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(54) STEEL SHEET AND MANUFACTURING METHOD THEREFOR

(57) The present invention relates to a steel sheet that can be used for automobiles, etc., and relates to a steel sheet that can ensure improved plating characteristics, and a manufacturing method therefor.

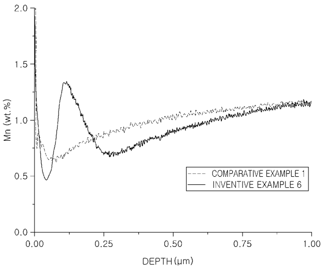

FIG. 1

Processed by Luminess, 75001 PARIS (FR)

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Description

Technical Field

[0001] The present disclosure relates to a steel sheet that can be used in automobiles, etc., and relates to a steel sheet that can ensure improved plating characteristics, and a manufacturing method therefor.

Background Art

[0002] Recently, issues such as energy saving, exhaust gas reduction, collision stability, durability improvement, or the like, may be important issues that automobile manufacturers should address. In order to effectuate energy savings and exhaust gas reductions, a decrease in weight of automobiles may be being emphasized. Meanwhile, in order to simultaneously reduce the weight of automobiles and effectuate collision stability and durability improvement, an increase in strength of a steel material is required, and excellent formability is also required.

[0003] In order to improve strength of the steel material, various alloy elements may be included to increase hardenability, but in this case, there may be a problem of deteriorating formability such as a springback phenomenon.

[0004] To solve such a problem, a hot forming method (hot press forming method) has been proposed. The hot press forming method may be a method of processing a steel material at a high temperature (800°C or higher) suitable for processing, and then rapidly cooling the steel material at a low temperature, to form a low-temperature structure such as martensite or the like, in the steel material, thereby increasing strength of a final product. This hot press forming method may minimize the problem of formability, when a member having a high strength is manufactured.

[0005] In order to improve hardenability such that martensite may be easily formed during cooling, various alloying elements may be added to a steel material for hot press forming. In particular, elements having a high oxidation tendency, such as Mn, Si, Al, Cr, B, or the like, as compared to Fe, may be added.

[0006] Meanwhile, in order to prevent decarburization or oxidation of a steel sheet during hot press forming, or to secure corrosion resistance of a component, various types of plating may sometimes be applied to a surface of a steel material. Thereamong, methods of plating the surface of the steel material by hot plating such as hot-dip galvanizing or hot-dip aluminum plating are widely used.

[0007] The hot-dip galvanizing may be generally performed by annealing before plating, but there may be a problem that a plating property deteriorates due to a surface oxide formed during annealing from alloy elements such as Mn, Si, Al, Cr, B, or the like, included in the steel material. That is, during the annealing process, the alloy elements may diffuse to the surface of the steel material, and may react with a small amount of oxygen or water vapor present in an annealing furnace to form single or composite oxides of the elements. These oxides may interfere with plating wettability during the plating process, causing non-plating or causing plating peeling, thereby lowering plating quality.

[0008] Various technologies have been proposed to improve plating quality, and thereamong, Patent Document 1 proposes a technology for controlling an air-fuel ratio of air and fuel to 0.80 to 0.95 during an annealing process, oxidizing a steel sheet in a direct flame furnace in an oxidizing atmosphere, forming an iron oxide including Si, Mn, or Al alone or composite oxides to a certain depth in the steel sheet, performing reduction-annealing of the iron oxide in a reducing atmosphere, and then performing hot-dip galvanizing, to provide a hot-dip galvanized steel sheet or an alloyed hot-dip galvanized steel sheet having excellent plating quality.

[0009] When a method of reducing after oxidation is used in the annealing process, as in Patent Document 1, components having high affinity for oxygen such as Si, Mn, Al, or the like, may be internally oxidized to a certain depth from a surface layer of the steel sheet, thereby suppressing diffusion to the surface layer, such that the surface layer relatively may include less Si, Mn, or Al alone or composite oxides, which improves wettability with zinc and reduces unplated ranges. However, in steel to which Si is added, during a reduction process, Si may be concentrated directly under an iron oxide, to form an Si oxide having a band shape, which causes peeling in the surface layer including a plating layer, that is, when peeling occurs at an interface between reduced iron and base iron thereunder, making it difficult to secure adhesion of the plating layer.

[0010] Meanwhile, as another method for improving a plating property of the hot-dip galvanized steel sheet, Patent Document 2 proposes a method for improving the plating property by maintaining a high dew point in an annealing furnace to internally oxidize alloy components such as Mn, Si, Al, or the like, which may be easy to oxidize, in the steel sheet, thereby reducing oxides that may be externally oxidized on a surface of the steel sheet after annealing. However, although the method according to Patent Document 2 may solve a problem of the plating property due to external oxidation of Si, which may be easy to oxidize internally, there may be a problem that an effect thereof is minimal when a large amount of Mn, which is relatively difficult to oxidize internally, is added.

[0011] In addition, even when the plating property is improved by internal oxidation, problems such as linear non-plating may occur due to surface oxides formed unevenly on the surface, or when manufacturing an alloyed hot-dip galvanized steel sheet (GA steel sheet) through alloying heat treatment after plating, linear defects may occur on the surface of the alloyed hot-dip galvanized steel sheet due to uneven alloying.

[0012] (Patent Document 1) Korean Patent Publication No. 2010-0030627

[0013] (Patent Document 2) Korean Patent Publication No. 2009-0006881

Summary of Invention

Technical Problem

[0014] An aspect of the present disclosure is to provide a steel sheet having excellent plating characteristics by suppressing non-plating or peeling of a plating layer during plating, and a method for manufacturing the same.

[0015] The problem of the present disclosure is not limited to the above-described contents. Those who have ordinary knowledge in the technical field to which the present disclosure belongs will have no difficulty in understanding additional problems of the present disclosure from the general contents of the present disclosure specification.

Solution to Problem

[0016] An aspect of the present disclosure is a steel sheet including one or two of Mn and Si in steel,
wherein, in a glow discharge optical emission spectrometer (GDS) profile in which one or two components of Mn and Si are observed in a depth direction from a surface of the steel sheet, the steel sheet comprises two or more valleys in which amounts of the one or two components of Mn and Si are 60% or less of an amount of a parent material within 1 μm from the surface of the steel sheet.

