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(54) Al-Si-Cr-PLATED STEEL SHEET EXCELLENT IN CORROSION RESISTANCE AND PRODUCTION THEREOF.

(57) A plated steel sheet having improved corrosion and heat resistances is produced by supplying chromium to an Al-Si plating layer formed on the surface of a steel sheet by hot dipping. The chromium source to be used comprises a chromium coating layer formed on the surface of a nonplated sheet by electroplating, vacuum deposition, etc. The wettability of the chromium coating layer with a plating metal can be improved by activating the surface of the layer by plasma etching, ion beam etching, etc., before dipping a chromium-coated steel sheet in a hot dipping bath. The plating layer L formed on the steel substrate S has a layered structure composed of the first layer L_1 based on chromium, the second layer L_2 based on Cr-Al-Si system and the third layer L_3 based on Al-Si-Cr system, when plating is conducted under the conditions of a thick chromium coating layer and a relatively suppressed diffusion of chromium. Since the plating layer L contains chromium, the resultant plated steel sheet is far more excellent in corrosion and heat resistances than the conventional Al-Si-plated steel sheets.

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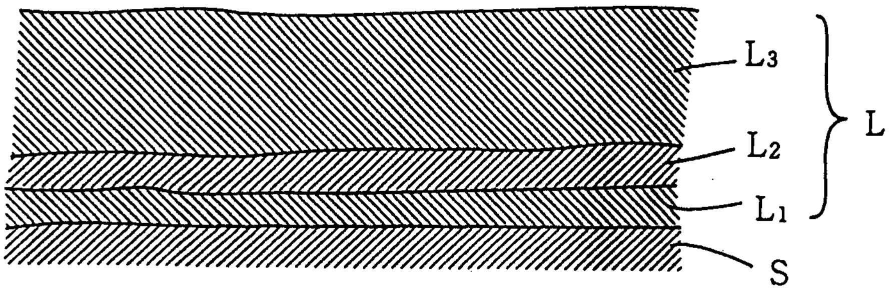
FIG.5



INDUSTRIAL APPLICATION OF THE INVENTION

The present invention relates to a hot-dip coated steel sheet remarkably improved in corrosion and heat resistance by the addition of Cr to a hot-dip Al-Si plating layer, and a method for manufacturing said coated steel sheet.

BACKGROUND OF THE INVENTION

An Al-Si alloy-coated steel sheet has been manufactured by introducing a steel sheet into a hot-dip coating bath prepared from an Al-Si alloy. The Al-Si alloy plating layer formed on the surface of the steel sheet is excellent in corrosion and heat resistance and provides a fine surface appearance. These properties of the Al-Si alloy plating layer broadens the use of the coated steel sheet, e.g. parts and members for the exhaust system of an automobile and structural members for building or civil engineering.

A conventional hot-dip Al-Si alloy coating method commonly uses a continuous hot-dip coating equipment involving an in-line reducing furnace. In this continuous hot-dip coating equipment, a steel sheet to be hot-dip coated is annealed in a reducing atmosphere in a pretreatment zone. In the annealing step, the steel sheet is subjected to gas cleaning reaction so that oxide films are reductively removed from the surface of the steel sheet. Hereby, the surface of the steel sheet is activated. The steel sheet is then introduced into a hot-dip Al-Si alloy coating bath.

The corrosion resistance of a steel sheet coated with a hot-dip Al-Si alloy plating layer is further improved by the addition of Cr to the plating layer. In this regard, Japanese Patent Application Laid-Open 2-88754 discloses the use of an Al-Si alloy coating bath containing Cr to let an Al-Si plating layer contain Cr in an amount of 0.01-2 wt.%. The resulting coated steel sheet can be used as a structural material which exhibits sufficient durability even in a severe corrosive atmosphere.

However, the addition of Cr to the coating bath raises the melting point of an Al-Si alloy, so that the coating bath shall be kept at an elevated temperature. Since a pot for the coating bath is subjected to severe eroding reaction due to the high-temperature Al-Si alloy melt, its life time substantially becomes shorter.

Taking into consideration the life time of the pot, there is a limitation on the possible amount of Cr to be added to the Al-Si coating bath. For instance, as for an Al-Si alloy coating bath commonly used in a conventional hot-dip coating line, Si content is 18 wt.% or less, and the coating bath is held at a temperature of 680 °C or lower. The addition of Cr to be added to the Al-Si coating bath shall be controlled in an amount of 0.5 wt.% or less, so as to prevent the coating bath from rising its temperature too higher. Hereby, Cr content in an objective Al-Si alloy plating layer could not be increased, and an obtained Al-Si alloy coated steel sheet is not improved so much in corrosion resistance.

In order to improve the corrosion resistance of an Al-Si alloy coated steel sheet, there is known the use of a parent sheet excellent in corrosion reistance itself, e.g. a Cr-contng. low-alloyed steel or stainless steel, instead of a common steel. However, these steels are expensive, and requires special pretreatment. Consequently, a product cost for the Al-Si alloy coated steel sheet as a whole is high. For instance, when a stainless steel sheet containing 16 wt.% or more of Cr is used as a parent sheet, the price of the product will be two times or more higher as compared with a product obtained from a parent sheet such as a common steel, e.g. Al-killed steel, or low-C steel. In this regard, the kind of a parent sheet is inevitably limited to a steel free of Cr or a low-grade stainless steel containing a small amount of Cr. Thus, the corrosion resistance of the Al-Si alloy coated steel sheet could not be substantially improved by the selection of the parent sheet.

When a steel sheet, e.g. a low-alloyed steel or stainless steel, containing an easily oxidizable element such as Cr, Si or Al is used as a parent sheet, it is difficult to remove oxide films from the surface of the steel sheet by the power of a reducing gas. A commonly used in-line reducing process is designed for hot-dip coating common steels, but unappropriate for alloyed steels, stainless steels or the like containing easily oxidizable elements. These elements are easily oxidized and converted to oxide films adherent to the surface of the steel sheet, so that the surface exhibits poor wettability to a hot-dip coating metal.

Japanese Patent Publication 63-44825 disclosed another method for improving the corrosion resistance of an Al-Si alloy coated steel sheet. In this method, a parent sheet is coated with Ni, Cu, Co or Cr and then processed in a hot-dip Al-Si coating line including a gas cleaning zone. The coated steel sheet obtained in this way is improved in corrosion resistance owing to the precoating of Ni, Cu, Co or Cr.

However, there is formed tough oxide fimes firmly adhering onto the surface of the parent sheet precoated with Cr. A reaction for reducing such oxide films does not occur thermodynamically under the conventional condition that the surface of a steel sheet coated with oxide films of Cr is heated at a temperature of 500-800 °C in an atmosphere comprising reducing gas such as H_2 or $H_2 + N_2$. For instance, oxide films were not removed from the surface of a Cr-precoated steel sheet by heating the steel sheet 5 min. at 700 °C in a reducing gas atmosphere of $H_2 + 25\% N_2$ having a dew point of -60 °C.

The incomplete removal of the oxide films would cause the formation of defects such as uncoating, when hot-dip coating is applied to the steel sheet after being reductively annealed. According to the results of our experiments, 60% or more of the surface area failed to be coated, when a Cr-coated steel sheet was hot-dip coated with an Al-Si alloy in a continuous hot-dip coating process including an in-line reductively annealing furnace. The obtained steel sheet on which uncoated parts are distributed can not be offered to a practical use.

Even at coated parts, the reaction between a substrate steel and a plating layer is incomplete. Most of the plating layer merely lies on the Cr coated steel sheet with a physical force. Hence, the formed plating layer has poor adhesiveness and would be easily peeled off the surface of the steel sheet by slight working. In this sence, even the coated part can not endure for practical use.

It is expected that the formation of defects such as uncoating and poor adhesiveness can be inhibited by the complete removal of oxide films from the surface of the steel sheet to effectively promote the reaction between the substrate steel and the plating layer. However, high-temperature heating is required for removing oxide films in a short time by the gas cleaning method. For instance, when oxide films are to be reductively removed in 10 sec. or shorter using the same reducing atmosphere as a conventional atmosphere for common steels, the reducing reaction to remove the oxide films does not occur at a temperature below 1000 °C. The high-temperature heating consumes a large amount of thermal energy and necessitates a heating furnace and other installation constructed by expensive material excellent in heat resistance. Besides, since the high-temperature heating deteriorates the mechanical property, e.g. elongation and strength, of the parent sheet iteslf, almost all kinds of steel can not be subjected to the high-temperature heating.

In order to inhibit the harmful influence of chromium oxide films, Japanese Patent Publication 63-44825 discloses the use of an Al coating bath containing Si only in an amount of impurity order in addition to maitaining the coating bath at a temperature of approximately 700 °C higher than that of a conventional Al-Si alloy coating bath which is held at 620-670 °C. The reactivity of the coating bath is enhanced effectively for lowering the surface area of uncoated parts by the limitation on Si content and the maintenance of the coating bath at a high temperature. However, the formation of uncoated parts can not be completely inhibited.

We observed the cross section of a coated steel sheet obtained in this method. It was noted that an Al plating layer was formed at a part where chromium oxide films were destroyed. It is supposed that the reaction between the substrate steel and the plating layer occured due to the destruction of the chromium oxide films. However, a brittle alloyed layer grew thick at the reacted part, since the reactivity of the Al coating bath free of Si was too high. Although the reacted part was thick, the plating layer was not substantially improved in adhesiveness.

In case where a steel sheet precoated with Ni, Co or Cu is used as a parent sheet, oxide films are removed from the surface of the steel sheet by gas cleaning. In this case, there are no problems such as those derived from oxide films formed on the Cr-precoated steel sheet. The influence in response to the kind of the precoating layer is suggested in the data disclosed in Japanese Patent Publication 63-44825.

When an alloyed steel containing an easily oxidizable element, stainless steel or Cr-precoated steel is used as a parent sheet, the adhesiveness of the Al-Si alloy plating layer to the substrate steel is improved by precoating the parent sheet with Fe or a Fe alloy. Oxide films are easily reductively removed from the surface of the steel sheet, when the precoated parent sheet is passed trough the in-line annealing furnace of a conventional continuous hot-dip coating equipment.

Japanese Patent Application Laid-Open 63-176482 discloses the pretreatment wherein a parent sheet is precoated with Co, Ni, Mn, Mo, Cu, Cr and/or W and then with Fe to improve the adhesiveness of an Al plating layer to a substrate steel. The precoating of Fe or a Fe alloy suppresses harmful influence originated in chromium oxide films. However, the precoating of Fe or a Fe alloy requires an additional step and needs expsenes for electroplating, so that production cost becomes higher in total. In addition, when the precoated parent sheet is dipped in an hot-dip Al-Si coating bath, the Fe or Fe alloy precoating layer dissolved in the plating layer before its solidification. Consequently, Fe content in the plating layer becomes higher, so that the coated steel sheet obtained in this way is not substantially improved in corrosion resistance.

An object of the present invention is to manufacture a steel sheet coated with a superior Al-Si-Cr layer without defects such as uncoated parts or poor adhesiveness derived from chromium oxide films. Such a Al-Si-Cr layer is formed by introducing a parent sheet, on which a Cr coating layer is formed in an active state free from oxide films, into a hot-dip Al-Si alloy copating bath.

Another object of the present invention is to obtain a coated steel sheet remarkably improved in corrosion and heat resistance by controlling the conditions of manufacturing to reform the structure of a plating layer.

Still another object of the present invention is to produce a steel sheet coated with an Al-Si-Cr plating layer excellent in corrosion and heat resistance with high productivity by arranging the formation of a Cr coating layer and the application of hot-dip Al-Si alloy layer coating in series.

SUMMARY OF THE INVENTION

According to the present invention, a parent sheet, on which there is formed a Cr layer having an active surface free of oxide films, is introduced into a hot-dip Al-Si alloy coating bath. Such a Cr layer is preformed on the surface of the parent sheet by electroplating or vapor deposition.

The Cr layer is held in the active state until the Cr coated parent sheet is introduced into the hot-dip coating bath, as follows:

① The Cr layer formed on the surface of the parent sheet is subjected to plazma etching or ion beam etching in a vacuum atmosphere and then introduced into the hot-dip coating bath held in the same vacuum atmosphere.

Oxide films are completely removed from the surface of the Cr coated parent sheet by plazma etching or ion beam etching, so that the Cr coated steel sheet while keeping its surface in an active state is introduced into the Al-Si coating bath. Hereby, the reaction between the substrate steel and the plating layer is not impeded at all by chromium oxide film, and an excellent plating layer is formed on the surface of the parent sheet.

The Cr layer may be formed by vapor deposition in a vacuum atmosphere or electroplating in the opened atmosphere. The Cr coated parent sheet may be hot-dip coated just after the formation of the Cr layer, or stored for future hot-dip coating in response to production schedules.

② After the Cr layer is formed by vapor deposition in a vacuum atmosphere, the Cr coated parent sheet is successively introduced into a hot-dip coating bath held in the same vacuum atmosphere.

This method, corresponding to the advancement of the method ①, effectively uses the phenomenon that oxide films are not formed on the surface of the Cr coating layer in a vacuum atmosphere. In this sense, this method may omit plazma etching or ion beam etching.

In case where a steel sheet hot-dip coated with an Al-Si-Cr plating layer is to be manufactured in a single process line arranging a vapor deposition device and a hot-dip coating bath in series, Cr is vapor deposited on the surface of a parent sheet in a vacuum atmosphere, and then the Cr coated parent sheet is introduced into the hot-dip Al-Si coating bath held in the same vacuum atmosphere. Hereon, the vapor deposition of Cr and the dipping of the Cr coated parent sheet in the coating bath are performed in the same vacuum atmosphere, so that the Cr coated parent sheet can be introduced into the coating bath without the oxidation of the Cr layer. Consequently, the Cr coated steel sheet is hot-dip coated under the condition that its surface is kept in a state highly active to the hot-dip Al-Si coating bath.

③ A parent sheet after being introduced into a vacuum chamber is treated by plazma etching or ion beam etching to activate its surface, a Cr layer is formed on the surface of the parent sheet by vapor deposition, and then the Cr coated parent sheet is introduced into a hot-dip Al-Si coating bath.

An apparatus for hot-dip coating a parent sheet after being activated by plazma etching or ion beam etching generally has a vacuum chamber. The inner atmosphere in the vacuum chamber is effectively utilized for vapor Cr deposition to the parent sheet after being activated by plazma etching or ion beam etching. Hereby, an Al-Si-Cr hot-dip coated steel sheet is manufactured at a lower running cost. In addition, a high-purity Cr plating layer is formed with high productivity at a low cost.

The continuous hot-dip coating apparatus for a parent sheet after being activated by plazma etching or ion beam etching is disclosed in Japanese Patent Application Laid-Open 3-86710, for instance.

The Cr layer may be formed on the surface of a parent sheet by electroplating or vapor deposition. The Cr layer preferably has a thickness of 0.02 µm or more to improve the corrosion resistance of a product.

