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FORMATION OF CHROMIUM-CONTAINING COATINGS ON BOTH SIDES OF
STEEL STRIP WITH ONE COATED SIDE HAVING A BRIGHT FINISH
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FORMATION OF CHROMIUM-CONTAINING COATINGS ON BOTH SIDES OF STEEL STRIP WITH ONE COATED SIDE HAVING A BRIGHT FINISH
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ABSTRACT OF THE DISCLOSURE

In a method of forming a chromium-containing coating on steel strip, a chromium-containing powder is applied uniformly to one side of the strip and compacted thereon. The thus-prepared strip is coiled and diffusion treated in a protective atmosphere, preferably of hydrogen, and including a halogen-containing gas at a temperature and for a time sufficient to form a stainless steel coating on both sides of the strip.

BACKGROUND OF THE INVENTION

This invention relates to the formation of a chromium-containing coating on sheet or continuous metal strip, and more particularly to a stainless steel coating on both surfaces of a steel strip or sheet.

In the manufacture of chromized coatings by the method known as roll bonding, wherein a chromium-containing metal powder is applied to the surface of a strip, compacted into the strip surface, and the article then subjected to a diffusion treating operation to produce a diffused coating of an iron-chromium alloy on the article, excellent stainless steel coatings can be produced on light gage strip. These coatings have corrosion resistance comparable to that of stainless steel strip, and for many applications the roll bonded coating is most acceptable.

A characteristic of the as-diffused roll bonded coating is the comparative roughness of the surface of the coating. When a bright stainless surface is required for esthetic purposes, the roll bonded coating must be applied in sufficient thickness to permit polishing, with consequent removal of a portion of the surface. To obtain a satisfactory product bearing a high polish may require repeating the process of applying powder, compacting and diffusing in order to provide sufficient powder on the strip to obtain the thickness of coating necessary to withstand the final polishing step.

Accordingly, a principal object of this invention is to obtain a chromized steel strip in which at least one side of the coated article has a bright finish.

Another object is to provide a chromized steel strip in which both sides of the strip bear a stainless steel coating.

A further object is to provide a method of forming a bright finish on a chromized surface produced from a roll bonded product without requiring a polishing step.

SUMMARY OF THE INVENTION

We have found that by applying a uniform layer of chromium-containing metal alloying powder to one side of a strip and following this with certain controlled treatment steps, a thin, adherent, ductile and corrosion-resistant coating is produced on both surfaces of the strip.

In accordance with this invention, a steel sheet or strip is preferably coated on one side with a thin film of liquid. The liquid should have such viscosity, volatility and tackiness characteristics as to render it suitable as a temporary bonding agent for subsequently applied metal powder. A chromium-containing metal powder is

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next applied uniformly over the filmed surface of the strip, and the strip is then subjected to a rolling operation, or equivalent pressure application, to compact the powder. In this step, the powder is rolled into a flat, compacted metallic layer in which adjacent grains of powder are bonded together. This metallic coating is in a semi-adherent condition in relation to the strip, the underside of the metallic coating having been mechanically bonded to the strip surface. The composite article of strip bearing a compacted metal powder on one surface is then given a diffusion treatment in a heat treating furnace, preferably in a coiled configuration in which a powder-coated surface and a non-powder coated surface are in close opposed relation. The diffusion treatment is performed in a protective environment in which there is present sufficient halogen-containing gas to promote transfer of chromium from the powder-coated surface to the uncoated surface of the strip. Treatment is performed at a controlled temperature and for a time sufficient to produce an adherent, corrosion resistant stainless steel coating on both sides of the strip.

The "effective carbon," hereinafter defined, in both the strip and the applied powder, should be kept below certain predetermined limits in order to develop coatings on the strip which are ductile and corrosion resistant.

BRIEF DESCRIPTION OF THE DRAWING

The drawing is a reproduction of a photomicrograph of a transverse section of a steel strip coated on both sides with an iron-chromium alloy.

DETAILED DESCRIPTION

In one specific embodiment of the invention, a five-ton coil of 20 gage strip of titanium-stabilized steel, having a total carbon content of 0.06%, was unwound from the coil, and a thin film of tridecyl alcohol was applied to one side of the strip by means of rubber rolls. The strip was then passed horizontally through a fluid bed of finely divided Simplex ferrochrome powder (—150 mesh, U.S. Standard Sieve Series), the powder being distributed uniformly on one side of the strip. In this operation, the underside of the strip, that coated with alcohol, contacted the fluidized powder and was coated therewith. The powder had the following analysis:

	Percent
Chromium	69.8
Silicon	1.75
Carbon	0.035
Iron, balance.	

