

DESCRIPTION



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HIGH CORROSION RESISTANCE GALVANNEALED STEEL MATERIAL
HAVING HAIRLINE APPEARANCE

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TECHNICAL FIELD

The present invention relates to a high corrosion
resistance galvanized steel material having a hairline
appearance used for interior materials or exterior
materials of buildings, cars, etc., surface materials of
electrical equipment, etc.

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BACKGROUND ART

As conventional steel materials having a hairline
appearance, stainless steel materials are well known.
That is, as a surface finish of stainless steel
materials, a "hairline finish (HL finish)" is defined in
JIS G 4305 and 4307. A "hairline finish", as defined by
"a finish obtained by polishing by a polishing material
of a suitable particle size to give a continuous polished
grain", means a surface finish where the polished surface
continues long like with hairs.

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FIG. 1 is a view showing an outline of a hairline
finish. The ordinary hairline finish method, as shown in
FIG. 1, comprises rotating at a high speed an endless
paper polishing belt 3 strung between a contact wheel 1
and an idler roll 2 by rotating the contact wheel so as
to polish the surface of a stainless steel material 6
moving from an uncoiler 4 to a coiler 5 by the polishing
belt (for example, see Japanese Patent Publication (A)
No. 1-306162 and Japanese Patent Publication (B) No. 7-
96183). A hairline finished stainless steel material has
corrosion resistance and has a unique surface pattern, so
is being widely used for interior materials or external
materials of buildings where design is stressed, surface
materials of electrical equipment, etc.

However, stainless steel materials are expensive, so



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a new inexpensive steel material taking the place of stainless steel materials, that is, a steel material having a hairline appearance provided with a high corrosion resistance similar to a stainless steel material and suitable for use for building materials or electrical equipment, is desired.

Therefore, the inventors took note of the inexpensive galvanized steel materials with their excellent corrosion resistance similar to stainless steel materials and studied how to give them a hairline finish.

As conventional art for giving a plating layer a hairline finish, art has been proposed for solving the problem of the underlayer of the plating coated layer being exposed, the corrosion resistance becoming poor, and stable good quality materials not being able to be obtained if forming a plating coating layer on the surface of a thin, light-weight magnesium-based member and applying a hairline finish to try to form a hairline pattern on the surface of the plating coated layer.

That is, there is the art of giving a hairline finish to the surface of an Mg-based part on which the dry plating method is used to form a plating coated layer (1) selected from Cu, a Cu alloy, Au, an Au alloy, Al, or an Al alloy and over said plating coated layer (1) the wet plating method is used to form a plating coated layer (2) selected from Cu, Ni, Au, Cr, Zn, Pa, Pt, Rh, Fe, Co, Sn, Cd, Ru, and their alloys (for example, see Japanese Patent Publication (A) No. 2000-219977). However, this art requires that two thick plating coated layers be provided. Further, the dry plating method and wet plating method have to be combined, so this art is difficult to apply as is to a galvanized steel material.

Further, various inventions have been made regarding high corrosion resistance galvanized steel sheets. For example, a Zn-Al-Mg-based alloy plated steel sheet plated using a plating bath comprised of, by mass%, Al: 3 to 17%, Mg: 1 to 5%, and the balance of Zn and a plated

steel sheet plated using a plating bath of this plus Ti and B (for example, see Japanese Patent Publication (A) No. 10-306357) or a Zn-Al-Mg-Si-based alloy plated steel sheet plated having a plating layer including, by mass%,
5 Al: 5 to 8%, Mg: 1 to 10%, Si: 0.01 to 2%, and, if needed, Fe: 1% or less or further Sn: 0.1 to 2% are known (for example, see Japanese Patent Publication (A) No. 2001-355053).

DISCLOSURE OF THE INVENTION

10 The present invention has as its object the provision of a high corrosion resistance galvanized steel material having a hairline appearance which can be used similarly for the same applications as the applications of a stainless steel material having a
15 hairline appearance.

The inventors engaged in in-depth research on giving a hairline finish to a galvanized steel material, which is a material less expensive than a stainless steel material but having a similar corrosion resistance, as a
20 material for taking the place of a stainless steel material having a hairline appearance. As a result, they found that if giving a pure galvanized steel material a hairline finish, since the zinc is soft, the hairlines formed are easily crushed and, further, the hairline
25 finish polishing belt easily becomes clogged at the time of the processing work, so good hairlines could not be obtained and a hairline finish was difficult. Further, the hairline finished galvanized steel material had the problem of formation of white rust on the zinc surface in
30 the atmosphere. If white rust formed, the hairline appearance ended up disappearing and the effect of formation of the hairlines ended up being lost.

Therefore, in the present invention, the inventors took note of high corrosion resistance galvannealing
35 process introducing a hard phase in the plating layer and discovered that if applying a hairline finish to this, a good high corrosion resistance galvanized steel material

having a hairline appearance can be obtained and thereby completed the present invention.

The present invention has as its gist the following:

5 (1) A high corrosion resistance galvanized steel material having a hairline appearance having a plating layer with a plating deposition of 10 to 600 g/m², containing Al: 1 to 60 mass%, Mg: 0.1 to 10 mass%, and a balance of Zn and unavoidable impurities, and having hairlines formed on the surface, said hairlines having a
10 surface roughness Ra of 0.2 to 2.5 μm and a peaks per inch PPI of 50 to 400 in a direction perpendicular to the hairlines, having a surface roughness Ra of 0.1 to 1.2 μm and a peaks per inch PPI of 1 to 100 in the hairline direction, and having a surface roughness Ra in a
15 direction perpendicular to the hairlines of 1.2 times or more the surface roughness Ra in the hairline direction and a PPI in a direction perpendicular to the hairlines of 2.0 times or more the PPI in the hairline direction.