When the parent sheet is introduced into a hot-dip Al-Si alloy coating bath, Cr diffuses into a plating layer being formed on the surface of the parent sheet. If the Cr layer has a sufficient thickness, the Cr layer remains as an intermediate layer between the substrate steel and the plating layer in the product. If the Cr layer is thin, Cr completely diffuses into the plating layer without remaining at the boundary between the substrate steel and the plating layer.

Whether the Cr layer remains between the substrate steel and the plating layer or not depends on the temperature and composition of the hot-dip Al-Si alloy coating bath, a period for dipping the parent sheet in the coating bath, etc. in addition to the thickness of the Cr layer. In any case, the coated steel sheet is remarkably improved in corrosion resistance, since the formed plating layer contains Cr. Especially in case where a sub-layer containing 0.7 wt.% or more Cr is formed in the plating layer, the corrosion resistance is excellent.

The plating reaction occurs on the surface of the parent sheet through the Cr layer having a surface activated, so that the formed plating layer exhibits excellent adhesiveness to the substrate steel without the formation of defects such as uncoated parts. In addition, since the Cr layer effectively suppresses the diffusion of Fe from the substrate steel, the formed plating layer itself is presented with excellent corrosion resistance and workability.

When the parent sheet is hot-dip coated under the condition that the Cr layer remains at the boundary between the substrate steel and the plating layer, the intermediate Cr layer suppresses the alloying reaction between the substrate steel and the plating layer, so as to inhibit the formation of a thick brittle alloyed layer. Consequently, the product is excellent in workability, too.

A large amount of Cr may be intentionally diffused into the plating layer to precipitate Cr-Si-Al alloy particles by controlling the hot-dip coating conditions, e.g. holding the hot-dip coating bath at a higher temperature or dipping the parent sheet in the coating bath for a longer time. The precipitation of the Cr-Si-Al alloy particles exhibits a remarkable effect on the improvement in the corrosion resitance of the hot-dip coated steel sheet.

Taking into cosideration the above-mentioned effects of the Cr layer, it is preferable to form the Cr layer of 0.1 μm or more in thickness on the surface of the parent sheet.

There are not particular restrictions on the composition and temperature of the hot-dip coating bath to be used according to the present invention. However, it is preferable to control Si content within the range of 1-13 wt.% and the temperature of the hot-dip coating bath below 680 °C, in order to prolong the life-time of a pot for the coating bath and to enhance the surface appearance of an obtained product. In case where a thin Al-Si-Cr alloy layer is to be formed on the surface of the parent sheet, it is preferable to maintain Si content within the range of 6-12 wt.% and the temperature of the coating bath below 680 °C.

The hot-dip coating bath may contain Cr as a third component. The use of the Cr-contng. Al-Si alloy coating bath is effective for raising an amount of Cr existent in the plating layer. The amount of Cr to be added to the coating bath, which does not limit the scope of the present invention, is 0.5 wt.% or less in the practical point of view. If the coating bath contains an excessive amount of Cr, the coating bath shall be maintained at a higher temperature in response to the elevation of the melting point of the Al-Si alloy.

Various elements dissolved from the pot remain as impurities in the hot-dip Al-Si coating bath. Among such element, Fe is the element mixed in the biggest amount in the coating bath. Fe concentration in the coating bath is ordinarily controlled at 3 wt.% or less. If the parent sheet is hot-dip coated using the coating bath containing a large amount of Fe under the condition to leave the Cr layer, there would be formed the Fe-contng. Al-Si-Cr alloy layer which unfavorably deteriorates the corrosion resistance of the coated steel sheet.

The dissolution of Fe from a structural material such as a pot may be inhibited by applying ceramic lining to the structural material. The dissolution of Fe from the parent sheet into the coating bath is also inhibited, since the parent sheet to be coated is covered with the Cr layer. Consequently, the coating bath is kept at very low Fe concentration, so as to sufficiently lower Fe content in the plating layer to be formed on the surface of the steel sheet.

There is not any restriction on the material of a parent sheet to which the present invention is applicable. For instance, a common steel such as Al-killed steel may be used in order to reduce the cost of a product. Even when a cheap common steel is used as a parent sheet, the obtained product exhibits excellent corrosion resistance similar to that of a high-grade steel material such as stainless steel.

When a low-alloyed steel or stainless steel is used as a parent sheet, the substrate steel itself has good corrosion resistance. Owing to the combination of this property with the hot-dip Al-Si coating layer formed on the Cr layer, the coated steel sheet exhibits corrosion and heat resistance superior to those of an expensive high-grade stainless steel containing large amounts of Cr and Ni.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic view illustrating a plant for continuing plazma etching, vapor Cr deposition and hot-dip coating in the same vacuum chamber according to the present invention.

Fig. 2 is a schematic view illustrating a plant for continuing ion beam etching, vapor Cr deposition and hot-dip coating in the same vacuum chamber according to the present invention.

Fig. 3 is a schematic view illustrating a plant for continuing vapor Cr deposition, plazma etching and hot-dip coating in the same vacuum chamber according to the present invention.

Fig. 4 is a schematic view illustrating a plant for continuing vapor Cr deposition, ion beam etching and hot-dip coating in the same vacuum chamber according to the present invention.

Fig. 5 shows the lamellar structure of a plating layer formed according to the present invention.

Fig. 6 shows the lamellar structure of another plating layer which contains a large amount of Cr.

Fig. 7 is a graph for explaining the effect of the thickness of a Cr layer on Cr content in the second sub-layer of a plating layer and the corrosion resistance of a coated steel sheet obtained in Example 1.

Fig. 8 illustrates a plating layer wherein Si-rich alloy particles are precipitated.

Fig. 9 is a graph for explaining the effect of the thickness of a Cr layer on Cr content in the second sub-layer of a plating layer and the corrosion resistance of a coated steel sheet obtained in Example 2.

Fig. 10 is a graph for explaining the effect of the thickness of a Cr layer on Cr content in the second sub-layer of a plating layer and the corrosion resistance of a coated steel sheet obtained in Example 3.

Fig. 11 shows the metallurgical structure and concentration of a plating layer formed on the surface of a steel sheet in Example 5.

Fig. 12 is a graph showing the relationship between the thickness of a Cr layer and the corrosion resistance of a coated steel sheet obtained in Example 5.

Fig. 13 is a graph for explaining the corrosion resistance of a hot-dip Al-Si alloy-coated steel sheet after being electroplated in comparison with that of the same coated steel sheet after being precoated with Fe.

Fig. 14 is a graph for explaining the effects of the thickness of a Cr layer and the temperature of a hot-dip coating bath on the corrosion resistance of a coated steel sheet obtained in Example 6.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

According to the present invention, a parent sheet coated with a Cr layer having a surface activated is introduced into a hot-dip Al-Si coating bath. The Cr layer may be fomed by electroplating or vacuum vapor deposition. The surface of the Cr layer is activated by plazma etching, ion beam etching, etc.. The Cr layer keeping its surface in the activated state may be brought into contact with the hot-dip coating bath, when vapor Cr deposition is successively followed by hot-dip coating using a coating bath maintained in the same vacuum chamber. When the surface of the parent sheet is activated by plazma etching or ion beam etching before the formation of the Cr layer, the substrate steel exhibits excellent affinity to the Cr layer to be formed by vapor deposition.

In response to the combination of the formation of the Cr layer with the activation and hot-dip coating, the present invention is realized in various processes classified as follows:

① electroplating a parent sheet with Cr → plazma etching to activate the surface of the Cr layer → hot-dip coating in the same vacuum chamber

② electroplating a parent sheet with Cr → ion beam etching to activate the surface of the Cr layer → hot-dip coating in the same vacuum chamber

③ vapor Cr deposition on a parent sheet → plazma etching to activate the surface of the Cr layer → hot-dip coating in the same vacuum chamber

④ vapor Cr deposition on a parent sheet → ion beam etching to activate the surface of the Cr layer→ hot-dip coating in the same vacuum chamber

⑤ vapor Cr deposition on a parent sheet → hot-dip coating in the same vacuum chamber

⑥ vapor Cr deposition on a parent sheet → plazma etching to activate the surface of the Cr layer in the same vacuum chamber → hot-dip coating in the same vacuum chamber

⑦ vapor Cr deposition on a parent sheet → ion beam etching to activate the surface of the Cr layer in the same vacuum chamber → hot-dip coating in the same vacuum chmaber

⑧ plazma etching to activate the surface of a parent sheet → vapor Cr deposition on the parent sheet in the same vacuum chamber → hot-dip coating in the same vacuum chamber

⑨ ion beam etching to activate the surface of a parent sheet → vapor Cr deposition on the parent sheet in the same vacuum chamber → hot-dip coating in the same vacuum chamber

There is designed a hot-dip coating plant corresponding to each process. For instance, Fig. 1 shows the layout wherein various devices are arranged according to the steps in the process ⑥.

A parent sheet 10 is fed out from a pay-off reel 11 and introduced into a vacuum chamber 20, while changing its running direction with deflector rolls 12, 13. A vacuum seal means 21 is provided in the vacuum chamber 20 at its inlet position. Inside the vacuum chamber 20, a high-frequency heater 30, a vapor Cr deposition device 40 and a plazma etching device 50 are successively aligned along the running direction of the parent sheet 10.

The outlet of the vacuum chamber 20 is immersed in a hot-dip coating bath 61 in a hot-dip coating zone 60 to make vacuum sealing at the outlet. Hereon, the hot-dip coating bath 61 is pumped from a pot 62 up to the height corresponding to the degree of vacuum in the vacuum chamber 20, to form a snout 63. Hereby, the outlet of the vacuum chamber 20 is completely vacuum sealed by the hot-dip coating bath 61.

The vacuum chamber 20 is evacuated by vacuum pumps 22, 23. The parent sheet 10 after being introduced into the vacuum chamber 20 is heated at a predetermined temperature by the high-frequency heater 30, coated with Cr by the vapor Cr deposition device 40 and then activated by the plazma etching device 50.

The parent sheet 10 is then introduced through the snout 63 into the hot-dip coating bath 61. The parent sheet 10 is carried along sunk rolls 64, 65 in the hot-dip coating bath 61, and raised from the bath 61. An excessive amount of a coating metal is removed by a gas wiper 66 to control the amount of the coating metal adherent onto the surface of the parent sheet 10. The coated sheet is further carried along deflector rolls 14-16 and then coiled onto a winding reel 17.

Fig. 2 shows the layout wherein various devices are arranged in the order of steps in the process ⑦. In this layout, a couple of ion beam etching devices 70, 70 are located in the state facing to each surface of the parent sheet 10, instead of the plazma etching device 50 shown in Fig. 1. The surface of the parent sheet 10 is bombarded with ion beams 71, 71 discharged from each ion beam etching device 70, 70. The bombardment of the ion beams 71, 71 induces the etching reaction to remove oxide films and/or denatured surface parts from the Cr layer which has been formed by the vapor Cr deposition device 40.

In any case, the Cr layer is formed by the vapor Cr deposition device 40 held in the same vacuum atmosphere as that for the hot-dip coating zone 60. Consequently, the Cr layer is maintained under the condition difficult to form oxide films or denatured surface parts, which would impede the adhesion of a coating metal, on the surface of the Cr layer. In this sence, there may be omitted the plazma etching device 50 or the ion beam etching device 70 to be provided at the downstream of the vapor Cr deposition device 40, when the Cr layer is not suffered from harmful influences such as oxide films. The layout which omits the activating device corresponds to the process ⑤.

Oxide films and/or denatured surface parts are removed from the surface of the Cr layer by plazma etching or ion beam etching. In this sense, the steel sheet on which the Cr layer is preformed by a device independent from the hot-dip coating equipment may be used as the parent sheet 10. Said Cr layer may be formed by either electroplating or vapor deposition. The process ① corresponds to the case where the surface of the Cr layer formed by electroplating is activated by plazma etching before the step of hot-dip coating. The process ② corresponds to the case where the same Cr layer is activated by ion beam etching. The process ③ or ④ is the case where the Cr layer is subjected to plazma etching or ion beam etching, respectively.

There are often formed oxide films and/or denatured layers on the surface of a steel sheet. Said oxide films and/or denatured layers deteriorate the adhesiveness of the Cr layer, to be formed by the vapor Cr deposition device 40, onto the substrate steel. When the steel sheet being in such surface condition is used as the parent sheet 10, the surface of the steel sheet is preferably activated before the formation of the Cr layer.

The process ⑧ shows the case where ion beam etching is employed for the activating treatment using the layout shown in Fig. 3. In this layout, the plazma etching device 50 is located at the upstream of the vapor Cr deposition device 40. If necessary, the same plazma etching device may be additionally provided at the downstream of the vapor Cr deposition device 40.

The process ⑨ uses the layout shown in Fig. 4, wherein the surface of the parent sheet 10 is activated by ion beam etching. In this layout, the ion beam etching device 70 is located at the upstream of the vapor Cr deposition device 40. If necessary, the same ion beam etching device may be additionally provided at the downstream of the vapor Cr deposition device 40.

Since the parent sheet 10 coated with the Cr layer having the surface activated is introduced into the coating bath 61, the Cr layer exhibits excellent wettability to the coating metal. Consequently, a fine plating layer is formed on the surface of the steel substrate. The plating layer has the lamellar structure which is changed in resposnse to the operational conditions, e.g. the composition and temperature of the cotaing bath, the thickness of the Cr layer and the kind of the substrate steel.

When the parent sheet is hot-dip coated under the condition to form a plating layer in which Cr concentration is relatively lower, the plating layer has the lamellar structure shown in Fig. 5. The lamellar structure comprises, in the order from the surface of the substrate steel S, the first sub-layer L_1 of an Al-Si-Fe alloy, the second sub-layer L_2 of an Al-Cr-Si-Fe alloy and the third sub-layer L_3 of an Al-Si ally. The second sub-layer L_2 is one formed by the diffusion of Cr during dipping the Cr-coated steel sheet in the coating bath. The second sub-layer L_2 has the effect to improve corrosion and heat resistance owing to high Cr concentration.

The effect of Cr on the corrosion and heat resistance is distinctly noted, when Cr concentration in the second sub-layer L_2 is 0.7 wt.% or higher. The Cr concentration is preferably adjusted by controlling the composition and temperature of the coating bath, the thickness of the Cr layer, etc..

A conventional hot-dip Al-Si alloy-coated steel sheet does not have a layer corresponding to the second sub-layer L_2, but depends on an Al-Si surface layer to protect the substrate steel from corrosion. Consequently, its corrosion resistance is substantially inferior to that of the steel sheet coated with the plating layer including the second sub-layer L_2.

Cr content in the second sub-layer L_2 has the effect to suppress the diffusion of Fe from the substrate steel S, so as to reduce the total amount of Fe in the plating layer. In addition, the plating layer is formed through the Cr layer excellent in adhesiveness and wettability. Consequently, the obtained product is improved in workability as well as corrosion resistance. For instance, the coated steel sheet can be reformed to an objective shape without flaking or powdering.

