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3,343,928

FERROUS SUBSTRATE HAVING AN IRON-CHROMIUM-ALUMINUM ALLOY COATING THEREON

Harold E. Bellis, North Tonawanda, N.Y., and Giles F. Carter, Wilmington, Del., assignors to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

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ABSTRACT OF THE DISCLOSURE

A ferrous metal substrate is provided with a ferritic alloy coating consisting of 12 to 50% by weight of chromium, 0.08 to 4% by weight of aluminum with the balance of the coating consisting essentially of iron.

This application is a continuation-in-part of application Ser. No. 335,378, filed Jan. 1, 1964, which is a continuation-in part of application Ser. No. 211,895, filed July 23, 1962, which is in turn a continuation-in-part of application Ser. No. 139,369, filed Sept. 20, 1961, said applications being now abandoned.

This invention relates to novel articles which exhibit outstanding corrosion resistance properties comprising a ferrous metal substrate having a ferritic chromium-aluminum-iron alloy coating that may or may not also include small amounts of nickel as an alloying element, wherein the surface composition of said coating is controlled to contain at least 12% by weight chromium and a content of aluminum within specified critical limits.

Metal coatings on dissimilar metal substrates are a known means of providing surface protection. Ferritic stainless steel coatings have been provided on ferrous metal articles in the past to provide corrosion resistance properties not possessed by the base metal originally. Ferritic stainless coatings have been formed on ferrous metal articles, for example, by cladding a sheet of ferritic stainless steel to a sheet of base metal such as mild steel. It has also been proposed to form such coatings on ferrous metal articles through chromium diffusion treatment whereby the surface of the base metal, such as mild steel or carbon steel, is alloyed with chromium. These prior ferritic alloy coatings have been essentially chromium-iron alloys.

Although such prior ferritic stainless coatings have been useful in enhancing the corrosion resistance properties of less expensive ferrous base metals, there is great demand for achieving ferritic stainless coatings which can impart increased corrosion resistance characteristics to inexpensive base metals. Furthermore, it has been found that articles having known ferritic stainless coatings are usually not formable; the ferritic coating in many instances actually separating from the formable base metal when the coated article is deformed to any appreciable extent. On the other hand, articles of the prior art, having a ferritic alloy coating, which are formable are found to exhibit relatively poor corrosion resistance at the plastically deformed areas. Apparently this condition is due to the fact that small cracks or fractures occur in the coating during forming so that the corrosion-susceptible base metal becomes exposed to corrosive media and rust appears on the surface of the coated articles.

It is the object of the present invention to provide an article of manufacture exhibiting increased corrosion resistance comprising a ferrous metal substrate having a ferritic chromium-aluminum alloy coating which may or may not also include nickel as an alloying element, said coating containing at its surface at least 12% by weight chromium and an appreciable content of aluminum but which is maintained below an upper critical limit.

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Surprisingly, in accordance with the present invention, it has been found that the corrosion resistance of a ferrous metal article having an iron-chromium alloy coating is markedly increased on the addition of aluminum to the coating so that top 0.3 mil of said resulting coating is ferritic and consists essentially of iron, at least 12% by weight of chromium and from about 0.08% to 4% by weight of aluminum. It has been found that if the content of aluminum in the top 0.3 mil of the coating reaches about 5% by weight the corrosion resistance of the coated article actually decreases over a ferrous metal article possessing a ferritic chromium-iron alloy coating. It has been found that nickel may be alloyed with the chromium-aluminum-iron alloy coating defined above, if desired, without adversely affecting the improved corrosion resistance performance obtained if the nickel content in the top 0.3 mil of the coating is maintained below approximately 6% by weight. The presence of nickel in the coating is found to offer an important advantage inasmuch as it confers a self-healing characteristic to the ferritic alloy coating. If a coating containing nickel as an alloying element develops a rust spot, the rust may be removed from the spot, and although a mark or scar remains at the site, the coating resists the continued showing of rust. By contrast, when the coating does not contain nickel, if rust is removed, more rust continues to form at the spot from the ferrous metal underlying the coating and, of course, this rust detracts from the visual attractiveness of the coated article.

Articles according to the present invention may be prepared by diffusion processes, as well as by any other coating processes in which the coating is metallurgically bonded to the base metal, such as, cladding by rolling, cladding by high energy impact, soldering, fusion joints, casting one metal to another or by any other coating process. The base metal underlying the coating may be any ferrous metal, such as, for example, cast iron, carbon steel, mild steel, low-carbon steel, stainless steel, low-alloy steels, such as those containing small amounts of chromium, niobium, vanadium, titanium, zirconium, or the like. The outstanding economic advantage offered by the coated articles of the invention, of course, is that a relatively inexpensive base metal, such as mild steel, may be provided the corrosion resistance characteristics of a very superior ferritic stainless steel with the use of only a very thin surface coating. The articles of the invention, for example, are found to possess superior corrosion resistance over many 300 and 400 series solid stainless steel products.