(2) A high corrosion resistance galvanized steel
20 material having a hairline appearance having a plating layer with a plating deposition of 10 to 600 g/m², containing Al: 1 to 60 mass%, Mg: 0.1 to 10 mass%, and a balance of Zn and unavoidable impurities, and having hairlines formed on the surface, said hairlines having a
25 peaks per inch PPI of 50 to 400 in a direction perpendicular to the hairlines, having a peaks per inch PPI of 1 to 100 in the hairline direction, and having a PPI in a direction perpendicular to the hairlines of 2.0 times or more the PPI in the hairline direction.

30 (3) A high corrosion resistance galvanized steel material having a hairline appearance having a plating layer with a plating deposition of 10 to 600 g/m², containing Al: 1 to 60 mass%, Mg: 0.1 to 10 mass%, and a balance of Zn and unavoidable impurities, and having
35 hairlines formed on the surface, said hairlines having a surface roughness Ra of 0.1 to 2.5 μm and a peaks per

inch PPI of 50 to 400 in a direction perpendicular to the hairlines, having a surface roughness Ra of 0.1 to 1.2 μm and a peaks per inch PPI of 1 to 100 in the hairline direction, and having a surface roughness Ra in a direction perpendicular to the hairlines of 1.2 times or more the surface roughness Ra in the hairline direction and a PPI in a direction perpendicular to the hairlines of 2.0 times or more the PPI in the hairline direction.

5 (4) A high corrosion resistance galvanized steel material having a hairline appearance as set forth in any one of (1) to (3), characterized in that the plating layer further contains Si in an amount of 0.001 to 3 mass%.

10 (5) A high corrosion resistance galvanized steel material having a hairline appearance as set forth in any one of (1) to (4), characterized in that the plating layer further contains one or two of Ti in an amount of 0.0001 to 0.1 mass% and B in an amount of 0.0001 to 0.1 mass%.

15 (6) A high corrosion resistance galvanized steel material having a hairline appearance as set forth in any one of (1) to (5), characterized in that plating layer is comprised of a Zn and Al binary eutectic in a volume ratio of 1 to 80 vol% and a Zn, Al, and ZnMg alloy ternary eutectic in a volume ratio of 10 to 90 vol%, with the total of the two being at least 50%.

20 (7) A high corrosion resistance galvanized steel material having a hairline appearance as set forth in any one of (1) to (6), characterized in that plating layer has a chromate treated layer of 1 to 1000 mg/m^2 on its surface.

25 (8) A high corrosion resistance galvanized steel material having a hairline appearance as set forth in any one of (1) to (6), characterized in that plating layer surface has a chromate-free treated layer of 1 to 200 mg/m^2 not containing any chrome on its surface.

30 (9) A high corrosion resistance galvanized steel

material having a hairline appearance as set forth in any one of (1) to (8), characterized by having a transparent resin coating layer of a thickness of 0.5 to 100 μm on its surface.

5 (10) A high corrosion resistance galvanized steel material having a hairline appearance as set forth in any one of (1) to (9), characterized in that the vicinity of the interface between the plating layer surface and chromate-free treated layer not containing any chrome has
10 a layer of a deposit of one or more of Co, Fe, Ni, Pt, and Mn in a metal state or hydroxide state of 0.1 to 10 mg/m^2 and the blackening resistance in a wet environment is excellent.

BRIEF DESCRIPTION OF THE DRAWINGS

15 FIG. 1 is a view showing an outline of a hairline finish.

 FIG. 2 gives views of the structure of a Zn-based alloy plating layer of the present invention, wherein (a) is a micrograph of a Zn-based alloy plating layer of the present invention and (b) is a schematic view of its
20 structure.

 FIG. 3 is a micrograph of the cross-section of the surface of a hairline finished high corrosion resistance galvanized steel material (Zn-11%Al-3Mg-0.2Si plating, plating weight: 90 g/m^2) after #80 emery polishing
25 (magnification: 1000X).

BEST MODE FOR CARRYING OUT THE INVENTION

 Below, the present invention will be explained in detail.

30 As steel materials having a hairline appearance, there are hairline finished stainless steel materials, but stainless steel materials are expensive. Therefore, the inventors focused on the galvanized/galvanized plated steel materials providing a high corrosion
35 resistance like that of stainless steel materials and studied giving galvanized/galvanized steel materials a hairline finish.

If giving a galvanized steel material a hairline finish, the ridges of the hairlines become deformed and the hairlines are crushed, so a good hairline appearance cannot be obtained. There are also parts where the base metal is exposed. Further, the problem arises of clogging of the hairline finishing polishing belt. Further, there is the problem that if leaving the material in the atmosphere after giving it the hairline finish, white rust is formed and the hairline appearance ends up being lost.

A good hairline appearance cannot be obtained in this way probably due to the fact that the galvanized layer has a hardness of about 50 Hv, i.e., is soft. Therefore, the inventors focused on galvanized layers including hard phases and found that if giving these a hairline finish, a good hairline appearance could be obtained. As galvanized layers including hard phases, they learned that a galvanized layer containing Al and Mg which contains Zn and Al binary eutectic and Zn, Al, and ZnMg alloy ternary eutectic hard layers is suitable. The plating layer should be one comprising, as ingredients, by mass%, Al: 1.0 to 60%, Mg: 0.1 to 10%, and the balance of Zn and unavoidable impurities, further selectively including, as needed, Si: 0.001 to 3.0% to improve the corrosion resistance and one or both of Ti: 0.0001 to 0.1% and B: 0.0001 to 0.1% to improve the appearance.

The reasons for limitation of the ingredients of the galvanized layer will be explained next.