The plating layer obtained under the condition to enhance Cr concentration comprises the first sub-layer L_1 of an Al-Si-Fe-Cr alloy, the second sub-layer L_2 of an Al-Cr-Si-Fe alloy and the third sub-layer L_3 of an Al-Si-Cr alloy.

The first sub-layer L_1 is excellent in corrosion inhibition, since it contains Cr with high Al concentration. Cr concentration in the first sub-layer L_1 is up to 0.7 wt.%, when the plating layer is formed on a parent sheet such as common steel which does not contain Cr. When an alloyed steel or stainless steel is used as a parent sheet, Cr concentration in the first sub-layer L_1 is higher owing to the diffusion of Cr from the substrate steel S. The corrosion resistance is more improved, as Cr concentration in the first sub-layer L_1 is higher. However, Cr concentration in the first sub-layer L_1 does not exceed 5 wt.%, even when a high-Cr steel containing 40 wt.% or more Cr is used as the parent sheet.

The second sub-layer L_2 is of the Al-Cr-Si-Fe alloy in which Cr is preferentially concentrated. The second sub-layer L_2 exhibits the highest effect to inhibit corrosion among the sub-layers L_1-L_3, since Cr and Al concentrations are both higher. Cr concentration in the second sub-layer L_2 is preferably adjusted by controlling the amount of Cr adhering to the parent sheet. For instance, the Cr concentration in the second sub-layer L_2 was approximately 3 wt.%, when a Cr layer of 0.1 μm in thickness was formed on the parent sheet. The thickness of the Cr layer is predetermined taking into consideration the corrosion resistance necessary for the use of a product.

The third sub-layer L_3 is the Al-Si-Cr alloy layer which is formed by the solidification of a coating metal. The sub-layer L_3 has nearly the same composition as that of the coating bath, except Cr. The sub-layer L_3 also contains Cr in a small amount of 0.1 wt.% or less due to the diffusion of Cr. Although Cr content is low, the third sub-layer L_3 is improved in corrosion inhibition, too.

When a parent sheet is to be hot-dip coated under the condition to leave the Cr layer at the boundary between the substrate steel and the plating layer, a Cr layer is formed in relatively large thickness on the surface of the parent sheet, and the diffusion of Cr is suppressed during hot-dip coating. The formed plating layer comprises the first sub-layer L_1 of Cr, the second sub-layer L_2 of Cr-Si-Al and the third sub-layer L_3 of Al-Si-Cr.

The second sub-layer L_2 promotes the segregation of Fe diffused from the coating bath or the like therein, so as to reduce Fe concentration in the third sub-layer L_3. Fe mixed as an impurity in the third sub-layer L_3 is preferably controlled in an amount of 0.7 wt.% or less, in order to enhance the effect of the plating layer L to inhibit corrosion reaction.

There is not any specified restriction on the concentration of each element, except Fe, in the second sub-layer L_2 and the third sub-layer L_3. However, in order to effectively improve the corrosion resistance by the combination of these sub-layers L_1-L_3, the second sub-layer L_2 preferably has the composition of 30-60 wt.% Cr, 30-60 wt.% Si, less than 30 wt.% Fe and the balance being substantially Al, while the third sub-layer L_3 preferably has the composition of 6-12 wt.% Si, 0.05-0.5 wt.% Cr and the balance being substantially Al.

The second sub-layer L_2 preferably contains 30-60 wt.% Cr with Fe concentration reduced below 30 wt.%, to improve the corrosion resistance by the co-operative effect with the first sub-layer L_1. However, the excessive growth of the second sub-layer L_2 would cause the formation of big cracks, when the obtained product is mechanically reformed to a certain shape by bending or the like. In this regard, Si content in the second sub-layer L_2 is preferably controlled at 30-60 wt.% to suppress the growth of the second sub-layer L_2.

The third sub-layer L_3 is excellent in ductility as well as corrosion resistance. When cracks are formed in the hard brittle first and second sub-layers L_1, L_2 during bending the obtained product, the cracks are sealed by the plastic flow of the third sub-layer L_3 to prevent the substrate steel from exposing to the atmosphere. When Cr content in the third sub-layer L_3 is controlled within the range of 0.05-0.5 wt.%, the corrosion resistance is improved without lowering the ductility. The third sub-layer L_3 preferably contains 6-12 wt.% Si to improve the coated steel sheet in surface appearance and flatness. Si in the third sub-layer L_3 is effective in corrosion inhibition, too.

Cr-Si-Al alloy particles G may be dispersed in the third sub-layer L_3, as shown in Fig. 6. The dispersion of the alloy particles G further enhances the effect of the third sub-layer L_3 to suppress the corrosion reaction. The alloy particles G are those precipitated from the first sub-layer L_1 and the second sub-layer L_2 by either holding the hot-dip Al-Si alloy coating bath at a higher temperature or dipping the parent sheet in the coating bath for a longer time.

The steel sheet hot-dip coated with the Al-Si-Cr plating layer as aforementioned is manufactured by coating a parent sheet with a Cr layer and then introducing the parent sheet into a hot-dip Al-Si alloy coating bath. When the Al-Si alloy coating bath does not contain Fe as an impurity, the Cr-Si-Al alloy layer is formed as the second sub-layer L_2. When Fe is mixed as an impurity in the coating bath, Fe is segregated in the second sub-layer L_2 during the solidification of the plating layer. Hereby, a Cr-Si-Al-Fe alloy layer is formed as the second sub-layer L_2.

EXAMPLE 1:

A parent sheet to be hot-dip coated was prepared from an Al-killed steel sheet of 0.5 mm in thickness and 100 mm in width. The Al-killed steel had the composition of 0.02 wt.% C, 0.04 wt.% Si, 0.19 wt.% Mn, 0.011 wt.% P, 0.011 wt.% S, 0.045 wt.% Al and the balance being substantially Fe. The parent sheet, after being degreased and acid-pickled, was offered to a hot-dip Al-Si coating process using the hot-dip coating plant shown in Fig. 1.

A vacuum chamber 20 was evacuated to 1×10^{-3} Pa by vacuum pumps 22, 23. After the interior of the vacuum chamber 20 reached a predetermined degree of vacuum, a high-frequency heater 30, a vapor Cr deposition device 40 and a plazma etching device 50 were put into operation. Hereon, the degree of vacuum in the vacuum chamber 20 was changed to 3 Pa by the introduction of raw gas. Plazma etching was performed under the conditions shown in Table 1.

TABLE 1

CONDITIONS FOR PLAZMA ETCHING	
RAW GAS FOR PLAZMA ETCHING	Ar
POWER FOR GENERATING PLAZMA	4 kW
VOLTAGE CHARGED ON ELECTRODE	350 V
FLOW RATE OF RAW GAS	1×10^{-6} m^3/sec.
LINE SPEED	30 m/min.

The parent sheet after being plazma etched was hot-dip coated with an Al-Si alloy under the conditions shown in Table 2.

TABLE 2

CONDITIONS FOR HOT-DIP Al-Si ALLOY COATING	
COMPOSITION OF COATING BATH	Si: 9.2 wt.%
	Fe: 1.6 wt.%
	BALANCE: Al except inevitable impurities
TEMP. OF COATING BATH	660 °C
ADHESION AMOUNT OF PLATING LAYER	30 g/m^2 per single surface

The obtained product had a multi-layered alloy plating layer. The third sub-layer L_3 in the plating layer was composed of a mixed phase comprising primary crystals of an Al-rich alloy and eutectically precipitated crystals of a Si-rich alloy. Under the third sub-layer L_3, there were formed the second sub-layer L_2 of Al-Cr-Si-Fe and the first sub-layer L_1 of Al-Si-Fe.

Cr concentration in the second sub-layer L_2 was variously changed by controlling the thickness of a Cr layer to be formed by vacuum deposition, to examine the effect of the thickness of the Cr layer on Cr concentration in the second sub-layer L_2 and the corrosion resistance of an obtained product. The results are shown in Fig. 7. Hereon, corrosion resistance was evaluated as a time period (hereinafter referred to as "5% rust formation time") until the surface area of a test piece was occupied by 5% or more with rust formed on the surface of said test piece in the salt water spray test regulated in JIS (Japanese Industrial Standard).

It is apparently understood from Fig. 7 that the formation of a thicker Cr layer resulted in the increase of Cr concentration in the second sub-layer L_2 as well as the elongation of the 5% rust formation time. There is recognized the effect of Cr in the plating layer to remarkably improve the corrosion resistance. When the Cr layer was formed in thickness of 0.03 μm or more, Cr concentration in the second sub-layer L_2 was of 0.7 wt.% or more.

The same relationship of Cr concentration in the second sub-layer L_2 with the improvement in corrosion resistance was obtained in the case where a parent sheet coated with a Cr layer was activated by ion beam etching in the plant shown in Fig. 2. Table 3 shows the conditions for ion beam etching in this case.

TABLE 3

CONDITIONS FOR ION BEAM ETCHING	
SORT OF ION	Ar^+
ENERGY	10 keV
DENSITY OF ELECTRIC CURRENT	10 A/dm^2
IRRADIATION ANGLE TO SURFACE OF STEEL SHEET	40 degree
LINE SPEED	30 m/min.

In another case, a Cr layer was preformed on the surface of a parent sheet by electroplating, and the parent sheet was introduced into the vacuum chamber 20 of the hot-dip coating plant shown in Fig. 1 or 2. The parent sheet was etched and hot-dip coated with an Al-Si layer. An obtained product was a multi-layered alloy-coated steel sheet which exhibited extremely excellent corrosion resistance as compared with a conventional Al-Si alloy-coated steel sheet, as far as Cr concentration in the second sub-layer L_2 was 0.7 wt.% or more.

EXAMPLE 2:

The same Al-killed steel as that in Example 1 was used as a parent sheet to be hot-dip coated in the plant shown in Fig. 3. The parent sheet was plazma etched under the conditions shown in Table 1 and then coated with a Cr layer by vacuum deposition. Thereafter, the parent sheet was hot-dip coated under the conditions shown in Table 4.

TABLE 4

CONDITIONS FOR HOT-DIP Al-Si ALLOY COATING	
COMPOSITION OF COATING BATH	Si: 9.3 wt.%
	Fe: 1.5 wt.%
	Cr: 0.11 wt.%
	BALANCE: Al except inevitable impurities
TEMP. OF COATING BATH	660 °C
ADHESION AMOUNT OF PLATING LAYER	30 g/m^2 per single surface

The obtained product had a multi-layered alloy plating layer. The third sub-layer L_3 in the plating layer was composed of a mixed phase comprising primary crystals of an Al-rich alloy and eutectically precipitated crystals of a Si-rich alloy. Under the third sub-layer L_3, there were formed the second sub-layer L_2 of Al-Cr-Si-Fe and the first sub-layer L_1 of Al-Si-Fe-Cr.

A test piece was cut out from the coated steel sheet which was obtained by coating a parent sheet with a Cr layer of 0.3 μm in thickness and then hot-dip coating it in an Al-Si coating bath. The test piece was examined by EPMA linear analysis to investigate the distribution of each element in the plating layer. Fig. 8 shows the result of analysis in comparison with the sectional structure.

Cr concentration in the second sub-layer L_2 was variously changed by controlling the thickness of a Cr layer to be formed by vacuum deposition. The effect of the Cr layer on corrosion resistance was researched in the same way as that in Example 1. The results are shown in Fig. 9. It is noted from Fig. 9 that the Cr layer of 0.02 μm or more in thickness effectively improved corrosion resistance. Cr concentration in the second sub-layer L_2 was of 0.7 wt.% or more owing to such a thicker Cr layer.

EXAMPLE 3:

Two kinds of stainless steels SUS410L and SUS430 were used as parent sheets. Each sheet was of 0.5 mm in thickness and 100 mm in width. The stainless steel SUS410L had the composition of 0.01 wt.% C, 0.48 wt.% Si, 0.23 wt.% Mn, 0.026 wt.% P, 0.003 wt.% S, 11.96 wt.% Cr and the balance being Fe except inevitable impurities. The stainless steel SUS430 had the composition of 0.06 wt.% C, 0.45 wt.% Si, 0.28 wt.% Mn, 0.025 wt.% P, 0.007 wt.% S, 16.44 wt.% Cr and the balance being Fe except inevitable impurities.

Each parent sheet was hot-dip coated under all the same conditions as those in Example 2.

A test piece was cut out from each obtained product and subjected to the salt water spray test to study the effect of the Cr layer on the 5% rust formation time. There was the relationship shown in Fig 10 between the thickness of the Cr layer and the 5% rust formation time. It is recognized from Fig. 10 that the product obtained from a stainless steel according to the present invention is remarkably improved in corrosion resistance as compared with the stainless steel itself or a product hot-dip coated without vapor Cr deposition.

EXAMPLE 4:

The combination of Cr coating with a hot-dip coating process was examined to search how to affect the corrosion resistance of an obtained product, as follows: The same Al-killed steel as that in Example 2 was hot-dip coated with an Al-Si alloy layer. The composition of a coating bath and the adhesion amount of a plating layer were adjusted to the same as those in Example 2. In case where a parent sheet was precoated with Cr in a separate apparatus and then immersed in a hot-dip Al-Si alloy coating bath, the Cr-coated parent sheet was intorduced into the vacuum chamber 20 shown in Fig. 3. In this case, the vapor Cr deposition device 50 was not put into operation, but the plazma etching device 40 was operated to activate the surface of the Cr layer. Thereafter, the Cr-coated parent sheet was intorduced into the coating bath.

Table 5 shows the corrosion resistance of each product in response to the hot-dip coating process. It is noted from Table 5 that the same excellent corrosion resitance as that in Example 2 is obtained even when hot-dip Al-Si alloy coating was applied to the steel sheet which had been precoated with a Cr layer by vapor deposition or electroplating.

TABLE 5 EFFECT OF COATING PROCESS ON CORROSION RESISTANCE

COATING PROCESS	THICKNESS OF Cr LAYER (μm)	5% RUST FORMATION TIME (hrs.)
(VAPOR Cr DEPOSITION) → (HOT-DIP Al-Si COATING)	0.1	2110
	0.3	3600
(Cr ELECTROPLATING) → (HOT-DIP Al-Si COATING)	0.1	2110
	0.3	3600
[Cr ELECTROPLATING →HOT-DIP Al-Si COATING]	0.1	2110
	0.3	3600

NOTE:- The steps in each parenthesis were done in the same apparatus.

EXAMPLE 5:

The same Al-killed steel as that in Example 1 was used as a parent sheet. After the parent sheet was degreased and pickled, a Cr layer was formed on the parent sheet by vapor deposition or electroplating. The Cr-coated parent sheet was hot-dip coated with an Al-Si alloy layer in the plant using the plazma etching device shown in Fig. 3 or the ion beam etching device shown in Fig. 4.

