in polishing with colloidal silica, automatic polishing may be performed for 1 hour at an output set to 40% using VibroMet 2 manufactured by Buehler.

[0084] However, if electrolytic polishing, chemical etching, or the like is applied in the process of removing the strain introduced by mechanical polishing, the oxide is dissolved, so that the actual state of the oxide present on the grain boundary cannot be grasped by observation. Similar caution is also required in the case of polishing using water as a solvent. A water-soluble oxide is dissolved during polishing with water as a solvent, so that the internal oxide on the grain boundary cannot be observed. Therefore, as the finishing step of polishing, a step not including the above-described procedure is adopted.

[0085] The surface layer area of the observed section of the sample prepared with the above-described procedure is observed using a SEM and SEM-EBSD. From an observation magnification of 1000 to 9000 times, a magnification is selected at which the microstructure includes 10 or more grains of ferrite, and for example, the magnification is set to 3000 times.

[0086] First, an oxide present at a grain boundary is confirmed from a reflected electron image in the SEM. In the reflected electron image, the color tone depends on the atomic number (or mass), and therefore the oxide and the steel structure can be easily distinguished.

[0087] In the microstructure observation of the reflected electron image, for example, when a state of a small atomic number (or mass) is set to be displayed in a "black color tone", an oxide having a smaller mass than iron is displayed in a black color tone in the observation image. Under this observation condition, the microstructure of the steel sheet surface layer area is photographed in five visual fields, and the state of presence of the internal oxide is confirmed. The observed maximum depth of the internal oxide layer is regarded as the thickness of the internal oxide layer.

[0088] Subsequently, crystal orientation data of BCC-iron is acquired by SEM-EBSD at the same position as the visual field observed in the above-described SEM-reflected electron image. The magnification for the measurement is any magnification selected from 1000 to 9000 times, and may be, for example, the same magnification as in the above-described observation of the SEM-reflected electron image. The interval of the measurement (step) is set to 0.01 to 0.1 μm , and an interval of 0.05 μm may be selected.

[0089] In the crystal orientation map data of BCC-iron obtained under these measurement conditions, a boundary having a crystal orientation difference of 15° or more is regarded as a grain boundary, excluding a region having a reliability value (CI value) of less than 0.1. The CI value is a numerical value that serves as an index of the reliability of crystal orientation determination shown by analysis software, and if the CI value is less than 0.1, the reliability is generally considered to be low.

[0090] In a case where an oxide is present at a grain boundary of ferrite, crystal orientation data of BCC-iron cannot be obtained, so that many regions having a CI value of less than 0.1 are present between adjacent grains. In this case, the grain boundary cannot be clearly confirmed, but at a boundary having an orientation difference between adjacent ferrite grains of 15° or more, a grain boundary is drawn on the map so as to pass through the center of the region having a CI value of less than 0.1.

[0091] In the grain boundary map of ferrite obtained by the above-described procedure, the length of the grain boundary covered with the oxide (hereinafter, described as "oxide covering length") is measured in the range from the surface to the maximum depth of the internal oxide layer obtained above. Subsequently, the length of the grain boundary not covered with the oxide (hereinafter, described as "oxide non-covering length") is measured. Then, the obtained oxide covering length is divided by the lengths of all the grain boundaries to calculate the grain boundary coverage (%).

"Fe-Al Alloy Layer"

[0092] In the steel sheet 1 according to the present embodiment, the Fe-Al alloy layer 20 having an average thickness of 1 nm or more is formed on the surface of the base steel sheet 10 at a coverage of 40% or more. The Fe-Al alloy layer 20 is formed between the base steel sheet 10 and the zinc-plated layer 30.

[0093] An LME crack is caused by penetration of zinc melted during welding into a grain boundary. Therefore, a Fe-Al alloy layer present at the interface between the plated layer and the base metal serves as a barrier against zinc penetration to improve the LME resistance.

[0094] When viewed in a cross section in the thickness direction (sheet thickness direction of the base steel sheet), if the average thickness of the Fe-Al alloy layer is less than 1 nm or the coverage is less than 40%, a sufficient barrier property cannot be ensured, and the LME resistance cannot be sufficiently improved. Therefore, the average thickness of the Fe-Al alloy layer is 1 nm or more, and the coverage is 40% or more. The average thickness of the Fe-Al alloy layer is preferably 5 nm or more, more preferably 10 nm or more, and still more preferably 20 nm or more. The coverage by the Fe-Al alloy layer is preferably 50% or more, and more preferably 60% or more.

[0095] Meanwhile, if the average thickness of the Fe-Al alloy layer is 100 nm or more, the bending resistance deteriorates. Therefore, the average thickness of the Fe-Al alloy layer is less than 100 nm.

[0096] The upper limit of the coverage is not required to be limited, but the cost to obtain a coverage of 100% is significantly high, and therefore the coverage may be less than 100%, or 98% or less.

[0097] Here, the coverage is the percentage (%) of the length of the interface between the Fe-Al alloy layer and the base steel sheet in the length of the surface of the base steel sheet when viewed in a cross section in the thickness direction.

[0098] The average thickness of the Fe-Al alloy layer and the coverage by the Fe-Al alloy layer are determined with the following method.

[0099] A sample is collected to have an observed section that is a cross section parallel to the rolling direction and the sheet thickness direction of the steel sheet. In this sample, the vicinity of the surface of the base steel sheet is photographed using a FE-SEM in the range of 1.5 μm^2 or more/1 visual field at a magnification of 50000 times.

[0100] The Fe-Al alloy layer is observed in a black color in the reflected electron image at the interface between the base phase and the plated layer, and thus the Fe-Al alloy layer is visually determined, and the thickness of the Fe-Al alloy layer is measured.

[0101] The photographing is performed at 5 locations/1 visual field for 5 visual fields, and the average value of the thickness of the Fe-Al alloy layer in 5 visual fields (25 locations) is regarded as the average thickness of the Fe-Al alloy layer of the steel sheet according to the present embodiment.

[0102] In addition, the length of the interface between the base steel sheet and the Fe-Al alloy layer is measured in the

length of the surface of the base steel sheet in the observed visual field and the coverage is determined. The measurement is performed for five visual fields, and the average of the coverages of the visual fields is regarded as the coverage of the steel sheet according to the present embodiment.

5 "Plated Layer"

[0103] The steel sheet 1 according to the present embodiment includes the zinc-plated layer 30 on the surface of the base steel sheet 10 (a portion without the Fe-Al alloy layer) and/or the Fe-Al alloy layer 20 (a portion having the Fe-Al alloy layer on the base steel sheet). The zinc-plated layer is, for example, a hot-dip galvanized layer. In the present embodiment, the zinc-plated layer means a plated layer containing 80 mass% or more of Zn. The presence of the hot-dip galvanized layer on the surface improves the corrosion resistance.

[0104] The adhesion amount of the zinc-plated layer is not particularly limited. However, if the adhesion amount is too large, the amount of molten zinc during welding is increased. Therefore, from the viewpoint of more effectively suppressing occurrence of LME, the adhesion amount is preferably 100 g/m² or less, and more preferably 80 g/m² or less.

[0105] Meanwhile, from the viewpoint of improving the corrosion resistance, the adhesion amount is preferably 10 g/m² or more.

[0106] The chemical composition of the zinc-plated layer is not limited, and, for example, preferably includes Al: 0.1 to 2.0% and Fe: 5.0% or less in mass%, with a remainder of Zn and an impurity. The amount of the impurity is preferably 0.1 mass% or less in total.

[0107] The adhesion amount and the chemical composition of the zinc-plated layer are determined with the following method.

[0108] The plated layer is melted using hydrochloric acid containing an inhibitor, and the weights before and after the melt are compared to determine the adhesion amount. In addition, the solution obtained by the melt is quantitatively analyzed by ICP to measure the chemical composition of the plated layer.