[0017] Another aspect of the present disclosure is a method for manufacturing a steel sheet, comprising: preparing a base steel sheet including one or two of Mn and Si in steel;

> forming an Fe plating layer by performing Fe pre-plating on a surface of the base steel sheet with a thickness of more than 0.5 g/m^2 to 3 g/m^2 or less; and
> annealing the base steel sheet on which the Fe plating layer has been formed, at a temperature of 600 to 950°C in an atmosphere having a dew point temperature of 10°C or less.

Advantageous Effects of Invention

[0018] The present disclosure may provide a steel sheet having excellent plating characteristics by suppressing formation of an oxide such as Mn, Si, or the like, on a surface of the steel sheet using a method different from the prior art, to suppress non-plating or plating peeling during hot-dip plating.

[0019] Various advantages and effects of the present disclosure are not limited to the above-described contents, and will be more easily understood in the process of explaining specific embodiments of the present disclosure.

Brief Description of Drawings

[0020]

> FIG. 1 is a schematic diagram of a glow discharge optical emission spectrometer (GDS) profile of Mn amount measured on surfaces of steel materials of Comparative Example 1 and Invention Example 6 in a depth direction, according to an embodiment of the present disclosure.
> FIG. 2 is a schematic diagram of a glow discharge optical emission spectrometer (GDS) profile of Si amount measured on surfaces of steel materials in a longitudinal direction, according to an embodiment of the present disclosure.

Best Mode for Invention

[0021] The terms used in this specification are for describing the present disclosure and are not intended to limit the present disclosure. In addition, as used herein, singular forms include plural forms unless the relevant definition clearly indicates the contrary.

[0022] The meaning of "comprising" or "including" used in the specification specifies a configuration and does not exclude the presence or addition of another configuration.

[0023] Unless otherwise defined, all terms, including technical and scientific terms, used in this specification have the same meaning as commonly understood by a person of ordinary skill in the technical field to which the present disclosure pertains. Terms defined in the dictionary are interpreted to have meanings consistent with related technical literature and current disclosure.

[0024] Hereinafter, the present disclosure will be described in detail.

[0025] First, a steel sheet, which may be an embodiment of the present disclosure, will be described in detail.

[0026] The steel sheet may comprise an oxide-forming element such as Mn, Si, or the like. Mn, Si, or the like, may form an oxide on a surface of the steel sheet during an annealing process prior to plating, thereby lowering plating characteristics.

[0027] The steel sheet may comprise the following characteristics in terms of a GDS concentration profile of Mn, Si, or the like, which may be an oxidizing element that form an oxide on the surface and deteriorate plating characteristics. The GDS concentration profile refers to a concentration and a concentration profile, measured using a glow discharge optical emission spectrometer.

[0028] FIGS. 1 and 2 illustrate concentration profiles of Mn and Si, measured from surfaces of steel sheets of Comparative Example 1 and Invention Example 6 in examples described below, in a depth direction, and it can be seen that concentration profiles measured from the surface illustrates a valley in which an amount decreases and a mountain in which an amount increases.

[0029] In the steel sheet of the present disclosure, in a glow discharge optical emission spectrometer (GDS) profile in which one or two components of Mn and Si are observed in a depth direction from a surface of the steel sheet, the steel sheet comprise two or more valleys in which amounts of the one or two components of Mn and Si are 60% or less of an amount of a parent material within 1 μm from the surface of the steel sheet.

[0030] In this case, an amount of a parent material may refer to an average amount of a component, corresponding thereto, in a steel sheet manufactured by controlling the same during a steelmaking process, and may be representatively used as a value measured at a 1/4 point (1/4*t) of a thickness (t, unit mm) of the steel sheet.

[0031] When the valleys are less than 2, surface concentration of Mn and Si elements may occur, which may deteriorate a plating property. However, when the valleys are 2 or more, a deficiency layer of an element corresponding thereto may be formed, which may suppress surface concentration, thereby improving a plating property.

[0032] Meanwhile, it may be effective that amounts of one or two of Mn and Si included in a grain or a grain boundary of the grains within 1 μm from the surface of the steel sheet in the thickness direction are 40% or more of an amount of each of the components measured at the 1/4 point (1/4*t) of the thickness (t, unit mm) of the steel sheet. In general, diffusion of elements in steel may be a function of concentration and time. To minimize diffusion of an element forming a surface oxide to a surface, it is desirable to anneal and pass the steel sheet at a fast speed, as possible. However, to satisfy mechanical properties, there may be a target temperature and time for each section of an annealing furnace, and considering an industrial production environment of the steel sheet that continuously passes through various facilities such as the annealing furnace, a plating bath, or the like, optimum effects may be achieved in terms of plating characteristics and manufacturing efficiency, when the amounts of the components are 40% or more.

[0033] The present disclosure is not particularly limited to the alloy composition of the steel sheet comprising Mn, Si, or the like, in the steel, and it is sufficient to be recognized by a person skilled in the art that may be used in the technical field to which the present disclosure belongs.

[0034] As an example, the steel sheet may comprise, by weight, C: 0.02 to 0.6%, Si: 0.001 to 2%, Al: 0.001 to 1%, Mn: 0.1 to 4%, P: 0.05% or less, S: 0.02% or less, Cr: 1% or less, N: 0.02% or less, Ti: 0 to 0.1%, B: 0.0001 to 0.01%, Cu: 0 to 1.00%, Mo: 0 to 1.00%, Cr: 0 to 1.00%, Ni: 0 to 1.00%, V: 0 to 1.00%, Ca: 0 to 0.01%, Nb: 0 to 0.1%, Sn: 0 to 1%, W: 0 to 1%, Sb: 0 to 1%, Mg: 0 to 0.1%, Co: 0 to 1%, As: 0 to 1%, Zr: 0 to 1%, Bi: 0 to 1%, REM: 0 to 0.3%, the remainder Fe, and unavoidable impurities.