The vacuum chamber 20 was evacuated to 1 × 10^{-3} Pa by the vacuum pumps 22, 23. After the interior of the vacuum chamber 20 reached a predetermined degree of vacuum, the plazma etching device 50 or the ion beam etching device 70 as well as the high-frequency heater 30 was operated to activate the surface of the parent sheet 10. Hereon, the degree of vacuum in the vacuum chamber 20 was changed to 0.05-5 Pa due to the inflow of raw gas Ar.

Before the vapor Cr deposition, the parent sheet 10 was heated by the high-frequency heater 30 and conditioned to the state having a surface activated by the plazma etching device 50 or the ion beam etching device 70. Consequently, the Cr layer formed by vapor deposition was uniformly formed on the whole surface of the parent sheet 10 with excellent adhesiveness. Hereon, plazma etching and ion beam etching were done under the conditions shown in Tables 1 and 3, respectively.

After the parent sheet 10 was coated with the Cr layer, a hot-dip Al-Si alloy plating was applied to the parent sheet 10 under the conditions shown in Table 6.

TABLE 6

CONDITIONS OF HOT-DIP Al-Si ALLOY PLATING	
COMPOSITION OF HOT-DIP COATING BATH (wt.%)	Si 9.2
	Fe 0.08 or 2.11
	BALANCE Al and inevitable impurities
ADHESION AMOUNT	30 g/m^2 per single surface

In order to study the effects of the thickness of the Cr layer and the temperature of the coating bath on the structure (i.e. the multi-layered structure shown in Fig. 5 or 6) of the plating layer L, the thickness of the

Cr layer and the temperature of the coating bath were variously changed. The results are shown in Tables 7 and 8 in combination with the presence or absence of Cr-Si-Al alloy particles G dispersed in the plating layer. There appeared the same tendency to form a plating layer L having the same multi-layered structure and to disperse alloy particles G, in case where the Cr layer was formed by vapor deposition or electroplating, and then only etching was applied to the surface of a parent sheet coated with the Cr layer before the hot-dip coating step.

TABLE 7

EFFECT OF THICKNESS OF Cr LAYER AND TEMPERATURE OF HOT-DIP COATING BATH			
THICKNESS OF Cr LAYER	TEMP. OF COATING BATH (°C)	FORMATION OF PLATING LAYER[*1]	DISPERSION OF ALLOY PARTICLES[*2]
0.05 µm	620°C	no	-
	640°C	no	-
	660°C	no	-
	680°C	no	-
0.08 µm	620°C	no	-
	640°C	no	-
	660°C	no	-
	680°C	no	-
0.10 µm	620°C	yes	no
	640°C	yes	-
	660°C	no	-
	680°C	no	-
0.50 µm	620°C	yes	no
	640°C	yes	yes
	660°C	no	-
	680°C	no	-

*1: a plating layer, in which Cr remained, having the multi-layered structure shown in Fig. 5 or 6
*2: alloy particles dispersed in the third sub-layer

TABLE 8

EFFECT OF THICKNESS OF Cr LAYER AND TEMPERATURE OF HOT-DIP COATING BATH			
THICKNESS OF Cr LAYER	TEMP. OF COATING BATH (°C)	FORMATION OF PLATING LAYER[*1]	DISPERSION OF ALLOY PARTICLES[*2]
1.0 µm	620°C	yes	no
	640°C	yes	yes
	660°C	no	-
	680°C	no	-
1.5 µm	620°C	yes	no
	640°C	yes	yes
	660°C	no	-
	680°C	no	-
2.0 µm	620°C	yes	no
	640°C	yes	yes
	660°C	yes	yes
	680°C	yes	yes
3.0 µm	620°C	yes	no
	640°C	yes	yes
	660°C	yes	yes
	680°C	yes	yes

*1: a plating layer, in which Cr remained, having the multi-layered structure shown in Fig. 5 or 6
*2: alloy particles dispersed in the third sub-layer

It is apparently shown in Table 7 that the use of a parent sheet coated with a Cr layer having thickness less than 0.1 µm did not cause the remaining of Cr and the formation of a plating layer having the multi-layered structure shown in Fig. 5 or 6. When a parent sheet coated with such a thin Cr layer was introduced into a hot-dip Al-Si alloy coating bath, the Cr layer was completely dissolved or diffused without remaining.

On the other hand, when a parent sheet coated with a Cr layer of 0.1-1.5 µm in thickness was introduced into the hot-dip Al-Si alloy coating bath held at a temperature below 640°C, an obtained product had a plating layer, wherein Cr remained, having the multi-layered structure shown in Fig. 5 or 6.

As for a product manufactured from a parent sheet coated with a Cr layer having thickness exceeding 1.5 µm, the Cr layer remained in the plating layer, even when the parent sheet was immersed in a hot-dip Al-Si allloy coating bath held at a temperature above 640 °C. The formed plating layer had the multi-layered structure shown in Fig. 5 or 6. When the coating bath was held at a temperature exceeding 640 °C, Cr-Si-Al alloy particles G were precipitated in the third sub-layer L_3.

The third sub-layer L_3 of the plating layer formed on the surface of a steel substrate was studied in the relationship with the compositions of the hot-dip coating bath. The results are shown in Table 9. The Cr layer shown in Table 9 was formed by vapor deposition, but the same results were obtained as for the Cr layer formed by electroplating. In this case, two kinds of coating bathes were used, one having the composition containing 0.08 wt.% Fe as an impurity mixed in the coating bath, and the other having the composition intentionally containing a large amount e.g. 2.11 wt.%, of Fe.

TABLE 9 RELATIONSHIP BETWEEN HOT-DIP COATING CONDITIONS AND THIRD SUB-LAYER

	SAMPLE	COATING BATH (wt.%)				TEMP. OF BATH	THICKNESS OF Cr LAYER	THIRD SUB-LAYER (wt.%)			
	NO.	Fe	Cr	Si	Al	(℃)	(μm)	Fe	Cr	Si	Al
PRESENT INVENTION	1	0.01	0.02	9.2	bal.	620	1	0.01	0.40	3.3	bal.
	2					640	1	0.01	0.38	3.3	bal.
	3	2.11	0.03	9.1	bal.	620	1	0.58	0.39	3.5	bal.
	4					640	1	0.62	0.43	3.4	bal.
	5	0.01	0.02	9.2	bal.	640	3	0.01	0.39	3.5	bal.
	6					660	3	0.01	0.40	3.3	bal.
	7	2.11	0.03	9.1	bal.	640	3	0.60	0.40	3.4	bal.
	8					660	3	0.62	0.42	3.4	bal.
COMPARISON	9	0.01	0.02	9.2	bal.	620	0	2.13	0.02	10.1	bal.
	10					640	0	2.09	0.02	10.0	bal.
	11					660	0	2.20	0.01	9.9	bal.
	12	2.11	0.03	9.1	bal.	620	0	2.08	0.02	9.9	bal.
	13					640	0	2.19	0.01	9.9	bal.
	14					660	0	2.15	0.02	10.0	bal.

It is noted from Table 9 that a product manufactured from a parent sheet coated with a Cr layer according to the present invention had the third sub-layer, i.e. the outmost layer, of low Fe concentration controlled below 0.62 wt.%, even when the coating bath containing a large amount (2.11 wt.%) of Fe was used for hot-dip coating. The low Fe concentraion is caused by the segregation of Fe in the second sub-layer resulting in the formation of a Cr-Si-Al-Fe alloy layer. In addition, the Cr layer formed on the surface of the parent sheet before the hot-dip coating was diffused into the third sub-layer, so that the Cr concentration in the third sub-layer became approximately 0.4 wt.%.

The amount of Cr in the third sub-layer means the Cr concentration of the third sub-layer itself except the Cr-Si-Al alloy particles. Thus, the third sub-layer exhibits an excellent corrosion inhibiting effect owing to the high Cr concentration and the low Fe concentration in the third sub-layer.

On the other hand, when a parent sheet uncoated with a Cr layer was hot-dip coated under the same conditions, there was formed the third sub-layer containing 2.0 wt.% or more of Fe regardless the Fe concentration of the coating bath. Such high Fe concentration is caused by the inclusion of Fe in the plating layer from the coating bath as well as the diffusion of Fe from the substrate steel. The third sub-layer was inferior in corrosion inhibition due to the high Fe concentration.

The cross section of the coated steel sheet No. 4 was examined by linear analysis using EPMA. Fig.11 shows the result of the analysis in comparison with the metallurgical structure of the plating layer. It is noted in Fig. 11 that the first sub-layer L_1 derived from the Cr layer remained on the surface of the substrate steel. Fe, diffused from the coating bath and the substrate steel, was segregated in the second sub-layer L_2 composed of a Cr-Si-Al-Fe alloy, while the presence of Fe was not detected in the third sub-layer L_3 composed of an Al-Si-Cr alloy. The concentrations of Cr and Si were selectively higher at the part where Cr-Si-Al alloy particles were dispersed in the third sub-layer L_3.

The metallurgical structure of the coated steel sheet No. 5 was observed by a microscope. It was clearly detected that the plating layer had the multi-layered structure comprising the Cr-contng. first sub-layer L_1, the second sub-layer L_2 of a Cr-Si-Al alloy and the third sub-layer L_3 of an Al-Si-Cr alloy successively formed on the surface of the substrate steel S. The Cr-Si-Al alloy particles were dispersed in the third sub-layer L_3.

Fig. 12 shows the relationship between the thickness of the Cr layer and corrosion resistance. It is apparent from Fig. 12 that the corrosion resistance was remarkably improved in response to the thickness of the Cr layer especially exceeding 0.1 µm. The corrosion resistance was further enhanced by the dispersion of the Cr-Si-Al alloy particles in the third sub-layer, when a parent sheet coated with a Cr layer of 2.0 µm or more in thicknees was immersed in a hot-dip coating bath held at 640°C. The excellent corrosion resistance was not deteriorated by the concentration of Fe included in the second sub-layer.

The corrosion resistance of a steel sheet coated with Cr only by vapor deposition was examined for comparison. Even when a thick Cr layer of 8.0 µm in thickness was formed on the substrate steel, the coated sheet sheel was inferior in corrosion resistance. That is, the 5% rust formation time was shorter than 500 hrs..

The excellent corrosion resistance is ensured by keeping the concentration of Cr in the thrid sub-layer. This effect is the same when the Cr-coated steel sheet was activated by ion beam etching.

Further, after a Cr layer was preformed on the surface of a parent sheet by electroplating, the Cr-coated steel sheet was introduced into the vacuum chamber 20 shown in Fig. 3 or 4, etched and then hot-dip coated in the Al-Si alloy bath. In this case, the obtained steel sheet coated with the multi-layered alloy plating layer exhibited excellent corrosion resistance as comapred with a conventional Al-Si alloy-coated steel sheet, as long as the Cr layer was of 0.1 µm or more in thickness.

When the results above-mentioned are summerized, it can be understood that there are formed plating layers having Cr-contng. multi-layered structure effective in corrosion resistance, as far as parent sheets are coated with Cr layers having predetermined thickness, even when each step was changed in order as shown in Table 10.

TABLE 10 ORDER OF VAPOR Cr DEPOSITION, ETCHING AND HOT-DIP COATING

	ORDER OF EACH STEP
I	VAPOR Cr DEPOSITION (APPARATUS ONLY FOR VAPOR DEPOSITION) → [PLAZMA ETCHING → HOT-DIP COATING]
II	VAPOR Cr DEPOSITION (APPARATUS ONLY FOR VAPOR DEPOSITION) → [ION BEAM ETCHING → HOT-DIP COATING]
III	Cr ELECTROPLATING → [PLAZMA ETCHING → HOT-DIP COATING]
IV	Cr ELECTROPLATING → [ION BEAM ETCHING → HOT-DIP COATING]
V	[VAPOR Cr DEOPOSITION → HOT-DIP COATING]
VI	[PLAZMA ETCHING → VAPOR Cr DEPOSITION → HOT-DIP COATING]
VII	[ION BEAM ETCHING → VAPOR Cr DEPOSITION → HOT-DIP COATING]

The steps in each parenthesis [ ] were done in the same apparatus.

A product manufactured by hot-dip coating a parent sheet coated with a Cr layer of 0.5 µm in thickness in any of the process I - VII was excellent in corrosion resistance well over 3500 hrs. by the 5% rust formation time, regardless of the means for forming a Cr layer or the order of the etching and Cr layer-forming steps. Especially, a product obtained from a parent sheet coated with a Cr layer of 2.0 µm in thickness had the 5% rust formation time exceeding 8500 hrs..

Fig. 13 shows the effect of Fe concentration in the third sub-layer on corrosion resistance. In this case, a parent sheet coated with a Cr layer of 1.5 µm in thickness was hot-dip coated in an Al-Si alloy coating bath held at 640 °C using the plant shown in Fig. 3. Hereon, Fe content included in the third sub-layer was 0.7 wt.% or lower. In this regard, a parent sheet was electroplated with a Fe layer and then hot-dip coated in the same way to prepare a test piece for comparative examples wherein Fe content in the third sub-layer was intentionally increased.

It is noted from Fig. 13 that products had excellent corrosion resistance near 6500 hrs. by 5% rust formation time when Fe content in the third sub-layer was below 0.7 wt.%. The corrosion resistance became worse as the increase of Fe concentration in the third sub-layer. For instance, a product having the third sub-layer wherein Fe concentration was 2.03 wt.% showed poor corrosion resistance below 4500 hrs. by 5% rust formation time. Taking into consideration the effect of Fe, the Cr layer is also effective in inhibiting the increase of Fe concentration in the third sub-layer. Thus, the Cr layer favorably suppresses the increase of Fe concentration in addition to the increase of Cr concentration in the third sub-layer, so as to remarkably improves the corrosion resistance of the coated steel sheet.

EXAMPLE 6

Parent sheets were coated with an Al-Si alloy plating layer using a Cr-contng. hot-dip coating bath having the composition shown in Table 11. The obtained product had corrosion resistance in the relationship shown in Fig. 14 with the thickness of Cr layers preformed on the surface of the parent sheets. Herein, each parent sheet was coated with the Cr layer and then hot-dip coated with the Al-Si alloy plating layer using the plant shown in Fig. 3. The corrosion resistance was examined by the salt water spray test under the same conditions as those in Example 1.

It is noted from Fig. 14 that a coated steel sheet further improved in corrosion resistance was obtained using a hot-dip coating bath containing Cr as compared with a product hot-dip coated in a coating bath free from Cr. When the plating layer formed on the steel sheet was observed by a microscope, it was detected that Cr-Al-Si alloy particles in an increased amount were dispersed in the third sub-layer. Hereby, it is thought that the further improvement of corrosion resistance is owing to the increase of the Cr-Al-Si alloy particles.