25 "Mechanical Property"

[0109] In the case of using the steel sheet according to the present embodiment as a steel sheet for a vehicle, the steel sheet is desired to have a high strength. Considering contribution to weight reduction of the vehicle, the tensile strength is 980 MPa or more. The tensile strength is preferably 1050 MPa or more, and more preferably 1100 MPa or more.

[0110] Meanwhile, if the tensile strength is more than 2000 MPa, the residual stress at the time of welding is increased and causes a crack in the internal oxide layer on the grain boundary, and thus the effect of suppressing an LME crack remarkably deteriorates. Therefore, the tensile strength is 2000 MPa or less.

35 "Manufacturing Method"

[0111] An effect of the steel sheet according to the present embodiment can be obtained as long as the steel sheet has the above-described characteristics regardless of the manufacturing method. However, the manufacturing conditions described below are preferable because the steel sheet can be stably manufactured.

[0112] That is, the steel sheet according to the present embodiment can be manufactured by annealing and plating a steel sheet (hot-rolled steel sheet or cold-rolled steel sheet) to be a base steel sheet under predetermined conditions.

[0113] The conditions for manufacturing the steel sheet to be subjected to the annealing step are not limited. For example, a hot-rolled steel sheet can be manufactured by casting molten steel having the above-described chemical composition under normal conditions to form a steel piece, and then subjecting the steel piece to hot rolling under normal conditions. A cold-rolled steel sheet can be manufactured by subjecting the hot-rolled steel sheet to cold rolling under normal conditions.

<Annealing Step>

[0114] The annealing step includes a heating process of heating a steel sheet having a predetermined chemical composition (the same chemical composition as that of the steel sheet according to the present embodiment to be obtained) to an annealing temperature (maximum heating temperature) of 700 to 1000°C and a holding process of holding the heated steel sheet at the annealing temperature for 1 second or more.

[0115] From the viewpoint of productivity, the annealing is preferably performed by passing the steel sheet through a continuous annealing line.

[0116] If an annealing temperature is less than 700°C, the amount of austenite is insufficient, and a sufficient amount of hard structure cannot be ensured in phase transformation during subsequent cooling, so that a sufficient tensile strength cannot be obtained. Therefore, the annealing temperature is 700°C or more. The annealing temperature is preferably

720°C or more.

[0117] Meanwhile, if the annealing temperature is more than 1000°C, the grain size of austenite becomes large, transformation is less likely to proceed during cooling, and it becomes difficult to obtain a sufficient soft structure contributing to improvement of the formability. Therefore, the annealing temperature is 1000°C or less. The annealing temperature is preferably 900°C or less.

(Heating Process)

[0118] In the heating process, the steel sheet is heated to an annealing temperature (maximum heating temperature: 700 to 1000°C).

[0119] In the heating process to the annealing temperature in the annealing step, the average heating rate in a first temperature range of 400 to 650°C is 2.0°C/sec or more, the average heating rate in a second temperature range of 650°C to the annealing temperature is 0.5 to 5.0°C/sec, and $(P(H_2O)/P(H_2))$ of the atmosphere is 0.05 to 2.00 in the second temperature range.

[0120] In the first temperature range of 400 to 650°C, dislocations are mainly recovered during heating. If the average heating rate in this temperature range is 2.0°C/sec or more, recovery of dislocations is suppressed, and thus many dislocations to be nuclei of recrystallization can remain. In this case, recrystallization that occurs in a temperature range of 650°C or more can occur in many places.

[0121] The upper limit of the average heating rate in the first temperature range is not limited, but the average heating rate is preferably 20.0°C/sec or less from the viewpoint of cost.

[0122] The second temperature range of 650°C to the annealing temperature is a temperature range in which recrystallization occurs, and is a temperature range in which an internal oxide layer is formed by controlling the atmosphere.

[0123] If the average heating rate in this temperature range is more than 5.0°C/sec, recrystallization of the steel sheet proceeds before an oxide is formed in the surface layer area, and coarse ferrite grains are generated. In this case, an internal oxide layer in which the grain boundary is covered with an oxide is not formed.

[0124] Meanwhile, if the average heating rate is less than 0.5°C/sec, a decarburization reaction may excessively proceed, and the tensile strength of the steel sheet may deteriorate.

[0125] At the time of heating in the second temperature range, if $(P(H_2O)/P(H_2))$, which is the ratio of the water vapor partial pressure $P(H_2O)$ to the hydrogen partial pressure $P(H_2)$ in the atmosphere in the furnace, is less than 0.05, a sufficient internal oxide layer cannot be ensured. Therefore, $(P(H_2O)/P(H_2))$ is 0.05 or more. $(P(H_2O)/P(H_2))$ is preferably 0.07 or more, and more preferably 0.10 or more.

[0126] Meanwhile, if $(P(H_2O)/P(H_2))$ is more than 2.00, decarburization excessively proceeds, the thickness of the decarburized layer is increased, and the tensile strength of the steel sheet decreases. Therefore, $(P(H_2O)/P(H_2))$ is 2.00 or less. $(P(H_2O)/P(H_2))$ is preferably 1.50 or less, and more preferably 1.20 or less.

[0127] By controlling the average heating rate and the atmosphere in the second temperature range, recrystallization is started from many recrystallization nuclei, and at the same time, an internal oxide is generated at the grain boundary. Thus, grain growth is inhibited, and at the same time, the grain boundary coverage by the oxide is set to 60% or more.

[0128] In order to control recovery of dislocations, recrystallization, and grain growth and generate an internal oxide at the grain boundary efficiently, the average heating rate in the first temperature range is preferably higher than the average heating rate in the second temperature range, and the average heating rate in the first temperature range is more preferably higher than the average heating rate in the second temperature range by 2.0°C/sec or more.

(Holding Process)

[0129] After heating to the annealing temperature as described above, the steel sheet is held at a predetermined maximum heating temperature for 1 second or more. If the holding time is less than 1 second, the steel sheet is not sufficiently austenitized. In this case, a sufficient amount of hard structure cannot be ensured in phase transformation during subsequent cooling, so that a sufficient tensile strength cannot be obtained.

[0130] The upper limit of the holding time is not particularly limited. However, if the holding time is too long, the manufacturability of the steel sheet is impaired, and therefore the upper limit value of the holding time is preferably 1000 seconds.

<Plating Step>

[0131] In the plating step, the steel sheet after the annealing step is cooled from the annealing temperature to a temperature of 440 to 550°C at an average cooling rate of 0.5°C/sec or more, and the steel sheet is immersed in a plating bath containing Zn as a main component and having an effective Al amount of 0.050 to 0.250 mass%, pulled up from the

plating bath, and then cooled so that the temperature of the steel sheet reaches 400°C within 10 seconds, and subsequently cooled to 350°C or less at an average cooling rate of 1.0°C/sec or more and 5.0°C/sec or less in a range of 400 to 350°C. As a result, a zinc-plated layer is formed on the surface of the steel sheet, and a Fe-Al alloy layer is formed on at least a part of the interface between the steel sheet and the plated layer.

[0132] If the average cooling rate to a temperature of 440 to 550°C is less than 0.5°C/sec, a hard structure is not formed in the base steel sheet, and the strength decreases.

[0133] If the cooling stop temperature (the temperature of the steel sheet at the time of immersion in the plating bath) is less than 440°C, application of a large amount of heat to the plating bath is necessary for maintaining the plating temperature, and thus the manufacturing cost is increased.

[0134] Meanwhile, if the temperature of the steel sheet at the time of immersing the steel sheet in the plating bath is more than 550°C, equipment for removing a large amount of heat from the plating bath is necessary for maintaining the plating bath temperature, and thus the manufacturing cost is increased.