The thus-treated coil was run through a two-roll temper mill to compact the powder on the strip. The pressure of the rolls during compacting was sufficient to produce an elongation in the strip of about 2.0%. After leaving the rolls, the strip was wound on a take-up reel, unwound and recoiled. During recoiling, a kinked wire spacer was inserted between coil convolutions to produce an open-coil effect. For most efficient diffusion, it is desirable to space each lap of the coil to permit the diffusion atmosphere to circulate freely, and to prevent possible welding of adjacent laps.

The open coil was placed on edge in an annealing furnace of the Lee-Wilson type, and, after properly sealing the furnace, an atmosphere of hydrogen and chlorine was introduced, as the coil temperature was raised to a diffusion treatment temperature of 1650° F. The chlorine represented about 1.0% of the total diffusion treatment atmosphere, and was fed to the furnace at a rate of 9 cu. ft. per hour. Hydrogen flow was maintained at 900 cu. ft. per hour. About 15 hours were required to bring the coil to the diffusion temperature of 1650° F., at which point the amount of chlorine being continuously introduced into the

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furnace, along with hydrogen, was reduced to an amount equal to about 0.5% by volume of the total treatment zone atmosphere. Once the 1650° F. temperature had been reached, the coil was allowed to soak at this temperature in the hydrogen and chlorine atmosphere for about 15 hours, during which time chromium in the ferrochrome powder-coated side of the strip diffused into the strip, and iron diffused outwardly into the powder coating. At the same time, chlorine in the treatment atmosphere reacted with a portion of the chromium in the powder and transported it to the uncoated side of the strip, where the chromium was deposited and then diffused into the strip.

Because the powder-coated side of the strip has a uniform distribution of powder at the outset, and thus permits a uniformly diffused coating on that side, it likewise permits a uniform transport of chromium to the non-powder-coated side by way of the even spacing of the laps of the coil and the even distribution of the treating atmosphere.

As there is a constant supply of hydrogen and chlorine to the furnace, there must also be a discharge of the gases. However, the mean retention time for any given amount of chlorine within the furnace is relatively high, and this chlorine used to transport chromium to the non-powder-coated side, and iron from the strip to the powder-coated side, may pass through a number of transport cycles in the confined spaces between coil laps before this chlorine is exhausted from the system.

Introduction of chlorine was discontinued after 15 hours at diffusion treatment temperature, to prevent further transport of chromium from the powder-coated to the non-powder-coated surface. The soak period was continued for an additional 13 hours in a hydrogen gas atmosphere to permit the proper amount of diffusion of chromium and iron at both surfaces to form coatings of the desired thickness and composition. In any event, chlorine should be exhausted from the atmosphere surrounding the charge before the cooling cycle reaches that point at which chlorine compounds condense to produce a deleterious effect on the surface of the alloy coating.

After cooling the strip in the furnace, during which a hydrogen atmosphere was maintained, the coil was removed, washed with dilute nitric acid and brushed to remove any loose powder or reaction products retained on the coating surface. The strip was then given a temper roll on polished rolls equivalent to about 2.0% reduction.

The continuous, pore-free, stainless steel coating produced by the method of this invention is adherent, ductile and corrosion resistant. The product has a matte finish coating surface on the previously powder-coated side and a bright finish on the opposite side of the strip. The continuous, pore-free portion of the coating on each side of the strip ranged from 0.0011 inch to 0.0014 inch in thickness. The product is illustrated in the drawing, which is a reproduction of a photomicrograph of a transverse section of the coated strip, etched in picral-nital, and taken at 100 magnifications. The bright surface coating is represented at A, while the matte surface coating is represented at B.

The non-powder coated side has a smoothness unattainable when both sides of the strip are coated by applying powder to each before the diffusion treatment, except by applying a double thickness of powder and then giving the surface a high polish. Such means for obtaining a bright finish would be very wasteful of powder. Our invention provides an inexpensive and efficient method of producing a stainless coating on both sides of the strip with one side having a bright finish. In many applications where a bright finish is required or desired, this type of finish may be necessary only on the side exposed to view.

It will be apparent that many alternative means or materials may be made use of in the various operating steps of the example. Alternatives in certain instances would cause little or no loss in efficiency.

