

1

2

3,481,769

ALLOY DIFFUSION COATING PROCESS

Giles F. Carter, Wilmington, Del., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

No Drawing. Continuation-in-part of application Ser. No. 139,369, Sept. 20, 1961. This application Mar. 2, 1964, Ser. No. 348,860

Int. Cl. C23c 1/08

U.S. Cl. 117—114

11 Claims

This invention relates to a process for coating ferrous metal articles. More particularly, the invention relates to a process for forming an alloy diffusion coating of aluminum and iron on a ferrous metal substrate by using a molten metal transfer agent.

This application is a continuation-in-part of my pending application Ser. No. 139,369, filed Sept. 20, 1961, which is a continuation of my applications Ser. No. 44,015 and Ser. No. 835,171, filed July 20, 1960, and Aug. 21, 1959, respectively, which are now abandoned.

Considerable difficulty has been experienced in providing aluminum-iron alloyed articles having acceptable properties for commercial uses. Alloys containing more than about 5% aluminum become brittle when cold worked. Cladding or coating a deformable metal substrate, e.g., mild steel, has not proved to be a fully satisfactory solution to the problem due to the difficulty in obtaining good adhesion or diffusion of the alloy onto the surface of the substrate. In attempting to prepare such articles, it has been necessary to use specialized gaseous treatments of the substrate either prior to or during the coating operation.

It is a primary object of this invention to provide an improved process for preparing high quality coatings of an aluminum alloy on various metal articles. This object is attained by the process of this invention whereby a ferrous metal article is contacted with a molten bath containing, as essential ingredients, a source of aluminum and a Group II-A metal selected from the class consisting of calcium, barium, magnesium, and strontium, which are hereinafter referred to as transfer agents.

In practicing this invention, a molten bath may be prepared in a number of ways. A mixture of one or more of the transfer agents and a source of aluminum may be melted by heating the mixture to a temperature between about 800° C. and the melting temperature of the article to be coated, or the transfer agent may be melted and the aluminum added thereto. The article to be coated is then immersed in the bath. The period of treatment in the bath may extend from a few minutes to an hour or more, depending on the particular coating characteristics desired. Deeper penetration of the diffusing element, i.e., the aluminum, occurs when longer periods of treatment are used. Generally, a period from about one minute to about one hour is preferred. At the end of the selected period, the article, which now has a diffusion coating on its surface, is removed from the bath, quenched, if desired, and then cleaned to remove the quenching medium and adherent bath.

The use of a blanket of inert gas over the molten bath is desirable but not essential since the bath may be operated under carefully controlled conditions in the ambient atmosphere. It is preferred to agitate the bath during operation by mechanical or other means but this is not essential.

The composition of the bath must be controlled. The amount of aluminum must be maintained at a level less than 70% by weight of the bath. It is essential that this limitation be adhered to since as the upper limit is approached etching of the ferrous substrate is first observed, and finally the substrate dissolves completely in the bath. The lower limit for aluminum is not critical and will de-

pend primarily on the treating time and temperature used, and the concentration of aluminum desired in the coating. Generally at least 0.5% by weight is used, with a preferred range being from 1% to 20%. Any source of aluminum metal may be used to provide coatings having a thickness from a fraction of a mil to 10 or more mils thick. Aluminum compounds which are reducible to the metallic form by the transfer agent, such as aluminum chloride and aluminum oxide, as well as ferro-aluminum alloys are illustrative.

The other essential ingredient of the bath, i.e., the transfer agent, when used alone must be present in an amount greater than 30% by weight of the bath. In a preferred embodiment, from about 60% to about 99% by weight of the transfer agent is used. These amounts may be varied by introducing a neutral diluent, i.e., a material which is not reactive with the ingredients in the bath and does not diffuse to a substantial degree into the substrate. Illustrative examples of such diluents which may be used to reduce the amount of transfer agent required and to modify the melting temperature of the bath include copper, lead, and tin. Minor amounts of one or more diffusing elements may also be included in the bath.

The operating temperature of the bath for the process is selected to favorably affect the rate of diffusion of aluminum and any other diffusing elements which may be present, and to maintain the transfer agent present in the bath in the molten state. A temperature less than about 800° C. is not considered practical because the rate of diffusion is too slow. The maximum practical operating temperature may be considered to be the normal boiling point of the particular transfer agent used, but in any event the temperature of operation must be maintained below the normal melting point of the solid ferrous metal article treated. A preferred operating temperature for the process is from about 900° to 1200° C.

The residence time of the ferrous article in the molten bath influences the thickness of coating obtained and may vary widely. Depending on the size of the molten bath and the treating time necessary for desired thickness of coating, coiled steel sheet or shaped ferrous metal articles may be passed continuously through the molten bath at a rate to provide the required residence time for a desired coating, or articles may be immersed batchwise in the molten bath to provide the required residence time for a desired coating and then withdrawn.