Al forms a hard phase Zn/Al binary eutectic and Zn/Al/Zn₂Mg ternary eutectic in the plating layer and acts to improve the corrosion resistance of the plating layer and suppress the formation of dross in the plating bath. If Al is less than 1.0%, the volume fraction of the binary eutectic and ternary eutectic forming the hard phase becomes insufficient, a good hairline appearance cannot be obtained by a hairline finish, and the plated

steel material becomes inferior in corrosion resistance. On the other hand, if Al is over 60%, the plated surface is formed with whisker-shaped relief shapes, a plating layer with a uniform appearance cannot be obtained, the effect of improvement of the corrosion resistance becomes saturated, and simultaneously the sacrificial corrosion action on the base iron is lost so the corrosion resistance of flawed parts deteriorates. Therefore, the Al content was made 1.0 to 60%.

Mg is an ingredient required for forming the ternary eutectic and has the effect of forming corrosion products on the plated surface to improve the corrosion resistance of the plated steel material. If Mg is less than 0.1%, the volume fraction of the ternary eutectic becomes insufficient, a good hairline appearance cannot be obtained by a hairline finish, and the corrosion products required for improving the corrosion resistance cannot be formed. On the other hand, if Mg exceeds 10%, the plating bath proceeds to oxidize due to contact with the air, black oxides (dross) are produced making treatment difficult, and the effect of improvement of the corrosion resistance becomes saturated. Therefore, the Mg content was made 0.1 to 10%.

Si is added as needed to improve the corrosion resistance and improve the plating adhesion. If the amount of addition is less than 0.001%, these effects are not obtained, while if over 3.0%, these effects become saturated and conversely the production of dross increases, so the amount of addition of Si was made 0.001 to 3.0%.

Ti is an ingredient added as needed for forming the nuclei for precipitation of the primary crystal Al phase, increasing the fineness of the structure, and improving the appearance. At least 0.0001% must be added. However, if adding over 0.1%, the solubility in the plating bath is exceeded, Ti-Al-based precipitates grow, the plating layer is formed with relief shapes on its surface, and

the quality of the appearance deteriorates, so Ti was made 0.0001 to 0.1%.

5 B, like Ti, has the effect of improving the plating appearance, but if less than 0.0001%, that effect cannot be obtained, while if over 0.1%, that effect becomes saturated, so B was made 0.0001 to 0.1%.

10 With a plating deposition of less than 10 g/m², the corrosion resistance becomes inferior, so this was made the lower limit, while with one of more than 600 g/m², the uniformity of deposition of the plating layer deteriorates and a dripping appearance results, which is not preferred, and bending or the like easily results in cracks in the plating layer. Therefore, 600 g/m² was made the upper limit.

15 FIG. 2(a) is a micrograph of the structure of a Zn-based alloy plating layer of the present invention, while FIG. 2(b) is a schematic view of the structure.

20 As shown in FIG. 2(b), for example, the Zn-11%Al-3%Mg-0.2%Si high corrosion resistance Zn-based alloy plating layer has, in its cross-sectional structure, a structure of a [Zn/Al/Zn₂Mg] ternary eutectic phase 7 in which a [Zn/Al] binary eutectic phase 8 is mixed and in which a [Zn₂Mg single phase] 9 is present in island shapes.

25 This ternary eutectic phase is comprised of a structure of soft Zn and Al phases in which hard Zn₂Mg is dispersed. The structure as a whole features both consistency and hardness. If giving a hairline finish to plated steel material in which this type of phase is also present at the surface, the plated surface is easily peeled off from the plated surface by the polishing belt, a beautiful hairline appearance is obtained without deformation of the ridges of the hairlines, the polishing belt does not become clogged, and a good hairline appearance is obtained.

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FIG. 3 is a micrograph of the cross-section of the surface of a hairline finished high corrosion resistance

galvannealed steel material (Zn-11%Al-3Mg-0.2Si plating, plating deposition: 90 g/m²) after #80 emery polishing (magnification: 1000X). As shown in FIG. 3, this has a good appearance with no deformation of the hairline grooves.

To give a high corrosion resistance galvannealed steel material a hairline finish to obtain a good hairline appearance, the plating layer is preferably structured with a [Zn/Al] binary eutectic phase in a volume fraction of 1 to 80 vol%, a [Zn/Al/Zn₂Mg] ternary eutectic phase in a volume fraction of 10 to 90 vol%, and the balance of Zn, Zn₂Mg alloy, Mg₂Si, TiAl₃, etc. The [Zn/Al] binary eutectic phase is soft compared with the ternary eutectic phase, but is hard compared with the Zn and Al single phases. Therefore, the smaller the volume fraction, the more improved the hairline finishability. If over 90 vol%, the plating layer as a whole softens and the hairline finishability deteriorates. Making it less than 1 vol% is difficult engineering wise. If the volume fraction of the ternary eutectic becomes small, the hardness and consistency characteristics of the plating layer deteriorate, the appearance at the time of hairline finishing deteriorates, and the scraps easily clog the abrasive material. Therefore, the lower limit of the volume fraction of the ternary eutectic was made 10 vol%. On the other hand, the upper limit is determined by the ease of formation of the Al phase and Zn₂Mg phase in the process of solidification of the plating layer. 90 vol% was the upper limit in engineering production. Further, if the volume fraction of the two eutectic phases combined falls, the overall plating layer falls in hardness and consistency and the hairline appearance becomes poor, so this fraction was made 50% or more.

The thickness of the plating layer suitable for application of a hairline finish is, in terms of plating deposition, 10 to 600 g/m², preferably 100 to 500 g/m². If the plating deposition is less than 10 g/m², since the

plating layer is thin, the corrosion resistance is insufficient and the hairline finishing ends up exposing the underlying steel material. If the plating deposition is over 600 g/m^2 , the plating layer is too thick and a plating layer with a uniform appearance cannot be obtained. Further, the plating layer easily peels off. This is also disadvantageous cost wise. Therefore, the plating deposition was made 10 to 600 g/m^2 .