[0035] Meanwhile, the steel sheet may comprise an oxide formed of one or two or more of Mn, Si, Al, Cr, and B is included in a grain boundary within 10 μm from the surface in the depth direction. During annealing, an oxidation-friendly element in steel, such as Mn, Si, Al, Cr, B, or the like, may mainly diffuse into a grain boundary of the base iron and move to the surface layer, and at the same time, oxygen included in an Fe plating layer may diffuse into the steel and combine with the oxidation-friendly element to form an oxide.

[0036] A depth at which the oxide is formed may be proportional to an absolute amount of the oxygen included in the Fe plating layer. As described below, the oxygen in the Fe plating layer may be included in an amount of 5 to 50 wt%. Therefore, a thickness of the oxide after annealing may be 1 μm or more and 10 μm or less. When it is less than 1 μm, since a suppression level of the surface thickening may be insufficient, the plating properties may not be improved. When it exceeds 10 μm, since an additional electroplating cell should be installed, and it causes a decrease in production speed, it is not desirable from an economical point of view.

[0037] The surface of the steel sheet may comprise a plating layer such as a hot-dip galvanized layer, a hot-dip aluminum plating layer, or the like. A type or a method of the plating layer is not particularly limited, and all types or methods that may be performed in the technical field to which the present disclosure belongs may be included.

[0038] Next, a method for manufacturing a steel sheet, which may be another aspect of the present disclosure, will be described in detail.

[0039] First, a base steel sheet comprising one or two of Mn and Si in steel may be prepared.

[0040] In the present disclosure, since a base steel sheet comprising the aforementioned alloy composition may be applied without limitation as a base steel sheet of a steel sheet for plating or a hot-dip galvanized steel sheet, according to the present disclosure, there may be no specific limitation on a method for manufacturing the base steel sheet. As an example, the steel sheet may comprise, by weight, C: 0.02 to 0.6%, Si: 0.001 to 2%, Al: 0.001 to 1%, Mn: 0.1 to 4%, P: 0.05% or less, S: 0.02% or less, Cr: 1% or less, N: 0.02% or less, Ti: 0 to 0.1%, B: 0.0001 to 0.01%, Cu: 0 to 1.00%, Mo: 0 to 1.00%, Cr: 0 to 1.00%, Ni: 0 to 1.00%, V: 0 to 1.00%, Ca: 0 to 0.01%, Nb: 0 to 0.1%, Sn: 0 to 1%, W: 0 to 1%, Sb: 0 to 1%, Mg: 0 to 0.1%, Co: 0 to 1%, As: 0 to 1%, Zr: 0 to 1%, Bi: 0 to 1%, REM: 0 to 0.3%, the remainder Fe, and unavoidable impurities.

[0041] An example of the above-mentioned method for manufacturing a steel sheet may be described in detail.

[0042] A steel sheet according to an embodiment of the present disclosure may be manufactured by reheating, hot-rolling, coiling, and cold-rolling a steel slab satisfying the above-mentioned alloy composition.

Reheating

[0043] A steel slab satisfying an alloy composition of the present disclosure may be reheated at a temperature range of 1200°C or higher. To re-dissolve most of precipitates present in steel, it may be reheated at a temperature of 1200°C or higher. In an embodiment of the present disclosure, the reheating temperature may be 1250°C or higher.

Hot-Rolling

[0044] The reheated steel slab may be hot-rolled at a finish-rolling temperature of Ar3 to 1000°C. In the hot-rolling, when the finish-rolling temperature is less than Ar3 ($\gamma \rightarrow \alpha$ transformation temperature during cooling), abnormal rolling may be likely to occur, causing a mixed grain structure on a surface, and it may be difficult to control a shape of the hot-rolled steel sheet. On the other hand, when the finish-rolling temperature exceeds 1000°C, uniform hot-rolling may not be performed across an entire thickness, which causes insufficient grain refinement.

Coiling

[0045] The hot-rolled steel sheet may be coiled at a temperature range exceeding Ms (martensite start temperature) and 750°C or less. When a coiling temperature is Ms or less, strength of the hot-rolled steel sheet may be too high, which may reduce cold-rollability. When the coiling temperature exceeds 750°C, an increase in thickness of an oxide layer and oxidation of a grain boundary of a surface layer occurs, which not only deteriorates a pickling property, but also causes the grain boundary of the surface layer to peel off during annealing in a continuous annealing furnace.

[0046] In the present disclosure, cooling conditions to the coiling temperature after hot-rolling are not particularly limited, and may be cooled under usual conditions applied in the same technical field. In an embodiment of the present disclosure, air cooling may be performed.

Pickling

[0047] The hot-rolled steel sheet that has undergone the above-described process may be pickled by placing it in a hydrochloric acid bath to remove a hot-rolled scale. A hydrochloric acid concentration of the hydrochloric acid bath during pickling may be performed in a range of 10 to 30%, and a pickling passing speed may be 100 to 250 mpm. When a pickling speed exceeds 250 mpm, a hot-rolled steel sheet surface scale may not be completely removed, and when the pickling speed is lower than 100 mpm, since a surface layer of base iron may be corroded by hydrochloric acid, it may be performed at 180 mpm or higher.

Cold-Rolling

[0048] The coiled steel sheet may be cold-rolled at a cumulative reduction ratio of 30 to 90% to obtain a cold-rolled steel sheet. When the reduction ratio is less than 30%, rolling and tension controlling may be inaccurate, which may cause a sheet to twist, and anisotropy of the material may increase even after hot forming due to insufficient recrystallization during annealing. On the other hand, when the reduction ratio exceeds 90%, a product may not be produced due to load of the cold-rolling during rolling.

[0049] Pre-plating of Fe may be performed on the surface of the steel sheet, before annealing, to form an Fe plating layer.

[0050] A method of forming the Fe plating layer is not particularly limited, but an electroplating method or the like, may be used.

[0051] It is effective that a plating adhesion amount of the pre-plating of Fe is more than 0.5 g/m^2 to 3 g/m^2 or less.