No special pretreatment of the ferrous metal articles is required before immersion in the molten bath. It is, of course, desirable that the surface of the ferrous metal article be clean and, for optimum results, it is preferable that the metal article be subjected to conventional degreasing treatment. Nevertheless, it has been observed that coatings formed by the process are not significantly influenced by the presence of scale or thin films of oil on the surface of the base metal.

The ferrous articles treated in accordance with the hereinbefore described method of the invention are termed coated articles although it must be appreciated that the diffusing element migrates into the solid surface of the ferrous articles and thus alters the characteristics of the articles. For the usual treating times, ranging from approximately one minute to several hours, the coating is characterized by different concentrations of the diffusing element at its outer surface than are found in the interior.

A better understanding of the invention will be gained from the following illustrative examples in which parts and percentages are by weight unless otherwise specified.

EXAMPLE I

Mild steel coupons containing 0.06% carbon were treated in a molten bath containing 500 grams of calcium

and 20 grams of aluminum. After remaining in the bath for one hour at 1060° C., ductile coatings of iron-aluminum were formed. The surface of the coupon was not covered by pure aluminum, the surface being an alloy of iron-aluminum having oxidation resistant properties far superior to those of the original base metal.

EXAMPLE II

A two-inch by two-inch cylinder of 316 stainless steel was immersed for two hours in a diffusion bath containing 220 grams of calcium and 80 grams of aluminum maintained at 1000° C. After removal, the cylinder was cleaned and heated for sixteen hours in air at 1230° C. Less than 1 mil of scale formed and there was no flaking of scale during cooling. These results are significant because the coated stainless steel proved to be extremely resistant to oxidation at high temperatures and repeated heating-cooling cycles did not induce excessive scaling. The absence of flaking indicates that the coated stainless steel may be heated and cooled many times without excessive scaling. Untreated stainless steel fails rapidly in heating-cooling cycles because of excessive scale flaking during cooling.

The procedure can be repeated substituting barium for the calcium in the bath with similar results.

EXAMPLE II

A bath was formed containing 120 grams of magnesium and 30 grams of powdered aluminum. The bath was agitated and operated under a blanket of argon gas. A mild steel coupon was immersed in this bath for ten minutes at 1000° C. A coating 1 mil thick was obtained on the base metal and the surface of coating contained approximately 10% aluminum.

EXAMPLE IV

A bath containing 500 grams of calcium and 20 grams of aluminum was heated to 1060° C., and 10 grams of manganese powder were added after the calcium-aluminum had been stirred under argon for one hour. After additional stirring, a mild steel coupon was treated for thirty minutes at 1060° C. and a thick coating of iron-aluminum-manganese alloy about 2.7 mils was formed. This coated coupon demonstrated excellent resistance to oxidation when exposed to air at high temperatures in the order of 1000° to 1100° C.

The procedure can be repeated substituting strontium for the calcium in the bath with similar results.

EXAMPLE V

A bath was formed containing 52 grams of calcium, 17 grams of aluminum, and 4 grams of yttrium. A mild steel sample was treated in this bath for two hours at 1100° C. A coating 0.6 mil thick was obtained having a surface concentration of 15% aluminum and 10% yttrium.

EXAMPLE VI

This example illustrates the critical nature of the transfer agent concentration in the molten bath.

Separate samples of 1008 killed steel, 20 mils thick, were treated for fifteen minutes at a temperature of 1140° C. by immersing them in a series of molten baths of calcium to which aluminum wire was added. The baths were under a protective argon atmosphere.

The first bath was composed of 500 grams of calcium to which 1180 grams of aluminum (70% by weight of aluminum) were added. Within five minutes after immersing the steel sample in the bath, the sample completely dissolved.

The second bath was composed of 500 grams of calcium and 910 grams of aluminum (65% by weight of aluminum). The sample was removed after fifteen minutes, inspected and weighed. It had lost about 10% by weight and had an irregular etched surface. It rusted when placed in hot water. Quantitative analysis by X-ray

fluorescence of the sample surface showed the presence of some aluminum on the surface of the panel.

To the third bath, 500 grams of calcium and 640 grams of aluminum (about 56% by weight of aluminum) were added. At the end of fifteen minutes, the sample was removed from the bath. The panel gained about 5% in weight, had a smooth, reflective surface and did not rust when treated with dilute acetic acid. The presence of aluminum on the surface was clearly indicated by X-ray fluorescence.