As the shape of the superior appearance hairlines formed on the plated steel material, in the direction perpendicular to the hairlines (C-direction), the surface roughness should be a surface roughness R_a of 0.2 to $2.5 \mu\text{m}$, preferably 1.2 to $1.8 \mu\text{m}$, and the peaks per inch PPI should be 50 to 400; in the hairline direction (L-direction), the surface roughness should be R_a : 0.1 to $1.2 \mu\text{m}$, preferably 0.5 to $1.0 \mu\text{m}$, and the peaks per inch PPI should be 1 to 100; the R_a in the direction perpendicular to the hairlines (C-direction) should be 1.2 times or more the R_a in the hairline direction (L-direction) ($\text{C-direction } R_a / \text{L-direction } R_a \geq 1.2$); and the PPI in the direction perpendicular to the hairlines (C-direction) should be 2 times or more the PPI in the hairline direction (L-direction) ($\text{C-direction PPI} / \text{L-direction PPI} \geq 2$).

If less than the limit limits of the C-direction and L-direction surface roughnesses R_a , peaks per inch PPI, and ratios prescribed here, the hairlines will no longer stand out and the hairline finish treatment will become wasted. Further, conversely, if more than the upper limits of the C-direction and L-direction surface roughnesses R_a and peaks per inch PPI, the hairlines will become too coarse, beautiful hairlines will not be obtained, the aesthetic design value of the hairlines will be lost, and the product will lose its value.

Therefore, the present invention defines the shape of the hairlines as above by the surface roughnesses,

peaks per inch, and their ratios. Note that the surface roughness Ra was measured in accordance with the method of measurement prescribed in JIS B060 (1997) employing a reference length of 0.8 mm. Further, the peaks per inch
5 PPI were measured in accordance with SAEJ911-1986 using a measured length of 1 inch and a width 2H between positive and negative reference levels of 50 μ inch.

To form hairlines satisfying the requirements of the surface roughnesses, peaks per inch, and their ratios
10 prescribed in the present invention, use of a #60 to #320 or so belt sander (polishing belt) for the hairline finish is preferable.

After application of the hairline finish, the plating layer is preferably treated by chromate treatment
15 or chromate-free treatment for primary rust proofing.

A galvanized steel material is susceptible to white rust, so to prevent this, after the plating layer is given the hairline finish, it is treated by chromate treatment or chromate-free treatment to form a
20 rustproofing coated layer for primary rust proofing.

In the case of chromate treatment, a known chromate treatment, for example, chromate treatment by a chromate treatment solution containing chromic acid and a reaction accelerator as main ingredients can be applied. The
25 amount of chromate deposition is made 1 to 200 mg/m².

If the amount of chromate deposition is less than 1 mg/m², a sufficient rust proofing effect cannot be obtained. Further, if over 200 mg/m², not only does the hairline finish no longer stand out, but also the rust
30 proofing effect will end up becoming saturated and, economically, the cost will rise.

Further, it is also possible to perform primary rust proofing by a known chromate-free treatment (nonchromate treatment) in the same way as a chromate treatment.

35 The chromate-free treatment (nonchromate treatment) uses a treatment solution not containing any environmentally harmful hexavalent chrome in the

solution. For example, there are treatment solutions containing Zr, Ti salts, treatment solutions containing silane coupling agents, etc. Known chromate-free treatment solutions may be used for chromate-free treatment. In such chromate-free treatment, a chromate-free treated layer containing Ti, Zr, P, Ce, Si, Al, Li, and other main ingredients and not containing chromic acid is formed. The amount of deposition is preferably 1 to 1000 mg/m².

If the amount of deposition in the chromate-free treatment is less than 1 mg/m², a sufficient rust preventing effect cannot be obtained. Further, if over 1000 mg/m², not only does the hairline finish no longer stand out, but also the rust preventing effect ends up becoming saturated and, economically, the cost rises.

Further, if giving a galvanized steel material a hairline finish and then leaving it in the atmosphere, the plated surface will oxidize and blacken. If blackening, the hairline finish will no longer stand out and the hairline appearance will be lost. Further, the galvanized layer will be easily damaged upon collision with a hard object. For this reason, if forming a transparent resin coated layer to a thickness of 0.5 to 100 μm on the hairline finished plated surface, the blackening resistance and the defect resistance can be improved. The transparent resin coated layer may be formed using a conventional known organic clear coating and a conventional known coating method. As such organic clear coatings, specifically an acryl-based baked clear coating, urethane-based clear coating, epoxy-based clear coating, polyester-based clear coating, melamine alkyd-based clear coating, etc. may be mentioned. Among these, polyester-based and acryl-based baked clear coatings are preferably used.

As the method of coating an organic clear coating, specifically the roll coater method, curtain coater method, spray can method, electrostatic method, etc. may

be mentioned. Among these, the roll coater method and the curtain coater method are preferable.

To impart blackening resistance, it is possible to give the vicinity of the interface with the chromate and chromate-free treated layer a layer of a deposit of one or more of Co, Fe, Ni, Pt, and Mn in a metal state or hydroxide state of 0.1 to 10 mg/m². This deposited layer should have an amount of deposition of 0.1 to 10 mg/m², preferably 0.5 to 3.0 mg/m². This treatment greatly improves the blackening resistance in a wet environment. If the amount of deposition is less than 0.1 mg/m², the effect of the blackening resistance is not sufficient, while if over 10 mg/m², the corrosion resistance deteriorates, so these are not preferred. The method of imparting this treated layer is not particularly limited, but as examples there are the above salt water solution dipping method or spraying method, the vacuum deposition method, etc. In the dipping method, the hairline finished plated steel sheet is dipped in a 0.1 to 10 g/liter metal salt aqueous solution for 0.5 to 10 seconds, then rinsed.

EXAMPLES

Below, examples will be used to explain the present invention in detail.

Low carbon steel sheets of two different types of thicknesses, that is, sheet thicknesses of 0.8 mm and 1.6 mm, were used as the sheets for plating.