[0135] The composition of the plating bath in which the steel sheet is immersed contains Zn as a main component (for example, at a content of 80 mass% or more), and is not limited as long as the effective Al amount (value obtained by subtracting the total Fe amount from the total Al amount in the plating bath) is 0.050 to 0.250 mass%. The composition may include another element, for example, one or more selected from Ag, B, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Ge, Hf, I, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, Pb, Rb, S, Si, Sn, Sr, Ta, Ti, V, W, Zr, and REM, as necessary.

[0136] If the effective Al amount in the plating bath is less than 0.050 mass%, the formation of a Fe-Al alloy layer becomes insufficient. Furthermore, intrusion of Fe into the plating layer may excessively proceed, leading to deterioration of the plating adhesion. The effective Al amount in the plating bath is preferably 0.065 mass% or more.

[0137] Meanwhile, if the effective Al amount in the plating bath is more than 0.250 mass%, an Al-based oxide that inhibits movement of Fe atoms and Zn atoms is generated at the boundary between the steel sheet and the plated layer, and the plating adhesion may deteriorate. The effective Al amount in the plating bath is preferably 0.180 mass% or less.

[0138] The plating bath temperature is not limited, but is preferably 450 to 490°C. If the plating bath temperature is less than 450°C, the viscosity of the plating bath excessively increases, control of the plated layer thickness becomes difficult, and the external appearance of the hot-dip galvanized steel sheet may be impaired. The plating bath temperature is preferably 455°C or more.

[0139] Meanwhile, if the plating bath temperature is more than 490°C, a large amount of fume is generated, and safe plating operation may be difficult. The plating bath temperature is preferably 480°C or less.

[0140] After the steel sheet is pulled up from the plating bath, the steel sheet is cooled so that the temperature of the steel sheet reaches 400°C within 10 seconds while the adhesion amount is adjusted by wiping with an N₂ gas or the like, and then cooled to 350°C or less at an average cooling rate of 1.0°C/sec or more and 5.0°C/sec or less in a range of 400 to 350°C.

[0141] Alloying of the plated layer with the base phase proceeds mainly at a temperature of 400°C or more. Therefore, excessive alloying of the plated layer can be prevented by cooling the steel sheet so that the time of pulling up from the plating bath to the time at which the temperature reaches 400°C is 10 seconds or less (so that the temperature reaches 400°C within 10 seconds). If the time to 400°C is more than 10 seconds, not a Fe-Al alloy layer but a Fe-Zn alloy layer is formed, and a predetermined Fe-Al alloy layer cannot be obtained.

[0142] Then, the average cooling rate in a range of 400 to 350°C is set to 5.0°C/sec or less so that the time at 400 to 350°C is 10.0 seconds or more, and thus a Fe-Al alloy layer is formed at the interface between the plated layer and the base phase, and the coverage can be 40% or more.

[0143] Meanwhile, if the time at 400 to 350°C is more than 50.0 seconds, the thickness of the Fe-Al alloy layer is 100 nm or more. Therefore, the average cooling rate in a range of 400 to 350°C is 1.0°C/sec or more.

[0144] Furthermore, it is preferable that the plating bath temperature is more than 450°C, and that the temperature reaches 400°C within 10 seconds (that is, the average cooling rate to 400°C is more than 5.0°C/sec) and then the average cooling rate in a range of 400 to 350°C is 5.0°C/sec or less so that the average cooling rate to 400°C is higher than the average cooling rate in a range of 400 to 350°C. The two-stage cooling as described above appropriately forms a Fe-Al alloy layer at the interface between the zinc-plated layer and the base steel sheet. The Fe-Al alloy layer formed at the interface between the zinc-plated layer and the base steel sheet takes in and integrates the internal oxide at the grain boundary of the steel sheet surface layer area. Therefore, the Fe-Al alloy layer is less likely to be peeled off from the base steel sheet, and an effect of obtaining a higher bending fatigue strength can be obtained. The average cooling rate to 400°C is more preferably 6.0°C/sec or more.

<Skin Pass Rolling Step>

[0145] In the method for manufacturing a steel sheet according to the present embodiment, the steel sheet after the plating step may be subjected to skin pass rolling for the purpose of shape adjustment and the like. In the case of performing skin pass rolling, the rolling rate is preferably 0.5% or less.

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Examples

[0146] A slab having a chemical composition described in Tables 1-1 to Tables 1-4 was hot-rolled and coiled to obtain a hot-rolled steel sheet having a sheet thickness of 3.0 mm. This hot-rolled steel sheet was cold-rolled to obtain a cold-rolled steel sheet having a sheet thickness of 1.6 mm.

[0147] This cold-rolled steel sheet was heated to an annealing temperature and held under conditions shown in Tables 2-1 and 2-2.

[0148] After the holding, as shown in Tables 2-1 and 2-2, the steel sheet was cooled to a temperature of 440 to 550°C, and then immersed in a plating bath to form a zinc-plated layer.

[0149] After immersion in the plating bath, the steel sheet was cooled so that the values of the cooling time and the average cooling rate to 400°C were as in Tables 2-1 and 2-2. Thereafter, cooling was switched, and the steel sheet was cooled to 350°C or less so that the value of the average cooling rate in a range of 400 to 350°C was as in Tables 2-1 and 2-2.

[0150] Thereafter, skin pass rolling was performed under conditions shown in Tables 2-1 and 2-2.

[Table 1-1]

No.	Chemical composition (unit: mass%, remainder: Fe and impurity)											
	C	Si	Mn	P	S	Al	N	O	Ti	B	Cr	Mo
A	0.30	2.56	2.52	0.0152	0.0016	0.384	0.0007	0.0050	-	-	-	-
B	0.38	1.10	1.54	0.0066	0.0019	0.365	0.0073	0.0017	-	-	-	-
C	0.32	0.35	2.18	0.0025	0.0013	0.795	0.0006	0.0007	-	-	-	-
D	0.22	0.81	2.31	0.0083	0.0020	0.021	0.0046	0.0010	0.022	0.0023	-	-
E	0.34	0.65	4.34	0.0048	0.0039	0.744	0.0014	0.0009	-	-	-	-
F	0.18	2.13	3.37	0.0029	0.0153	0.088	0.0012	0.0064	0.021	-	0.793	0.097
G	0.36	2.16	3.40	0.0024	0.0020	1.060	0.0010	0.0078	-	-	0.042	-
H	0.35	2.32	1.19	0.0066	0.0018	0.635	0.0050	0.0010	0.051	0.0019	-	-
I	0.19	0.71	2.47	0.0124	0.0023	1.278	0.0040	0.0031	-	-	-	-
J	0.23	2.16	1.72	0.0134	0.0017	0.905	0.0014	0.0005	-	-	0.056	-
K	0.12	1.24	4.79	0.0153	0.0060	1.185	0.0011	0.0009	-	0.0005	-	-
L	0.35	1.29	2.27	0.0038	0.0017	0.214	0.0009	0.0006	-	0.0015	0.154	-
M	0.36	1.58	2.78	0.0026	0.0016	0.890	0.0007	0.0005	-	-	-	-
N	0.16	1.63	4.40	0.0027	0.0021	0.211	0.0009	0.0007	0.128	0.0023	-	-
O	0.21	2.47	4.64	0.0033	0.0021	0.583	0.0009	0.0011	-	-	-	-
P	0.37	2.68	1.88	0.0026	0.0167	0.156	0.0008	0.0007	-	-	-	-
Q	0.16	0.74	3.99	0.0033	0.0021	1.074	0.0007	0.0012	0.009	0.0012	0.076	-
R	0.24	2.69	3.10	0.0026	0.0023	0.320	0.0007	0.0011	0.015	-	-	0.068
S	0.18	1.57	4.56	0.0024	0.0013	1.403	0.0009	0.0023	-	-	0.085	-
T	0.34	2.67	3.42	0.0049	0.0017	0.875	0.0010	0.0010	0.016	-	-	0.039
U	0.23	1.24	3.64	0.0196	0.0030	0.688	0.0013	0.0018	-	0.0010	-	0.769