[0052] To secure quality of hot-dip plating of the steel sheet comprising Mn and Si, it is preferable to process a plating amount of the Fe plating layer to be more than 0.5 g/m^2 and less than 3.0 g/m^2, based on an iron concentration. An upper limit of the Fe plating amount is not particularly limited, but when it exceeds 3.0 g/m^2 in the continuous plating process, a plurality of plating cells may be required or a production speed may decrease, which may not be economical. In addition, when an Fe plating amount is large, an Fe electroplating solution may be rapidly denatured in the continuous process, causing a decrease in pH and a significant decrease in plating efficiency, making it difficult to manage the solution. On the other hand, when the Fe plating amount is 0.5 g/m^2 or less, since oxygen included in the Fe plating layer may be rapidly reduced and removed, diffusion of Mn and Si from the base iron and formation of surface oxides may not be effectively suppressed, which causes a problem in that quality of hot-dip plating deteriorates. The Fe plating amount may be a concentration of iron included in the plating layer, and when the Fe plating layer is completely reduced during annealing, it may have a thickness of about 0.05 to 0.4 μm.

[0053] In an embodiment of the present disclosure, the Fe plating layer may be formed on the surface of the base iron through an electroplating method, and an oxygen concentration of the Fe plating layer formed may be controlled by appropriately controlling conditions of the electroplating solution and the plating conditions.

[0054] That is, to form the Fe plating layer in the present disclosure, an electroplating solution comprising iron ions including ferrous ions and ferric ions; a complexing agent; and inevitable impurities, and in which a concentration of the ferric ions among the iron ions is 5 to 60 wt%, may be used.

[0055] According to an embodiment of the present disclosure, the electroplating solution may include ferrous ions and ferric ions. To obtain high plating efficiency, it may be advantageous to include only ferrous ions. However, when only ferrous ions are included, since the solution may be deteriorated and the plating efficiency may rapidly decrease, which may cause quality deviation in the continuous electroplating process, the ferric ions may be further included. In this case, a concentration of the ferric ions may be 5 to 60 wt% of the total of ferrous and ferric ions, and is more preferably 5 to 40 wt%. When it is less than 5%, since a rate at which ferric iron is reduced to ferrous iron in an negative electrode may be lower than a rate at which ferrous iron is oxidized to ferric iron in a positive electrode, a ferric concentration may rapidly increase, a pH may rapidly decrease, and plating efficiency may continuously decrease. On the other hand, when the concentration of ferric ions exceeds 60%, since a reaction amount at which ferric iron is reduced to ferrous iron may increase significantly more than a reaction amount at which ferrous iron is reduced and precipitated as metallic iron, in the negative electrode, plating efficiency may significantly decrease and plating quality may deteriorate. Therefore, considering equipment and process characteristics such as a plating amount, a working current density, a solution supply amount, a solution amount lost by being deposited on a strip, a rate of change in concentration due to evaporation, or the like, it is preferable to set a concentration of ferric ions among the iron ions to 5 to 60 wt%.

[0056] A concentration of the iron ions may be preferably 1 to 80 g per 1 L of the electroplating solution, and more preferably 10 to 50 g per 1 L. When it is less than 1 g/L, there may be a problem that plating efficiency and plating quality may be rapidly reduced, while when it exceeds 80 g/L, solubility may be exceeded, which may cause precipitation, and since loss of raw materials due to solution loss in the continuous plating process may increase, it may not be economical.

[0057] The electroplating solution of the present disclosure may comprise a complexing agent, and to include a large amount of ferric iron without generating sludge and maintain high plating efficiency, it is preferable to use an amino acid or an amino acid polymer as the complexing agent.

[0058] The amino acid refers to an organic molecule in which carboxyl groups (-COOH) and amine groups (-NH_2) are combined, and the amino acid polymer refers to an organic molecule formed by polymerization of two or more amino acids, and the amino acid polymer may exhibit complexing properties, similar to the amino acid. Therefore, in the following description, the amino acid and the amino acid polymer may be collectively referred to as an amino acid.

[0059] When amino acids are dissolved in neutral water, since amines may be coupled to hydrogen ions to have a positive charge, and carboxyl groups may dissociate hydrogen ions to have a negative charge, amino acid molecules may maintain charge neutrality. On the other hand, when the solution is acidified, since carboxyl groups may be recoupled to hydrogen ions to be charge neutral, and amines may have a positive charge, amino acid molecules may form cations. In other words, the amino acids may form charge neutrality or cations in a weakly acidic aqueous solution.

[0060] When amino acids are added to an acidic electrolyte including iron ions, they may be complexed with the ferrous ions and the ferric ions, and the iron ions complexed with the amino acids may maintain a cation state even in a complexed state. Therefore, they exhibit electrically opposite properties to conventional complexing agents having a plurality of carboxyl groups, which may be negatively charged in the weakly acidic aqueous solution.

[0061] In addition, amino acids may form fewer bonds with iron ions, and may have weaker bonding strength, as compared to complexing agents including a plurality of carboxyl groups such as citric acid, EDTA, or the like, but bonding strength thereof with ferric ions that generate sludge may be sufficiently strong, and thus may prevent precipitation by ferric ions. In addition, even when ferric ions are complexed, since they may maintain cations, ferric ions may be easily transferred to the negative electrode, and may reduced to ferrous ions to participate in the plating reaction, while movement thereof to the positive electrode may be suppressed, so the production speed of ferric ions may be slowed down. Therefore, even when continuous plating is performed for a long period of time, the ferric ion concentration may be maintained at a constant level, plating efficiency may be maintained constant, and there may be no need to replace the electrolyte.

[0062] Meanwhile, when iron ions in the solution are exhausted by plating in the continuous electroplating process, the solution becomes acidic, and even when the same amount of iron ions are precipitated, a pH change of the solution including ferric ions may be reduced, as compared to the solution including only ferrous ions. When the pH increases, some of the ferric ions may be coupled to the hydroxide ions, and when the pH decreases, the hydroxide ions may be separated and neutralized, so the solution including the ferric ions may act as a pH buffer by slowing down the pH change even without a separate pH buffer, such that electroplating efficiency may be maintained at a constant level in the continuous electroplating process.

