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(54) **Electroplating of hot-galvanized steel sheet and continuous plating line therefor**

Elektroplattierung von feuerverzinkten Stahlbändern und kontinuierliche Vorrichtung dafür

Electroplacage de bandes d'acier galvanisées à chaud et installation en continu à cet effet

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EP 0 545 908 B1

Description

This invention relates to a plating method for steel sheet. More particularly, it relates to an electroplating method of hot-galvanized steel sheet. It also relates to a plating line in which a steel sheet is continuously subjected to hot-galvanizing and then electroplating. The resulting plated steel sheet has an electroplated top coating with excellent covering power and adhesion to the underlying hot-galvanized coating.

In the automotive and construction industries, there is always a great demand for materials having good corrosion resistance and a long life span. In particular, the corrosion resistance demanded of rust-preventive steel sheets for automobile bodies has become extreme.

In order to meet these demands, various new types of electroplated steel sheets have been proposed, such as steel sheets electroplated with a Zn-Ni, Zn-Fe, or Zn-Mn alloy, steel sheets hot-dip plated with a Zn-Fe, Zn-Al-Si, or Zn-Al-Mg alloy. Steel sheet having multiple plated layers in which the top layer is an Fe-rich (Fe $\geqq$ 60%) Fe-Zn alloy plated coating has also been developed with the intention to improve the coatability of the plated steel sheet by cationic electrodeposition performed thereon and to increase the adhesion of the electrodeposited coating in water (see Japanese Published Unexamined Patent Application No. 56-133488).

Steel sheet with a plurality of layers of plated coating (hereinafter referred to as multi-layer plated steel sheet) is highly suitable for use in automobiles and as a construction material not only on account of its coatability but also because of its excellent press forming characteristics (sliding properties), weldability, and various other properties.

The multi-layer electroplating that have been proposed in the prior art include a Zn-Ni/Fe or Fe-Zn coating (Japanese Published Examined Patent Application No. 60-57518), a Zn-Ni/Zn or Zn-Ni or Zn-Fe/Cr(Cr-oxide) coating (Japanese Published Unexamined Patent Application No. 60-197893), a Zn-Mn/Zn-Fe coating (Japanese Publised Unexamined Patent Application No. 58-42787), and a Zn or Zn alloy/minute particle-dispersed Zn or Zn alloy coating (Japanese Publised Unexamined Patent Application No. 62-230999).

Recently, it has also been proposed to perform electroplating on an alloyed hot-galvanized steel sheet (Japanese Publised Unexamined Patent Applications Nos. 56-133488 and 61-253397).

When forming multi-layer electroplated coating using a single electroplating line, normally, plating baths for different types of coatings are arranged in series along the line. Equipment for dip water rinsing and, if necessary, equipment for rinsing with hot water or with brushes is installed between successive baths. However, no treatment other than rinsing or scrubbing is performed on the steel sheet as it is passed from one bath to another.

Similarly, when a steel sheet is hot-galvanized and then electroplated in a continuous process, equipment for continuous electroplating is simply connected in series with equipment for continuous hot-galvanizing, and no special treatments are performed on the steel sheet as it travels between the two sets of equipment.

For example, Japanese Published Unexamined Patent Application No. 60-224791 discloses a continuous plating apparatus in which a pretreatment apparatus, a hot-galvanizing bath, an alloying furnace, and an electroplating apparatus are connected in series. A skin-pass rolling mill and, if necessary, a water rinse tank may be disposed between the hot-galvanizing bath and the electroplating apparatus.

Japanese Published Unexamined Patent Application No. 62-17200 discloses a continuous one-sided plating apparatus in which a pretreatment apparatus, a hot-galvanizing bath for plating one side of a steel sheet, an alloying furnace, a cleaning apparatus for cleaning the unplated side of the sheet, and an electroplating apparatus are connected in series.

In these continuous plating apparatuses, no special chemical treatment is performed on the hot-dipped coating of the sheet before electroplating.

Document GB-A-0 417 411 discloses a method of electroplating hot-dip galvanized steel involving a cleaning step prior to electroplating.

The present inventors' research has shown that when two different processes, such as hot-galvanizing and electroplating, are arranged in sequence, the following problems occur.

(1) If continuous electroplating is performed after hot-galvanizing of a steel sheet, electroplated coatings such as a Fe or Fe-based alloy (Fe-Zn, etc.), Cr(Cr-oxide), Ni, and Zn-Ni alloy coatings have poor adhesion to the galvanized coating, and these coatings tend to readily peel off either while the coated sheet is still flat or after it has been subjected to working (bending, drawing, etc.).