TABLE 11

COATING CONDITIONS USING Cr-CONTG. HOT-DIP Al-Si COATING BATH	
COMPOSITION OF HOT-DIP COATING BATH (wt.%)	Si : 9.2
	Fe : 1.7
	Cr : 0.13
	bal: Al and impurities
ADHESION AMOUNT	30 g/m^2 per single surface

According to the present invention as aforementioned, a Cr layer preformed on the surface of a steel sheet to be hot-dip coated serves as a Cr supply source to a plating layer. The steel sheet can be introduced into a hot-dip coating bath under the condition that the Cr layer keeps good wettability to a coating metal, when oxide films formed on the surface of the Cr layer are removed by plazma etching or ion beam etching, or when hot-dip coating continuously follows vapor Cr deposition in the same vacuum chamber. Hereby, the formed plating layer is effective in corrosion resistance and heat resistance owing to Cr content therein as well as adhesiveness to the steel substrate.

The formed plating layers have multi-layered structures each different from the others in response to the thickness of the Cr layers, hot-dip coating conditions, kinds of parent sheets, etc.. The coated shteel sheet having any multi-layered structure exhibits excellent corrosion resistance and heat resistance as compared with a conventional hot-dip Al-Si alloy-coated steel sheet. The obtained product will be used as a material in broad industrial fields, e.g. parts and members for the exhaust system of an automobile, and structural sheets for building and civil engineering.

In addition, a coating process as well as a plant therefor are simplified, when a steel sheet is hot-dip coated in the same vacuum chamber as that for vapor Cr deposition, Hereby, a product excellent in corrosion resistance and heat resistance is manufactured at a low cost.

Claims

1. A method of manufacturing an Al-Si-Cr alloy coated steel sheet comprising the steps of:
  - forming a Cr layer on the surface of a parent sheet, and
  - introducing said sheet into a hot-dip Al-Si alloy coating bath while keeping the surface of said Cr layer in an activated state.

2. The method according to Claim 1, wherein the coating bath is free from Cr.

3. The method according to Claim 1, wherein the coating bath contains Cr.

4. The method according to Claim 1, wherein the parent sheet is a Cr-containing low-allloyed steel or a stainless steel.

5. The method according to Claim 1, wherein the parent sheet is a common steel or a low-alloyed steel free from Cr.

6. The method according to Claim 1, wherein the Cr layer is formed by electroplating.

7. The method according to Claim 1, wherein the Cr layer is formed by vapor Cr deposition.

8. A method of manufacturing an Al-Si-Cr alloy-coated steel sheet comprising the steps of:
- forming a Cr layer on the surface of a parent sheet by vapor deposition in a vacuum atmosphere, and
- introducing said sheet into a hot-dip Al-Si alloy coating bath held in the same vacuum atmosphere.

9. The method according to Claim 8, wherein the coating bath is free from Cr.

10. The method according to Claim 8, wherein the coating bath contains Cr.

11. The method according to Claim 8, wherein the parent sheet is a Cr-containing low-allloyed steel or a stainless steel.

12. The method according to Claim 8, wherein the parent sheet is a common steel or a low-alloyed steel free from Cr.

13. A method of manufacturing an Al-Si-Cr alloy-coated steel sheet comprising the steps of:
- forming a Cr layer on the surface of a parent sheet by vapor deposition in a vacuum atmosphere,
- activating the surface of said Cr layer by plazma etching or ion beam etching in the same vacuum atmosphere, and
- introducing said sheet into a hot-dip Al-Si alloy coating bath held in the same vacuum atmosphere.

14. The method according to Claim 13, wherein the coating bath is free from Cr.

15. The method according to Claim 13, wherein the coating bath contains Cr.

16. The method according to Claim 13, wherein the parent sheet is a Cr-containing low-allloyed steel or a stainless steel.

17. The method according to Claim 13, wherein the parent sheet is a common steel or a low-alloyed steel free from Cr.

18. A method of manufacturing an Al-Si-Cr alloy-coated steel sheet comprising the steps of:
- activating the surface of a parent sheet by plazma etching or ion beam etching in a vacuum atmosphere,
- forming a Cr layer on the surface of said parent sheet by vapor deposition in the same vacuum atmosphere, and
- introducing said sheet into a hot-dip Al-Si alloy coating bath held in the same vacuum atmosphere.

19. The method according to Claim 18, wherein the coating bath is free from Cr.

20. The method according to Claim 18, wherein the coating bath contains Cr.

21. The method according to Claim 18, wherein the parent sheet is a Cr-containing low-allloyed steel or a stainless steel.

22. The method according to Claim 18, wherein the parent sheet is a common steel or a low-alloyed steel free from Cr.

23. An Al-Si-Cr alloy-coated steel sheet comprising a steel substrate coated with a plating layer having a multi-layered structure composed of the first sub-layer of an Al-Si-Fe alloy, the second sub-layer of an Al-Cr-Si-Fe alloy and the third sub-layer of an Al-Si alloy formed in oder on the surface of said steel substrate.

24. The Al-Si-Cr alloy-coated steel sheet according to Claim 23, wherein the second sub-layer contains 0.7 wt.% or more of Cr.

25. The Al-Si-Cr alloy-coated steel sheet in Claim 23, wherein the steel substrate is a common steel or a low-alloyed steel free from Cr.

26. The Al-Si-Cr alloy-coated steel sheet according to Claim 23, wherein the steel substrate is a Cr-containing low-alloyed steel or a stainless steel.

27. An Al-Si-Cr alloy-coated steel sheet comprising a steel substrate coated with a plating layer having a multi-layered structure composed the first sub-layer of an Al-Si-Fe-Cr alloy, the second sub-layer of an Al-Cr-Si-Fe alloy and the third sub-layer of an Al-Si-Cr alloy formed in order on the surface of said steel substrate.

28. The Al-Si-Cr alloy-coated steel sheet according to Claim 27, wherein the second sub-layer contains 0.7 wt.% or more of Cr.

29. The Al-Si-Cr alloy-coated steel sheet according to Claim 27, wherein the third sub-layer includes Si-rich alloy particles precipitated therein.

30. The Al-Si-Cr alloy-coated steel sheet according to Claim 27, wherein the steel substrate is a common steel or a low-alloyed steel free from Cr.

31. The Al-Si-Cr alloy-coated steel sheet according to Claim 27, wherein the steel substrate is a Cr-containing low-alloyed steel or a stainless steel.

32. An Al-Si-Cr alloy-coated steel sheet comprising a steel substrate coated with a plating layer having a multi-layered structure composed of the first sub-layer of Cr, the second sub-layer of an Cr-Si-Al alloy and the third sub-layer of an Al-Si-Cr alloy formed in order on the surface of said steel substrate.

33. The Al-Si-Cr alloy-coated steel sheet according to Claim 32, wherein the third sub-layer includes Cr-Si-Al alloy particles precipitated therein.

34. The Al-Si-Cr alloy-coated steel sheet according to Claim 32, wherein the steel substrate is a common steel or a low-alloyed steel free from Cr.

35. The Al-Si-Cr alloy-coated steel sheet according to Claim 27, wherein the steel substrate is a Cr-containing low-alloyed steel or a stainless steel.

Amended claims

1. A method of making an Al-Si-Cr alloy-coated steel sheet comprising the steps of:
- forming a Cr layer on the surface of a parent sheet, and
- introducing said sheet into a hot-dip Al-Si alloy coating bath while keeping the surface of said Cr layer in an activated state.

2. A method of making an Al-Si-Cr alloy-coated steel sheet comprising the steps of:
- forming a Cr layer on the surface of a parent sheet by vapour deposition in a vacuum atmosphere, and

- introducing said sheet into a hot-dip Al-Si alloy coating bath held in the same vacuum atmosphere.

3. A method of making an Al-Si-Cr alloy-coated steel sheet comprising the steps of:
- forming a Cr layer on the surface of a parent sheet by vapour deposition in a vacuum atmosphere,
- activating the surface of said Cr layer by plazma etching or ion beam etching in the same vacuum atmosphere, and
- introducing said sheet into a hot-dip Al-Si alloy coating bath held in the same vacuum atmosphere.

4. A method of making an Al-Si-Cr alloy-coated steel sheet comprising the steps of:
- activating the surface of a parent sheet by plazma etching or ion beam etching in a vacuum atmosphere,
- forming a Cr layer on the surface of said parent sheet by vapour deposition in the same vacuum atmosphere, and
- introducing said sheet into a hot-dip Al-Si alloy coating bath held in the same vacuum atmosphere.

5. A method according to any preceding claim, wherein the coating bath is free from Cr.

6. A method according to any one of claims 1 to 4, wherein the coating bath contains Cr.

7. A method according to any preceding claim, wherein the parent sheet is a Cr-containing low-alloyed steel or a stainless steel.

8. A method according to any one of claims 1 to 6, wherein the parent sheet is a common steel or a low-alloyed steel free from Cr.

9. A method according to any preceding claim, wherein the Cr layer is formed by electroplating.

10. A method according to any one of claims 1 to 8, wherein the Cr layer is formed by vapour Cr deposition.

11. An Al-Si-Cr alloy-coated steel sheet comprising a steel substrate coated with a plating layer having a multi-layered structure composed of a first sub-layer of Al-Si-Fe alloy, a second sub-layer of Al-Cr-Si-Fe alloy and a third sub-layer of Al-Si alloy in said order on the surface of said steel substrate.

12. An Al-Si-Cr alloy-coated steel sheet comprising a steel substrate coated with a plating layer having a multi-layered structure composed of a first sub-layer of Al-Si-Fe-Cr alloy, a second sub-layer of Al-Cr-Si-Fe alloy and a third sub-layer of Al-Si-Cr alloy in said order on the surface of said steel substrate.

13. An Al-Si-Cr alloy-coated steel sheet comprising a steel substrate coated with a plating layer having a multi-layered structure composed of a first sub-layer of Cr, a second sub-layer of Cr-Si-Al alloy and a third sub-layer of Al-Si-Cr alloy in said order on the surface of said steel substrate.

14. An Al-Si-Cr alloy-coated steel sheet according to claim 11 or 12, wherein the second sub-layer contains 0.7 wt.% or more of Cr.

15. An Al-Si-Cr alloy-coated steel sheet according to any one of claims 11 to 14, wherein the steel substrate is a common steel or a low-alloyed steel free from Cr.

16. An Al-Si-Cr alloy-coated steel sheet according to any one of claims 11 to 14, wherein the steel substrate is a Cr-containing low-alloyed steel or a stainless steel.

17. An Al-Si-Cr alloy-coated steel sheet according to any one of claims 12 or 14 to 16 when dependant upon claim 12, wherein the third sub-layer includes Si-rich alloy particles precipitated therein.

18. An Al-Si-Cr alloy-coated steel sheet according to any one of claims 13 or 14 to 16 when dependant upon claim 13, wherein the third sub-layer includes Cr-Si-Al alloy particles precipitated therein.