It is not necessary that the strip be diffusion heat treated in coil form, although treatment of a coil is the most effi-

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cient method from the standpoint of handling and utilization of furnace space. The strip bearing the compacted powder on one side can be cut into convenient lengths of sheet, and the sheets can be placed vertically on edge in the furnace with a powder-coated side and an uncoated side in facing, or closed opposed, relation during the diffusion operation. This modification would require guides within the furnace to support the sheets in position.

Generally, if the steel strip stock is excessively soiled, it should be cleaned with a cleaning medium such as a hydrocarbon solvent or an alkali cleaner before applying the powder.

The powder-retaining material, which is applied to the strip in the form of a thin film, and which acts temporarily as a powder retaining medium, may be any liquid substance having the proper viscosity, volatility and tackiness characteristics previously referred to, and which, in addition, leaves no carbon deposit on the steel surface, and meets safety requirements. The metal powder can be applied to the steel backing member without a liquid substance having the above-stated characteristics first being applied, but use of a liquid film is preferred, for the film lends mechanical efficiency to the steps of applying and compacting the powder.

While not critical, it is desirable to control both the amount of liquid applied and the grain size of the metal powder. The alcohol, or other substance, used for retaining the metal powder, should be applied in a rather thin film of a thickness just sufficient to cause adequate adherence of the powder particles. An excess of the liquid may cause problems of slippage and inefficient compacting during the rolling operation.

In selecting a particular liquid as the powder-retaining medium, care should be taken to select one which will not leave any substantial carbon deposit in the compacted metal, which in turn could produce brittleness of the resultant coating. Kerosene is an alternative liquid which has been used successfully as the powder-retaining agent. Transformer oil and straw oil may be used also, although with less efficiency than either tridecyl alcohol or kerosene.

Metal powder which passes a 150 mesh screen has been found to be very satisfactory, although larger particles may be used. The size of powder particles desired will depend somewhat on the physical manner by which the powder is applied. It has been found desirable to have the powder particles in a granular or angular shape, rather than flattened or spherical, to obtain the best control of powder coating weight and adherence of the compacted powder layer to the strip.

If the powder is applied to the strip in an amount of from 8 to 10 grams per square foot of backing strip surface, quite satisfactory results are obtained, and this amount of powder is held on the strip readily by a very light film of tridecyl alcohol. Heavier or lighter applications of powder may be used, depending to some extent on the desired distribution of chromium and the thickness of the diffused coating. By using a heavier alcohol film, the amount of powder applied can be increased by approximately twice the 10 grams per sq. ft. figure given above.

While application of powder to the strip is accomplished satisfactorily by passing the strip through a fluid bed of powder, alternative methods for this application include use of a vibrator dispenser, electrophoretic deposition and electrostatic spray technique.

When the powder has been compacted onto the base steel, it is in the form of a porous "shell" which is held mechanically to the base. Porosity of the "shell" is advantageous, for, during the heating-up period prior to diffusing, the volatile, oily liquid, originally applied to hold the powder to the strip, is vaporized and escapes through the pores of the compacted layer.

The different types of powder contemplated for use in this invention are those containing chromium, or iron

and chromium. Metal powders answering this description are iron-chromium alloy, a mixture of iron and chromium and commercial grade chromium powder. In the case of alloy powders, it will be apparent that iron or chromium powder may be added if desired. Small amounts of metallic impurities, which do not affect the resultant coating, can be tolerated in the powder.

We have found that excellent results are obtained with powder of the type given in the process example, i.e. ferrochrome powder containing approximately 70% chromium with the balance substantially iron. This type of powder produces, upon diffusion treatment, a stainless steel type coating, which coating, when continuous and pore-free, will resist a boiling 20 volume percent aqueous solution of nitric acid (based on 100% HNO_3). While a relatively high amount of chromium in the powder is preferred for efficient formation of the coating, a stainless steel coating can be obtained when the chromium in the powder represents considerably less than 70% of the total powder. Both the amount of powder applied and the amount of chromium required in the powder depend on the desired thickness and chromium composition of the coating.

The temperature during diffusion treatment should range preferably between approximately 1550° F. and 1900° F. for not less than about 12 hours, although considerably longer times may be desirable, depending on the amount of alloying required. Actually, there is no upper limit for diffusion temperature other than that which may be dictated by practical considerations. At temperatures above 1550° F., the minimum time required will be lowered in an inverse manner.