The sheets were plated by heating, annealing, and plating by a continuous hot dip galvanization line of a non-oxidizing furnace type. The annealing atmosphere was made 10% hydrogen and the remaining 90% nitrogen gas. The dew point was made -30°C. The annealing temperature was made 730°C and the annealing time 3 minutes. The plating bath was comprised of, by mass%, Al: 11.0%, Mg: 3.0%, Si: 0.2%, and the balance of Zn and unavoidable impurities, while the plating bath temperature was 450°C. The plating deposition was adjusted by the ordinary nitrogen gas

wiping method.

After the plating, different number belt sanders (size 100 mmx915 mm) were used to give hairline finishes under conditions of a belt speed of about 3.5/seconds and a polishing time of 3 to 4 seconds. After this, the surface roughness (Ra) and peaks per inch (PPI) were investigated.

The results are shown in Table 1.

As shown in Table 1, Nos. 1, 2, and 5 were the high corrosion resistance plated steel materials having a beautiful hairline appearance satisfying the surface roughnesses (Ra), peaks per inch (PPI), and their ratios prescribed in the present invention.

As opposed to this, the #80 bead blasted No. 3 was formed with uniform fine relief over its surface, but the L-direction surface roughness and peaks per inch were small, the ratios of the surface roughness and peaks per inch were also small, and the requirements prescribed in the present invention were not satisfied. The bead blasting and hairline finish were clearly difficult.

No. 4 was given a hairline finish, but the belt sander was a #600 type or too fine and therefore the requirements for hairlines prescribed in the present invention were not satisfied. Hairlines could not be clearly observed in the appearance.

Further, No. 6 and No. 7 are cases with hairline finish given. In these cases, the C-direction surface roughness and peaks per inch were small and the ratios were also small. In these cases as well, naturally no hairlines were observed.

From the above test results, only the plated steel sheets with hairline finishes satisfying the requirements prescribed in the present invention were plated steel sheets with beautiful hairline appearances.

Next, the inventors prepared plated steel sheets with different compositions of plating layers then used a #80 belt sander (size 100 mmx915 mm) to give them a

hairline finish at a belt speed of about 3.5/second and a polishing time of 3 to 4 seconds. The inventors investigated the hairline appearance and state of deposition of scraps at that time.

5 The results are shown in Table 2. Nos. 1 to 17 have the plating compositions prescribed in the present invention and were good in terms of hairline appearance, clogging of sanders by scraps, and corrosion resistance. On the other hand, Nos. 18 to 20 had platings outside the
10 composition prescribed by the present invention. While they had values of surface roughness satisfying the values prescribed in the present invention, the hairline appearance could not be clearly observed and the sheets were poor in terms of scrap production and corrosion
15 resistance. The reason why the hairline appearance could not be clearly observed is believed to be because of the production of scraps and deformation of the polishing marks etc.

 Further, the inventors performed plating while
20 changing the volume fractions of the eutectic phases in the plating layers and investigated the resultant performances. The results are shown in Table 3. Nos. 1 to 5 had the phase structures prescribed in the present invention and were good in all of the hairline
25 appearance, sander scrap clogging, and corrosion resistance. On the other hand, Nos. 6 and 7 had platings outside the phase structure prescribed by the present invention and were inferior in hairline appearance and poor in terms of production of scraps.

30 Further, plated steel sheets having a composition of Zn-11Al-3Mg-0.2Si were used for chromate treatment, chromate-free treatment, clear coating treatment, and blackening resistance treatment. The chromate treatment comprised coating the sheet with a chromic acid 100
35 g/liter solution, then drying it in a 60°C hot air furnace for 30 seconds. The chromate-free treatment comprised coating the sheet with a chemical comprised of zirconium

aluminum carbonate, cobalt nitrate, silica, and ammonium phosphate, then drying in a 60°C hot air furnace for 30 seconds. Further, sheets were coated with a melamine alkyd-based clear coating (solvent-based) and acryl-based clear coating (aqueous dispersion based) and heated until sheet temperatures of 220°C (melamine alkyd-based) and 150°C (acryl-based). The blackening resistance treatment comprised dipping the sheet in a 1 g/liter Ni sulfate aqueous solution for 3 seconds, then rinsing and drying it, then treating it by the chromate-free treatment and coating it by a melamine alkyd-based clear coating. The corrosion resistance of the flat parts was evaluated by the amount of formation of white rust after 240 hours of a JIS Z2331 salt water spray test with "Good" indicating 1% or less formation of white rust and "Poor" indicating 10% or more. The cross-cut parts were evaluated by the blisters after 1000 hours of a salt water spray test with "Good" indicating less than 2 mm and "Poor" 2 mm or more. The blackening resistance was evaluated by allowing a treated steel material to stand in a high humidity tank of a temperature of 60°C and a relative humidity of 85% for seven days and comparing the color difference δE values before and after. The color difference δE was measured in accordance with JIS Z8722. A δE of 1 or less indicated no blackening or a good result (Good), 1 to 2 indicated slight observance or a fair result (Fair), and larger than 2 indicated blackening observed or a poor result (Poor).

Nos. 1 to 46 satisfy the requirements of the blackening resistance treatment, pretreatment, and coating prescribed by the present invention and were excellent in corrosion resistance both at the flat parts and the cross-cut parts. Further, Nos. 23 and 46 treated for blackening resistance were also excellent in blackening resistance. On the other hand, Nos. 47 to 49 were outside the requirements of the present invention

and were poor in corrosion resistance.