[0063] Therefore, by using amino acids as a complexing agent, sludge may be prevented, and not only ferrous ions but also ferrous ions may be used as plating raw materials, and when ferrous ions and ferrous ions may be mixed and used, the pH change of the solution may be slowed down, and accumulation of ferrous ions may be easily prevented, such that the electroplating efficiency and plating quality may be maintained at a constant level in the continuous electroplating process.

[0064] Meanwhile, the complexing agent may be added in an amount such that a molar concentration ratio of the iron ions and the complexing agent is 1:0.05 to 2.0, and is more preferably added in an amount such that the ratio is 1:0.5 to 1.0. When it is less than 0.05, the ferric ion included in excess cannot be suppressed from combining with hydroxide ion or oxygen to form sludge, and even when the ferric irons are not included, the plating efficiency may be greatly reduced, and furthermore, burning may be induced, resulting in poor plating quality. On the other hand, even when it exceeds 2.0, a sludge suppression effect and plating quality may be maintained, but overvoltage may increase, reducing plating efficiency, and since amino acids, which may be relatively expensive, as compared to raw materials including iron ions such as iron sulfate, may be unnecessarily excessively included, the raw material cost may increase, which may not be economical.

[0065] The complexing agent may be at least one selected from the amino acids or the amino acid polymers, and for example, may be at least one selected from alanine, glycine, serine, threonine, arginine, glutamine, glutamic acid, and glycylglycine.

[0066] When the amino acid is used as the complexing agent, and electroplating is performed at a current density of 3 to 120 A/dm^2 while maintaining a solution temperature at 80°C or lower and pH at 2.0 to 5.0, the Fe plating layer having high plating efficiency and a high oxygen concentration may be obtained.

[0067] A temperature of the Fe electroplating solution may not significantly affect quality of the Fe plating layer, but when it exceeds 80°C, evaporation of the solution becomes severe, such that a concentration of the solution may continuously change, making uniform electroplating difficult.

[0068] When a pH of the Fe electroplating solution is less than 2.0, electroplating efficiency may decrease, making it unsuitable for a continuous plating process, and when the pH exceeds 5.0, the plating efficiency increases, but sludge may be generated during continuous electroplating in which iron hydroxide is precipitated, causing problems such as pipe clogging and contamination of rolls and equipment.

[0069] When a current density is less than 3 A/dm^2, plating overvoltage of the negative electrode may decrease, which reduces Fe electroplating efficiency, making it unsuitable for a continuous plating process. When it exceeds 120 A/dm^2, burning may occur on the plating surface, making the electroplating layer uneven and causing problems in that the Fe plating layer easily peels off.

[0070] As described above, the present disclosure may comprise 5 to 50 wt% of oxygen in the Fe plating layer. The reason for incorporation of oxygen into the Fe plating layer may be as follows. In a process of precipitating iron on the surface of the steel sheet to which the negative electrode is applied, hydrogen ions may be simultaneously reduced to hydrogen gas, thereby increasing the pH. Therefore, both ferrous and ferric ions temporarily may be coupled to OH-ions, and may be incorporated together when the Fe plating layer is formed. When anionic complexing agents such as acetic acid, lactic acid, citric acid, EDTA, or the like, are used, the iron ions coupled to the OH- ions of the complexing agent may comprise an average negative charge, and when the negative electrode is applied for electroplating, an electrical repulsion may occur, which suppresses incorporation into the Fe plating layer. On the other hand, amino acids may be electrically neutral at pH 2.0 to 5.0, and become cations in strong acids with pH lower than 2.0. Even when 1 to 2 OH- ions are coupled to the iron ions coupled to the amino acids, they become cations, so an electrical attraction may be generated with the negative electrode performing electroplating, causing a large amount of oxygen to be incorporated. Therefore, when an amino acid is used as a complexing agent such that a molar concentration ratio of iron ions and amino acids may be 1:0.05 to 1:2.0 and the pH may be maintained at 2.0 to 5.0, Fe electroplating may be performed, thereby obtaining an Fe plating layer having high plating efficiency, suppressing occurrence of sludge, and including 5 to 50 wt% of oxygen.

[0071] Next, the base steel sheet on which the Fe plating layer is formed may be annealed.

[0072] The annealing may be performed by maintaining a dew point temperature at +10°C or lower and 600 to 950°C for 1 to 1000 seconds.

[0073] When the dew point temperature exceeds +10°C during the annealing heat treatment, there may be a risk that the base steel sheet itself is oxidized. However, since there may be a problem that plating performance deteriorates when the dew point temperature is excessively low, a lower limit of the dew point temperature may be set to -50°C in consideration thereof, and preferably -10°C.

[0074] The annealing may be performed in a temperature range of 600 to 950°C. When the heat treatment temperature is less than 600°C, it may be difficult for the rolled structure created by cold-rolling to recover and recrystallize, and it may be difficult to secure sufficient tensile properties, while when it exceeds 950°C, excessive decarburization may occur, resulting in poor fatigue properties, and a large amount of B oxide may be formed, which may reduce plating adhesion during plating, and may cause deterioration of the sintering equipment, which may lead to frequent equipment replacement, which may increase process costs.

[0075] In addition, an annealing time may be 1 to 1000 seconds. When the annealing time is less than 1 second, it may be difficult to secure an annealing effect, and when it exceeds 1000 seconds, a production line may be reduced.

[0076] Meanwhile, during heating for the annealing heat treatment, moist nitrogen may be injected during the heating section, preferably when the temperature is raised to 700°C or higher. This may be to induce internal oxidation of oxidizing elements, and moist nitrogen may be injected at a flow rate of 50 to 200 Nm^3/h (meanwhile, an amount of moisture within the 50 to 200 Nm^3/h moist nitrogen range may be calculated as 5 to 40 L/h). When an amount of moist nitrogen is less than 50 Nm^3/h, since a dew point rising effect may be insufficient, formation of the internal oxidation layer may be weak, and when it exceeds 200 Nm^3/h, the dew point exceeds +10°C and becomes excessively high, causing a problem in which the base iron itself is oxidized.

[0077] After the annealing, the annealed steel sheet may be cooled. Since cooling conditions in the cooling after the annealing may not significantly affect surface quality of a final product, i.e., plating quality, there may be no need to specifically limit the cooling conditions in the present disclosure. However, to prevent oxidation of iron components during the cooling process, an atmosphere that may be reducing at least for iron may be applied.

