The text describes a method for manufacturing a high manganese steel sheet. The method involves pickling a slab, immersing it into a hot dip galvanizing bath, allowing it to create a plated layer on the surface of the steel sheet. This process is part of the patenting process under the Patent Cooperation Treaty (PCT). The inventors mentioned are Jeon, Il, Young, and Sohn, Il, with the application containing a search report, as indicated by the provided title and abstract.
Description
HIGH MANGANESE COATED STEEL SHEET HAVING HIGH STRENGTH AND DUCTILITY AND MANUFACTURING METHOD THEREOF

Technical Field

[1] The present invention relates to a high manganese galvanized steel sheet having high ductility and strength as well as excellent corrosion resistance and workability, in which high manganese steel containing 15 to 30 wt% manganese (Mn) is plated with zinc (Zn) so as to form a single galvanized layer or a plated layer composed of 5 wt% or less Mn, 5 to 15 wt% iron (Fe), balance Zn, and inevitable impurities introduced from a base metal when plated.

Background Art

[2] In recent years, regulations on automotive emissions become serious due to exhaust and environmental problems of fossil fuel. In this respect, reduction in the weight of an automotive body in order to improve fuel efficiency becomes very important. In order to reduce the weight of the automotive body, a variety of automotive high strength steel sheets have been developed. However, these steel sheets are restricted in workability of parts due to reduction in ductility in connection with the increase in strength.

[3] Many researches have been made in order to notably overcome the shortage of the ductility of this high strength steel. As a result, there has been developed a technique that secures sufficient strength by containing manganese (Mn) at a large amount of 7 wt% to 35 wt%, and that induces twin deformation during plastic deformation of steel to significantly improve the ductility.

[4] However, since Mn is an element having strong ionization tendency, corrosion is rapidly proceeding when a content of Mn is high, as compared to ordinary steel. Thus, anti-corrosion is essentially required. Nevertheless, there has not yet been developed a technique on galvanizing and/or galvannealing for preventing corrosion of the steel sheet containing 15 wt% to 30 wt% Mn.

[5] Thus, an embodiment of the present invention is directed to provide a plating method for endowing high manganese steel, a kind of high-quality steel, with corrosion resistance.

Disclosure of Invention
Technical Problem

[6] Embodiments of the present invention provide high manganese steel containing a great deal of Mn through an optimum alloy design, and a galvanizing and/or galvannealing method as a processing technique suitable for the high manganese steel.

Technical Solution

[7] According to an aspect of the present invention, there is provided a high manganese plated steel sheet, which contains, by weight, 0.3% to 0.9% carbon (C), 15% to 30% manganese (Mn), 0.1% to 5.0% aluminum (Al), 0.04% or less nitrogen (N), 0.03% or less sulfur (S), 0.1% or less phosphor (P), one or two or more selected from the group consisting of 1.0% or less chrome (Cr), 1.0% or less molybdenum (Mo), 0.5% or less copper (Cu), 5.0% or less silicon (S), 0.0005% to 0.04% boron (B), 2.0% or less nickel (M), 0.5% or less niobium (Nb), 0.5% of less vanadium (V), 0.005% to 0.1% antimony (Sb), 0.001% to 0.3% titanium (Ti), 0.0005% to 0.04% lanthanum (La), 0.0005% to 0.04% cesium (Ce), 0.005% to 0.10% zirconium (Zr), and 0.0005% to 0.030% calcium (Ca), inevitable impurities, and balance iron (Fe). An oxide film of Zn alone or Zn-Fe-Mn composite may be formed on a surface of the steel sheet. Particularly, the oxide film of Zn-Fe-Mn composite contains, by weight, 5% or less Mn, and 5% to 15% Fe, inevitable impurities, and balance Zn on a basis of the oxide film.