[Table 1-2]

No.	Chemical composition (unit: mass%, remainder: Fe and impurity)											
	C	Si	Mn	P	S	Al	N	O	Ti	B	Cr	Mo
V	0.26	0.33	3.79	0.0235	0.0028	0.839	0.0045	0.0033	0.008	-	-	0.090
W	0.29	1.54	3.67	0.0030	0.0159	0.104	0.0077	0.0078	-	0.0009	-	-
X	0.30	2.37	1.51	0.0028	0.0009	0.456	0.0008	0.0055	0.031	0.0056	0.083	-

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(continued)

No.	Chemical composition (unit: mass%, remainder: Fe and impurity)											
	C	Si	Mn	P	S	Al	N	O	Ti	B	Cr	Mo
5	Y	0.20	2.06	4.53	0.0028	0.0021	0.747	0.0009	0.0011	0.100	-	0.122
	Z	0.37	0.74	2.10	0.0221	0.0015	0.688	0.0012	0.0007	0.013	0.0009	0.111
	AA	0.31	2.90	2.30	0.0075	0.0170	0.752	0.0009	0.0010	-	-	-
10	AB	0.28	1.01	3.91	0.0037	0.0061	0.650	0.0015	0.0076	-	-	-
	AC	0.22	1.64	1.80	0.0038	0.0028	0.646	0.0018	0.0076	-	0.0021	0.049
	AD	0.24	2.68	3.79	0.0134	0.0020	0.256	0.0008	0.0007	-	-	0.589
	AE	0.15	1.26	1.65	0.0112	0.0101	1.105	0.0008	0.0011	-	0.0012	0.059
15	AF	<u>0.09</u>	0.84	4.53	0.0037	0.0010	0.786	0.0005	0.0010	-	-	-
	AG	<u>0.41</u>	0.94	3.81	0.0027	0.0022	0.558	0.0005	0.0013	-	-	-
	AH	0.20	<u>0.07</u>	3.93	0.0153	0.0137	1.411	0.0052	0.0008	0.167	0.0073	0.102
20	AI	0.14	1.04	<u>0.91</u>	0.0228	0.0169	1.204	0.0082	0.0013	-	0.0006	-
	AJ	0.17	1.38	<u>5.11</u>	0.0037	0.0010	1.329	0.0079	0.0009	0.021	-	0.066
	AK	0.27	0.48	2.00	<u>0.0311</u>	0.0020	0.947	0.0007	0.0074	-	-	-
	AL	0.15	2.68	1.42	0.0029	<u>0.0206</u>	0.586	0.0009	0.0015	-	-	-
25	AM	0.23	0.35	2.87	0.0078	0.0017	<u>1.553</u>	0.0006	0.0087	0.022	0.0078	0.047
	AN	0.20	1.36	1.85	0.0067	0.0024	0.574	<u>0.0103</u>	0.0011	-	-	-
	AO	0.12	2.72	4.33	0.0028	0.0019	0.253	<u>0.0103</u>	-	-	0.085	0.041

30

[Table 1-3]

No.	Chemical composition (unit: mass%, remainder: Fe and impurity)											
	Ni	Cu	Sn	Nb	V	W	Ca	Mg	Bi	Sb	Zr	REM
35	A	-	-	-	-	-	-	-	-	-	-	-
	B	-	-	-	-	-	-	-	-	-	-	-
	C	-	-	-	-	-	-	-	-	-	-	-
	D	-	-	-	-	-	-	-	-	-	-	-
40	E	-	-	-	-	-	-	-	-	-	-	-
	F	-	0.040	-	-	0.107	-	0.0078	0.0019	-	-	-
	G	-	0.055	0.048	0.033	-	-	0.0061	0.0028	0.0165	-	-
45	H	-	-	-	0.054	-	0.0010	0.0010	0.0076	0.0046	-	-
	I	0.095	-	-	-	-	-	-	-	-	0.0009	-
	J	-	-	-	-	-	-	0.0010	-	0.0084	-	0.0077
	K	0.801	-	-	0.028	0.026	0.0077	-	0.0010	0.0080	-	0.0233
50	L	-	0.098	0.040	-	0.042	-	-	-	0.0134	-	0.0120
	M	-	-	0.041	-	0.136	-	0.0010	-	-	0.0014	-
	N	-	-	-	0.084	-	-	0.0080	0.0012	0.0045	0.0071	-
55	O	-	0.813	-	0.103	-	-	0.0010	0.0060	0.0086	-	0.0100
	P	-	0.200	-	-	0.047	-	-	-	0.0190	-	-
	Q	0.097	0.068	-	-	-	0.034	-	-	-	-	-

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(continued)

No.	Chemical composition (unit: mass%, remainder: Fe and impurity)											
	Ni	Cu	Sn	Nb	V	W	Ca	Mg	Bi	Sb	Zr	REM
R	-	-	-	-	-	0.052	0.0012	-	0.0012	0.0820	-	-
S	0.794	-	-	-	-	-	0.0006	0.0005	-	-	-	-
T	-	-	-	-	-	0.334	0.0035	-	0.0008	0.0085	-	-
U	0.377	-	-	-	-	-	-	-	-	-	-	-

[Table 1-4]

No.	Chemical composition (unit: mass%, remainder: Fe and impurity)											
	Ni	Cu	Sn	Nb	V	W	Ca	Mg	Bi	Sb	Zr	REM
V	0.819	0.584	-	-	0.031	0.241	-	-	-	-	-	-
W	-	-	0.261	-	-	-	-	0.0008	0.0006	0.0201	-	-
X	-	-	0.045	-	-	0.023	-	0.0074	0.0079	-	0.0007	0.0059
Y	-	0.058	0.309	-	-	-	-	-	-	-	-	-
Z	-	-	-	0.166	0.051	-	0.0011	-	0.0005	0.0458	0.0013	-
AA	-	-	-	0.132	-	-	0.0014	-	-	0.0672	0.0006	0.0134
AB	-	-	0.124	-	0.042	0.0-56	-	-	0.0057	-	0.0077	0.0057
AC	0.078	-	-	-	0.423	0.030	0.0010	-	0.0016	0.0097	-	0.0706
AD	0.477	-	0.040	-	-	-	0.0007	-	-	-	0.0008	-
AE	0.794	0.108	-	-	-	0.073	0.0082	0.0052	0.0023	-	0.0007	-
AF	-	-	-	0.019	-	-	0.0009	-	-	0.0229	0.0005	-
AG	-	-	-	-	-	-	-	-	-	-	-	-
AH	0.119	0.795	-	-	-	0.377	-	-	-	-	-	-
AI	0.830	-	-	-	0.033	0.168	0.0018	-	0.0010	0.0321	-	0.0228
AJ	-	-	-	-	-	0.047	0.0023	-	0.0008	0.0753	-	-
AK	-	-	-	0.016	-	-	-	-	-	-	-	0.0677
AL	-	-	-	-	-	-	-	-	-	-	-	-
AM	-	-	-	0.009	-	-	0.0010	-	-	-	-	0.0058
AN	-	-	-	0.010	-	-	-	-	-	-	-	0.0114
AO	0.069	-	0.415	-	-	-	0.0016	-	-	-	0.0048	-

[Table 2-1]

