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CHROMIZING FERROUS METAL SUBSTRATES
 Kenneth Urmston Holker, Harrogate, England, assignor
 to National Steel Corporation, Pittsburgh, Pa.
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20 Claims

ABSTRACT OF THE DISCLOSURE

In order to mitigate the formation of a layer of sintered powder on the surface of ferrous substrates chromized by the application of an adhesive layer followed by the application of chromium powder and a heat treatment to bring about the formation of a diffusion alloy surface layer, hydrated magnesium or aluminum halides or magnesium oxyhalide is applied to the substrate before, with or after the chromium. Preferably the halide is applied as an aqueous solution before the chromium so as to form the adhesive layer. pH modifiers may be incorporated to reduce the acidity of the solution in the case where aluminum chloride is used as the halide.

The present invention relates to a process of the type described in application No. 35,252 filed on May 6, 1970. In that application there is described a process for chromizing ferrous metal substrates in which there is first formed on the substrate a layer of adhesive material to which is then applied a chromium-containing metal powder, a halide being incorporated in the coating either as part of the adhesive layer or separately, and the coated substrate is then subjected to a heat treatment to bring about the formation of a chromium diffusion layer. A wide range of halides for incorporation in the layer is suggested, iron halides being stated to be the most preferred.

Unfortunately we have found that when many of the halides suggested in that application are employed in processes for chromizing ferrous substrates, having a low free carbon content either by virtue of decarburization or by being "stabilized" by the addition of a carbide-forming element there is a tendency for the chromium-containing metal powder applied to the substrate to sinter together to form an unsightly surface on the final diffusion product. It is necessary to remove this sintered coating by, for example, the use of wire brushes.

We have now found that this problem can be mitigated if either a hydrated aluminum halide or a hydrated magnesium halide or magnesium oxyhalide is employed in the process.

Accordingly, the present invention provides a process for the chromizing of ferrous metal substrates having a low free carbon content as hereinafter defined which comprises:

- (1) applying an adhesive layer to at least one surface of the substrate, optionally comprising or consisting of a hydrated magnesium halide or oxyhalide or hydrated aluminum halide;
- (2) applying a chromium-containing metal powder to the adhesive layer and if one is not already present, also applying one or more of a hydrated aluminum halide magnesium halide and magnesium oxyhalides; and
- (3) subjecting the coating substrate to a heat treatment to bring about the formation of a chromium diffusion alloy coating on the substrate.

When employed herein the term "having a low free carbon content" should be taken to denote steels which

have either been decarburized, for example, by treatment with wet hydrogen or contain a carbide-forming element—such as titanium or niobium to reduce the carbon available in the steel for migrating during the diffusion process, such steels will contain no more than 0.01% of unbound carbon.

The process of the invention is particularly suitable for use in processes in which the diffusion stage is carried out with coated surfaces of the substrate in contact either with another coated surface or an uncoated surface of steel. Thus the process enables the diffusion stage to be carried out with the substrate arranged in the form of a close coil or a stack of steel plates. The process can of course be employed alternatively in the case of an open coil or where there is no contact with adjacent substrates. We have found in the case where adjacent surfaces are placed in contact that it is unnecessary to apply the adhesive layer and the chromium-containing metal powder to both of the surfaces in order to obtain a satisfactory diffusion coating on both surfaces, but that application to one side only is sufficient.

Substrates suitable for use in the process of the invention are particularly substrates in which the carbon contained in the substrate has been bound by a carbide-former. The process of the invention is particularly suitable for titanium-stabilized steels. The form of substrate for which the process is most particularly suitable is steel strip or plate.

The hydrated aluminum, magnesium halides or magnesium oxyhalides employed for the process of the invention are the chlorides or oxychlorides. We have found that these halides can, if applied from a solution in a volatilizable solvent, preferably water, be employed as the adhesive layer onto which the chromium-containing metal powder is deposited. However the halides may also be applied as dry solids. If dry solids are employed they may be applied before with, or after the chromium-containing metal powder. Magnesium oxychloride can be applied either as a solid or as an aqueous slurry. If desired, however, some other adhesive may also be employed and if this is the case the halide need not be applied from a solution. For example, halide powder can be applied to the substrate after the adhesive layer and the chromium-containing metal powder. However, it is preferred to apply the halide first from an aqueous solution. If this is done the halide can conveniently be applied by passing the substrate, particularly when it is in the form of a strip, through a bath of an aqueous solution of the halide.