[8] According to another aspect of the present invention, there is provided a method of manufacturing a high manganese plated steel sheet. The method includes: a heating step of heating a continuously cast slab at a temperature of 1050°C to 1300°C, the continuously cast slab containing, by weight, 0.3% to 0.9% carbon (C), 15% to 30% manganese (Mn), 0.1% to 5.0% aluminum (Al), 0.04% or less nitrogen (N), 0.03% or less sulfur (S), 0.1% or less phosphor (P), one or two or more selected from the group consisting of 1.0% or less chrome (Cr), 1.0% or less molybdenum (Mo), 0.5% or less copper (Cu), 5.0% or less silicon (S), 0.0005% to 0.04% boron (B), 2.0% or less nickel (M), 0.5% or less niobium (Nb), 0.5% of less vanadium (V), 0.005% to 0.1% antimony (Sb), 0.001% to 0.3% titanium (Ti), 0.0005% to 0.04% lanthanum (La), 0.0005% to 0.04% cesium (Ce), 0.005% to 0.10% zirconium (Zr), and 0.0005% to 0.030% calcium (Ca), inevitable impurities, and balance iron (Fe); a finish hot rolling step of performing finish hot rolling on the slab at a temperature of 850°C to 950°C; a hot rolling and coiling step of performing hot rolling and coiling on the slab at a temperature of 750°C or less; a pickling step of pickling the slab in a hydrochloric acid (HCl) solution having a concentration of 5% to 25% for 20 seconds or more; a cold
rolled steps; an annealing step of annealing the slab at a recrystallization temperature of 600°C or higher; and a plating step of immersing the slab into a hot dip galvanizing bath so as to create a plated layer on a surface of the steel sheet. In addition to these steps, the method may further include a galvannealing step so as to introduce Mn, Fe, etc. of base metal into the plated layer to form a stable composite oxide plated layer, thereby providing the high manganese plated steel sheet having high strength and toughness and improving corrosion resistance.

Advantageous Effects

According to embodiments of the present invention, the high manganese plated steel sheet has Zn-Fe-Mn composite hot-dip galvanized layer that secures high ductility and strength and that has corrosion resistance better than existing hot-dip galvanized steel.

Best Mode for Carrying out the Invention

Exemplary embodiments of the present invention provide a high manganese galvanized steel sheet having high ductility and strength as well as excellent corrosion resistance and workability, in which high manganese steel containing 15 to 30 wt% of manganese (Mn) is plated with zinc (Zn) so as to form a single galvanized layer or a galvannealed layer composed of 5 wt% or less Mn, 5 to 15 wt% iron (Fe), balance Zn, and inevitable impurities introduced from a base metal during plating, and a method of manufacturing the same.

Hereinafter, the composition of a high manganese galvanized steel sheet according to an exemplary embodiment of the present invention will be described in detail (on the basis of weight).

Carbon (C): 0.3% to 0.9%

Since C contributes to stabilization of an austenite phase, it is favorable to increase an added amount of C. However, when the added amount of C is less than 0.3%, austenite stability is not maintained, and thus the fraction of a ferrite phase or an ε-martensite phase other than the austenite phase is increased. In contrast, when the added amount of C exceeds 0.9%, the austenite stability is greatly increased, and thus workability is reduced by transition of a deformation behavior caused by slip deformation. Thus, the added amount of C is limited to a range of 0.3% to 0.9%.

Manganese (Mn): 15% to 30%
Mn is an essential element that stabilizes an austenite phase as well as an important element that serves as a source that supplies Mn from a base metal to a plated layer in a galvannealing process during plating, and is added to a level of 15% to 30% for high manganese steel to which an embodiment of the present invention is applied. When Mn is added at an amount less than 15%, the fraction of a ferrite phase or an ε-martensite phase other than the austenite phase is increased. In contrast, when Mn is added at an amount exceeding 30%, high-temperature oxidation sharply occurs in a reheating process for hot rolling due to a high content of Mn, and thus deteriorates a quality of surface of a final product. Further, since a great deal of expensive Mn is added to increase production costs of the steel sheet, the added amount of Mn has an upper limit of 30%.

Aluminum (Al): 0.1% to 5.0%

AI is typically added for deoxidation of steel, but for improvement of ductility in an embodiment of the present invention. In detail, Al is an element for stabilizing a ferrite phase, but increases stacking fault energy in a slip plane, thereby inhibiting creation of an ε-martensite phase to improve the ductility. In addition, when the added amount of Mn is low, Al inhibits the creation of the ε-martensite phase. As such, Al goes far toward minimizing the added amount of Mn and improving formability. Thus, when the added amount of Al is less than 0.1%, the ε-martensite phase is created, thereby increasing strength but sharply decreasing ductility. For this reason, Al is added at an amount of 0.1% or more. In contrast, when the added amount of Al is more than 5.0%, creation of twins is inhibited to reduce ductility and continuous castability, and surface oxidation becomes serious to deteriorate the surface quality of a product when hot rolling. Thus, the added amount of Al has an upper limit of 5.0%.