Although any desirable coating technique may be employed, the preferred means for obtaining the coated articles of the invention, is the diffusion process disclosed in United States Patent No. 3,184,331, which is assigned to our assignee. The process involves the diffusion of various elements including chromium and nickel into the surface of a ferrous metal article by use of a metal transfer agent selected from the group consisting of calcium, barium, magnesium, and strontium, whereby the transfer agent acts principally as a solvent and transfer medium to bring the diffusing elements into contact with the surface of the solid ferrous metal article. At the high temperatures employed in the contacting, inward diffusion of the diffusing elements, dictated by well-known laws of solid state diffusion, then causes coating growth. The preferred embodiment for executing the diffusion process is by immersing the base ferrous metal article in a molten bath of the metal transfer agent having incorporated therein a source of the desired diffusing elements wherein said contacting is carried out at a temperature between about 800° C. and the melting point of said article. Calcium is the preferred transfer agent and the process when using calcium is preferably carried out at a tem-

perature between about 1000 to 1200° C. A more complete description of the process and its theory of operation is disclosed in the aforementioned United States patent, which is incorporated herein by reference.

It has been found in accordance with the present invention that the ferritic alloy composition within the range required for the coated surface of the articles of the invention can be obtained by maintaining the amounts of chromium, aluminum, and nickel in the metal transfer bath based on the amount of transfer agent present therein during the diffusion process. Within the range permissible for aluminum in the coating; namely, about 0.08% to 4% by weight, the concentration of aluminum in the top 0.3 mil of the ferritic alloy coating formed on the ferrous base metal is approximately equivalent to 1.5 to 2 times the concentration of dissolved aluminum in the bath based on the amount of transfer agent present. The amount of aluminum in the bath for the diffusion process, therefore, may range from about 0.04% to about 3% by weight based on the amount of transfer agent present in the bath. Within the range permissible for nickel in the coating; namely, up to approximately 6% by weight, the concentration of nickel in the top 0.3 mil of the ferritic alloy coating formed on the ferrous base metal is approximately equivalent to the amount of nickel present in the bath. The amount of nickel in the bath for the diffusion process, therefore, may range up to approximately 6% by weight based on the amount of transfer agent present. Chromium is completely miscible in iron and only slightly soluble in the transfer agent, the amount of chromium soluble in calcium, for example, at 1000° C., being in the order of about 0.1% by weight. Due to this fact, a saturated solution of chromium in the transfer agent favors rapid diffusion of chromium into ferrous base metals.

For usual coating times, of from 5 to 60 minutes, it is preferred that in executing the diffusion process that the amount of chromium in the bath, preferably in finely divided form, be in a range of from 3% up to 10% by weight based on the amount of transfer agent present therein. This provides an excess of chromium insuring a saturated solution of chromium in the transfer agent for optimum liquid-to-solid transfer of chromium to occur. Amounts of chromium above 10% by weight based on transfer agent may be used but little or no advantage is gained thereby. It will be appreciated from the foregoing that amounts considerably less than 3% by weight may be used successfully but usually it is not commercially feasible to operate with the amount of chromium in the bath below approximately 0.25% by weight based on the amount of transfer agent present.

The coatings of the articles of the invention formed by the above-described diffusion process may contain small amounts of diffused transfer agent. The coatings of the novel articles of the invention may also contain small amounts of other elements in addition to chromium-aluminum-iron which may diffuse into the coating from the ferrous metal substrate during the coating process or which may be purposely added so long as the novel and basic characteristics with respect to improved corrosion resistance set forth herein for the novel ferritic alloy coating of chromium-aluminum-iron are not altered.

A better understanding of the invention will be gained from the following examples demonstrating the features and advantages of the articles of the invention. These articles illustrating the invention were prepared by means of the above-described diffusion process and a showing of typical preparations by such means are included. It is to be appreciated that the ferritic alloy coatings of these articles formed by a diffusion coating technique are characterized by greater concentrations of the diffusing elements chromium, aluminum, and nickel at the outer surface of the coating and decreasing concentrations of these metals downward to the ferrous metal substrate. Therefore, it can be clearly expected that the maximum

limits for aluminum and nickel contents at the surface of the ferritic alloy coating which are established by the following examples as limits below which aluminum and nickel must be maintained in order to gain the improvements of the invention constitute as well as the maximum content of such alloying elements that may be tolerated at any level in the ferritic alloy coating for the articles of the invention.