The concentration of the halide in the volatilizable liquid solvent, if this is employed, may vary over wide ranges, such as, for example, from at least 10–100 g./l. up to 500–1,000 g./l., or up to the amount required to produce a saturated solution of the halide. In general, it is only necessary that the halide be present in a concentration to assure that the quantity of liquid to be applied on the substrate surface will deposit the desired amount of the halide upon evaporation. Thus, it will be largely determined by the volume of volatilizable liquid which can be evaporated in the drying stage without forming blisters or other imperfections in the coating. However the halide or oxyhalide is applied, it will be employed in an amount so as to provide approximately 1–10 or 1–20 grams, and preferably about 2–5 grams of the halide or oxyhalide per square foot per side of surface area to be wetted. The halide or oxyhalide may be applied to only one or to both surfaces of the sheet material. If a solution is used this may be applied to one side only by spraying or other suitable techniques such as by using wetted rolls. In instances where the solution is applied to both surfaces, then the sheet material may be immersed in a body of the solution, followed by withdrawing the wet sheet material

from the solution and passing it between squeege or metering rolls to remove excess liquid. The substrate surface should be uniformly wetted with a thin film of the solution without pooling or run off of liquid for best results, and preferably the solution is applied on one or both sides of the substrate by spraying a controlled amount of solution or by contacting with wetted grooved rolls having a controlled amount of the solution thereon. In instances where the solution is too dilute to apply the desired amount of the halide in one application, then a plurality of applications may be made followed by evaporation of solvent between stages, with the exception of the last stage as the sheet material should be wetted with the solution during the application of the metallic chromium-containing material in the coating step which follows. Applying the halide to both sides of the substrate permits better control and overcomes many practical problems of application. Moreover it may result in an improved product especially in cases where the chromium-containing material is applied to one surface only. More dilute solutions may be used to apply a given weight of halide per unit weight of metallic chromium without the problem of run off or pooling of the solution discussed above, or blistering of the coating during drying. Higher weight ratios of halide to metallic chromium may be obtained, and the more dilute halide solutions that are required to achieve a given weight ratio are easier to work with.

It is of course highly desirable that the solution used to apply the halide is not so acid as to result in attack on the sheet substrate. We have found that this may occur if either magnesium or aluminum halides are employed and is particularly a problem if the halide is aluminum chloride. In such cases satisfactory solutions can be obtained by incorporating sufficient basic material which does not itself affect the chromizing reaction to raise the pH to more than 1.2. Suitable compounds include alkali metal hydroxides and carbonates, such as sodium and potassium hydroxides and carbonates and alkaline earth metal oxides, hydroxides and carbonates such as magnesium and calcium oxides, hydroxides and carbonates. We have found the addition of magnesium oxide or carbonate is a particularly suitable method for this purpose and that solutions of aluminum chloride containing either of these having a pH in the range 1.2-2.5 preferably from 1.7 to 2.3 are particularly suitable. If alkaline earth metal oxides are employed then these will be added as solids to the coating. Normally such addition will be after a solution of the halide has been applied. In the case where magnesium chloride is employed with magnesium oxide these may react together to form magnesium oxychloride in situ.

The source of metallic chromium may be commercially pure chromium, or chromium alloyed with metals which do not have an adverse affect on the chromizing process. Ferrochromium is usually preferred and for best results it should have a carbon content of 0.05% or less. The metallic chromium content of the source material should be at least 20%, and for better results at least 50%. In instances where ferrochromium is employed, the chromium content is preferably at least 70% and ferrochromium containing about 72-84% chromium is very satisfactory.

The source of metallic chromium may be commercial and the particles are of a size useful in the selected method of application. While a number of methods of application are suitable, it is usually preferred to contact the substrate surface with a gaseous suspension of the dry metallic particles under conditions whereby they are directed onto the wet surface. Methods suitable for applying the source of chromium, include electrostatic deposition, or use of a vibrating table, a metering drum, or a fluidized bed. The presently preferred method is by electrostatic deposition using prior art apparatus and techniques described in the literature and patents such as U.S.