Silicon (Si): 5.0% or less

S is typically known that, when added excessively, S forms a S oxide layer on a surface of steel to degrade hot dip coating characteristics. However, in the case of Mn-enriched steel, when S is added at an appropriate amount, the S oxide layer is formed on the surface of the steel to inhibit oxidation in air. Thus, after cold-rolled, the steel sheet can be prevented from forming a thick Mn oxide layer. After annealed, the cold rolled steel sheet can be prevented from corrosion, and thus the surface quality of the cold rolled steel sheet, particularly the base steel sheet, can be improved. Since the thick Mn oxide layer is inhibited from being formed when hot dip coating is carried
out, the hot dip coating characteristics are greatly improved. In addition, physical properties of material, for instance tensile strength and elongation, are increased. In other words, when S is not added, the thick Mn oxide layer is formed on the surface of the steel sheet, and thus the steel sheet is easily subjected to corrosion. As such, when the steel sheet is plated, the thick Mn oxide layer exerts an adverse influence on the surface quality of the steel sheet. However, when S is excessively added, S oxide is formed on the surface of the steel sheet when the steel sheet is subjected to hot rolling, and thus lowers pickling characteristics. As a result, the surface quality of the hot rolled steel sheet is lowered. When the steel sheet is subjected to high-temperature annealing in a continuous annealing process and a continuous hot dip coating process, S is segregated to the surface of the steel sheet. Thus, when the hot dip coating is carried out, the segregation of S reduces wettability of melted Zn with respect to the surface of the steel sheet. For this reason, Zn coatability and weldability of steel can be greatly reduced. Accordingly, the added amount of S has an upper limit of 5.0%. Of course, since S has a content of 0.04% or more in the steel, a desired purpose can be accomplished without separately adding S in an embodiment of the present invention.

[25]  
[26] **Chrome (Cr): 1.0% or less**  
[27] Like S, Cr has an effect of forming a passivation film in air to inhibit corrosion. In detail, Cr prevents decarburization of the steel, thereby inhibiting creation of an α-martensite phase from the surface of the steel sheet to improve formability of steel. However, when an added amount of Cr, a ferrite stabilizing element, is increased, the creation of the α-martensite phase is accelerated to reduce ductility of steel. For this reason, the added amount of Cr has an upper limit of 1.0%.

[28]  
[29] **Copper (Cu): 0.5% or less**  
[30] Cu is a component added to increase corrosion resistance and strength. When an added amount of Cu exceeds 0.5%, red brittleness occurs to damage hot workability. Thus, the added amount of Cu is preferably limited to 0.5% or less.

[31]  
[32] **Nickel (Ni): 2.0% or less**  
[33] M increases stability of an austenite phase to inhibit creation of an α'-martensite phase damaging formability, and thus is favorable in terms of improving workability of steel. However, when an added amount of M is increased, internal oxidation sharply occurs along grain boundaries, leading to causing cracks during hot rolling. Further, M
is expensive. Thus, the added amount of M is limited to 2.0% or less.

[34] Molybdenum (Mo): 1.0% or less

Mo is an element added to improve secondary working embbrittlement resistance and platability. However, when an added amount of Mo exceeds 1.0%, Mo reduces the improving effect and is made economically unfavorable. Thus, the added amount of Mo is limited to 1.0% or less.

[37] Niobium (Nb) and Vanadium (V): 0.5% or less

Nb and/or V are components added to increase strength. When an added amount of Nb is more than 0.5%, Nb causes cracks during hot working. When an added amount of V is more than 0.5%, V creates a low-melting-point compound to damage hot workability. Thus, the added amounts of Nb and V are each limited to 0.5% or less.

[41] Nitrogen (N): 0.04% or less

N precipitates fine nitride in austenite grains in reaction with Al in the solidification process, thereby facilitating generating twins to improve strength and ductility when the steel sheet is formed. When an added amount of N exceeds 0.04%, the nitride is excessively precipitated to reduce hot workability and elongation. Thus, the added amount of N is limited to 0.04% or less.

[44] Sulfur (S): 0.03% or less

S is an element that is inevitably added on manufacturing steel. Thus, an added amount of S is limited to 0.03% or less. Particularly, S forms coarse Mn sulfide (MnS) to generate defects such as flange cracks, and reduces stretch flangability (hole expandability). Thus, the added amount of S is preferably limited to 0.03% or less.