Table 1

No.	Conditions	Ra (μm)		PPI	Ra ratio C/L	PPI ratio C/L	Evaluation
1	0.8t HL#150	L	0.65	48.2	2.47	7.10	Good
		C	1.61	342.4			
2	0.8t HL#80	L	0.65	57.0	2.14	3.76	Good
		C	1.39	214.6			
3	0.8t bead blast #80	L	1.36	245.8	1.04	6.94	Poor
		C	1.42	232.0			
4	1.6t HL#600	L	0.08	1.8	1.88	25.0	Fair
		C	0.15	45			
5	1.6t HL#150	L	0.73	55.0	2.21	5.72	Good
		C	1.61	315.2			
6	0.8t no polishing	L	0.93	70.0	0.71	1.21	Poor
		C	0.66	85.8			
7	1.6t no polishing	L	0.56	79.2	0.98	0.92	Poor
		C	79.2	72.8			

(Note) Good: Beautiful hairlines observed.

Fair: Hairlines cannot be clearly observed.

Poor: No hairlines.

Table 2

No.	Plating composition	Ra (μm)		PPI	Ra ratio C/L	PPI ratio C/L	Evaluation of hairline appearance	Evaluation of clogging of sander by scraps	Appearance of corrosion resistant SST after 240 hours	Remarks
1	Zn-1%Al-0.1%Mg	L	0.40	50	3.25	3.20	Good	Good	Good	Inv. mat.
		C	1.30	160						
2	Zn-1%Al-1%Mg	L	0.42	53	3.45	3.11	Good	Good	Good	Inv. mat.
		C	1.45	165						
3	Zn-6%Al-1%Mg	L	0.51	33	2.82	5.30	Good	Good	Good	Inv. mat.
		C	1.44	175						
4	Zn-6%Al-3%Mg	L	0.36	45	4.89	4.09	Good	Good	Good	Inv. mat.
		C	1.76	184						
5	Zn-6%Al-10%Mg	L	0.66	56	2.86	3.39	Good	Good	Good	Inv. mat.
		C	1.89	190						
6	Zn-11%Al-0.1%Mg	L	0.46	52	3.22	3.25	Good	Good	Good	Inv. mat.
		C	1.48	169						
7	Zn-11%Al-2%Mg	L	0.64	49	2.58	7.04	Good	Good	Good	Inv. mat.
		C	1.65	345						
8	Zn-11%Al-3%Mg	L	0.61	63	2.82	5.63	Good	Good	Good	Inv. mat.
		C	1.72	355						
9	Zn-11%Al-5%Mg	L	0.59	69	3.19	4.72	Good	Good	Good	Inv. mat.
		C	1.88	326						
10	Zn-11%Al-10%Mg	L	0.72	71	2.76	4.07	Good	Good	Good	Inv. mat.
		C	1.99	289						
11	Zn-11%Al-3%Mg-0.0001%Ti	L	0.71	56	2.62	5.30	Good	Good	Good	Inv. mat.
		C	1.86	297						
12	Zn-11%Al-3%Mg-0.01%Ti	L	0.79	63	2.48	4.51	Good	Good	Good	Inv. mat.
		C	1.96	284						
13	Zn-11%Al-3%Mg-0.1%Ti	L	0.72	45	2.57	8.13	Good	Good	Good	Inv. mat.
		C	1.85	366						
14	Zn-11%Al-3%Mg-0.0001%B	L	0.56	88	3.55	4.39	Good	Good	Good	Inv. mat.
		C	1.99	386						
15	Zn-11%Al-3%Mg-0.01%B	L	0.54	56	3.43	6.09	Good	Good	Good	Inv. mat.
		C	1.85	341						
16	Zn-11%Al-3%Mg-0.1%B	L	0.55	39	3.25	8.36	Good	Good	Good	Inv. mat.
		C	1.79	326						
17	Zn-11%Al-3%Mg-0.01%Ti-0.01%B	L	0.10	45	22.50	8.13	Good	Good	Good	Inv. mat.
		C	2.25	366						

18	Zn-0.5%Al	L	0.45	56	2.18	1.80	Fair	Poor	Poor	Comp. mat.
		C	0.98	101						
19	Zn-0.5%Al-0.5%Mg	L	0.39	51	2.85	1.90	Fair	Poor	Poor	Comp. mat.
		C	1.11	97						
20	Zn-65%Al-11%Mg	L	1.35	120	1.93	1.80	Fair	Good	Poor	Comp. mat.
		C	2.61	216						

Good: Beautiful hairlines observed
 Fair: Hairlines not clearly observable
 Poor: No hairlines

Good: Scraps not deposited on sander
 Poor: Scraps deposited on sander, polishing drops

Good: White rust slight, change in appearance small
 Poor: White rust remarkable, change in appearance large

Table 3

No.	Plating composition	Zn/Al binary eutectic fraction vol%	Zn/Al/Zn ₂ Mg ternary eutectic fraction vol%	Total of two phases	Evaluation of hairline appearance	Evaluation of clogging of sander by scraps	Remarks
1	Zn-5Al-3Mg	1	49	50	Good	Good	Inv. mat.
2	Zn-7Al-3Mg	10	45	55	Good	Good	Inv. mat.
3	Zn-45Al-2Mg	68	25	93	Good	Good	Inv. mat.
4	Zn-55Al-1.5Mg	80	13	93	Good	Good	Inv. mat.
5	Zn-11Al-3.3Mg	35	56	91	Good	Good	Inv. mat.
6	Zn-6Al-0.05Mg	25	1	26	Poor	Poor	Comp. mat.
7	Zn-0.5Al	0	0	0	Poor	Poor	Comp. mat.