In the following examples, amounts of the various ingredients are given in terms of percent by weight, unless otherwise indicated. All samples prepared were cooled to room temperature by quenching in oil upon removal from the coating bath. The concentrations of chromium, aluminum, and nickel reported represent a measure of their average concentrations in approximately the top 0.3 mil of the coating as determined by X-ray fluorescence. The surface of each sample was lightly polished before the concentration was determined. The thicknesses of the coatings reported were determined by microscopic examinations of cross-sections of the coated articles, after etching by 3% by weight concentrated nitric acid, 97% by weight ethanol in 30-60 seconds.

Example 1

A series of specimen articles were prepared comprising a ferrous metal substrate having a ferritic alloy coating with the top 0.3 mil of said coating having a composition consisting essentially of iron, chromium, and aluminum in which the chromium content varied over a wide range above a minimum value of 12% and the aluminum content varied from 0.05% to about 4%. The following represents a typical preparation of an article illustrative of this class of products.

An iron container having a bath prepared from 2300 grams calcium, 125 grams of powdered chromium (-325 mesh), and 12 grams of aluminum was heated to 1100° C. The bath was agitated by a mechanical stirrer and was covered by an inert atmosphere of argon. A mild steel specimen containing 0.04% carbon was introduced for a treating time of 28 minutes. The coated specimen was then removed from the bath and was cooled to room temperature. A coating of 1.7 mils was formed on the base metal, the top 0.3 mil of said coating having a concentration of 28% chromium and 1.1% aluminum. The coating procedure was repeated to prepare specimens listed in Table I with the amount of aluminum in the coating bath and coating time being varied as indicated in the table.

A series of such specimens each measuring 2" x 4" were then tested for corrosion resistance on the flat coated surface of the specimen (without deformation) in accordance with the copper acetic acid salt spray (CASS) test. This test was run in accordance with the procedure and apparatus published Nov. 14, 1960, by the Chemical and Metallurgical Dept., Quality Control Office of the Ford Motor Company, identified as Quality Laboratory and Chemical Engineering and Physical Test Methods BQ5-1. The description of the procedure and apparatus for this test is quite lengthy and will not be repeated herein in view of the reference provided. In this test, the sample is subjected to an acetic acid salt spray solution to which small amounts of copper chloride are added to promote corrosion. The test is now in broad use throughout the portion of the chromium plating industry concerned with out-of-door durability, being regarded as an excellent accelerated corrosive test which simulates the corrosion behavior and durability of chromium plated steel and zinc alloy parts in out-of-door service. The specimens were inspected for rust spots on the 2" x 4" coated surface after 16 hours and every 24 hours thereafter through 112 hours in the test with the total number of rust spots observed after each inspection being reported as the result of the test.

Data tabulated in Table I below are representative of the increased corrosion resistance provided by articles

of the invention comprising a ferritic chromium-aluminum-iron alloy coating formed on a mild steel substrate over the corrosion resistance provided by a coated article comprising a ferritic chromium-iron alloy coating formed on the same mild steel substrate and that provided by coated articles having a ferritic chromium-aluminum-iron alloy coating but wherein the aluminum content signifi-

a specimen measuring 4" x 6" was exposed to the CASS test. Failure for the test was considered to be ten (10) visually observed rust spots on the coated surface of the specimen. The specimens were observed after 16 hours and every 24 hours thereafter until failure occurred; with the hours to failure being reported as the result of the test.

TABLE II

Run No.	Percent Ni	Percent Al	Percent Cr	Coating Thickness	CASS Life in Hours to Failure
1-----	0.5	1.0	40	1.6	112+
2-----	1.7	0.9	43	1.5	112+
3-----	2.2	1.0	42	1.5	112+
4-----	3.0	1.1	39	1.0	112+
5-----	3.5	1.2	44	1.9	112+
6-----	4.2	1.6	38	1.3	112+
7-----	4.8	1.0	37	1.5	112+
8-----	5.9	2.0	46	2.1	112+
9-----	7.0	1.0	32	1.9	64
10-----	8.2	1.0	28	1.5	64
11-----	10.2	1.0	27	2.1	40

cantly exceeds 4% in the top 0.3 mil of said coating. Each run reported represents six (6) 2" x 4" panels having the same coating composition so that the rust spots reported for each exposure period to the CASS test is the total number observed for 48 sq. in.

The above results indicate clearly that nickel may be added as an additional alloying element in the ferritic coating up to amounts of about 6% without adversely affecting the improved corrosion resistance of the coated article of the invention.