(2) If a hot-galvanized steel sheet is heated to perform alloying of the galvanized coating prior to electroplating, the resulting alloyed galvanized coating has microscopic surface irregularities, i.e., bumps and depressions, which are inherent in an alloyed galvanized steel sheet (usually called GA steel sheet). The irregularities include those which are caused by the crystalline form of the Zn-Fe alloy and microscopic depressions which are formed during alloying. They generally have a size of 3 - 20 micrometers.

Such microscopic surface irregularities, and particularly the depressions, cannot be adequately covered by the

overlaid electroplated coating. When the electroplated coating is one such as an Fe coating which is intended to increase the coatability of the plated steel sheet by cationic electrodeposition, the electroplated coating cannot adequately perform its intended function.

The covering power of an electroplated coating with respect to microscopic irregularities will hereunder be referred to as its microcovering power.

Thus, it is not possible to achieve a hot-galvanized electroplated steel sheet of high quality simply by connecting a continuous hot-galvanizing apparatus and a continuous electroplating apparatus in sequence.

Accordingly, it is an object of the present invention to provide a plating line for performing continuous galvanizing and electroplating of steel sheet which can form an electroplated coating having excellent microcovering power.

It is another object of the present invention to provide a continuous plating line of steel sheet in which conventional hot-galvanizing and electroplating equipment is used.

It is a further object of the present invention to provide a method for electroplating a galvanized steel sheet to form an electroplated coating having excellent microcovering power.

It is a still further object of the present invention to provide a continuous galvanizing and electroplating method which can be performed in a single plating line to form a hot-galvanized electroplated steel sheet of high quality.

According to the method of the present invention, a hot-galvanized steel sheet is subjected to post-galvanizing surface treatment prior to electroplating in order to remove oxide and other surface contaminants (hereinafter collectively referred to as surface oxide contaminants) and activate the surface of the galvanized coating, the post-galvanizing surface treatment being performed by skin-pass rolling using a alkali solution having a pH of at least 12 which can dissolve aluminium oxide as a skin-pass rolling liquid.

The post-galvanizing surface treatment employed in the present invention greatly increases the adhesion and covering power of an electroplated coating. The reasons for these improvements are not yet clear. However, it is thought that the surface treatment improves properties by dissolving away aluminum oxide and an Zn-containing aluminum oxide which are formed on the surface of a galvanized coating of a steel sheet by the heat applied by hot-galvanizing or alloying and which have poor electrical conductivity. Furthermore, It can remove A1 and other metallic contaminants which segregates on the surface and which are thought to influence electrodeposition of an electroplated coating.

A continuous plating line according to the present invention comprises a continuous hot-galvanizing apparatus for forming a galvanized coating on a steel strip which is optionally equipped with an alloying apparatus, a continuous electroplating apparatus connected in series with the hot-galvanizing apparatus for forming an electroplated coating on the galvanized coating, and at least one post-galvanizing surface treatment apparatus disposed between the hot-galvanizing apparatus and the electroplating apparatus for removing surface oxide contaminants and activating the surface of the galvanized coating, the post-galvanizing surface treatment apparatus comprising a skin-pass rolling mill employing a strong alkali solution having a pH of at least 12 which can dissolve aluminum oxide as a skin-pass rolling liquid.

Figure 1 is a schematic illustration of an embodiment of a continuous plating line according to the present invention;

Figures 2a and 2b are schematic cross-sectional views of a multi-layer plated steel sheet manufactured by the method of the present invention and by a conventional method, respectively.

The present invention will be described in greater detail while referring to the accompanying drawings. The drawings illustrate embodiments of the plating line of the present invention having an alloying furnace after the hot-galvanizing bath. However, an alloying step is optional and the present invention is not limited to such embodiments.

Figure 1 schematically illustrates a continuous plating line according to the present invention.

As shown in this figure, a steel strip 2 is unwound from a pay-off reel 1 and passed through a prewashing apparatus 3 and then through a pretreatment apparatus comprising a rapid heating furnace 4, a reduction furnace 5, and a cooling furnace 6 in which the surface of the steel strip is cleaned.

If necessary, the strip 2 can be annealed. It is then passed through a hot-galvanizing bath 7 where hot galvanizing is carried out and a galvanizing coating is formed on one side or both sides of the strip. Then, if necessary, the strip 2 is passed through an alloying furnace 8 in which Fe in the steel strip 2 and Zn in the hot-galvanized coating are alloyed.

The hot-galvanizing bath 7 can be a bath of either zinc or a zinc alloy such as GALFAN [5% Al, 0.1% (La + Ce), the remainder Zn], GALVALUME (55% Al, 1.5% Si, the remainder Zn), or the like.