No.	Component No.	Annealing step						Plating step						Skin pass rolling step
		Average heating rate in first temperature range (°C/s)	Average heating rate in second temperature range (°C/s)	(P(H2O)/P(H2)) in second temperature range	Annealing temperature (°C)	Holding time (sec)	Average cooling rate (°C/s)	Cooling stop temperature before immersion in plating bath (°C)	Effective Al amount in plating bath (mass%)	Plating bath temperature (°C)	Cooling time to 400° C after immersion in plating bath (s)	Average cooling rate to 400° C (°C/s)	Average cooling rate in range of 400 to 350° C (°C/s)	
1	A	12.3	3.2	0.89	847	143	3.3	503	0.073	478	3.8	20.3	1.8	0.3
2	A	<u>1.6</u>	3.1	1.08	883	163	0.5	540	0.170	480	4.0	20.1	1.5	0.3
3	A	10.2	<u>0.3</u>	0.52	784	61	13.3	493	0.105	455	2.4	22.4	4.2	0.3
4	A	7.3	<u>7.1</u>	0.40	779	94	64.1	539	0.079	465	4.0	16.2	1.3	0.3
5	A	16.5	0.5	<u>0.02</u>	780	5	3.2	524	0.145	452	5.2	9.8	3.4	0.3
6	A	14.8	0.8	<u>2.31</u>	753	16	35.2	517	0.168	455	2.8	20.0	1.9	0.3
7	A	15.8	is	0.73	<u>683</u>	193	12.4	499	0.102	480	4.0	19.9	4.6	0.3
8	A	10.7	2.8	0.92	729	39	11.0	534	0.168	467	7.4	9.2	1.9	0.3
9	A	6.0	3.0	0.27	754	<u>0</u>	0.6	539	0.175	481	2.5	32.0	2.4	0.3
10	A	5.1	4.9	0.68	805	80	<u>0.3</u>	546	0.152	479	5.1	15.4	2.4	0.3
11	A	13.8	2.9	1.50	808	131	2.9	440	0.057	453	4.8	11.2	3.1	0.3
12	A	6.9	0.8	0.52	812	35	1.3	472	0.214	463	6.1	10.4	3.2	0.3
13	A	18.3	2.3	1.37	836	134	0.5	522	0.153	482	<u>13.4</u>	6.1	3.8	0.3
14	A	8.2	2.6	1.70	751	170	61.2	449	0.092	480	<u>32.1</u>	2.5	1.9	0.3
15	A	9.6	3.8	1.92	773	173	26.7	505	0.080	467	9.7	6.9	<u>0.5</u>	0.3
16	A	13.7	4.6	0.82	877	149	67.9	462	0.094	469	9.1	7.6	<u>0.7</u>	0.3
17	B	13.6	2.8	1.08	812	192	26.5	455	0.112	454	3.0	18.0	1.7	0.3
18	C	10.2	1.1	1.68	776	7	62.7	537	0.121	460	3.0	20.2	1.9	0.3

(continued)

No.	Component No.	Annealing step						Plating step						Skin pass rolling step
		Average heating rate in first temperature range (°C/s)	Average heating rate in second temperature range (°C/s)	(P(H2O)/P(H2)) in second temperature range	Annealing temperature (°C)	Holding time (sec)	Average cooling rate (°C/s)	Cooling stop temperature before immersion in plating bath (°C)	Effective Al amount in plating bath (mass%)	Plating bath temperature (°C)	Cooling time to 400° C after immersion in plating bath (s)	Average cooling rate to 400° C (°C/s)	Average cooling rate in range of 400 to 350° C (°C/s)	
19	D	3.2	2.0	0.33	755	193	66.2	535	0.151	470	5.1	13.8	1.1	0.3
20	E	18.8	3.6	1.26	808	144	12.4	538	0.123	463	3.9	16.3	1.0	0.3
21	F	7.0	5.0	1.58	776	30	52.0	458	0.112	481	8.5	9.5	1.2	0.3
22	G	9.6	0.8	1.72	892	40	1.6	505	0.146	460	6.1	9.9	1.4	0.3
23	H	4.5	0.8	2.00	839	27	0.5	473	0.117	482	9.4	8.8	2.2	0.3
24	I	8.9	0.7	0.67	888	184	0.5	445	0.141	462	4.3	14.2	3.1	0.3
25	J	2.5	3.5	0.17	795	42	26.3	510	0.167	456	6.2	9.2	2.6	0.3
26	K	14.2	2.1	1.83	750	88	78.6	486	0.075	470	2.9	24.3	2.4	0.3
27	L	16.4	4.4	0.10	790	18	1.8	473	0.070	473	2.8	26.1	4.7	0.3
28	M	6.6	2.9	1.99	863	87	13.1	517	0.111	482	4.8	17.2	1.2	0.3

[Table 2-2]

No.	Component No.	Annealing step						Plating step						Skin pass rolling step
		Average heating rate in first temperature range (°C/s)	Average heating rate in second temperature range (°C/s)	(P(H2O)/P(H2)) in second temperature range	Annealing temperature (°C)	Holding time (sec)	Average cooling rate (°C/s)	Cooling stop temperature before immersion in plating bath (°C)	Effective Al amount in plating bath (mass%)	Plating bath temperature (°C)	Cooling time to 400° C after immersion in plating bath (s)	Average cooling rate to 400° C (°C/s)	Average cooling rate in range of 400 to 350° C (°C/s)	
29	N	17.6	2.3	1.18	865	178	96.6	520	0.163	466	4.2.	15.7	4.7	0.3
30	O	14.2	2.2	1.86	776	138	10.1	456	0.139	467	3.1	21.4	1.3	0.3
31	P	2.7	2.4	0.85	757	44	13.8	444	0.156	483	3.7	22.5	2.3	0.3
32	Q	5.9	3.7	0.37	785	90	65.6	532	0.100	462	9.7	6.4	2.1	0.3
33	R	16.7	2.4	1.93	820	44	11.8	523	0.069	480	7.4	10.9	1.2	0.3
34	S	12.0	1.3	0.21	856	153	0.6	516	0.076	458	7.1	8.2	3.9	0.3
35	T	7.2	3.7	1.15	838	152	94.6	469	0.072	476	6.9	11.0	2.9	0.3
36	U	2.6	4.9	1.61	816	186	5.8	492	0.172	484	8.1	10.3	20	0.3
37	V	16.0	4.4	1.10	794	49	66.5	529	0.080	475	3.8	19.7	2.0	0.3
38	W	14.8	1.5	1.37	799	37	3.7	473	0.067	478	4.0	19.2	3.1	0.3
39	X	19.8	2.1	1.42	844	104	8.1	550	0.145	468	9.7	7.0	3.6	0.3
40	Y	10.8	4.7	1.66	864	134	71.1	531	0.107	453	8.6	6.1	3.4	0.3
41	Z	19.7	1.0	0.44	849	138	36.7	495	0.177	459	4.8	12.3	1.1	0.3
42	AA	13.9	3.3	1.08	818	154	1.5	495	0.101	456	8.8	6.3	3.6	0.3
43	AB	8.0	2.6	1.34	852	168	6.4	531	0.125	465	7.9	8.3	2.2	0.3
44	AC	13.1	3.9	1.59	763	115	66.6	489	0.106	457	2.4	23.4	3.4	0.3
45	AD	2.4	3.3	0.66	807	37	2.9	520	0.106	471	7.9	9.0	1.8	0.3
46	AE	4.2	2.2	0.54	853	56	83.3	500	0.114	486	7.4	11.5	2.2	0.3

(continued)