[47] Phosphor (P): 0.1% or less

P has a significant role in improving pickling characteristics of a hot rolled steel sheet. P is an element that causes interfacial precipitation, and forms scales and chemically unstable Fe-P compounds precipitated on interfaces of the steel sheet to facilitate removal of the scales when pickling is carried out. As a content of P increases, a superficial shape becomes uniform, and the pickling characteristics are improved. However, when the content of P is too high, castability is deteriorated, and red brittleness occurs during hot rolling. Thus, the added amount of P is preferably
limited to 0.1% or less.

[49] **Boron (B): 0.0005% to 0.04%**

B is resolved in columnar grain boundaries at a temperature of 1000°C or more, and thus inhibits creation and movement of vacancies to strengthen the columnar grain boundaries. However, when an added amount of B is less than 0.0005%, B has little effect. When the added amount of B exceeds 0.04%, B creates a large quantity of carbide and nitride to act as a nucleus for precipitation of Al nitride, thereby promoting the precipitation of coarse Al nitride to embrittle the grain boundaries. Thus, the proper added amount of B ranges from 0.0005% to 0.040%.

[52] **Titanium (Ti): 0.001% to 0.3%**

Ti is an element that is effective for an increase in strength of steel and grain refinement. When a content of Ti is less than 0.001%, it is difficult to obtain this effect. In contrast, when the content of Ti exceeds 0.3%, manufacturing costs are increased, and ductility of ferrite can be reduced due to excessive precipitates. Thus, the content of Ti is preferably limited to a range from 0.001% to 0.3%.

[55] **Zirconium (Zr): 0.005% to 0.10%**

Zr is resolved in columnar grain boundaries, thereby increasing a melting temperature of an Al-enriched low-melting-point compound to prevent a liquid phase film from being formed at a temperature of 1300°C. Further, Zr has high affinity for nitrogen (N) to act as a nucleus for precipitation of coarse Al nitride that is attributable to embrittlement of the columnar grain boundaries, thereby strengthening the columnar grain boundaries. However, when an added amount of Zr is less than 0.005%, these effects are insignificant. In contrast, when the added amount of Zr exceeds 0.10%, Zr is segregated in the grain boundaries, thereby causing embrittlement of the grain boundaries. Thus, the added amount of Zr is limited to a range from 0.005% to 0.10%.

[58] **Lanthanum (La) and Cesium (Cs): 0.0005% to 0.04%**

La and Ce are rare earth elements that serve to create a nucleus of a dendrite structure when molten steel is solidified, thereby refining a dendrite to inhibit growth of a columnar grain structure and facilitate creation of an equiaxed grain structure. Thus, La and CE reduces size and amount of columnar grains attributable to grain boundary embrittlement, and increases an amount of equiaxed grains having excellent
high-temperature ductility to improve hot workability. Further, La and Ce form compounds with P and S which are segregated in the grain boundaries to reduce rupture strength of a grain boundary, thereby reducing adverse influence of P and S. However, when added amounts of La and Ce are less than 0.0005%, this effect is insignificant. When the added amounts of La and Ce exceed 0.040%, La and Ce are saturated. Thus, the added amounts of La and Ce are preferably limited to a range from 0.0005% to 0.040%.

[61]

**Calcium (Ca): 0.0005% to 0.030%**

Ca forms compounds with non-metallic inclusions such as Al$_2$O$_3$, MnO, MnS, etc. in molten steel to spheroidize the non-metallic inclusions, thereby increasing rupture strength of a columnar grain boundary, releasing sensitivity of generating flange cracks from the steel sheet, and increasing stretch flangibility (hole expandability) of the steel sheet. However, when an added amount of Ca exceeds 0.030%, Ca is saturated. Thus, the added amount of Ca is limited to a range from 0.0005% to 0.030%.

[62]

**Antimony (Sb): 0.005% to 0.1%**

Sb contributes to inhibition of growth of various sub-scales generated in a hot-rolling process. Alloy elements such as S, Mn, Al, etc. show a selective oxidation behavior along an interface of the surface of the hot-rolled steel sheet, whereas Sb is segregated at the interfaces or the surface of the steel sheet without oxidation in a hot-rolling process, thereby effectively inhibiting growth of sub-scales. However, when Sb is excessively added, an amount of Sb precipitated from the interfaces is increased, and there is a possibility of the interfaces being mechanically weakened. When an added amount of Sb is less than 0.005%, it is difficult to produce a desired effect. In contrast, when Sb exceeds 0.1%, there is a possibility of causing working embrittlement of material. Thus, the added amount of Sb is limited to a range from 0.005% to 0.1%.