Any type of alloying furnace 8 can be employed, such as a gas-heated furnace, an electromagnetic induction furnace, or a laser heating furnace. The degree of alloying is controlled by adjusting the temperature and the heating time.

In the manufacture of rust-preventive steel sheet for automobiles, the galvanized coating typically has a Zn coating weight of 30 - 80 g/m^2 and it can be alloyed into a Zn-Fe alloy containing 7 - 12% Fe. When alloying is not performed, the steel strip 2 can be simply passed through the alloying furnace without alloying treatment.

The optionally alloyed galvanized steel strip 2 is then passed through a post-galvanizing surface treatment appa-

ratus, and the treated steel strip 2 is wound onto a tension roll 18.

According to the present invention, the post-galvanizing surface treatment is performed during skin-pass rolling, using a strong alkali solution with a pH of at least 12 which can dissolve aluminum oxide as a skin-pass rolling liquid (lubricant).

Figure 1 schematically illustrates a continuous plating line according to the present invention in which the post-galvanizing surface treatment apparatus is a skin-pass rolling mill 11. If necessary, this embodiment can be further equipped with a water cooling tank (not shown) for cooling the steel strip 2 to a suitable temperature for skin-pass rolling.

An example of a strong alkali solution which can be used as a skin-pass rolling liquid is a 1M sodium hydroxide solution. However, any alkali solution can be used which does not adversely affect the subsequent electroplating when a minor amount thereof is introduced into the electroplating solution. A pH of at least 12 is effective, but when performing mass production, the pH is preferably at least 12.5.

The skin-pass rolling liquid formed from a strong alkali solution can be used by spraying onto the strip 2 or the work rolls of the skin-pass rolling mill. The treating time may be varied by the distance between the skin-pass rolling mill 11 and ringer rolls (not shown) downstream of the mill. The effectiveness of post-galvanizing surface treatment during skin-pass rolling is not significantly affected by manufacturing conditions such as the travelling speed of the steel strip or the roughness of skin-pass rolls. The temperature of the skin-pass rolling liquid is preferably at least 50 °C.

It is known that an inhibitor may be added to water which is used as a skin-pass rolling liquid during temper rollling after hot galvanizing of a steel strip. However, the addition of an inhibitor is performed for the purpose of removing greases from the steel strip and for preventing corrosion. It has no effect on the microcovering power of an electroplated coating, and is thus totally different from the skin-pass rolling liquid which can be employed in the present invention.

A skin-pass rolling liquid in the form of a strong alkali with a pH of at least 12 which can dissolve aluminum oxide chemically removes surface oxide contaminants deposited on the galvanized coating which deteriorate the microcovering power of an electroplated coating formed thereon. At the same time, these contaminants are mechanically removed by the skin-pass rolling.

By performing the post-galvanizing surface treatment prior to electroplating, the adhesion and covering power of the electroplated coating are greatly increased.

After the post-galvanizing surface treatment, the steel strip 2 is passed through an electroplating apparatus to deposite an electroplated coating on the galvanized coating. When both sides of the steel strip are galvanized, electroplating can be applied to either one or both sides. When galvanizing is performed on one side of the strip, usually electroplating is applied to the same side, i.e., on the galvanized coating, although there is no limitation in this respect.

The electroplating apparatus includes the pretreatment tank 13, the electroplating cell 14, and the washing tank 15 (a water scrubber). In the pretreatment tank 13, the galvanized steel strip 2 is washed with water which may contain a certain additive which improves the surface condition of the steel strip. In the electroplating cell 14, various types of electroplating can be performed. In the washing tank 15, the electroplated steel strip is rinsed with water. If necessary, the steel strip 2 can be dried with hot air or by electric heating in the drier 16.

The electroplated coating is not restricted to any particular type. For example, it can be one which improves coatability of the galvanized coating by cationic electrodeposition overlaid thereon such as a pure Fe or Fe-X coating (wherein X is Zn, P, Ni, B, Sn, Ti or the like), a coating which improves the sliding properties of the galvanized coating such as a Cr (Cr-oxide), Ni, Ni-Zn coating, or various dispersion-type coatings such as a Ni-SiC, Zn-SiO_2, Ni-Zn-SiO_2, or a Zn-Al_2O_3 coating. Depending on the desired coating weight, a plurality of electroplating cells can be used.

Next, if necessary, finishing surface treatment such as chromate treatment, zinc phosphate treatment, or resin coating using a roll coater can be performed in the finishing surface treatment apparatus 17 to obtain a finished product.