No.	Component No.	Annealing step						Plating step						Skin pass rolling step
		Average heating rate in first temperature range (°C/s)	Average heating rate in second temperature range (°C/s)	(P(H2O)/P(H2)) in second temperature range	Annealing temperature (°C)	Holding time (sec)	Average cooling rate (°C/s)	Cooling stop temperature before immersion in plating bath (°C)	Effective Al amount in plating bath (mass%)	Plating bath temperature (°C)	Cooling time to 400° C after immersion in plating bath (s)	Average cooling rate to 400° C (°C/s)	Average cooling rate in range of 400 to 350° C (°C/s)	
47	<u>AF</u>	6.0	1.7	0.25	801	26	25.5	472	0.112	476	9.2	8.3	4.5	0.3
48	<u>AG</u>	17.6	2.8	1.34	845	171	0.6	458	0.176	455	8.4	6.5	1.8	0.3
49	<u>AH</u>	18.9	3.8	1.88	778	83	0.5	502	0.149	486	9.6	8.9	2.8	0.3
50	<u>AI</u>	5.7	3.0	1.62	837	14	3.0	483	0.121	463	7.0	9.0	1.2	0.3
51	<u>AJ</u>	7.2	2.9	0.62	775	115	62.8	493	0.094	453	6.9	7.7	3.7	0.3
52	<u>AK</u>	13.6	1.0	0.70	777	83	5.1	515	0.133	464	3.4	19.0	44	0.3
53	<u>AL</u>	16.9	2.8	1.55	894	166	1.5	491	0.113	474	7.9	9.3	4.7	0.3
54	<u>AM</u>	12.8	1.0	1.76	773	42	1.8	479	0.069	483	4.9	17.1	3.0	0.3
55	<u>AN</u>	5.9	1.4	1.06	793	27	2.2	540	0.138	455	6.2	8.9	4.5	0.3
56	<u>AO</u>	12.1	1.6	0.88	886	117	78.7	539	0.117	488	8.0	11.0	1.7	0.3

[0151] In the obtained zinc-plated steel sheet (hot-dip galvanized steel sheet), the base steel sheet was observed with the above-described method, and the thickness of the internal oxide layer, the grain boundary coverage of the internal oxide layer, and the microstructure at the 1/4 thickness position were observed. Tables 3-1 and 3-2 show the results.

[0152] Although not shown in the tables, the adhesion amount of the zinc-plated layer was 10 to 80 g/m².

[0153] Furthermore, in the obtained zinc-plated steel sheet, the thickness of the Fe-Al alloy layer and the coverage by the Fe-Al alloy layer were measured with the above-described method. Tables 3-1 and 3-2 show the results.

[0154] The obtained zinc-plated steel sheet was evaluated for tensile strength (TS), LME resistance, bending fatigue strength, and bending resistance in the following manner.

<Tensile Strength>

[0155] A JIS No. 5 tensile test piece was collected in the direction (width direction) perpendicular to the rolling direction and the thickness direction of the zinc-plated steel sheet (the rolling direction and the sheet thickness direction of the base steel sheet), and subjected to a tensile test in accordance with JIS Z 2241: 2011 to measure the tensile strength (TS).

[0156] A tensile strength of 980 MPa or more was determined to be a high strength.

<LME resistance>

[0157] An evaluation material having a size of 30 mm × 30 mm was collected from the zinc-plated steel sheet, and two sheets of this evaluation material were overlapped each other and energized under the following conditions to perform a spot welding test.

Electrode: φ8, R40

Pressurizing force: 4.5 kN

Inclination angle of electrode: 4°

Up-slope: 0.02 seconds

Energization time: 0.4 seconds

Retention time after energization: 0.3 seconds

The current was set so that the nugget diameter was 5 mm.

[0158] The cross section of the evaluation material after the spot welding was observed with a SEM, and the length of the crack was evaluated as follows.

Length of crack is 80 μm or less: OK (excellent in LME resistance)

Length of crack is more than 80 μm: NG

<Bending Resistance>

[0159] A bending test was performed in accordance with VDA238-100, and the bending angle (°) at this time was evaluated as follows. The test piece was collected in the direction in which the bending ridgeline was parallel to the rolling direction.

Bending angle > 110 - TS × 0.03: Ex (particularly excellent in bending resistance)

Bending angle > 110 - TS × 0.04: OK (excellent in bending resistance)

Bending angle ≤ 110 - TS × 0.04: NG

<Bending Fatigue Strength>

[0160] A plane bending fatigue test was performed in accordance with JIS Z 2275: 1978. The test piece was a No. 1 test piece having a width of 30 mm and an R of 40 mm.

[0161] As a result of the test, the fatigue strength at a number of repetitions of 10⁶ was evaluated as follows.

Fatigue strength at number of repetitions of 10⁶ > 0.35 × TS: Ex (particularly excellent in bending fatigue strength)

Fatigue strength at number of repetitions of 10⁶ > 0.30 × TS: OK (excellent in bending fatigue strength)

Fatigue strength at number of repetitions of 10⁶ ≤ 0.30 × TS: NG

[Table 3-1]

No.	Base steel sheet			Fe-Al alloy layer		Properties				Note
	Thickness of internal oxide layer (μm)	Grain boundary coverage by oxide (%)	Total volume percentage of fresh martensite and tempered martensite at 1/4 thickness position (%)	Thickness (nm)	Coverage of steel sheet surface (%)	TS (MPa)	LME resistance	Bending fatigue strength	Bending resistance	
1	5.4	71	96	30	53	1506	OK	Ex	Ex	Invention Example
2	<u>0.1</u>	<u>37</u>	90	37	54	1398	NG	NG	OK	Comparative Example
3	3.1	66	58	15	46	<u>947</u>	OK	OK	Ex	Comparative Example
4	1.5	<u>18</u>	95	34	57	1490	OK	NG	OK	Comparative Example
5	<u>0.0</u>	<u>0</u>	96	22	47	1485	NG	NG	OK	Comparative Example
6	186	92	48	22	45	<u>963</u>	OK	OK	Ex	Comparative Example
7	6.1	73	59	18	45	<u>894</u>	OK	OK	Ex	Comparative Example
8	5.6	69	58	40	69	1025	OK	Ex	Ex	Invention Example
9	0.9	64	47	19	47	<u>749</u>	OK	OK	OK	Comparative Example
10	1.8	69	58	28	53	<u>841</u>	OK	Ex	OK	Comparative Example
11	10.8	82	97	23	51	1549	OK	Ex	Ex	Invention Example
12	2.0	66	88	28	48	1496	OK	OK	OK	Invention Example
13	117	82	83	5	<u>25</u>	1093	NG	OK	Ex	Comparative Example

(continued)

No.	Base steel sheet			Fe-Al alloy layer		Properties				Note
	Thickness of internal oxide layer (μm)	Grain boundary coverage by oxide (%)	Total volume percentage of fresh martensite and tempered martensite at 1/4 thickness position (%)	Thickness (nm)	Coverage of steel sheet surface (%)	TS (MPa)	LME resistance	Bending fatigue strength	Bending resistance	
14	77	72	94	<u>0</u>	<u>0</u>	1553	NG	OK	Ex	Comparative Example
15	8.6	82	95	<u>134</u>	94	1516	OK	Ex	NG	Comparative Example
16	5.7	75	98	<u>167</u>	94	1580	OK	Ex	NG	Comparative Example
17	7.1	75	97	27	52	1660	OK	Ex	Ex	Invention Example
18	9.6	78	98	26	46	1478	OK	OK	Ex	Invention Example
19	0.8	64	80	54	65	1332	OK	Ex	OK	Invention Example
20	11.2	81	98	42	58	1556	OK	Ex	Ex	Invention Example
21	5.6	70	90	65	83	1378	OK	Ex	Ex	Invention Example
22	7.7	81	97	53	72	1554	OK	Ex	Ex	Invention Example
23	5.0	71	83	46	71	1659	OK	Ex	Ex	Invention Example
24	3.0	67	78	23	48	1128	OK	OK	Ex	Invention Example
25	0.4	64	83	29	56	1622	OK	Ex	OK	Invention Example
26	13.0	82	77	19	48	1269	OK	OK	Ex	Invention Example