[63]

Now, the reason why a method of manufacturing the steel sheet according to an embodiment of the present invention is controlled will be described in detail.

[64]

Generally, a hot-rolled steel sheet of high manganese steel is manufactured using continuous casting as in the process of manufacturing ordinary steel sheet. Steel melted with the above-mentioned composition is homogenized at a temperature of 1050°C to 1300°C similar to typical conditions, and a homogenized sample is subjected
to finish hot rolling at a temperature of 850°C to 950°C under typical conditions, hot rolling for coiling at a temperature of 650°C or less, and pickling.

[71]

**Heating Temperature of Continuously Cast Slab: 1050°C to 1300°C**

[72] The heating temperature of a continuously cast slab is set to 1300°C as its upper limit. This is because a trace of alloy element strengthening a columnar grain boundary is added to increase the melting point of a low-melting-point compound of the columnar grain boundary up to about 1300°C. When the continuously cast slab is heated at a temperature of 1300°C or more, a liquid phase film is generated from the columnar grain boundary of the continuously cast slab, and thus cracks occur during hot rolling. However, when the heating temperature is too low, a temperature gap up to a finish rolling temperature is narrow to make it impossible to sufficiently carry out the rolling up to a predetermined thickness. Thus, the heating temperature is set to 1050°C as its lower limit.

[73]

**Finish Hot Rolling Temperature: 850°C to 950°C**

[74] A typical finish rolling temperature is about 900°C in a hot rolling process. The steel sheet according to an embodiment of the present invention is subjected to hot rolling at this temperature. When the finish rolling temperature is excessively lowered, a rolling load is increased, which not only overloads a rolling mill but also exerts a bad influence on a quality of the interior of the steel sheet.

[75]

**Hot Rolling and Coiling temperature: 750°C or less**

[76] When a coiling temperature is too high, a thick oxide layer is formed on the surface of the hot rolled steel sheet, and internal oxidation occurs. As such, the oxide layer is not easily removed in a pickling process. Thus, the coiling temperature of the hot rolled steel sheet is preferably low. For this reason, in an embodiment of the present invention, the coiling temperature is limited to 750°C or less that is a sufficiently low temperature.

[77]

**After the hot rolling, the steel sheet is subjected to pickling in a solution of HCl in order to remove oxidized scales formed on the surface thereof. If necessary, the steel sheet is subjected to cold rolling in order to adjust shape and thickness thereof. The pickling is preferably carried out at HCl concentration of 5% to 25% within a range from 60°C to 90°C for 20 seconds or more.**
Continuous Annealing Temperature: 600 °C or more

When an annealing temperature is too low, it is difficult to secure sufficient workability, and transformation into austenite is not enough to maintain an austenite phase at a low temperature. As such, the annealing temperature is limited to 600°C or more. Since the high manganese steel according to an embodiment of the present invention is austenite steel free of phase transformation, workability can be sufficiently secured when the steel is heated at a recrystallization temperature or more. As such, the annealing is carried out under typical annealing conditions.

In order to plate the steel sheet undergoing recrystallization annealing with zinc, the steel sheet is immersed into a hot galvanizing bath, thereby creating a uniform plated layer on the surface thereof.

The hot galvanizing bath is a typical galvanizing bath based on a composition of Zn-Al. In this embodiment, the plating is carried out in a plating bath of Zn-0.013%Al by weight. However, although a trace of third element is added into the plating bath in order to improve the plating process, the plated layer does not undergo a great change in physical properties and corrosion resistance.

Galvannealing Temperature: 440 °C to 580 °C

In order to alloy a plated layer after plating, the steel sheet is subjected to galvannealing at a temperature of 440°C to 580°C, thereby forming a galvannealed layer. At this time, the galvannealed layer is created in such a manner that Mn, Fe or the other components contained in base metal during galvannealing are diffused to react with a plating element of Zn. In this case, a composition of the galvannealed layer includes, by weight, 5% or less Mn, 5% to 15% Fe, balance Zn, and a trace of other impurities introduced in the plating process among constituent elements of steel.

Since the alloy elements introduced into the galvannealed layer are introduced from the base metal, contents of Mn, Fe, etc. of the base metal can be somewhat reduced. However, in comparison with the base metal, the plated layer is thin, and thus an amount of the alloy elements such as Fe introduced into the galvannealed layer is very small on the basis of the base metal. Thus, a basis content of the base metal is not greatly changed due to the alloy elements introduced into the galvannealed layer.
A oxide film formed after annealing. The oxide film consist of Al alone or Mn-Al composite. An average thickness of the oxide film is 500 nm or less. Further, the oxide film is required not to continuously formed 10\(\mu\text{m}\) (micrometer) or more when its thickness is 50nm or more.