FIG.1

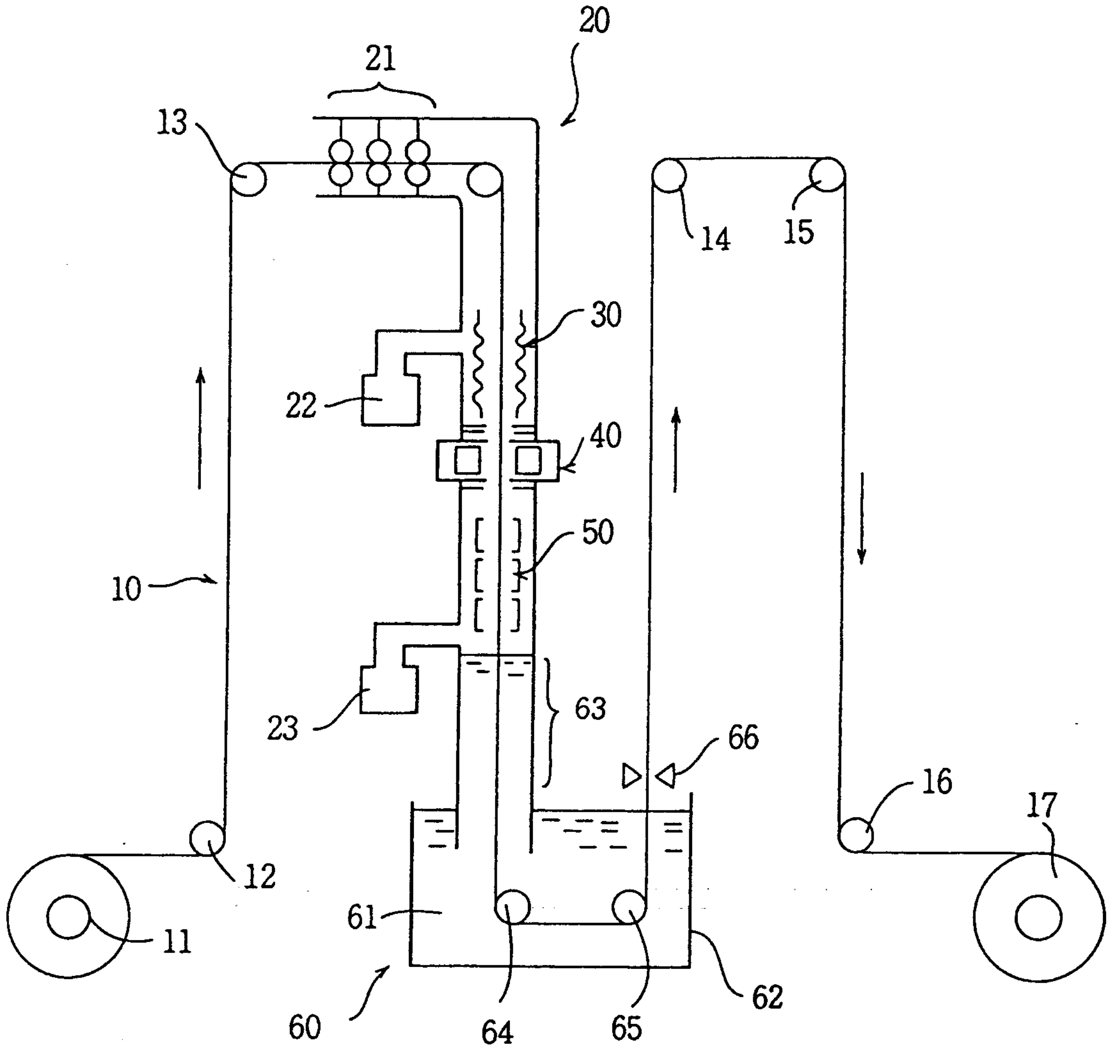


FIG.2

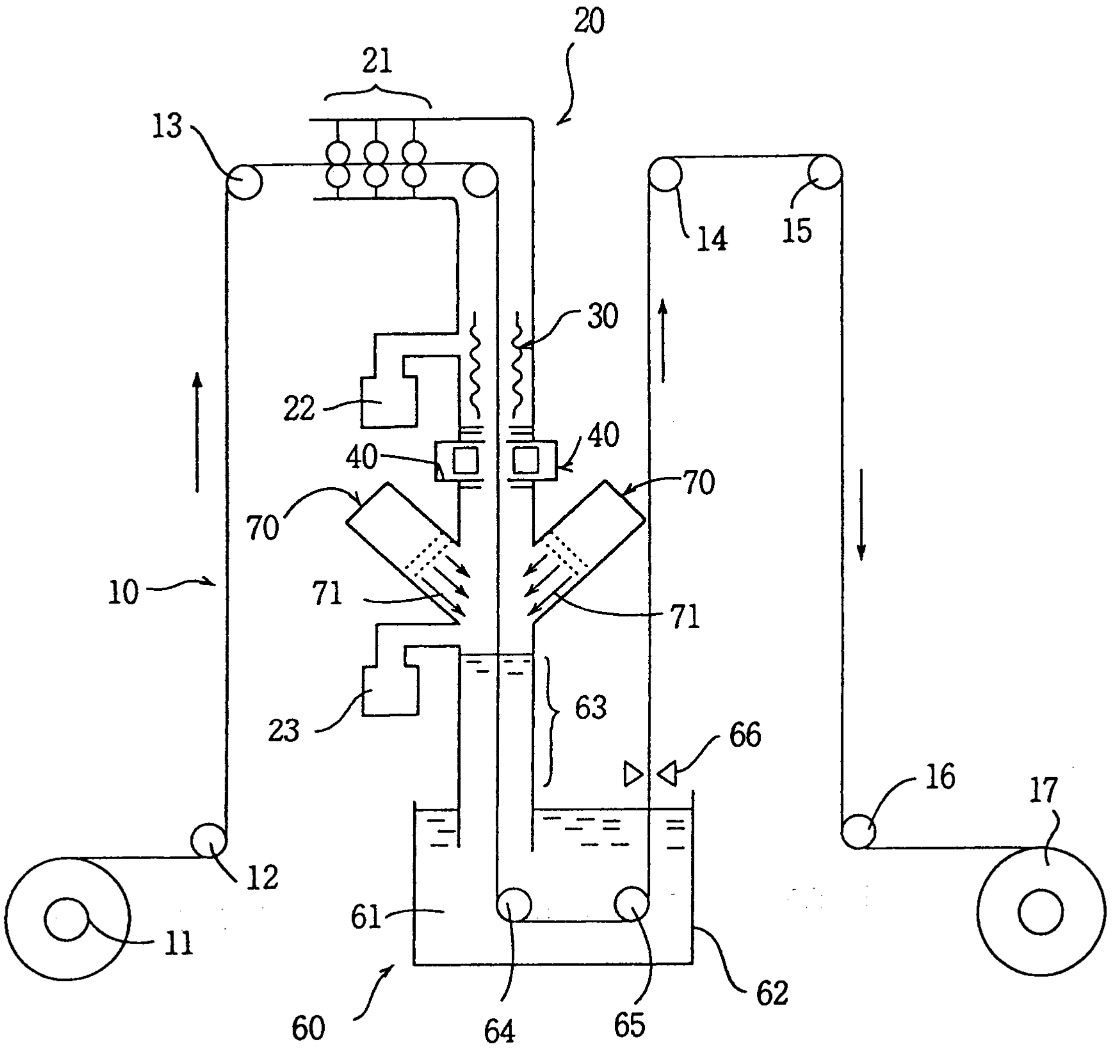

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FIG.3

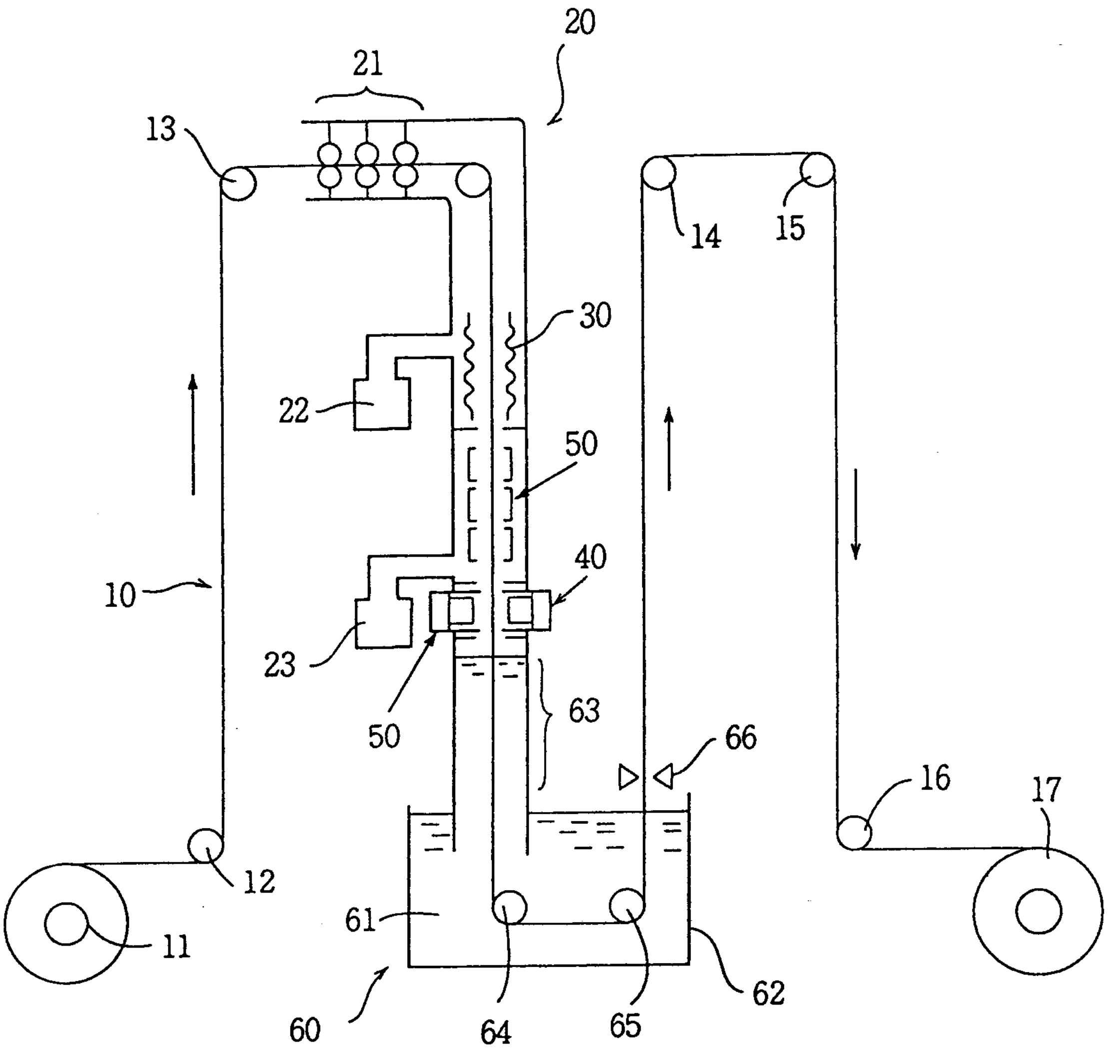
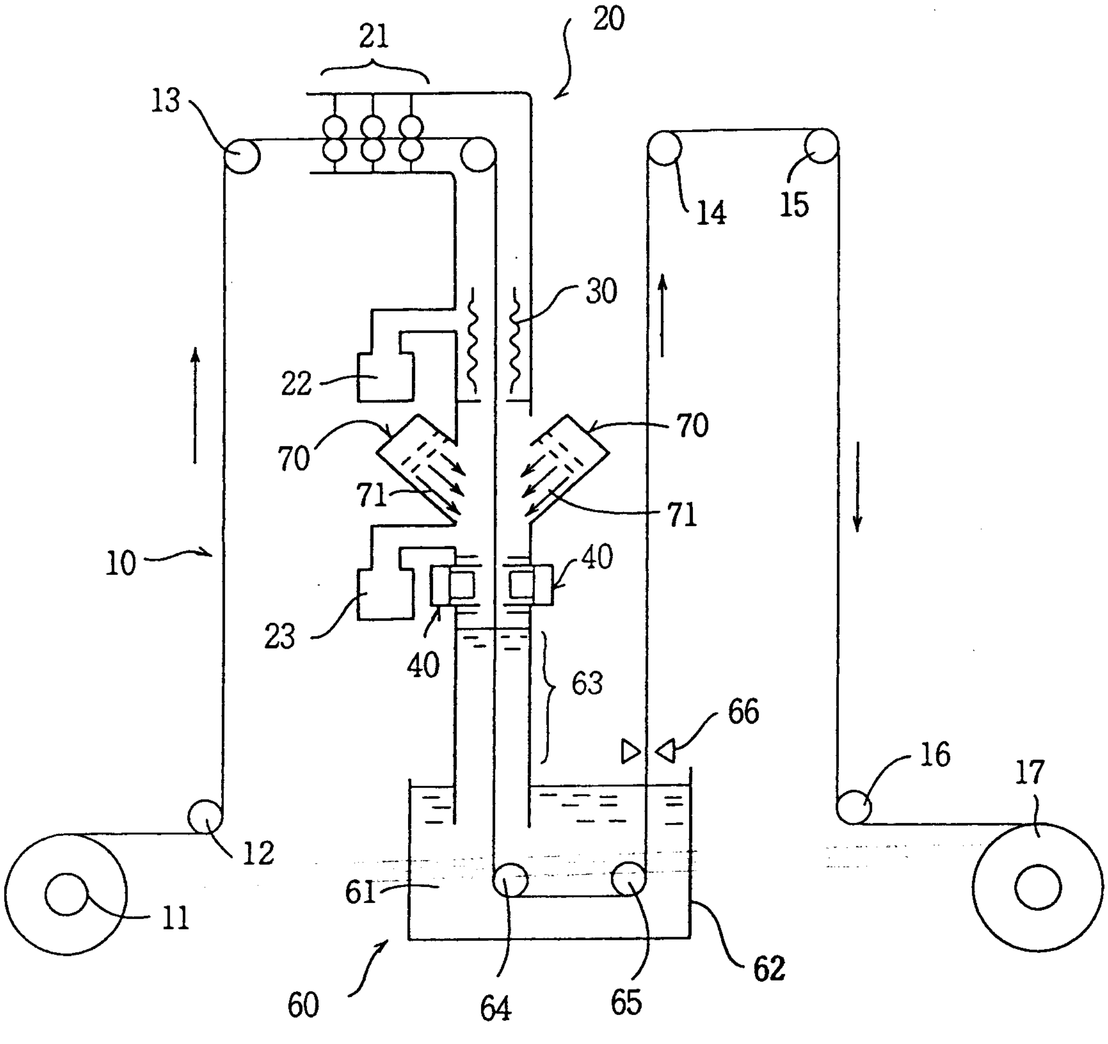


FIG.4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11
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60
64
65
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FIG.5

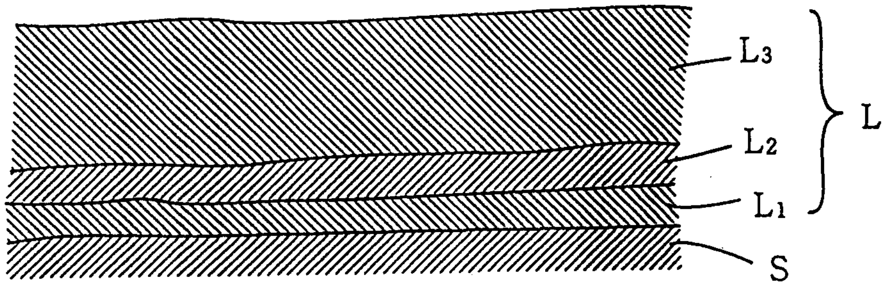


FIG.6

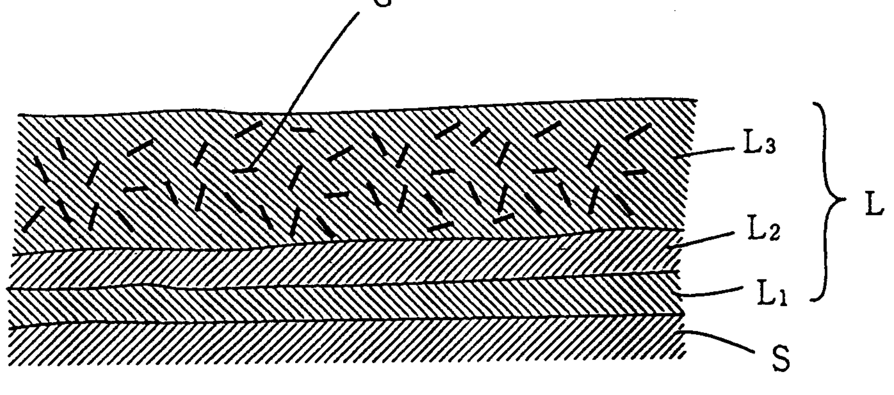


FIG.7

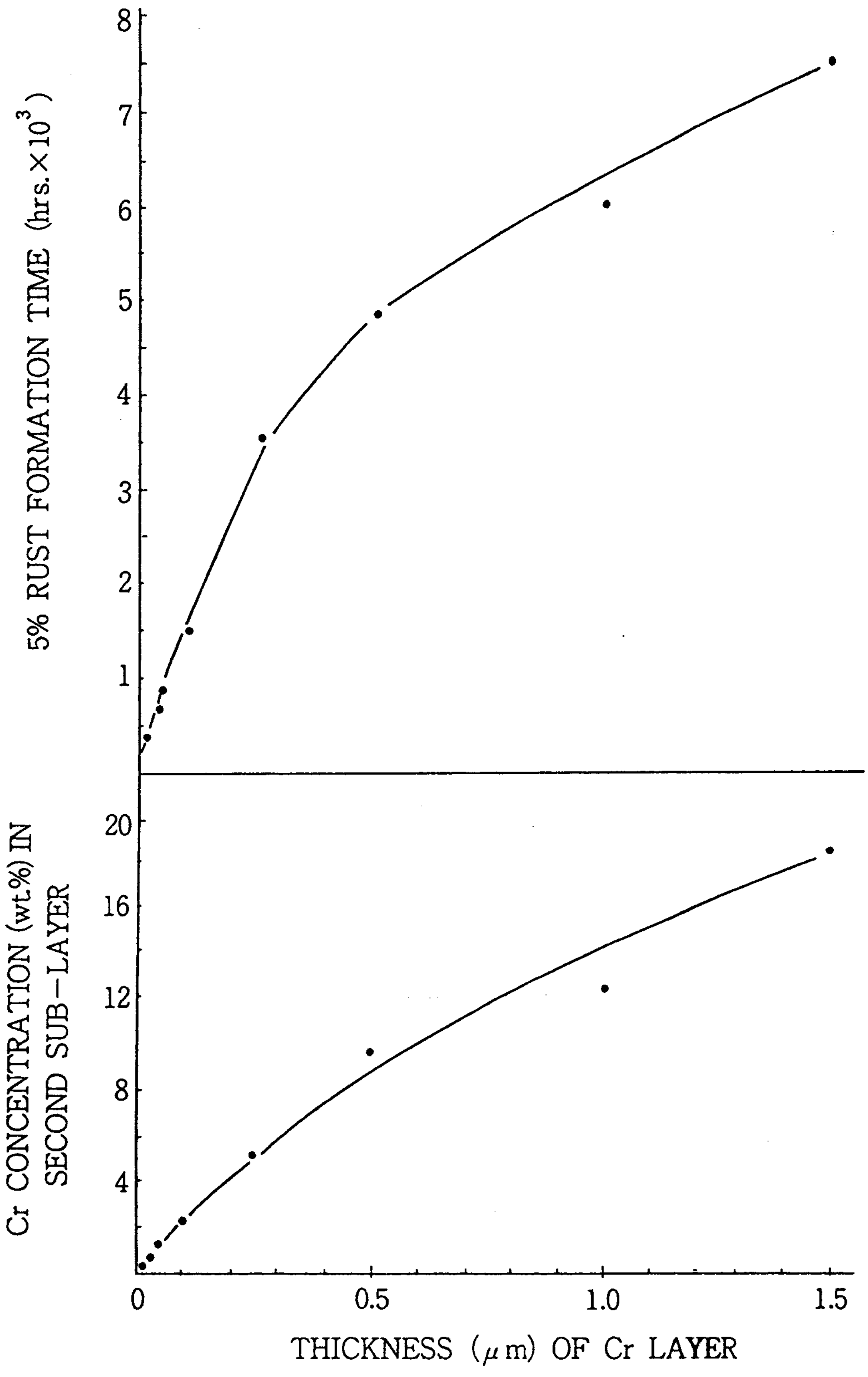

5% RUST FORMATION TIME (hrs.×10³)
8
7
6
5
4
3
2
1
Cr CONCENTRATION (wt%) IN SECOND SUB-LAYER
20
16
12
8
4
0
0.5
1.0
1.5
THICKNESS (μm) OF Cr LAYER