Pat. No. 3,090,353 and the patents mentioned hereinbefore. In instances where the substrate surface is contacted with an aerosol of the chromium containing particles, then the particle size (Tyler screen) should not be greater than about number five mesh, and preferably should not be greater than about number 30 mesh. Commercially available particles having a Tyler screen size between approximately minus 30 mesh and minus 350 mesh, preferably about minus 90-200 mesh, and for best results minus 150-200 mesh are very satisfactory and are practical particle sizes which are useful for producing uniform coating by well known prior art electrostatic deposition processes.

The chromium-containing material is deposited on the ferrous metal substrate in an amount to provide a desired weight of metallic chromium per unit of surface area. In instances where the source has a relatively low chromium content, the amount of the deposited coating is adjusted accordingly to provide the desired weight of metallic chromium. As a general rule, the metallic chromium content of the coating should be at least 5 grams per square foot of surface area to be chromized and preferably at least 9 to 10 grams. Better results usually are produced when the coating contains about 11-15 grams of chromium per square foot of surface area to be chromized and the coating weight may be increased as desired up to the upper limit, which is approximately 35 to 50 grams of metallic chromium per square foot of surface area to be chromized. The weight ratio of chromium to halide is normally from 1:1 to 10:1 preferably from 2:1 to 5:1. It is understood that the coating weights are given on a per side basis and are based on the metallic chromium content thereof.

The particulate source of chromium is applied to the substrate while it is still wet or tacky with the solution of halide and/or binder, and preferably immediately after application of the solution. When applied in this manner, the solution acts as a temporary binder for the metal particles. The particles are deposited and retained on the wet surface in the form of a uniform particulate chromium coating, and a more uniform chromized layer is produced on the substrate.

The liquid content in the particulate coating may be removed by heating at an elevated temperature. This may conveniently be accomplished by passing the coated substrate through an oven maintained at a temperature high enough to cause rapid evaporation of the liquid and preferably above the boiling point for a sufficient period of time to dry the substrate surface. When water is the liquid, a temperature of about 95-175° C. and preferably about 125-155° C. is satisfactory and the substrate may be heated for up to about 15 minutes normally from 1 to 60 seconds, preferably 5 to 30 seconds to ensure substantially complete evaporation of the water and loss of at least some water of hydration when present in the halide. The removal of the liquid produces an adherent particulate coating on the substrate containing the halide and the source of chromium. The dried coated surface may be coiled or passed under a roll without substantial loss of the particulate chromium coating and a compacting step is not necessary.

Substrates having coated surfaces can be arranged for the heat treatment in any convenient manner. For example, they may be arranged in stacks or disposed separately in a furnace. Lengths of steel strip can be coiled in either open or closed coil manner.

Preferably, however, a plurality of layers of the dried coated sheet material are assembled for chromizing the surfaces thereof with the adjacent layers or convolutions of the sheet material having at least one adherent particulate chromium coating therebetween. In instances where the sheet material is in the form of discrete sheets, this may be conveniently accomplished by stacking the dried coated sheets in superimposed relationship without compacting the coating. When the sheet material is in the form of continuous strip, the dried coated strip is coiled

without compacting the metallic chromium-containing particles in the coating. The strip may be coiled under a line tension of approximately 50-200 pounds per inch of width of the strip, and this amount of coiling is satisfactory without resulting in compacting or deforming of the particles in the coating to any substantial extent.

The assembly prepared from the dried coated sheet material is subjected to a heat treatment cycle under conventional chromizing conditions in a protective atmosphere. Preferably, the assemblies are placed in a closed vessel which is provided with an exhaust conduit and conduits for supplying desired gases thereto to purge air from the vessel with nitrogen or an inert gas, and to maintain a protective atmosphere. Heating means is provided for maintaining the vessel at a desired temperature over the heat treatment cycle. In one suitable heat treatment cycle, air is replaced with nitrogen, then the nitrogen atmosphere is replaced with a protective atmosphere including hydrogen or a mixture of hydrogen and inert gas, and the assemblies are heated to approximately 370-425° C. and preferably to about 400° C. while passing the protective atmosphere through the vessel to remove volatile materials. This temperature may be held for approximately 5-20 hours and preferably for about 10 hours. After the purging is completed, the temperature is raised to approximately 840°-1,010° C. and preferably to about 940-950° C., and this chromizing temperature is held for a sufficient period of time to chromize the sheet metal surfaces. For example, the chromizing temperature may be held for 10-80 hours and preferably about 20-40 hours. During this period of time, the vessel is not purged and the atmosphere is maintained at a positive pressure of 1-2 inches of water. The atmosphere in the vessel may be pure hydrogen or an inert gas such as argon or helium or a mixture of an inert gas and hydrogen. During the chromizing step, the halide provides halogen between the adjacent layers of sheet material in the assembly and especially next to the sheet material. As is well understood in the art, the halogen aids and promotes the chromizing of the adjacent surfaces in a minimum period of time.