The coating on each side of the strip, resulting after the diffusion treatment, will generally have a thickness of from about 0.001 to 0.003 inch. This coating will contain not less than about 12% chromium throughout, and will be characterized by a sharp interface between the alloy coating and the metal therebelow. Beneath the interface, the chromium content of the steel drops rapidly to zero.

Preferably, our coating has an average chromium content ranging from about 15% to 25%. Higher chromium contents may be used, but there would probably be little or no added benefit from the standpoint of corrosion resistance.

In this invention, "effective carbon" previously referred to, is that carbon, either in the base steel or in the applied powder, which by diffusion is free to combine with the chromium to form deleterious chromium carbides in the coating. Stated differently, it is that carbon which has a greater affinity for chromium at the diffusion temperature than for other elements in the substrate or coating. If chromium carbides are present in the coating of the finished product in sufficient amount, the coating is embrittled, and formability of the coated product is limited. Furthermore, a chromium alloy coating, containing considerable chromium carbide, has lower corrosion resistance than a coating substantially free of carbide.

Most metal powder will contain some carbon, and this carbon must be held to a value which will not produce the deleterious chromium carbides in the ultimate alloy coating. The amount of carbon which may be introduced into the compacted article by the powder should be not more than 0.25% by weight of the powder used.

There is no limitation on the type of steel which may be used as base material in our invention, as long as the effective carbon content of the base material is maintained at a figure no greater than 0.01% during diffusion treatment.

Maintaining the low value for effective carbon in the base steel during diffusion may be accomplished in various ways. The steel strip or sheet, for example a rimmed steel of 0.06% carbon, may be decarburized to below 0.01% carbon before any of the processing steps of the invention are applied.

Another procedure for obtaining the low effective carbon value in the base steel during diffusion is to decarburize the powder coated strip in the treatment furnace prior to the diffusion step. Successful decarburizing can be performed in this manner by introducing a moist hydrogen atmosphere (dew point, +95° F., or 5.5% by volume) into the furnace during the heating-up period, then, when the temperature reaches about 1250° F., holding at that temperature for about five hours. At the end of the five-hour period, the furnace is purged of the moist hydrogen atmosphere, and dry hydrogen is introduced. The required amount of halogen-containing gas must also be present in the diffusion treatment zone before the diffusion temperature is reached, to produce the chromized coating effectively.

A third means, by which the effective carbon can be maintained at or below 0.01% during diffusion treatment, is that shown in the specific detailed example of the process, wherein a titanium-stabilized steel is used as the substrate. Titanium is a carbide-former having considerable affinity for carbon, and acts as a carbon-sequestering agent, and in this manner carbon is tied up and is not free to migrate to the chromium in the coating. Examples of other sequestering agents are zirconium and columbium. When carbide-formers, or sequestering agents, are used in the strip base metal to tie up carbon in this invention, it is still essential that any unbound, effective carbon in solution in the strip, that which is free to react with chromium in the compacted powder, be held to a quantity not in excess of 0.01%.

When the carbon in the base steel is greater than 0.01%, and titanium is used to combine with the excess carbon, the amount of titanium necessary will, of course, depend on the amount of carbon to be sequestered. As a practical matter, when using a titanium-stabilized steel, it is desirable to maintain the titanium in an amount ranging from 0.2% to 0.5%, preferably in the range of from 0.25% to 0.35%, and always in an amount at least four times the amount by weight of carbon it is necessary to sequester.

In the specific process example of this invention, the base strip had an analysis of 0.3% titanium and 0.06% carbon. This amount of titanium combines with substantially all of the carbon to form a stable titanium carbide. An advantage of using titanium-stabilized steel strip, over decarburized strip, is in the fact that the stabilized strip has the strength characteristics of a low-carbon steel.

Regardless of the source of carbon, the coating of the chromized product should contain not more than 0.10% carbon. This refers especially to the main body of the coating. Carbides at the coating surface only may or may not be detrimental.

The diffusion treatment must be performed in a protective atmosphere or environment including a halogen-containing gas and substantially free of carbon, oxygen or nitrogen. To this end, any one of the noble gases may be used as a surrounding atmosphere along with the halogen-containing gas, although a more practical atmosphere is one composed of substantially pure hydrogen and the halogen-containing gas. Hydrogen has the added advantage of being able to remove oxygen from oxides which may have formed during processing.