Now, the high manganese galvanized steel sheet according to Examples of the present invention will be described in detail.

**Examples**

A steel slab was prepared with composition of steel as in Table 1 below. In Table 1, Inventive Examples 1 through 13 were steels corresponding to a component range of the present invention, and Comparative Examples 14 through 18 were steels beyond the component range of the present invention.
<table>
<thead>
<tr>
<th>Type of Steel</th>
<th>Chemical Components (weight %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>IE 1</td>
<td>0.44</td>
</tr>
<tr>
<td>2</td>
<td>0.44</td>
</tr>
<tr>
<td>3</td>
<td>0.5</td>
</tr>
<tr>
<td>4</td>
<td>0.48</td>
</tr>
<tr>
<td>5</td>
<td>0.434</td>
</tr>
<tr>
<td>6</td>
<td>0.56</td>
</tr>
<tr>
<td>7</td>
<td>0.61</td>
</tr>
<tr>
<td>8</td>
<td>0.55</td>
</tr>
<tr>
<td>9</td>
<td>0.58</td>
</tr>
<tr>
<td>10</td>
<td>0.59</td>
</tr>
<tr>
<td>11</td>
<td>0.55</td>
</tr>
<tr>
<td>12</td>
<td>0.31</td>
</tr>
<tr>
<td>13</td>
<td>0.45</td>
</tr>
</tbody>
</table>
The steel slab prepared as in Table 1 was subjected to heating at a temperature of 1200°C, finish rolling at a finish hot rolling temperature of 860°C, coiling and air cooling at a temperature of 750°C, removal of oxide from the surface thereof using a HCl solution, and cold rolling at a rolling reduction of 70%. Thereby, a cold rolled steel sheet was manufactured.

Plating was performed in the following two methods. In the first method, the cold rolled steel sheet was annealed under N\(_2\)-10%H\(_2\) atmosphere at a temperature of 620°C to 880°C, and was immersed into Zn-0.021%Al bath maintained at a temperature of 460°C, thereby forming a zinc plated layer on a surface thereof. In the second method, the cold rolled steel sheet was annealed under N\(_2\)-10%H\(_2\) atmosphere at a temperature of 620°C to 880°C, and was immersed into Zn-0.013%Al bath maintained at a temperature of 460°C, formed a zinc plated layer on a surface thereof, and is subjected to galvannealing at a temperature of 540°C. Thereby, a galvannealed steel sheet was manufactured. As a result, In Inventive Examples 1 through 13, the plated layer free of plating defects was created. However, as in Comparative Examples 14 and 15, when contents of S and Al deviate from the component range of the present invention, non-plating or plating defects such as blisters were shown.

Furthermore, properties and corrosion resistance of the plated layer were evaluated.
with respect to Embodiments and Comparative Examples. The results were shown in Table 2 below.

[HO]