After the chromizing step has been completed, the temperature is lowered to approximately 340-400° C. or below and the hydrogen-containing protective atmosphere may be replaced with gaseous nitrogen. After reducing the temperature still further to approximately 150-210° C. or below, the furnace may be opened and the chromized sheet material is removed. The chromized sheet material is subjected to washing with water sprays and/or is contacted with mechanically driven brushes to remove residual chemicals and inert filler when present. Thereafter, the chromized sheet material may be brushed or given other mechanical treatment to produce a lustrous finish, or it may be temper rolled.

The process of the invention may be readily adapted to the operation of continuous strip coating lines and especially high speed lines which operates at strip speeds of several hundred feet per minute and higher wherein the critical treatments to produce the adherent coating are performed while the strip travels in a substantially straight line. The strip is continuously uncoiled and is passed through successive zones for wet cleaning the strip, drying the cleaned strip, applying a solution of an halide and/or binder on the top surface of the dried strip and preferably also on the bottom surface, electrostatically depositing the particulate source of chromium on at least the top surface of the wet strip and if desired also on the under surface, drying the coating to form an adherent particulate coating and then coiling. The strip is preferably passed horizontally through the electrostatic deposition zone and through the oven without being contacted by a roll on the chromium-coated side, whereby the particulate chromium coating on the upper surface is not disturbed prior to drying the solution and coiling.

In instances where the adherent powdered chromium

coating is applied only to the upper surface of the strip, surprisingly it is still possible to chromize both surfaces. This is achieved without the need for a filler for spacing material between adjacent convolutions of the strip as there is no tendency for the adjacent sheets to adhere. When desired, open coil annealing may be employed for the chromizing step when the substrate is coated with chromium on one or both sides.

The process of the invention is illustrated by the following examples:

COMPARATIVE EXPERIMENT

Some pieces (6 ins. x 5 ins.) of titanium stabilized 20 gauge steel of free carbon content less than 0.01% were degreased in an alkaline degreasing bath, pickled in nitric acid, washed with water and dried. One surface of each of the pieces of steel was then treated with a solution of ferrous chloride tetrahydrate (4 parts) in water (5 parts). The amount of solution applied was such that, after drying, 4 grams per sq. ft. of steel surface of solid remained. To the wet surface, ferrochromium powder (200 B.S. Mesh) containing 83% chromium was evenly applied at the rate of 12 grams of chromium per sq. ft. of steel surface. The composite was dried at approximately 120° C. and after drying it was found that the ferrochromium coating was adherent and could not be readily removed by rubbing with the fingers. The pieces of treated steel were then stacked together so that a coated side was in contact with the uncoated side of the adjacent piece of steel, and the stack was then bolted tightly between two heavy gauge steel end plates in order to simulate the conditions which would occur in a closed coil of steel. The pack was then placed in a suitable furnace from which the air was removed by purging with gaseous nitrogen. After removal of the air, the nitrogen atmosphere was replaced with a hydrogen atmosphere and the furnace heated to 400° C. The flow of gas was continued through the furnace for 10 hours to ensure the complete removal of harmful products. The flow of gas was then stopped and the temperature was raised to 950° C. and maintained at this temperature for 16 hours.

After cooling, the pieces of steel were separated from one another and washed in water. The alloy diffusion layers contained an average of 23.5% chromium and were 0.002 in. thick. However, the surfaces of the treated steel were extremely rough and had sintered on them particles of ferrochrome which could not be removed by brushing.

Example 1

An experiment was conducted identical to that described in the comparative experiment, apart from the fact that the ferrous chloride solution was replaced by a solution containing aluminum chloride, which had added to it magnesium carbonate sufficient to give the solution a pH of 1.7. The amount of solution applied was sufficient to give rise to 4 grams of aluminum chloride per sq. ft. of steel surface after drying.

A stack of pieces of steel was prepared and furnished in the way described in the comparative experiment.