[0078] Additional plating may be performed on the manufactured steel sheet. The plating is not particularly limited, and for example, the annealed steel sheet may be immersed in a hot-dip galvanizing bath or a hot-dip aluminum plating bath to form a hot-dip plating layer or an alloyed hot-dip plating layer. The hot-dip plating layer may be a hot-dip aluminum plating layer, a hot-dip Al-Si plating layer, a hot-dip Al-Si-Mg plating layer, a hot-dip galvanizing layer, a hot-dip Zn-Mg plating layer, or the like, and the alloyed hot-dip plating layer may be an alloyed hot-dip aluminum plating layer, an alloyed hot-dip Al-Si plating layer, an alloyed hot-dip Al-Si-Mg plating layer, an alloyed hot-dip galvanizing layer, an alloyed hot-dip Zn-Mg plating layer, or the like.

[0079] The plating layer may also comprise Mn, Cr, Cu, Mo, Ni, Sb, Sn, Ti, Ca, Sr, Mg, or the like. An adhesion amount of the plating layer is not particularly limited, and for example, an adhesion amount within a general range may be used. As with the steel sheet, a plating layer or an alloyed plating layer may be provided on a steel member after heat treatment.

Mode for Invention

[0080] Hereinafter, embodiments of the present disclosure will be described. It may be obvious that various modifications may be made to the following embodiments by those skilled in the art without departing from the scope of the present disclosure. The following embodiments may be intended to help understand the present disclosure, and the scope of the rights of the present disclosure should not be limited to the following embodiments, but should be determined by the claims described below as well as their equivalents.

(Examples)

[0081] After preparing a cold-rolled steel sheet comprising C: 0.22%, Si: 0.28%, Al: 0.036%, Mn: 1.2%, P: 0.009%, S: 0.0006%, N: 0.0039%, B: 0.0031%, Ti: 0.03%, Cr: 0.21%, the remainder including Fe, and inevitable impurities, an Fe plating layer was formed in an Fe adhesion amount of Table 1 below, and annealing was performed under dew point and temperature conditions of Table 1 below. Meanwhile, after the annealing, the cold-rolled steel sheet was immersed in an Al plating bath including 9 wt% Si to perform aluminum plating.

[0082] The Fe plating layer was formed by immersing the cold-rolled steel sheet in an Fe plating solution and applying a current density of 20 A/dm^2 to perform Fe electroplating, and an adhesion amount was controlled by controlling a plating time. (In this case, a temperature of the solution was maintained at 50°C.) The plating time according to a target adhesion amount was calculated by calculating an electroplating adhesion amount and plating efficiency by measuring dissolution of the Fe plating layer and a total amount of Fe with a 5 to 10 wt% hydrochloric acid solution after performing Fe electroplating using a copper plate in advance, and was based thereon.

[0083] For a steel sheet manufactured as described above, a glow discharge optical emission spectrometer (GDS) analysis was performed to measure an amount profile of Mn and Si from a surface of the steel sheet in a depth direction, and GDS profiles of Comparative Example 1 and Invention Example 6 were illustrated in FIGS. 1 and 2 below.

[0084] The GDS analysis of the present disclosure used LECO's GDS850A equipment, and measured from the surface to 2 μm in the depth direction at intervals of 0.01 to 0.03 μm in an RF mode.

[0085] In the GDS analysis results analyzed for each of the steel sheets, the number of valleys where an amount of each element was 60% or less of a parent material amount from the surface to 1 μm in a thickness direction was referred to as A, and an amount of the deepest valley was referred to as B (unit: wt%), and were illustrated in Table 1 below. The valley does not mean the lowest point in the GDS, but means tendency observed in the profile. In FIG. 1, the number of valleys in Comparative Example 1 for Mn was observed to be 1, and the number of valleys in Inventive Example 6 for Mn was observed to be 2, and in FIG. 2, the number of valleys in Comparative Example 1 for Si was observed to be zero, but the number of valleys in Inventive Example 6 for Si was observed to be 1.

[0086] Meanwhile, plating properties for each of the steel sheets were evaluated, and results therefrom were illustrated together in Table 1 below. The plating properties were evaluated by plating adhesion. This was evaluated using a structural adhesive SA-1607E from Bogwangsa. First, the adhesive was applied as a rectangular solid shape measuring 10x50x10 mm^3 in width x length x height using a Teflon jig on a plated steel sheet measuring 30x80 mm^2, and then baked at a sintering temperature of 170°C for 20 minutes. After baking was completed, the adhesive was stored at room temperature for a day, and then the steel sheet was bent 90° to forcibly separate the adhesive and the plated steel sheet. When peeling occurred in the adhesive, it was judged as normal, and when separation occurred between the plating layer and the adhesive, it was judged as peeled. Specifically, when a peeled area was 3 mm or more in diameter, it was judged as peeled, and when peeling occurred in a very small area of 3 mm or less in diameter, it was re-examined and reevaluated. Samples that peeled more than three times out of five tests were marked as 'X,' 2 or fewer times, 1 or more times, and no peeling were marked as '○.'

[Table 1]

No.	Fe Adhesion Amount (mg/m^2)	Anneal Temp. (° C)	Anneal Furnace Dew Point (°C)	Plating	Mn		Si		Example
					A (no.)	B (wt%)	A (no.)	B (wt%)	
1	0	781	-50	X	1	0.635	0	-	Comparative Ex. 1
2	500	785	-49	X	1	0.523	0	-	Comparative Ex. 2
3	1000	754	-45	○	2	0.559	0	-	Inventive Ex. 1
4	1500	783	-41	○	2	0.579	0	-	Inventive Ex. 2
5	2000	782	-45	○	2	0.532	0	-	Inventive Ex. 3
6	0	782	5	Δ	1	0.600	0	-	Comparative Ex. 3
7	500	781	4	Δ	1	0.622	0	-	Comparative Ex. 4
8	1000	780	3	○	1	0.665	1	0.163	Inventive Ex. 4
9	1500	788	6	○	1	0.639	1	0.079	Inventive Ex. 5
10	2000	780	7	○	2	0.460	1	0.064	Inventive Ex. 6
11	3000	789	-49	○	2	0.517	0	-	Inventive Ex. 7
12	3500	-	-	No annealing and plating due to peeling of Fe plating layer					Comparative Ex. 5
13	4000	-	-	No annealing and plating due to peeling of Fe plating layer					Comparative Ex. 6
14	3000	777	6	○	2	0.249	1	0.044	Inventive Ex. 8