When hydrogen gas is used along with the halogen-containing gas, it should preferably be 100% pure hydrogen. However, even when allegedly pure hydrogen is used, certain impurities may enter the furnace atmosphere in large scale operations, through leaks in the system, from the furnace walls or other portions of the equipment or, possibly, in the hydrogen employed. Chromium has a strong affinity for carbon, nitrogen and oxygen, any of which might find its way into the treating atmosphere. Oxygen will normally be the chief source of trouble.

At the diffusion temperature, and even considerably below such temperature, the highly reactive chromium powder reacts with any small amount of oxygen present in

the atmosphere, and the resultant chromium oxide may completely surround the exposed portions of the powder particles. The formation of the oxide shell on the particles hinders the normal diffusion of the chromium particles into the steel base. For this reason, when oxygen is present as impurity in the treating atmosphere, it may be necessary to provide a means whereby the chromium powder is freed of its oxide and can then diffuse readily with the iron, both in the steel strip base, and in the powder itself in the case where there is iron in the powder.

Inclusion of a halogen-containing material in the furnace atmosphere has been found to promote the rapid diffusion of chromium into the iron and, contrariwise, the iron into the chromium, even when oxygen impurities have been introduced into the furnace inadvertently. Halogens, or halogen compounds, act as scavengers, or energizers, in that they remove the oxide film from the chromium powder particles, ensuring metal to metal contact.

While any halogen or halogen compound may be used as the energizer which is volatile at the diffusion temperature, or a few hundred degrees Fahrenheit below the diffusion temperature, it is preferable to use as the energizer, one which can be introduced as a gas at a relatively low temperature. When the energized is introduced in gaseous form, the amount and rate of introduction can be closely controlled. Hydrogen chloride, iodide, bromide or fluoride gas, among other halogen-containing vapors, may be used for this purpose. Suitable halogen-containing materials, in the form of solid compounds, which may be inserted into the furnace in solid form, and which volatilize at or near diffusion temperatures, include ammonium chloride, chromic fluoride, and ammonium bifluoride. Of the halogens themselves, chlorine gas has been found to be especially advantageous when injected in gaseous form into the hydrogen atmosphere in the treatment furnace.

In this invention, the halogen-containing gas has an additional and major function in the treating atmosphere. The halogen component reacts with chromium on the powder-coated side of the strip, and transports the chromium as a gaseous chromium halide to the uncoated side of the strip, where chromium is deposited as it is displaced from the halide by iron. The newly formed iron halide returns to the powder-coated side of the strip, again forming chromium halide, and this process of exchange is repeatedly indefinitely during diffusion.

As shown in the specific example, the halogen-containing gas should be introduced into the furnace during the heating-up period to provide a clean powder surface and effective transport of chromium at the outset of diffusion. Also, all halogen-containing gas should be purged from the furnace before any solid halides are deposited on the strip surface during cooling of the coil.

As an alternate procedure to introducing the halogen-containing material into the furnace as a gas, a solid halide may be introduced between the coil convolutions before the furnace inner cover is installed. The solid material will volatilize with the increasing temperature of the furnace, and will perform the same functions as the halogen-containing compound when introduced into the furnace in gaseous form.

Because of the poisonous and corrosive nature of the halogens, proper precautions should be taken to prevent escape of these materials into the ambient atmosphere, by using approved dispensing equipment and by installing proper venting facilities on the treatment furnace.

Care should be exercised in the use of halogens to avoid formation of an explosive mixture with hydrogen. For example, in Bureau of Mines Bulletin No. 503, entitled "Limits of Flammability of Gases and Vapors," it is shown that chlorine and hydrogen are known to produce an explosive mixture when the chlorine content of the mixture is above 11.0%. While it may thus be possible to use chlorine in an amount up to 9 or 10% of the treating atmosphere, for practical operations a halo-

gen content between 0.10% and 1.0% has proved entirely satisfactory.

It has been found that in certain instances, an erosive condition may be created in the coating in the presence of an excessive amount of chlorine or other halogen-containing gas. The introduction of the halogen-containing gas in large amounts apparently creates a physical disturbance on sections of the open wound coil, and consequently produces an uneven distribution of the alloy coating layer. While this unevenness of the coating has no effect on the surface appearance, nor on the resistance of the coating to boiling nitric acid in a static test, it may produce localized areas where the coating is quite thin. Thin spots in the coating would limit the amount of deformation or surface finishing which could be performed on the coated article, as the thin areas would tend to split or rupture more readily than the remainder of the coating.