Examination of the pieces of steel after furnacing revealed very little sintering of the ferrochrome to the surfaces and the diffusion coatings so obtained contained an average of 20.5% chromium and were 0.0023 in. thick.

Example 2

An experiment similar to that described in Example 1 was carried out, except that the ferrous chloride solution was replaced by a solution of magnesium chloride of pH 5.2. The amount of solution applied was such that, after drying, 4 grams of a solid magnesium chloride per sq. ft. of steel surface would remain.

A stack of plates was constructed and furnished in the way described in Example 1. On examination of the pieces of steel after furnacing, it was revealed that little sintering had taken place, and the diffusion alloy layers which

had been formed contained an average chromium content of 22.2% and had a thickness of 0.0021 in.

We claim:

1. In a process for chromizing ferrous metal substrates which comprises applying an adhesive layer to the substrate, subsequently applying chromium-containing powder thereto and then subjecting the substrate having the chromium-containing powder thereon to a heat treatment in the presence of a halide so as to bring about diffusion of the chromium into the substrate, the improvement which comprises employing as the halide at least one halogen-containing substance selected from the group consisting of hydrated magnesium halide, aluminum halide and magnesium oxyhalide, the said halogen-containing substance being applied to the substrate from an aqueous medium and a pH modifier being employed in conjunction with the said halogen-containing substance, the pH modifier being capable of reducing the acidity of the said halogen-containing substance and being employed in an amount to reduce the acidity thereof.

2. A process as claimed in claim 1 wherein the said halogen-containing substance is applied to the substrate from an aqueous medium prior to the application of the chromium-containing powder so as to form the said adhesive layer.

3. A process according to claim 1 wherein the said halogen-containing substance is applied to the substrate from an aqueous solution.

4. A process according to claim 3 wherein the pH modifier is present in an amount to adjust the pH of the solution to be within the range 1.2 to 2.5.

5. A process according to claim 4 wherein the pH modifier is selected from the group consisting of alkali metal hydroxides, alkali metal carbonates, alkaline earth metal oxides, alkaline earth metal hydroxides and alkaline earth metal carbonates.

6. A process according to claim 5 wherein aluminum chloride is employed in conjunction with magnesium carbonate.

7. A process according to claim 1 wherein the said halogen-containing substance is magnesium oxychloride.

8. A process according to claim 1 wherein the said halogen-containing substance is applied to the substrate in an amount of from 2 to 5 grams per sq. ft.

9. A process according to claim 1 wherein said halogen-containing substance is applied from an aqueous solution prior to the application of the chromium-containing powder and provides the adhesive layer to which the chromium-containing powder is applied.

10. A process according to claim 1 wherein the substrate is arranged for the heat treatment so that adjacent surfaces are in contact with each other.

11. A process according to claim 1 wherein the chro-

mium-containing powder is applied to only one surface of the substrate.

12. A process according to claim 1 wherein the chromium-containing powder is applied at a rate equivalent to that required to provide from 11 to 15 grams of chromium per square foot to be chromized based on the entire surface area to be chromized.

13. In a process for chromizing ferrous metal substrates which comprises applying an adhesive layer to the substrate, subsequently applying chromium-containing powder thereto and then subjecting the substrate having the chromium-containing powder thereon to a heat treatment in the presence of a halide so as to bring about diffusion of the chromium into the substrate, the improvement which comprises employing as the halide an oxyhalide of magnesium.

14. A process according to claim 13 wherein the oxyhalide is applied to the substrate from an aqueous medium.

15. A process according to claim 13 wherein the oxyhalide is applied to the substrate from an aqueous medium prior to the application of the chromium-containing powder so as to form the said adhesive layer.

16. A process according to claim 13 wherein the oxyhalide employed is magnesium oxychloride.

17. A process according to claim 13 wherein the oxyhalide is applied to the substrate in an amount of from 2 to 5 grams per sq. ft.

18. A process according to claim 13 wherein the substrate is arranged for the heat treatment so that adjacent surfaces are in contact with each other.

19. A process according to claim 13 wherein the chromium-containing powder is applied to only one surface of the substrate.

20. A process according to claim 13 wherein the chromium-containing powder is applied at a rate equivalent to that required to provide from 11 to 15 grams of chromium per square foot to be chromized, based on the entire surface area to be chromized.

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