[0087] In Inventive Examples 1 to 4, Fe plating layers were attached at 1000 to 3000 mg/m^2 or less. As results of GDS analysis of annealed and plated materials, two Mn minimum points were formed, which means that a section lacking Mn was formed in an extreme surface layer. Therefore, since a surface Mn oxide was reduced, it was judged that plating adhesion was good. In Inventive examples 5 to 8, Fe plating layers were attached to a steel sheet at 1000 to 3000 mg/m^2 or less, and then annealed while maintaining in an annealing furnace at dew points of 3 to 7°C, and then hot-dip galvanized. An internal oxidation effect due to oxygen included in the Fe plating layer and moisture in the annealing furnace may be weighted, which may dramatically improve plating adhesion.

[0088] In contrast, in Comparative Example 1, annealing and hot-dip aluminum plating were performed on a base iron without forming an Fe plating layer under the same conditions as described above. Based on GDS measurement results therefrom, it was judged that plating performance was poor due to formation of surface oxides, as surface concentrations of Mn and Si were high. In Comparative Example 2, 500 mg/m^2 of Fe plating was attached, but it was insufficient to secure stable plating adhesion.

[0089] In Comparative Example 3, a dew point was raised to 5°C in an annealing furnace, and oxidizing elements were formed as internal oxides to suppress surface concentration, but an effect was insufficient, resulting in poor plating adhesion. In Comparative Example 4, 500 mg/m^2 of Fe plating was attached, before annealing, at a dew point of 4°C, but plating adhesion was only slightly improved, and it was judged that this was because surface suppression levels of Mn and Si were still insufficient.

[0090] In Comparative Examples 5 and 6, 3000 mg/m^2 or more of Fe plating was formed on a steel sheet, but when observing a sample after electroplating, peeling occurred within a plating layer, and dust was thus generated, making subsequent annealing and plating processes impossible.

Claims

1. A steel sheet comprising:

   one or two of Mn and Si in steel,
   wherein, in a glow discharge optical emission spectrometer (GDS) profile in which one or two components of Mn and Si are observed in a depth direction from a surface of the steel sheet, the steel sheet comprises two or more valleys in which amounts of the one or two components of Mn and Si are 60% or less of an amount of a parent material within 1 μm from the surface of the steel sheet.

2. The steel sheet of claim **1,** wherein amounts of the one or two of Mn and Si included in a grain or a grain boundary within 1 μm in the depth direction from the surface are 40% or more of an amount of each of the components in the parent material.

3. The steel sheet of claim **1,** wherein the steel sheet comprises an oxide formed of one or two or more of Mn, Si, Al, Cr, and B is included in a grain boundary within 10 μm from the surface in the depth direction.

4. The steel sheet of claim 1, wherein the steel sheet comprises, by weight, C: 0.02 to 0.6%, Si: 0.001 to 2%, Al: 0.001 to 1%, Mn: 0.1 to 4%, P: 0.05% or less, S: 0.02% or less, Cr: 1% or less, N: 0.02% or less, Ti: 0 to 0.1%, B: 0.0001 to 0.01%, Cu: 0 to 1.00%, Mo: 0 to 1.00%, Cr: 0 to 1.00%, Ni: 0 to 1.00%, V: 0 to 1.00%, Ca: 0 to 0.01%, Nb: 0 to 0.1%, Sn: 0 to 1%, W: 0 to 1%, Sb: 0 to 1%, Mg: 0 to 0.1%, Co: 0 to 1%, As: 0 to 1%, Zr: 0 to 1%, Bi: 0 to 1%, REM: 0 to 0.3%, the remainder Fe, and unavoidable impurities.

5. The steel sheet of any one of claims 1 to 4, wherein the steel sheet comprises a hot-dip galvanized layer or a hot-dip aluminum-plated layer formed on the surface.

6. A method for manufacturing a steel sheet, comprising:

   preparing a base steel sheet comprising one or two of Mn and Si in steel;
   forming an Fe plating layer by performing Fe pre-plating on a surface of the base steel sheet with a thickness of more than 0.5 g/m^2 to 3 g/m^2 or less; and
   annealing the base steel sheet on which the Fe plating layer has been formed, at a temperature of 600 to 950°C in an atmosphere having a dew point temperature of 10°C or less.

7. The method of claim 6, wherein the Fe pre-plating is performed by electroplating.

8. The method of claim 6, wherein a period in time for the annealing is 1 to 1000 seconds.

9. The method of claim 6, wherein moist nitrogen is injected at a flow rate of 50 to 200 Nm^3/h during heating for the annealing.

10. The method of claim 6, wherein the base steel sheet comprises, by weight, C: 0.02 to 0.6%, Si: 0.001 to 2%, Al: 0.001 to 1%, Mn: 0.1 to 4%, P: 0.05% or less, S: 0.02% or less, Cr: 1% or less, N: 0.02% or less, Ti: 0 to 0.1%, B: 0.0001 to 0.01%, Cu: 0 to 1.00%, Mo: 0 to 1.00%, Cr: 0 to 1.00%, Ni: 0 to 1.00%, V: 0 to 1.00%, Ca: 0 to 0.01%, Nb: 0 to 0.1%, Sn: 0 to 1%, W: 0 to 1%, Sb: 0 to 1%, Mg: 0 to 0.1%, Co: 0 to 1%, As: 0 to 1%, Zr: 0 to 1%, Bi: 0 to 1%, REM: 0 to 0.3%, the

remainder Fe, and unavoidable impurities.