(continued)

No.	Base steel sheet			Fe-Al alloy layer		Properties				Note
	Thickness of internal oxide layer (μm)	Grain boundary coverage by oxide (%)	Total volume percentage of fresh martensite and tempered martensite at 1/4 thickness position (%)	Thickness (nm)	Coverage of steel sheet surface (%)	TS (MPa)	LME resistance	Bending fatigue strength	Bending resistance	
27	1.1	66	90	15	48	1350	OK	OK	OK	Invention Ex-ample
28	65	76	96	49	62	1663	OK	Ex	Ex	Invention Ex-ample

[Table 3-2]

No.	Base steel sheet			Fe-Al alloy layer		Properties				Note
	Thickness of internal oxide layer (μm)	Grain boundary coverage by oxide (%)	Total volume percentage of fresh martensite and tempered martensite at 1/4 thickness position (%)	Thickness (nm)	Coverage of steel sheet surface (%)	TS (MPa)	LME resistance	Bending fatigue strength	Bending resistance	
29	11.3	81	73	19	47	1305	OK	OK	Ex	Invention Example
30	12.4	88	99	33	52	1352	OK	Ex	Ex	Invention Example
31	1.4	65	87	26	47	1593	OK	OK	OK	Invention Example
32	1.3	68	77	55	63	1292	OK	Ex	OK	Invention Example
33	16.1	85	99	64	81	1418	OK	Ex	Ex	Invention Example
34	1.3	68	98	29	54	1342	OK	Ex	OK	Invention Example
35	4.0	74	97	31	53	1639	OK	Ex	Ex	Invention Example
36	2.3	67	96	50	69	1378	OK	Ex	OK	Invention Example
37	8.9	81	84	28	54	1459	OK	Ex	Ex	Invention Example
38	10.6	84	99	23	46	1546	OK	OK	Ex	Invention Example
39	12.9	85	92	33	59	1606	OK	Ex	Ex	Invention Example
40	9.9	77	68	30	57	1307	OK	Ex	Ex	Invention Example
41	4.2	74	92	48	70	1703	OK	Ex	Ex	Invention Example

(continued)

No.	Base steel sheet			Fe-Al alloy layer		Properties				Note
	Thickness of internal oxide layer (μm)	Grain boundary coverage by oxide (%)	Total volume percentage of fresh martensite and tempered martensite at 1/4 thickness position (%)	Thickness (nm)	Coverage of steel sheet surface (%)	TS (MPa)	LME resistance	Bending fatigue strength	Bending resistance	
42	7.3	77	88	35	57	1676	OK	Ex	Ex	Invention Example
43	5.4	72	93	45	64	1488	OK	Ex	Ex	Invention Example
44	9.7	83	95	17	44	1522	OK	OK	Ex	Invention Example
45	1.0	64	89	53	71	1465	OK	Ex	OK	Invention Example
46	1.2	65	98	36	61	1482	OK	Ex	OK	Invention Example
47	0.9	66	46	27	53	<u>849</u>	OK	Ex	OK	Comparative Example
48	12.2	80	91	51	62	1611	NG	Ex	Ex	Comparative Example
49	<u>0.1</u>	<u>20</u>	91	44	59	1084	NG	NG	OK	Comparative Example
50	5.0	73	70	61	73	<u>934</u>	OK	Ex	Ex	Comparative Example
51	2.4	72	95	27	52	1376	NG	Ex	OK	Comparative Example
52	5.3	71	94	16	49	1631	NG	NG	NG	Comparative Example
53	12.7	83	77	23	47	1778	NG	OK	NG	Comparative Example
54	11.8	84	92	27	47	<u>942</u>	OK	OK	Ex	Comparative Example

(continued)

No.	Base steel sheet			Fe-Al alloy layer		Properties				Note
	Thickness of internal oxide layer (μm)	Grain boundary coverage by oxide (%)	Total volume percentage of fresh martensite and tempered martensite at 1/4 thickness position (%)	Thickness (nm)	Coverage of steel sheet surface (%)	TS (MPa)	LME resistance	Bending fatigue strength	Bending resistance	
55	3.2	69	91	23	47	1450	OK	OK	NG	Comparative Example
56	5.3	76	78	50	72	1216	OK	Ex	NG	Comparative Example

[0162] As can be seen from Tables 1-1 to 3-2, in Nos. 1, 8, 11, 12, and 17 to 46 in which the chemical composition and the manufacturing method were within the scope of the present invention, a preferred Fe-Al alloy layer and an internal oxide layer were formed, and all of the tensile strength, the LME resistance, the bending fatigue strength, and the bending resistance were excellent.

[0163] Meanwhile, in Nos. 47 to 56 in which the chemical composition was out of the scope of the present invention, at least one of the tensile strength, the LME resistance, the bending fatigue strength, or the bending resistance was poor.

[0164] In Nos. 2 to 7, 9, 10, and 13 to 16 in which the manufacturing method was out of the scope of the present invention although the chemical composition was within the scope of the present invention, the tensile strength was low, or the internal oxide layer and the Fe-Al alloy layer were not formed in a preferable state, and therefore at least one of the LME resistance, the bending fatigue strength, or the bending resistance was poor. Brief Description of the Reference Symbols

[0165]

1 Steel sheet (zinc-plated steel sheet)

10 Base steel sheet

11 Internal oxide layer

20 Fe-Al alloy layer

30 Zinc-plated layer

Field of Industrial Application

[0166] According to the present invention, a zinc-plated steel sheet that has high strength and sufficient bending resistance and is excellent in LME resistance and bending fatigue strength can be provided. Such a steel sheet is useful as a high-strength steel sheet for a vehicle.

Claims

1. A zinc-plated steel sheet comprising:

a base steel sheet;
a Fe-Al alloy layer formed on at least a part of a surface of the base steel sheet; and
a zinc-plated layer formed on the surface of the base steel sheet or a surface of the Fe-Al alloy layer,
wherein, the base steel sheet has a chemical composition including, in mass%,
C: 0.10 to 0.40%,
Si: 0.10 to 3.00%,
Mn: 1.00 to 5.00%,
sol.Al: 0.001 to 1.500%,
P: 0.0010 to 0.0300%,
S: 0.0200% or less,
N: 0.0100% or less,
O: 0.0100% or less,
Ti: 0 to 0.200%,
B: 0 to 0.0100%,
Cr: 0 to 1.000%,
Mo: 0 to 1.000%,
Ni: 0 to 1.000%,
Cu: 0 to 1.000%,
Sn: 0 to 0.500%,
Nb: 0 to 0.200%,
V: 0 to 0.500%,
W: 0 to 0.500%,
Ca: 0 to 0.0100%,
Mg: 0 to 0.0100%,
Bi: 0 to 0.0100%,
Sb: 0 to 0.1000%,
Zr: 0 to 0.0100%,
REM: 0 to 0.1000%, and
a remainder: Fe and an impurity,

the base steel sheet has an internal oxide layer of 0.2 μm or more in a sheet thickness direction from the surface of the base steel sheet,
the Fe-Al alloy layer has an average thickness of 1 nm or more and less than 100 nm,
in a cross section in a thickness direction,
a grain boundary coverage by an oxide is 60% or more in the internal oxide layer,
a coverage of the surface of the base steel sheet by the Fe-Al alloy layer is 40% or more, and
a tensile strength is 980 MPa or more and 2000 MPa or less.