[111] Table 2
<table>
<thead>
<tr>
<th>No.</th>
<th>IE*</th>
<th>52</th>
<th>Good</th>
<th>45</th>
<th>Good</th>
<th>0.9</th>
<th>8.1</th>
<th>○</th>
<th>○</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>55</td>
<td>Good</td>
<td>○</td>
<td>48</td>
<td>Good</td>
<td>1.9</td>
<td>9.1</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>3</td>
<td>56</td>
<td>Good</td>
<td>○</td>
<td>52</td>
<td>Good</td>
<td>3.2</td>
<td>8.8</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>4</td>
<td>54</td>
<td>Good</td>
<td>○</td>
<td>47</td>
<td>Good</td>
<td>3.7</td>
<td>10.7</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>5</td>
<td>59</td>
<td>Good</td>
<td>○</td>
<td>46</td>
<td>Good</td>
<td>2.2</td>
<td>8.8</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>6</td>
<td>52</td>
<td>Good</td>
<td>○</td>
<td>52</td>
<td>Good</td>
<td>1.7</td>
<td>7.5</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>7</td>
<td>49</td>
<td>Good</td>
<td>○</td>
<td>55</td>
<td>Good</td>
<td>1.2</td>
<td>8.9</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>8</td>
<td>55</td>
<td>Good</td>
<td>○</td>
<td>51</td>
<td>Good</td>
<td>1.4</td>
<td>7.8</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>9</td>
<td>54</td>
<td>Good</td>
<td>○</td>
<td>48</td>
<td>Good</td>
<td>2.1</td>
<td>8.8</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>10</td>
<td>55</td>
<td>Good</td>
<td>○</td>
<td>48</td>
<td>Good</td>
<td>1.8</td>
<td>9.5</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>11</td>
<td>56</td>
<td>Good</td>
<td>○</td>
<td>51</td>
<td>Good</td>
<td>2.1</td>
<td>9.9</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>12</td>
<td>53</td>
<td>Good</td>
<td>○</td>
<td>45</td>
<td>Good</td>
<td>4.5</td>
<td>12</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>13</td>
<td>54</td>
<td>Good</td>
<td>○</td>
<td>52</td>
<td>Good</td>
<td>3.5</td>
<td>11</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>CE</td>
<td>14</td>
<td>56</td>
<td>Bad</td>
<td>X</td>
<td>49</td>
<td>Bad</td>
<td>1.1</td>
<td>2.1</td>
<td>○</td>
</tr>
<tr>
<td>15</td>
<td>58</td>
<td>Very Bad</td>
<td>X</td>
<td>51</td>
<td>Very Bad</td>
<td>1.0</td>
<td>1.2</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>16</td>
<td>54</td>
<td>Good</td>
<td>○</td>
<td>48</td>
<td>Good</td>
<td>-</td>
<td>8.9</td>
<td>△</td>
<td>△</td>
</tr>
<tr>
<td>17</td>
<td>56</td>
<td>Good</td>
<td>○</td>
<td>48</td>
<td>Good</td>
<td>-</td>
<td>10</td>
<td>△</td>
<td>△</td>
</tr>
</tbody>
</table>
As seen from Table 2, it was shown that the galvanized steel and the galvannealed steel of Inventive Examples were good in strippability and platability as compared to Comparative Examples, particularly that the galvannealed steel of each Inventive Example which contains the alloy elements diffused from the base metal was very good in corrosion resistance.
Claims

[1] A high manganese plated steel sheet comprising, by weight,
0.3% to 0.9% carbon (C),
15% to 30% manganese (Mn),
0.1% to 5.0% aluminum (Al),
0.04% or less nitrogen (N),
0.03% or less sulfur (S),
0.1% or less phosphor (P),
one or two or more selected from the group consisting of 1.0% or less chrome (Cr), 1.0% or less molybdenum (Mo), 0.5% or less copper (Cu), 5.0% or less silicon (S), 0.0005% to 0.04% boron (B), 2.0% or less nickel (Ni), 0.5% or less niobium (Nb), 0.5% of less vanadium (V), 0.005% to 0.1% antimony (Sb), 0.001% to 0.3% titanium (Ti), 0.0005% to 0.04% lanthanum (La), 0.0005% to 0.04% cesium (Ce), 0.005% to 0.10% zirconium (Zr), and 0.0005% to 0.030% calcium (Ca),
evitable impurities, and
balance iron (Fe),
wherein an oxide film of Al alone or Mn-Al composite is formed on a surface of the steel sheet.

[2] The high manganese plated steel sheet of claim 1, wherein the oxide film of Mn-Al composite comprises, by weight, 5% or less Mn, and 5% to 15% Fe,
evitable impurities, and a balance of Zn on a basis of the oxide film.

[3] The high manganese plated steel sheet of claim 1, wherein the oxide film of Al alone or Mn-Al composite has an average thickness of 500 nm or less.

[4] The high manganese plated steel sheet of claim 3, wherein the oxide film of Al alone or Mn-Al composite is not continuously formed 10/M or more when its thickness is 50nm or more.

[5] A method of manufacturing a high manganese plated steel sheet, the method comprising:
heating a continuously cast slab at a temperature of 1050°C to 1300°C, the continuously cast slab containing, by weight, 0.3% to 0.9% carbon (C), 15% to 30% manganese (Mn), 0.1% to 5.0% aluminum (Al), 0.04% or less nitrogen (N), 0.03% or less sulfur (S), 0.1% or less phosphor (P), one or two or more selected from the group consisting of 1.0% or less chrome (Cr), 1.0% or less
molybdenum (Mo), 0.5% or less copper (Cu), 5.0% or less silicon (S), 0.0005% to 0.04% boron (B), 2.0% or less nickel (M), 0.5% or less niobium (Nb), 0.5% of less vanadium (V), 0.005% to 0.1% antimony (Sb), 0.001% to 0.3% titanium (Ti), 0.0005% to 0.04% lanthanum (La), 0.0005% to 0.04% cesium (Ce), 0.005% to 0.10% zirconium (Zr), and 0.0005% to 0.030% calcium (Ca), inevitable impurities, and balance iron (Fe);
performing finish hot rolling on the slab at a temperature of 850°C to 950°C;
performing hot rolling and coiling on the slab at a temperature of 750°C or less;
pickling the slab in a hydrochloric acid solution having a concentration of 5% to 25% for 20 seconds or more;
annealing the slab at a recrystallization temperature of 600°C; and
immersing the slab into a hot dip galvanizing bath so as to create a plated layer on a surface of the steel sheet.