Normally, in an electroplating line, an alkali degreasing apparatus is installed as a pre-treatment apparatus. Such an apparatus is used merely for the purpose of removing dirt and grease (oil and fat) adhering to the steel strip, and its operation and effects are totally different from those of the post-galvanizing surface treatment employed in the present invention.

A hot-galvanized coating sometimes contains elements such as Al, Mg, and Mn. The post-galvanizing surface treatment of the present invention activates only the surface of the galvanized coating and does not reach the inside of the coating, so there is no adverse effect on these elements.

Figures 2a and 2b schematically illustrate the structure of a multi-layer coating according to the present invention and the prior art, respectively. In the example of the present invention (Figure 2a), minute irregularities 24 and 26 can be observed in the alloyed hot-galvanized coating layer 22 formed on a steel strip 20, but an electroplated coating 28 is uniformly formed over the irregularities. Surface contaminants which obstruct electrodeposition are previously removed.

In contrast, in the example of the prior art (Figure 2b), the electroplated coating layer 28 is able to cover the protrusions of the underlying alloyed galvanized coating 22, but the coating 22 is exposed where it contains depressions. Therefore, the coatability and workability of the resulting steel strip are not adequately improved by the electroplated coating.

Example

Hot-galvanizing followed by electroplating was performed on both sides of a steel strip using an apparatus like that illustrated in Figure 1. The coating weight of the galvanized Zn layer was 45 g/m^2 for each side. A 1M NaOH solution at a temperature of 50 °C with a pH of 13.5 was used as a skin-pass rolling liquid during skin-pass rolling of the alloyed galvanized strip which was performed with a reduction of 0.6%.

Continuous electroplating was carried out under the following conditions:

TABLE 2

Sulfate bath:			
Total Fe	80 g/l,	current density	60 A/dm^2
Fe^{3+}	1000 ppm,	plating weight	5 g/m^2
Zn^{2+}	2 g/l,	pH	1.6
Na^{+}	25 g/l	Temperature	50°C

The resulting plating had good microcovering power.

In contrast, when water (or water + an inhibitor) at 50°C or when an NaOH solution with a pH of 11.0 was used as a skin-pass rolling liquid, the electroplated layer formed atop the GA coating had poor microcovering power.

Claims

1. A continuous plating line for steel sheet comprising :

   a continuous hot-galvanizing apparatus (7) for forming a galvanized coating on at least one side of a steel sheet ;
   a continuous post-galvanizing surface treatment apparatus (9) which is connected in series with the hot galvanizing apparatus ;
   a continuous electroplating apparatus (13-15) connected in series with the post-galvanizing surface treatment apparatus for forming an electroplated coating atop of the galvanized coating, characterized in that the post-galvanizing surface treatment apparatus comprises a skin-pass rolling mill (11) which is disposed between the hot galvanizing apparatus (7) and the electroplating apparatus (13-15) and which uses an alkali solution with a pH of at least 12, in order to increase the adhesion and covering power of the electroplated coating.

2. A method for electroplating hot-galvanized steel sheet, wherein the hot-galvanized steel sheet is subjected prior to electroplating to post-galvanizing surface treatment, characterized in that the post-galvanizing surface treatment comprises skin-pass rolling using an alkali solution with a pH of at least 12 as a skin-pass rolling liquid, in order to increase the adhesion and covering power of the electroplated coating.

3. A method as claimed in claim 2, wherein the said alkali solution having a pH of at least 12 is sprayed onto the strip or the work rolls of the skin-pass rolling mill.

Patentansprüche

1. Kontinuierliche Plattierstraße für Stahlblech, umfassend

   eine kontinuierliche Feuerverzinkungsvorrichtung (7) zur Bildung einer Verzinkungsschicht an wenigstens einer Seite des Stahlblechs;
   eine kontinuierliche Nachverzinkungsoberflächenbehandlungsvorrichtung (9), welche in Reihe mit der Feuerverzinkungsvorrichtung verbunden ist;
   eine kontinuierliche Elektroplattiervorrichtung (13 bis 15), welche in Reihe mit der Nachverzinkungsoberflächenbehandlungsvorrichtung zur Bildung einer elektroplattierten Schicht auf der Verzinkungsschicht verbunden ist, dadurch gekennzeichnet, dass die Nachverzinkungsoberflächenbehandlungsvorrichtung ein Dressierwalzwerk (11) umfaßt, welches zwischen der Feuerverzinkungsvorrichtung (7) und der Elektroplattiervorrichtung (13 bis 15) angeordnet ist und welche eine Alkalilösung mit einem pH von mindestens 12 verwendet.