As used herein and in the appended claims, a halogen-containing gas is one which may include a gaseous halogen such as chlorine, bromine, etc., a halogen acid gas such as, for example, hydrogen chloride, or a normally solid halide such as, for example, ammonium chloride, ammonium bifluoride or chromic fluoride.

In the appended claims, percentages relating to chlorine or other halogen component of the halogen-containing gas are expressed as volume percent. All other claimed percentages refer to weight percent.

We claim:

1. A method of forming a coating on steel strip which comprises applying to one side of the strip a uniform distribution of metal powder group consisting of chromium, ferrochrome and chromium-iron mixture, compacting the powder on the strip, treating the strip in coil configuration in a protective atmosphere including a halogen-containing gas wherein the halogen represents not less than 0.1% of the protective atmosphere volume in a diffusion treatment zone for a time and at a temperature sufficient to cause diffusion between a portion of the compacted powder and the powder-coated side of the strip, and to cause transfer of a portion of the chromium in said powder to, and diffusion of the transferred chromium into the uncoated side of said strip, and to thereby form a stainless steel coating on both sides of said strip.

2. A method of forming a coating on steel sheets which comprises applying to one side of said sheets a coating of metal powder of the group consisting of chromium, ferrochrome and chromium-iron mixture, compacting the powder on the sheets, disposing the sheets in a diffusion treatment zone with a powder-coated side of one sheet facing an uncoated side of an adjacent sheet, diffusion treating the sheets and compacted powder in said treatment zone in a protective atmosphere including a halogen-containing gas wherein the halogen represents not less than 0.1% of the protective atmosphere volume for a time and at a temperature sufficient to cause diffusion between a portion of the compacted powder and the powder-coated side of the sheets, and to cause transfer of a portion of the chromium in said powder to, and diffusion of the transferred chromium into the uncoated side of the adjacent sheet, and to thereby form a stainless steel coating on both sides of said sheets.

3. A method according to claim 1 wherein the effective carbon content of the steel base is maintained at not more than 0.01% during diffusion.

4. A method according to claim 3 wherein the protective atmosphere is hydrogen and halogen-containing gas.

5. A method according to claim 4 wherein the metal powder contains not more than 0.25% carbon.

6. A method according to claim 5 wherein the halogen-containing gas is chlorine.

7. A method according to claim 4 wherein the amount of chromium in the coating is not less than 12%.

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8. A method according to claim 6 wherein the amount of chromium in the stainless steel coating is not less than 12%.

9. A method according to claim 4 wherein the strip is decarburized in the treatment zone during heating prior to diffusion treatment in the absence of halogen-containing gas, and halogen-containing gas is added to the protective atmosphere after decarburizing but prior to diffusion.

10. A method according to claim 9 wherein the strip is decarburized in the treatment zone prior to diffusion in an atmosphere comprising hydrogen and water vapor until the strip contains not over 0.01% carbon.

11. A method according to claim 6 wherein the metal powder is chromium.

12. A method according to claim 6 wherein the strip is in the configuration of an open coil during treatment.

13. A method according to claim 6 wherein the powder is ferrochrome powder.

14. A method according to claim 8 wherein the diffusion-treated strip is cooled, at least in the early stages, in a hydrogen atmosphere.

15. A method according to claim 11 wherein chlorine is removed from the diffusion treatment zone no later than the point at which chlorine compounds condense in the cooling step.

16. A method according to claim 5 wherein the stainless steel coating contains not more than 0.10% carbon.

17. A method according to claim 8 wherein the stainless steel coating contains not more than 0.10% carbon.

18. A method according to claim 17 wherein the steel

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strip contains a carbide-forming metal in an amount sufficient to maintain the effective carbon in the strip at not more than 0.01%.

19. A method according to claim 18 wherein the carbide-forming metal is titanium.

20. A method according to claim 8 wherein the diffusion treatment temperature is not less than 1550° F. for not less than twelve hours.

References Cited

UNITED STATES PATENTS

2,836,513	5/1958	Samuel (I)	----- 117—107.2 P X
3,061,462	10/1962	Samuel (II)	----- 117—107.2
3,163,553	12/1964	Commanday et al.	
3,222,212	12/1965	Samuel et al.	
3,312,546	4/1967	Mayer et al.	
3,340,054	9/1967	Ward et al.	----- 117—107.2 UX

FOREIGN PATENTS

1,513,264	1/1968	France	----- 117—107.2
-----------	--------	--------	-----------------

OTHER REFERENCES

"Applicants' Non-Pat. Citations," Abstract of Belgian Patent 711,292.

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