TABLE I

Run No.	Al in Bath (grams)	Coating Time (minutes)	Composition of Coating		Coating Thickness (mils)	CASS Hours of Exposure				
			Percent Al	Percent Cr		16	40	64	88	112
1-----	0	55	0	36	1.82	4	15	17	18	20
2-----	(*)	30	0.08	28	1.12	0	6	6	8	8
3-----	3.0	30	0.30	33	1.36	2	3	3	3	6
4-----	5.8	28	0.50	31	1.32	0	2	2	1	1
5-----	9.6	28	0.70	29	1.41	1	4	2	-----	5
6-----	11.5	28	1.1	28	1.66	4	4	3	6	6
7-----	38.0	28	1.8	31	3.21	1	3	4	4	4
8-----	65.0	50	2.2	30	3.39	1	5	5	5	7
9-----	92.0	56	3.4	32	3.81	3	3	5	7	6
10-----	127.0	62	4.9	33	4.43	6	25	29	30	30
11-----	154.0	10	6.8	28	2.5	72	118	-----	-----	-----

* Run carried out in container previously containing Ca-Al bath. No additional aluminum added.

It is obvious from the above results that only very small amounts of aluminum are necessary to effect significant increases in the corrosion resistance of a coated article having a chromium-iron alloy coating; 0.08% aluminum offering a surprising improvement. As will be noted when the aluminum content is 4.9%, the article actually exhibits somewhat less corrosion resistance than an article having a chromium-iron alloy coating without aluminum being present. The maximum limit for aluminum in the ferritic alloy coating is therefore somewhere between 3.4 and 4.9% and may be reasonably set at about 4%. Amounts of aluminum above 5% in the coating exhibit quite an adverse effect on corrosion resistance.

Example 2

To determine the effect of adding nickel to chromium-aluminum-iron alloy coatings, a series of specimen articles were prepared comprising a ferrous metal substrate having a ferritic alloy coating with the top 0.3 mil of said coating having a composition consisting essentially of iron, chromium, aluminum, and nickel in which the chromium content varied over a wide range above a minimum value of 12%, the aluminum content varied from 0.05 to about 4% and the nickel content was permitted to vary over a range above and below 6%, the articles in which the nickel concentrations in the top 0.3 mil of the coating were below 6% being within the invention and the articles in which the nickel concentrations in the top 0.3 mil of the coating were above 6% being outside the invention. Data tabulated in Table II below are representative of such series showing the effect on corrosion resistance caused by the addition of varying amounts of nickel. In this series of tests, for each run

As will be obvious from the foregoing description, the thickness of the ferritic alloy coating for the novel articles of the invention may vary over a wide limit. It is preferred, however, that the ferritic alloy coating on the article, as thickness was determined for the articles of the examples, be at least about 0.5 mil. Usually there is little advantage in the coating thickness being in excess of from 3 to 5 mils but thicker coatings may be formed, if desired. Although, as it has been previously stated, the chromium content in the top 0.3 mil of the coating may range over a broad range above the 12% by weight considered a minimum content necessary herein to impart stainless steel characteristics to the coating, it is most preferred that the content of chromium be in a range of from about 25 to 50% by weight.

The novel articles of the invention formed by the above-described diffusion process are also found to exhibit the desirable property of having a lower tendency for other materials to adhere to the surface of the ferritic alloy coating. For example, when formed into cooking utensils, such as frying pans, it is found that eggs and meat may be fried on the coated surface with little or no fats or oils being present without these substances exhibiting a tendency to stick to the coated surface. Similarly, it has been found that it is extremely difficult to electroplate metallic layers over the surface of the coatings of these articles due to the failure of the electroplate layer to adhere to the coated surface of the article.

It is to be appreciated that although outstanding corrosion resistance has been shown for the novel articles of the invention, even increased corrosion resistance can be obtained by well-known post-treatment techniques for such purposes. For example, corrosion resistance can be

markedly improved by passivating the article after coating in 50% nitric acid or 20% nitric acid-2% sodium dichromate solutions.

In like manner, many well-known treatments can be employed to improve the surface appearance of the coated article, 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 articles can also usually be polished or buffed after being formed without such treatment being deleterious to corrosion resistance.

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.

We claim:

1. An article of manufacture comprising a ferrous metal substrate having a ferritic alloy coating, wherein the top 0.3 mil of said coating is an alloy consisting of from 12 to 50% by weight of chromium, from about 0.08% to 4% by weight of aluminum, and the balance consisting essentially of iron.

2. The article of claim 1 wherein said coating is applied to a mild steel substrate.

3. The article of claim 2 wherein the top 0.3 mil of said coating is an alloy containing from about 25 to 50% by weight of chromium.

4. The article of claim 2 wherein the top 0.3 mil of said coating contains an amount of nickel not exceeding 6% by weight.

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HYLAND BIZOT, *Primary Examiner*.