FIG.8

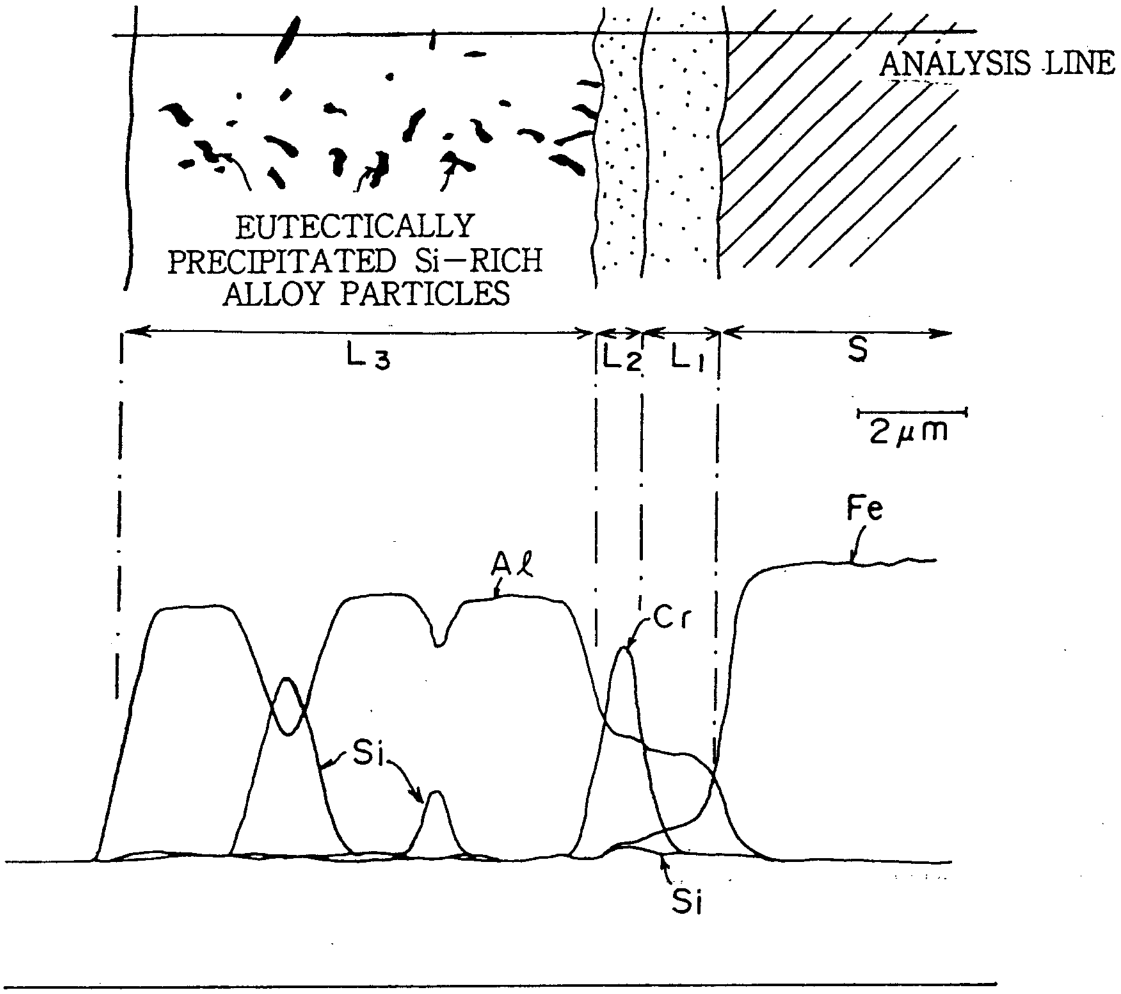

ANALYSIS LINE
EUTECTICALLY PRECIPITATED Si-RICH ALLOY PARTICLES
L3
L2
L1
S
2 μm
Fe
Aℓ
Cr
Si
Si

FIG.9

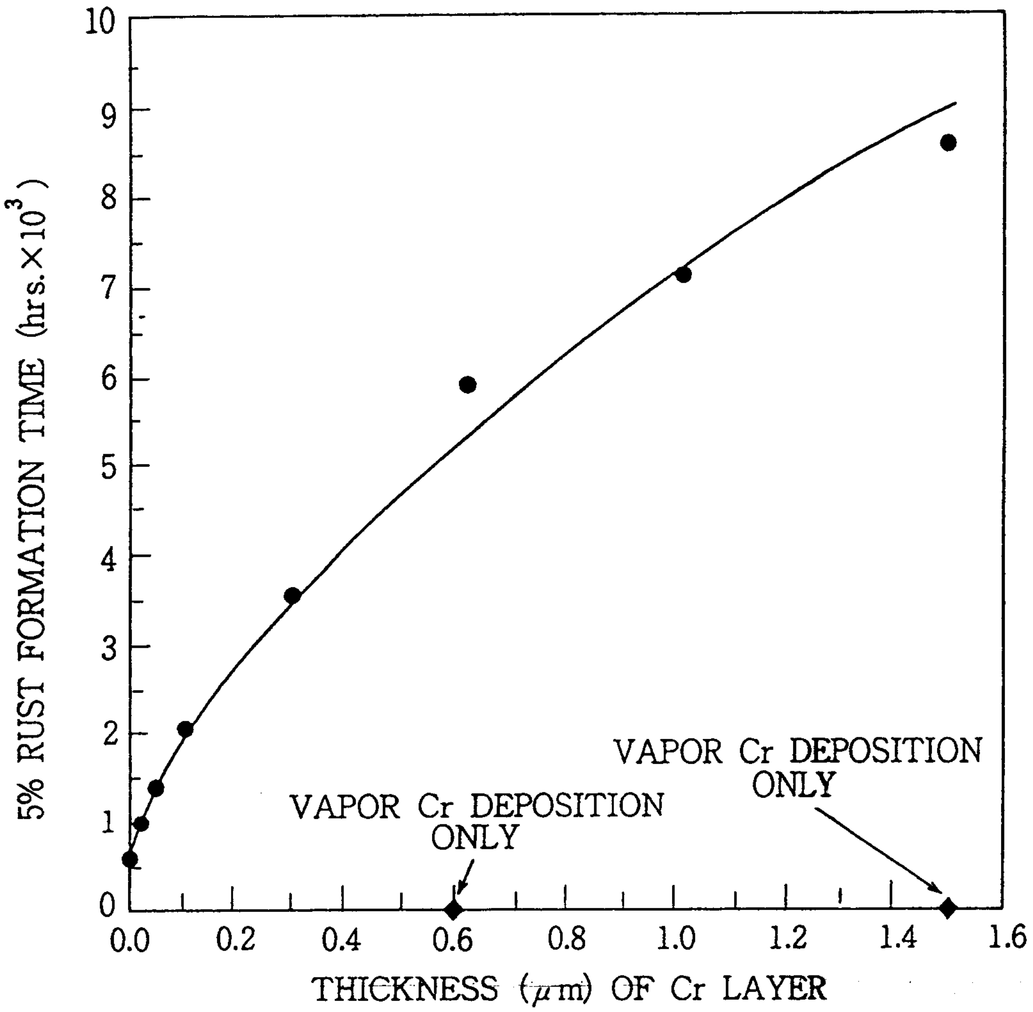

10
9
8
7
6
5
4
3
2
1
0
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
5% RUST FORMATION TIME (hrs.×10³)
THICKNESS (μm) OF Cr LAYER
VAPOR Cr DEPOSITION ONLY
VAPOR Cr DEPOSITION ONLY

FIG.10

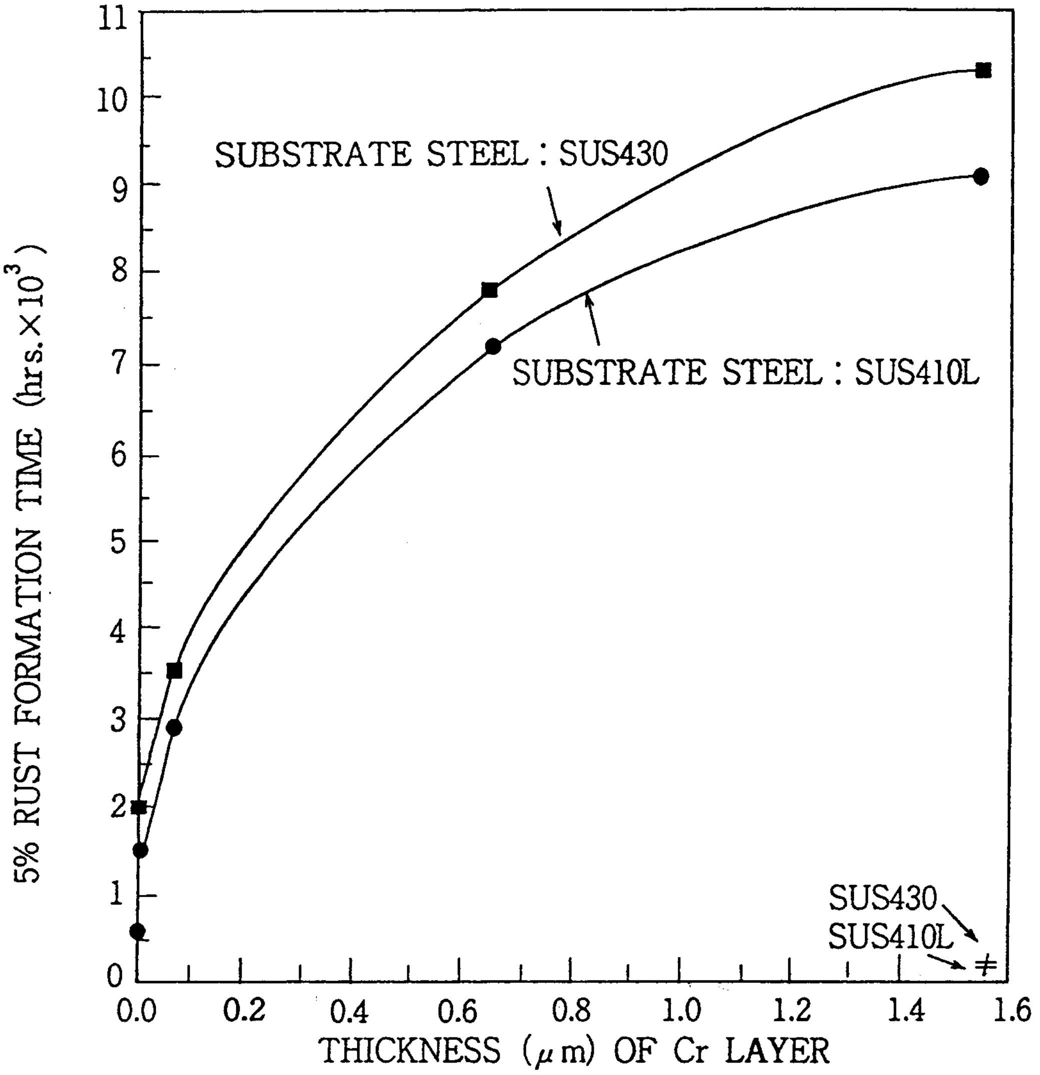

5% RUST FORMATION TIME (hrs.×10³)
THICKNESS (μm) OF Cr LAYER
SUBSTRATE STEEL : SUS430
SUBSTRATE STEEL : SUS410L
SUS430
SUS410L
0
1
2
3
4
5
6
7
8
9
10
11
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6