2. Verfahren zum Elektroplattieren von feuerverzinktem Stahlblech, wobei das feuerverzinkte Stahlblech vor dem Elektroplattieren einer Nachverzinkungsoberflächenbehandlung unterworfen wird, dadurch gekennzeichnet, dass die Nachverzinkungsoberflächenbehandlung ein Dressieren unter Verwendung einer Alkalilösung mit einem pH von wenigstens 12 als Dressierflüssigkeit umfaßt, um die Adhäsion und die Deckkraft der elektroplattierten Schicht zu erhöhen.

3. Verfahren nach Anspruch 2, wobei die besagte Alkalilösung, die einen pH von wenigstens 12 aufweist, auf das Blech oder die Arbeitswalzen des Dressierwalzwerks aufgesprüht wird.

Revendications

1. Chaîne de placage en continu pour de la tôle d'acier comprenant:

   - un appareil galvanisant à chaud en continu (7) pour former un revêtement galvanisé sur au moins une face d'une tôle d'acier;
   - un appareil de traitement de surface après galvanisation en continu (9) qui est relié en série à l'appareil galvanisant à chaud;
   - un appareil d'électroplacage en continu (13-15) relié en série à l'appareil de traitement de surface après galvanisation pour former un revêtement électroplaqué par-dessus le revêtement galvanisé, caractérisé en ce que l'appareil de traitement de surface après galvanisation comprend un laminoir de passe de peau (11) qui est disposé entre l'appareil galvanisant à chaud (7) et l'appareil d'électroplacage (13 à 15) et qui utilise une solution basique avec un pH d'au moins 12.

2. Procédé pour électroplaquer de la tôle d'acier galvanisée à chaud, dans lequel la feuille d'acier galvanisée à chaud est soumise avant l'électroplaquage à un traitement de surface après galvanisation, caractérisé en ce que le traitement de surface après galvanisation comprend le laminage de passe de peau en utilisant une solution basique avec un pH d'au moins 12 comme liquide de laminage de passe de peau, afin d'augmenter l'adhérence et le pouvoir de recouvrement du revêtement électroplaqué.

3. Procédé selon la revendication 2, dans lequel ladite solution basique ayant un pH d'au moins 12 est pulvérisée sur la bande ou sur les rouleaux de travail du laminoir de passe de peau.

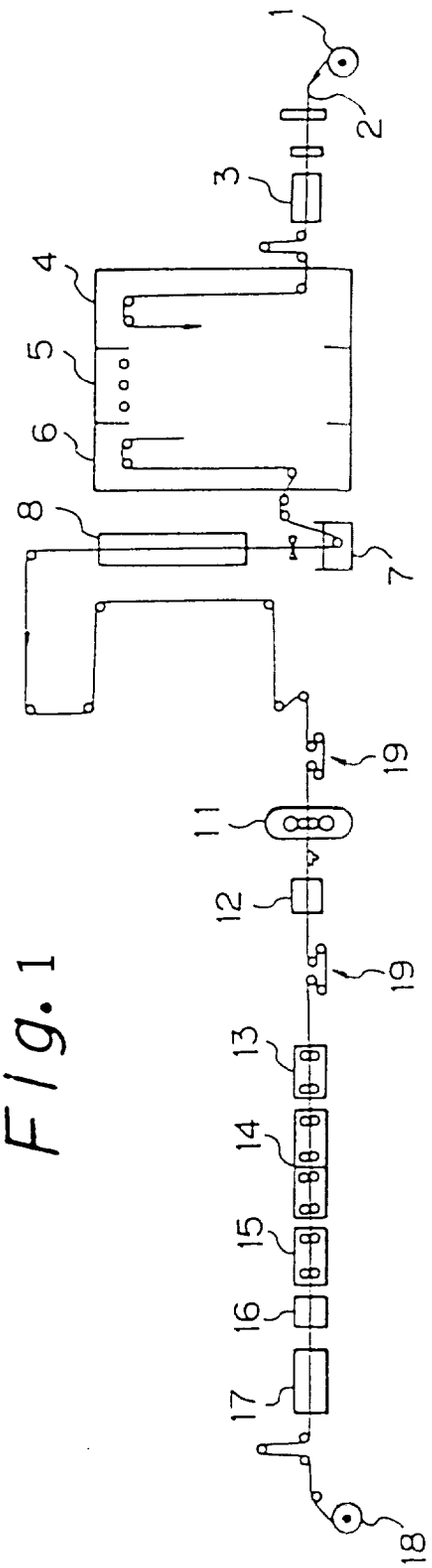

Fig. 1

Fig. 2