Good: Beautiful hairlines observed
 Fair: Hairlines not clearly observable
 Poor: No hairlines

Good: Scraps not deposited on sander
 Poor: Scraps deposited on sander, polishing drops

Table 4

No.	Plating composition	Blackening resistance treatment	Pretreatment	Amount of deposition mg/m ²	Type of coating	Thickness μm
1	Zn-11Al-3Mg-0.2Si	None	Chromate	10		
2	Zn-11Al-3Mg-0.2Si	None	Chromate	20		
3	Zn-11Al-3Mg-0.2Si	None	Chromate	50		
4	Zn-11Al-3Mg-0.2Si	None	Chromate	200		
5	Zn-11Al-3Mg-0.2Si	None	Chromate	10	Melamine alkyd	0.5
6	Zn-11Al-3Mg-0.2Si	None	Chromate	10	Melamine alkyd	2
7	Zn-11Al-3Mg-0.2Si	None	Chromate	10	Melamine alkyd	3
8	Zn-11Al-3Mg-0.2Si	None	Chromate	10	Melamine alkyd	5
9	Zn-11Al-3Mg-0.2Si	None	Chromate	10	Melamine alkyd	25
10	Zn-11Al-3Mg-0.2Si	None	Chromate	10	Melamine alkyd	100
11	Zn-11Al-3Mg-0.2Si	None	Chromate	10	Polyester	0.5
12	Zn-11Al-3Mg-0.2Si	None	Chromate	10	Polyester	2
13	Zn-11Al-3Mg-0.2Si	None	Chromate	10	Polyester	3
14	Zn-11Al-3Mg-0.2Si	None	Chromate	10	Polyester	5
15	Zn-11Al-3Mg-0.2Si	None	Chromate	10	Polyester	25
16	Zn-11Al-3Mg-0.2Si	None	Chromate	10	Polyester	100
17	Zn-11Al-3Mg-0.2Si	None	Chromate	10	Acryl	0.5
18	Zn-11Al-3Mg-0.2Si	None	Chromate	10	Acryl	2
19	Zn-11Al-3Mg-0.2Si	None	Chromate	10	Acryl	3
20	Zn-11Al-3Mg-0.2Si	None	Chromate	10	Acryl	5
21	Zn-11Al-3Mg-0.2Si	None	Chromate	10	Acryl	25
22	Zn-11Al-3Mg-0.2Si	None	Chromate	10	Acryl	100
23	Zn-11Al-3Mg-0.2Si	Yes	Chromate	10	Acryl	100
24	Zn-11Al-3Mg-0.2Si	None	Chromate-free	10		
25	Zn-11Al-3Mg-0.2Si	None	Chromate-free	20		
26	Zn-11Al-3Mg-0.2Si	None	Chromate-free	50		
27	Zn-11Al-3Mg-0.2Si	None	Chromate-free	1000		
28	Zn-11Al-3Mg-0.2Si	None	Chromate-free	10	Melamine alkyd	0.5
29	Zn-11Al-3Mg-0.2Si	None	Chromate-free	10	Melamine alkyd	2
30	Zn-11Al-3Mg-0.2Si	None	Chromate-free	10	Melamine alkyd	3
31	Zn-11Al-3Mg-0.2Si	None	Chromate-free	10	Melamine alkyd	5
32	Zn-11Al-3Mg-0.2Si	None	Chromate-free	10	Melamine alkyd	25
33	Zn-11Al-3Mg-0.2Si	None	Chromate-free	10	Melamine alkyd	100
34	Zn-11Al-3Mg-0.2Si	None	Chromate-free	10	Polyester	0.5
35	Zn-11Al-3Mg-0.2Si	None	Chromate-free	10	Polyester	2
36	Zn-11Al-3Mg-0.2Si	None	Chromate-free	10	Polyester	3
37	Zn-11Al-3Mg-0.2Si	None	Chromate-free	10	Polyester	5
38	Zn-11Al-3Mg-0.2Si	None	Chromate-free	10	Polyester	25
39	Zn-11Al-3Mg-0.2Si	None	Chromate-free	10	Polyester	100
40	Zn-11Al-3Mg-0.2Si	None	Chromate-free	10	Acryl	0.5
41	Zn-11Al-3Mg-0.2Si	None	Chromate-free	10	Acryl	2
42	Zn-11Al-3Mg-0.2Si	None	Chromate-free	10	Acryl	3
43	Zn-11Al-3Mg-0.2Si	None	Chromate-free	10	Acryl	5
44	Zn-11Al-3Mg-0.2Si	None	Chromate-free	10	Acryl	25
45	Zn-11Al-3Mg-0.2Si	None	Chromate-free	10	Acryl	100
46	Zn-11Al-3Mg-0.2Si	Yes	Chromate-free	10	Acryl	100
47	Zn-11Al-3Mg-0.2Si	None	None		None	
48	Zn-11Al-3Mg-0.2Si	None	Chromate	0.5	None	
49	Zn-11Al-3Mg-0.2Si	None	Chromate	10	Acryl	0.4

Table 4 (continued)

No.	Corrosion resistance		Blackening	Remarks
	Flat parts	Cross-cut parts		
1	Good	Good	Fair	Inv. mat.
2	Good	Good	Fair	Inv. mat.
3	Good	Good	Fair	Inv. mat.
4	Good	Good	Fair	Inv. mat.
5	Good	Good	Fair	Inv. mat.
6	Good	Good	Fair	Inv. mat.
7	Good	Good	Fair	Inv. mat.
8	Good	Good	Fair	Inv. mat.
9	Good	Good	Fair	Inv. mat.
10	Good	Good	Fair	Inv. mat.
11	Good	Good	Fair	Inv. mat.
12	Good	Good	Fair	Inv. mat.
13	Good	Good	Fair	Inv. mat.
14	Good	Good	Fair	Inv. mat.
15	Good	Good	Fair	Inv. mat.
16	Good	Good	Fair	Inv. mat.
17	Good	Good	Fair	Inv. mat.
18	Good	Good	Fair	Inv. mat.
19	Good	Good	Fair	Inv. mat.
20	Good	Good	Fair	Inv. mat.
21	Good	Good	Fair	Inv. mat.
22	Good	Good	Fair	Inv. mat.
23	Good	Good	Good	Inv. mat.
24	Good	Good	Fair	Inv. mat.
25	Good	Good	Fair	Inv. mat.
26	Good	Good	Fair	Inv. mat.
27	Good	Good	Fair	Inv. mat.
28	Good	Good	Fair	Inv. mat.
29	Good	Good	Fair	Inv. mat.
30	Good	Good	Fair	Inv. mat.
31	Good	Good	Fair	Inv. mat.
32	Good	Good	Fair	Inv. mat.
33	Good	Good	Fair	Inv. mat.
34	Good	Good	Fair	Inv. mat.
35	Good	Good	Fair	Inv. mat.
36	Good	Good	Fair	Inv. mat.
37	Good	Good	Fair	Inv. mat.
38	Good	Good	Fair	Inv. mat.
39	Good	Good	Fair	Inv. mat.
40	Good	Good	Fair	Inv. mat.
41	Good	Good	Fair	Inv. mat.
42	Good	Good	Fair	Inv. mat.
43	Good	Good	Fair	Inv. mat.
44	Good	Good	Fair	Inv. mat.
45	Good	Good	Fair	Inv. mat.
46	Good	Good	Good	Inv. mat.
47	Poor		Poor	Comp. mat.
48	Poor		Poor	Comp. mat.
49	Good	Poor	Fair	Comp. mat.