FIG.11

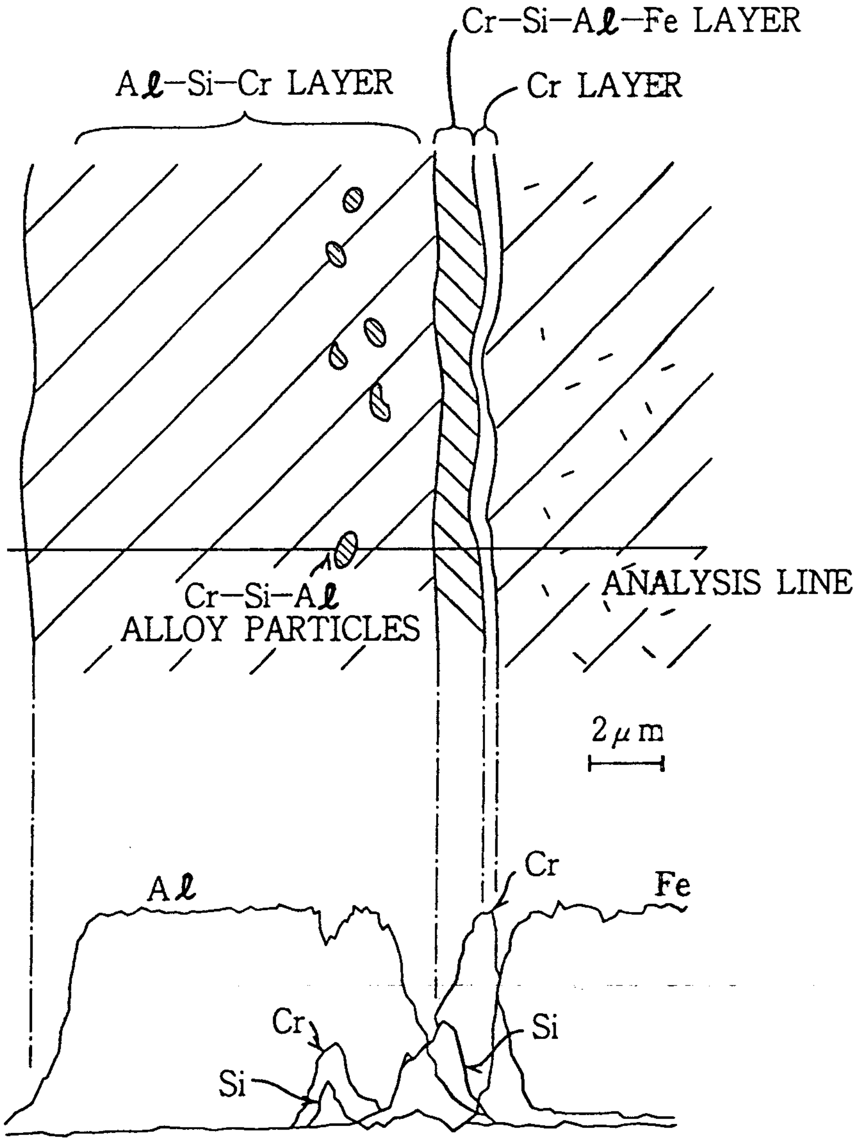

Cr−Si−Aℓ−Fe LAYER
Aℓ−Si−Cr LAYER
Cr LAYER
Cr−Si−Aℓ
ALLOY PARTICLES
ANALYSIS LINE
2μm
Aℓ
Cr
Fe
Cr
Si
Si

FIG.12

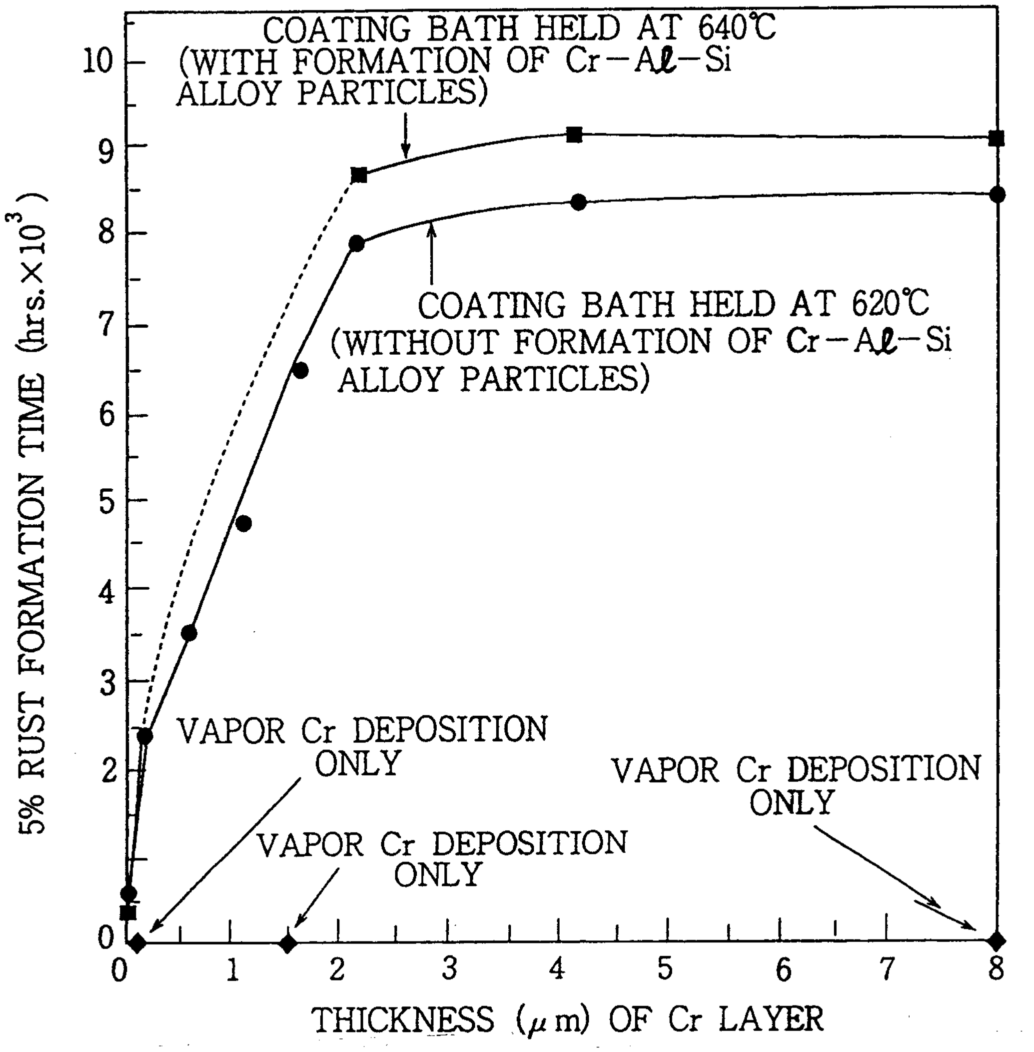
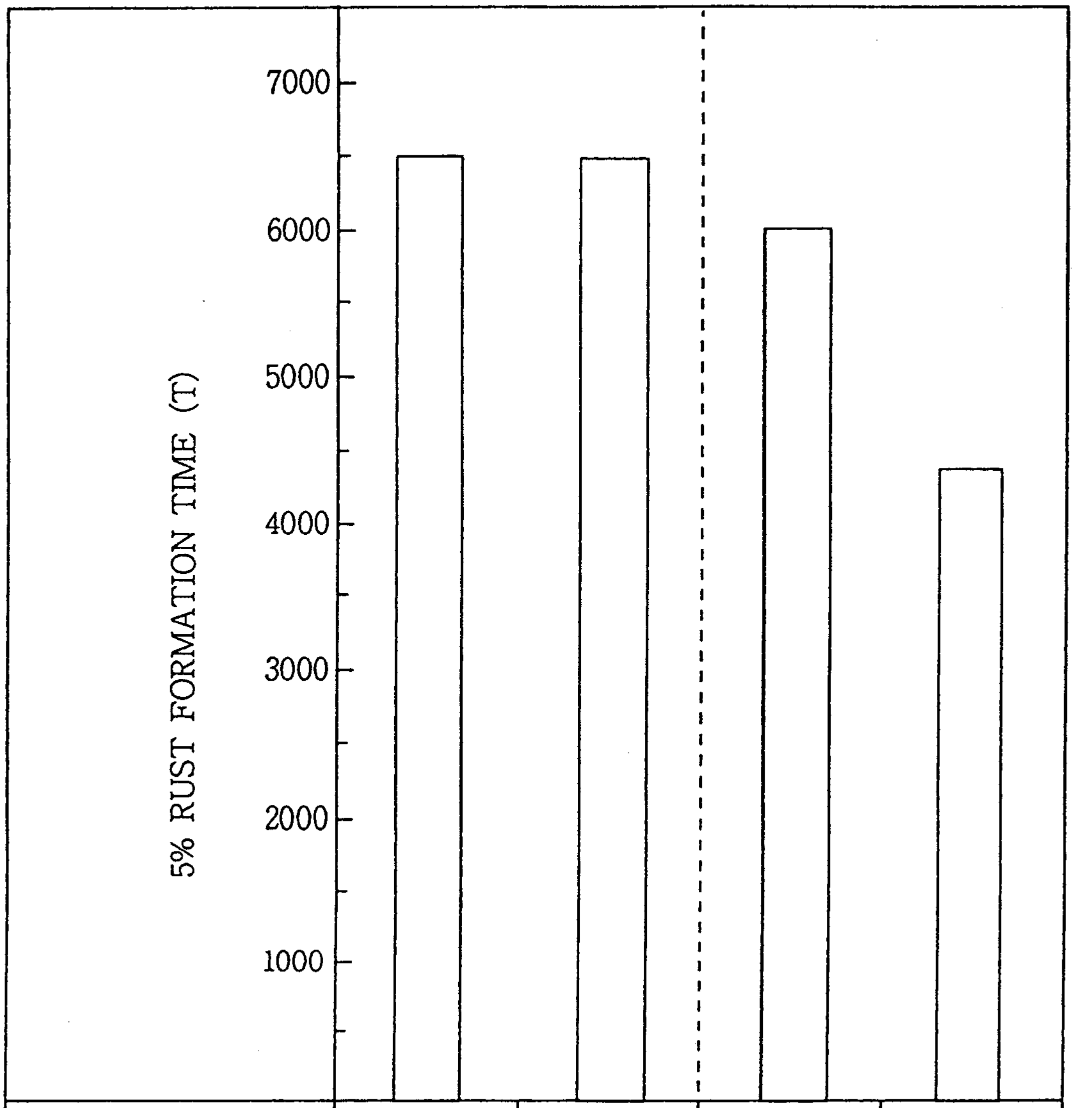

COATING BATH HELD AT 640℃
(WITH FORMATION OF Cr−Aℓ−Si
ALLOY PARTICLES)
COATING BATH HELD AT 620℃
(WITHOUT FORMATION OF Cr−Aℓ−Si
ALLOY PARTICLES)
VAPOR Cr DEPOSITION
ONLY
VAPOR Cr DEPOSITION
ONLY
VAPOR Cr DEPOSITION
ONLY
5% RUST FORMATION TIME (hrs.×10³)
0
2
3
4
5
6
7
8
9
10
0
1
2
3
4
5
6
7
8
THICKNESS (μm) OF Cr LAYER

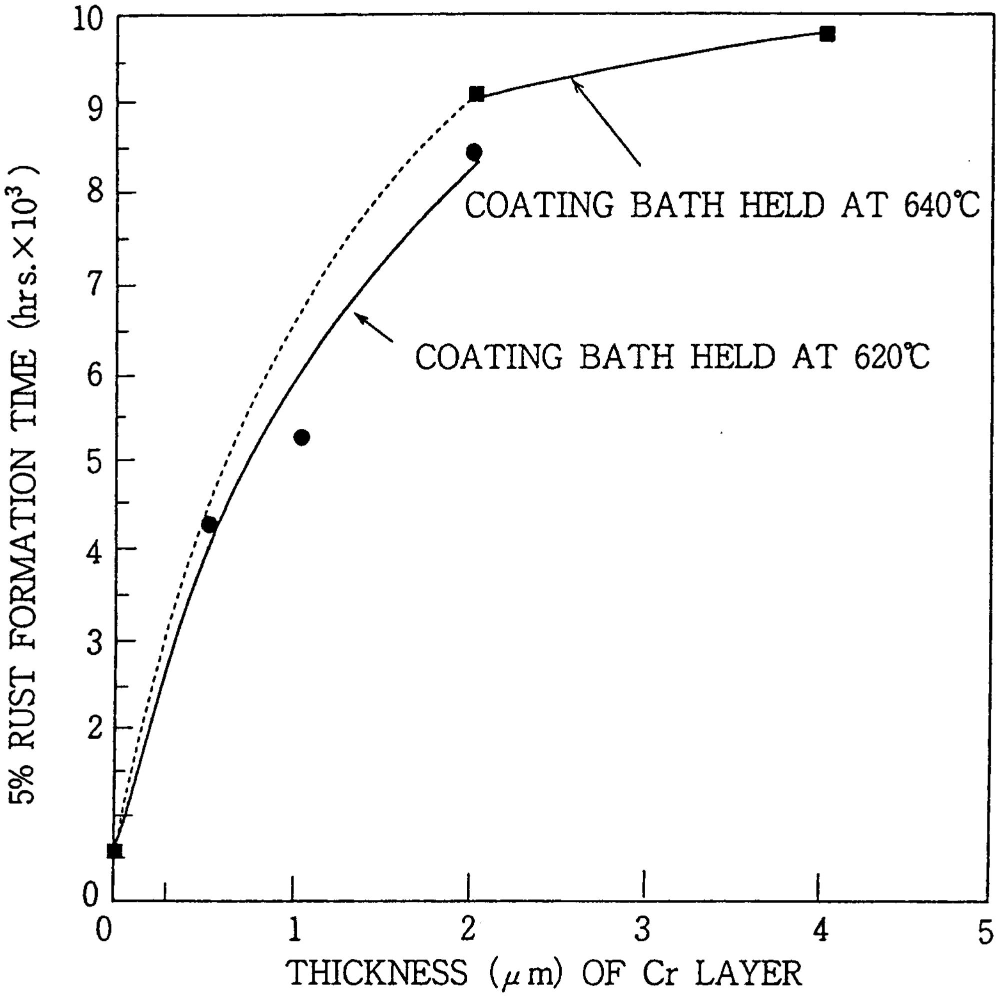
FIG.13



ADHESION AMOUNT (g/m^2) OF Fe	0	0	0.5	2.0
Fe CONCENTRATION (wt.%) IN THIRD SUB-LAYER	0.01	0.66	0.80	2.03
TYPE OF PROCESS	Cr ELECTROPLATING → HOT-DIP COATING		Cr ELECTROPLATING → Fe ELECTROPLATING	
	PRESENT INVENTION		COMPARATIVE EXAMPLES	

Cr LAYER OF 1.5μm IN THICKNESS   COATING BATH HELD AT 640C

FIG.14


10
9
8
7
6
5
4
3
2
0
5% RUST FORMATION TIME (hrs.×10³)
0
1
2
3
4
5
THICKNESS (μm) OF Cr LAYER
COATING BATH HELD AT 640℃
COATING BATH HELD AT 620℃

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP93/00163

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl^5 C23C2/12, C23C2/02

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)

Int. Cl^5 C23C2/12, C23C2/02, C23C28/02

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

Jitsuyo Shinan Koho	1926 - 1992
Kokai Jitsuyo Shinan Koho	1971 - 1992

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, A, 4-28852 (Nisshin Steel Co., Ltd.), January 31, 1992 (31. 01. 92), (Family: none)	1-35
A	JP, A, 58-58261 (NKK Corp.), April 6, 1983 (06. 04. 83), (Family: none)	1-35
A	JP, A, 55-76017 (Kawasaki Steel Corp.), June 7, 1980 (07. 06. 80), (Family: none)	1-35

☐ 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 document 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 another 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 April 20, 1993 (20. 04. 93)	Date of mailing of the international search report May 18, 1993 (18. 05. 93)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.