11. The method of claim 6, wherein the base steel sheet is manufactured by comprising reheating a steel slab to a temperature range of 1200°C or higher;

hot-rolling at a finish-rolling temperature of Ar3 to 1000°C after the reheating;
coiling at a temperature range more than a martensite start temperature (Ms) to 750°C or less; and
cold-rolling at a cumulative reduction ratio of 30 to 90%.

12. The method of any one of claims 6 to 11, further comprising forming a plating layer by immersing the steel sheet in a hot-dip galvanizing bath or a hot-dip aluminum plating bath after the annealing.

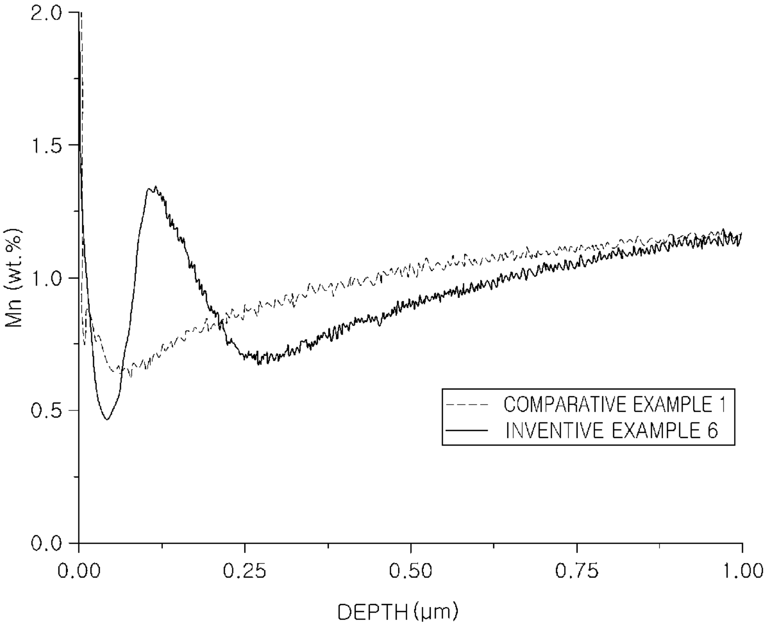
2.0
1.5
1.0
0.5
0.0
Mn (wt.%)
0.00
0.25
0.50
0.75
1.00
DEPTH (μm)
COMPARATIVE EXAMPLE 1
INVENTIVE EXAMPLE 6

FIG. 1

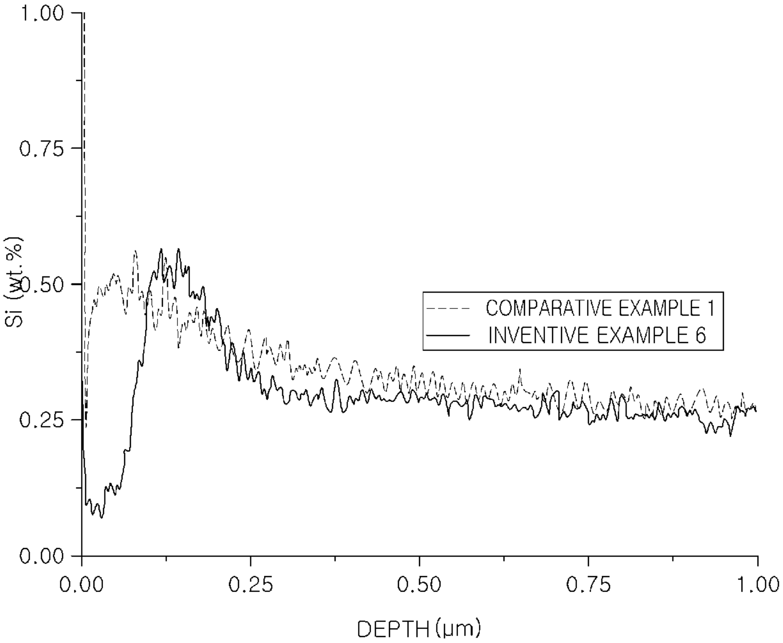
1.00
0.75
0.50
0.25
0.00
Si (wt.%)
0.00
0.25
0.50
0.75
1.00
DEPTH (μm)
COMPARATIVE EXAMPLE 1
INVENTIVE EXAMPLE 6

FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2023/008374

A. CLASSIFICATION OF SUBJECT MATTER

C25D 5/50(2006.01)i; **C25D 3/20**(2006.01)i; **C25D 7/06**(2006.01)i; **C23C 28/00**(2006.01)i; **C23C 28/02**(2006.01)i; **C23C 2/06**(2006.01)i; **C23C 2/40**(2006.01)i; **C22C 38/58**(2006.01)i; **C22C 38/44**(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)

C25D 5/50(2006.01); B05D 3/02(2006.01); B32B 15/18(2006.01); C21D 8/02(2006.01); C21D 9/46(2006.01); C22C 38/58(2006.01); C23C 2/02(2006.01); C23C 2/06(2006.01)

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

Korean utility models and applications for utility models: IPC as above
Japanese utility models and applications for utility models: IPC as above

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

eKOMPASS (KIPO internal) & keywords: 망간(Mn), 규소(Si), 용융아연도금(galvanized), 강판(steel sheet), 소둔(annealing), 산화물(oxide)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	KR 10-1647223 B1 (POSCO) 10 August 2016 (2016-08-10) See paragraphs [0031] and [0112] and claims 1 and 9.	4,10-11
X	US 5447802 A (TOBIYAMA et al.) 05 September 1995 (1995-09-05) See column 7, line 21 - column 8, line 17 and claims 3, 9 and 14.	6-9,12
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A	US 2010-0304183 A1 (HONDA et al.) 02 December 2010 (2010-12-02) See claims 26-27.	1-12

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

* Special categories of cited documents:
- "A" document defining the general state of the art which is not considered to be of particular relevance
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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
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search **20 September 2023**	Date of mailing of the international search report **21 September 2023**
Name and mailing address of the ISA/KR **Korean Intellectual Property Office** **Government Complex-Daejeon Building 4, 189 Cheongsa-ro, Seo-gu, Daejeon 35208** Facsimile No. **+82-42-481-8578**	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 2022)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/KR2023/008374

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