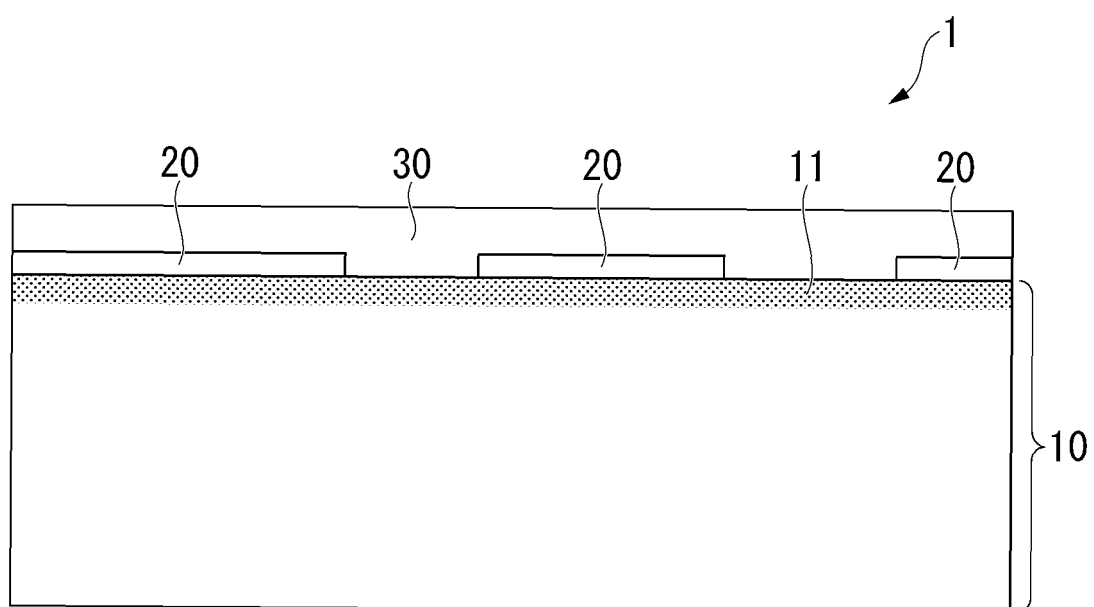
2. The zinc-plated steel sheet according to claim 1, wherein

the chemical composition of the base steel sheet contains, in mass%, one or more selected from the group consisting of
Ti: 0.005 to 0.200%,
B: 0.0005 to 0.0100%,
Cr: 0.001 to 1.000%,
Mo: 0.001 to 1.000%,
Ni: 0.001 to 1.000%,
Cu: 0.001 to 1.000%,
Sn: 0.001 to 0.500%,
Nb: 0.001 to 0.200%,
V: 0.001 to 0.500%,
W: 0.001 to 0.500%,
Ca: 0.0001 to 0.0100%,
Mg: 0.0001 to 0.0100%,
Bi: 0.0001 to 0.0100%,
Sb: 0.0001 to 0.1000%,
Zr: 0.0001 to 0.0100%, and
REM: 0.0001 to 0.1000%.

3. A method for manufacturing a zinc-plated steel sheet, the method comprising:

an annealing step of holding a steel sheet at an annealing temperature of 700 to 1000°C for 1 second or more to anneal the steel sheet, the steel sheet having a chemical composition including, in mass%, C: 0.10 to 0.40%, Si: 0.10 to 3.00%, Mn: 1.00 to 5.00%, sol.Al: 0.001 to 1.500%, P: 0.0010 to 0.0300%, S: 0.0200% or less, N: 0.0100% or less, O: 0.0100% or less, Ti: 0 to 0.200%, B: 0 to 0.0100%, Cr: 0 to 1.000%, Mo: 0 to 1.000%, Ni: 0 to 1.000%, Cu: 0 to 1.000%, Sn: 0 to 0.500%, Nb: 0 to 0.200%, V: 0 to 0.500%, W: 0 to 0.500%, Ca: 0 to 0.0100%, Mg: 0 to 0.0100%, Bi: 0 to 0.0100%, Sb: 0 to 0.1000%, Zr: 0 to 0.0100%, REM: 0 to 0.1000%, and a remainder: Fe and an impurity; and
a plating step of forming a zinc-plated layer on a surface of the steel sheet after the annealing step, wherein
in the annealing step, in a heating process to the annealing temperature, an average heating rate in a first temperature range of 400 to 650°C is 2.0°C/sec or more, and an average heating rate in a second temperature range of 650°C to the annealing temperature is 0.5 to 5.0°C/sec and an atmosphere having $(P(\text{H}_2\text{O})/P(\text{H}_2))$ in the second temperature range is 0.05 to 2.00,
in the plating step, the steel sheet is cooled to a temperature of 440 to 550°C at an average cooling rate of 0.5°C/sec or more, is immersed in a plating bath containing Zn as a main component and having an effective Al amount of 0.050 to 0.250 mass%, is pulled up from the plating bath, then is cooled so that a temperature of the steel sheet reaches 400°C within 10 seconds, and subsequently is cooled to 350°C or less so that at an average cooling rate from 400°C to 350°C is 1.0°C/sec or more and 5.0°C/sec or less.

FIG. 1



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2023/002565

A. CLASSIFICATION OF SUBJECT MATTER

C21D 9/46(2006.01)i; **C22C 18/04**(2006.01)i; **C22C 38/00**(2006.01)i; **C22C 38/60**(2006.01)i; **C23C 2/02**(2006.01)i;
C23C 2/06(2006.01)i; **C23C 2/40**(2006.01)i

FI: C22C38/00 301T; C22C38/60; C21D9/46 J; C23C2/06; C23C2/40; C23C2/02; C22C18/04

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)

C21D8/02; C21D9/46; C22C18/04; C22C38/00-C22C38/60; C23C2/02; C23C2/06; C23C2/40

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

Published examined utility model applications of Japan 1922-1996
 Published unexamined utility model applications of Japan 1971-2023
 Registered utility model specifications of Japan 1996-2023
 Published registered utility model applications of Japan 1994-2023

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.
A	WO 2019/116531 A1 (NIPPON STEEL CORP) 20 June 2019 (2019-06-20) entire text, all drawings	1-3
A	WO 2020/213686 A1 (NIPPON STEEL CORP) 22 October 2020 (2020-10-22) entire text, all drawings	1-3
A	WO 2013/047821 A1 (NIPPON STEEL & SUMITOMO METAL CORPORATION) 04 April 2013 (2013-04-04) entire text	1-3
A	WO 2021/224662 A1 (ARCELORMITTAL) 11 November 2021 (2021-11-11) entire text, all drawings	1-3

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

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“O” document referring to an oral disclosure, use, exhibition or other means

“P” document published prior to the international filing date but later than the priority date claimed

“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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“&” document member of the same patent family

Date of the actual completion of the international search

06 April 2023

Date of mailing of the international search report

18 April 2023

Name and mailing address of the ISA/JP

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Authorized officer

Telephone No.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/JP2023/002565

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WO 2019/116531 A1	20 June 2019	US 2020/0325554 A1 entire text, all drawings EP 3725904 A1 KR 10-2020-0092351 A CN 111492075 A CA 3085282 A1 BR 112020008427 A2 RU 2020123267 A MX 2020005828 A	
WO 2020/213686 A1	22 October 2020	US 2022/0145425 A1 entire text, all drawings EP 3957764 A1 CN 113557318 A KR 10-2021-0123384 A	
WO 2013/047821 A1	04 April 2013	US 2014/0234660 A1 entire text EP 2762582 A1 CA 2850340 A1 TW 201329251 A CN 103842541 A KR 10-2014-0052072 A MX 2014003718 A RU 2014117645 A BR 112014007498 A2 ZA 201402352 B PL 2762582 T3 ES 2725803 T3	
WO 2021/224662 A1	11 November 2021	EP 4146835 A1 entire text, all drawings KR 10-2022-0156089 A CN 115516117 A CA 3180099 A1 BR 112022021048 A2	

Form PCT/ISA/210 (patent family annex) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

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