[6] The method of claim 5, wherein the plating step is performed in a Zn plating bath or a Zn-Al plating bath.

[7] The method of claim 5, further comprising: after the plating, galvannealing the slab at a temperature of 440°C to 580°C to form a galvannealed layer.

[8] The method of claim 7, wherein the galvannealed layer includes, by weight, 5% or less of Mn, and 5% to 15% of Fe, inevitable impurities, and a balance of Zn.
A. CLASSIFICATION OF SUBJECT MATTER

C22C 38/04(2006.01)

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)

IPC C21D 1/76, C21D 7/02, C21D 7/13, C21D 9/46, C22C 38/00, C22C 38/04, C22C 38/06, C22C 38/08, C22C 38/12, C22C 38/14, C22C 38/18, C22C 38/58, C23C 2/02, C23C 2/06, C23C 2/28

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 since 1975

Japanese Utility models and applications for Utility models since 1975

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

eKIPASS(KIPO internal) & keywords high manganese steel, alloying hot dip coating, and similar terms

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>WO 2007-075006 Al(POSCO) 5 July 2007 See the abstract, claims 1-13, tables 1, 2, and example</td>
<td>1-8</td>
</tr>
<tr>
<td>A</td>
<td>US 5647922 A(TAI WOUNG KIM et al) 15 July 1997 See the abstract, and claim 1</td>
<td>1-8</td>
</tr>
<tr>
<td>A</td>
<td>US 5810950 A(TAI WOUNG KIM et al) 22 September 1998 See the abstract, and claim 1</td>
<td>1-8</td>
</tr>
</tbody>
</table>

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
  "E" earlier application or patent but published on or after the international filing date
  "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)
  "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 JANUARY 2009 (20 01 2009)

Date of mailing of the international search report
20 JANUARY 2009 (20.01.2009)

Name and mailing address of the ISA/KR

Korean Intellectual Property Office
Government Complex-Daejeon, 139 Seoonsa-ro, Seogu, Daejeon 302-701, Republic of Korea

Facsimile No 82-42-472-7140

Authorized officer

LEE, SUNG JOON

Telephone No 82-42-481-5530

Form PCT/ISA/210 (second sheet) (July 2008)
<table>
<thead>
<tr>
<th>Patent document cited in search report</th>
<th>Publication date</th>
<th>Patent family member(s)</th>
<th>Publication date</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>KR 10-2007-0067950 A</td>
<td>29.06.2007</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DE 69517376 T2</td>
<td>12.10.2000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EP 0700451 A1</td>
<td>13.03.1996</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EP 0700451 B1</td>
<td>07.06.2000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 08-507107 A</td>
<td>30.07.1996</td>
</tr>
<tr>
<td></td>
<td></td>
<td>KR 9701324 B1</td>
<td>05.02.1997</td>
</tr>
<tr>
<td></td>
<td></td>
<td>wo 95-26423 A1</td>
<td>05.10.1995</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DE 69619653 T2</td>
<td>21.11.2002</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EP 0812365 B1</td>
<td>06.03.2002</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 10-503243 A</td>
<td>24.03.1998</td>
</tr>
<tr>
<td></td>
<td></td>
<td>wo 97-24467 A1</td>
<td>10.07.1998</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CA 2520814 A1</td>
<td>14.10.2004</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CN 1771348 A</td>
<td>10.05.2006</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EP 1634975 A1</td>
<td>15.03.2006</td>
</tr>
<tr>
<td></td>
<td></td>
<td>RU 2005133422 A</td>
<td>27.04.2006</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TW 241360 B</td>
<td>11.10.2005</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TW 241360 A</td>
<td>11.10.2005</td>
</tr>
</tbody>
</table>

Form PCT/ISA/210 (patent family annex) (July 2008)