Good: White rust 1% or less
 Good: Blisters less than 2 mm
 Good: Less than ΔE1
 Fair: ΔE: 1 to 2
 Poor: More than ΔE2
 Poor: White rust 10% or more
 Blisters 2 mm or more

INDUSTRIAL APPLICABILITY

The high corrosion resistance galvanized steel material having a hairline appearance of the present invention is provided with a good hairline appearance and is excellent in corrosion resistance as well, so can be

used for applications similar to the applications of conventional stainless steel material having a hairline appearance. Further, it can be provided at less of a price than expensive stainless steel material.

CLAIMS

1. A high corrosion resistance galvanized steel material having a hairline appearance having a plating layer with a plating deposition of 10 to 600 g/m²,
5 containing Al: 1 to 60 mass%, Mg: 0.1 to 10 mass%, and a balance of Zn and unavoidable impurities, and having hairlines formed on the surface, said hairlines having a surface roughness Ra of 0.2 to 2.5 μm and a peaks per inch PPI of 50 to 400 in a direction perpendicular to the
10 hairlines, having a surface roughness Ra of 0.1 to 1.2 μm and a peaks per inch PPI of 1 to 100 in the hairline direction, and having a surface roughness Ra in a direction perpendicular to the hairlines of 1.2 times or more the surface roughness Ra in the hairline direction
15 and a PPI in a direction perpendicular to the hairlines of 2.0 times or more the PPI in the hairline direction.

2. A high corrosion resistance galvanized steel material having a hairline appearance having a plating layer with a plating deposition of 10 to 600 g/m²,
20 containing Al: 1 to 60 mass%, Mg: 0.1 to 10 mass%, and a balance of Zn and unavoidable impurities, and having hairlines formed on the surface, said hairlines having a peaks per inch PPI of 50 to 400 in a direction perpendicular to the hairlines, having a peaks per inch
25 PPI of 1 to 100 in the hairline direction, and having a PPI in a direction perpendicular to the hairlines of 2.0 times or more the PPI in the hairline direction.

3. A high corrosion resistance galvanized steel material having a hairline appearance having a plating
30 layer with a plating deposition of 10 to 600 g/m², containing Al: 1 to 60 mass%, Mg: 0.1 to 10 mass%, and a balance of Zn and unavoidable impurities, and having hairlines formed on the surface, said hairlines having a surface roughness Ra of 0.1 to 2.5 μm and a peaks per
35 inch PPI of 50 to 400 in a direction perpendicular to the hairlines, having a surface roughness Ra of 0.1 to 1.2 μm

and a peaks per inch PPI of 1 to 100 in the hairline direction, and having a surface roughness Ra in a direction perpendicular to the hairlines of 1.2 times or more the surface roughness Ra in the hairline direction and a PPI in a direction perpendicular to the hairlines of 2.0 times or more the PPI in the hairline direction.

5 4. A high corrosion resistance galvanized steel material having a hairline appearance as set forth in any one of claims 1 to 3, characterized in that the plating
10 layer further contains Si in an amount of 0.001 to 3 mass%.

 5. A high corrosion resistance galvanized steel material having a hairline appearance as set forth in any one of claims 1 to 4, characterized in that the plating
15 layer further contains one or two of Ti in an amount of 0.0001 to 0.1 mass% and B in an amount of 0.0001 to 0.1 mass%.

 6. A high corrosion resistance galvanized steel material having a hairline appearance as set forth in any one of claims 1 to 5, characterized in that plating layer
20 is comprised of a Zn and Al binary eutectic in a volume ratio of 1 to 80 vol% and a Zn, Al, and ZnMg alloy ternary eutectic in a volume ratio of 10 to 90 vol%, with the total of the two being at least 50%.

25 7. A high corrosion resistance galvanized steel material having a hairline appearance as set forth in any one of claims 1 to 6, characterized in that plating layer has a chromate treated layer of 1 to 1000 mg/m² on its surface.

30 8. A high corrosion resistance galvanized steel material having a hairline appearance as set forth in any one of claims 1 to 6, characterized in that plating layer surface has a chromate-free treated layer of 1 to 200 mg/m² not containing any chrome on its surface.

35 9. A high corrosion resistance galvanized steel material having a hairline appearance as set forth in any one of claims 1 to 8, characterized by having a

transparent resin coating layer of a thickness of 0.5 to 100 μm on its surface.

5 10. A high corrosion resistance galvanized steel material having a hairline appearance as set forth in any one of claims 1 to 9, characterized in that the vicinity of the interface between the plating layer surface and chromate-free treated layer not containing any chrome has a layer of a deposit of one or more of Co, Fe, Ni, Pt, and Mn in a metal state or hydroxide state of 0.1 to 10
10 mg/m^2 and the blackening resistance in a wet environment is excellent.