A fourth sample was immersed in a bath containing 500 grams of calcium and 190 grams of aluminum (about 27% by weight of aluminum). After fifteen minutes, the panel was removed from the bath and found to have a surface concentration of aluminum of about 25% by weight, with the balance being iron. The sample had a smooth, reflective surface.

As indicated in the foregoing examples, minor amounts of various metals in addition to aluminum may be included in the molten bath. Such metals as manganese and yttrium may be included in small amounts in the bath.

It is, of course, to be appreciated that many well-known treatments can be employed to improve the surface appearance of a coated article made by the process of this invention, if desired. For example, an improved surface finish can be obtained by cold working the base metal to a mirror finish before coating or, alternatively, the surface of the coated article may be cold worked to improve surface appearance. The coated article prepared by the invention also may be subjected to subsequent thermal treatments in order to enhance the physical properties such as quenching or annealing, if desired.

The products prepared by the process of this invention are particularly useful in applications in which oxidative resistance, flue gas corrosion resistance at high temperatures, and immunity from attack of various kinds of sulfurous gases such as H₂S, SO₂, and SO₃ is desired. These coated articles may be used for pots for salt, cyanide, and lead where operating temperatures approach 1550° F. They may be used as tubes for air heaters, radiant steam superheaters, and oil and gas polymerizers. They are also useful in fabricating electrical apparatus. Surface enrichment of an electrical iron with aluminum provides desirable electrical properties without the accompanying brittleness of the commonly known bulk alloys. In addition, the decarburization of the ferrous substrate which is provided by the process of this invention further reduces energy losses attributable to the presence of carbon in prior art products. By using the process of this invention, the additional decarburizing procedure commonly used is no longer necessary.

As many widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that this invention is not to be limited to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. A process for forming an aluminum-iron alloy diffusion coating on a ferrous metal article, said article being selected from the group consisting of mild steel and stainless steel articles, comprising contacting said article in a molten bath for a period of time sufficient to obtain an aluminum-iron diffusion coating thereon, said bath consisting essentially of an admixture of a Group II-A metal selected from the class consisting of calcium, barium, magnesium, and strontium and a source of aluminum wherein said metal is present in an amount from about 5% to about 99% by weight and said aluminum is present during said period of contacting in an amount less than 70% by weight of said bath, the temperature of said bath being maintained between about 800° C. and the melting point of said article.

2. The process of claim 1 wherein said bath contains from about 1% to 20% by weight of aluminum and at least 30% by weight of calcium.

5

3. The process of claim 2 wherein said temperature is between 900° and 1200° C.

4. The process of claim 3 wherein said article is immersed in said bath for a period from one to sixty minutes.

5. The method of impregnating a solid ferrous base metal with a controlled amount of aluminum which method comprises contacting a surface of said base metal, free of scale, with a liquid solution of aluminum in magnesium at a temperature between about 1472° F. and 2150° F. for a time sufficient to obtain an aluminum-iron diffusion layer of a desired thickness on the surface of said article, said liquid solution containing between about 0.1 and 20 atomic percent aluminum.

6. The method of claim 5 wherein said liquid solution contains between about 0.5 and 10 atomic percent aluminum.

7. The method of claim 5 wherein said liquid solution contains between about 0.5 and 5 atomic percent aluminum.

8. The method of claim 5 wherein said contacting is carried out in an inert gas atmosphere.

9. The method of aluminizing a steel article which comprises contacting a surface of said article, free of scale, with a magnesium-aluminum liquid solution at a temperature between about 1472° F. and 1800° F. under an inert gas atmosphere for a time sufficient to provide an aluminum-iron diffusion layer of a desired thickness on the surface of said article, said solution containing about 0.5 to 10 atomic percent aluminum.

6

10. The method of impregnating a solid ferrous base metal with a controlled amount of aluminum which method comprises contacting a surface of said base metal with a liquid solution of aluminum in magnesium at a temperature between 850° F. and 2150° F. for a time sufficient to obtain an aluminum-iron diffusion layer of a desired thickness on the surface of said article, said liquid solution containing between about 0.1 to 20 atomic percent aluminum.

11. The method of aluminizing a steel article which comprises contacting a surface of said article with a magnesium-aluminum liquid solution at a temperature between about 1200° F. and 1800° F. under an inert gas atmosphere for a time sufficient to provide an aluminum-iron diffusion layer of a desired thickness on the surface of said article, said solution containing about 0.5 to 10 atomic percent aluminum.

References Cited

UNITED STATES PATENTS

2,550,709	5/1951	Moe et al.	117—52
2,912,346	11/1959	Kanter	117—51
3,134,685	5/1964	Dravnieks	117—114
3,184,292	5/1965	Argyriades et al.	117—114

RALPH S. KENDALL, Primary Examiner

U.S. Cl. X.R.

117—131; 29—196.2