

Dec. 27, 1966

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3,294,498

CR-FE DIFFUSION COATING FERROUS METAL SUBSTRATE

Filed Sept. 24, 1963

3 Sheets-Sheet 1

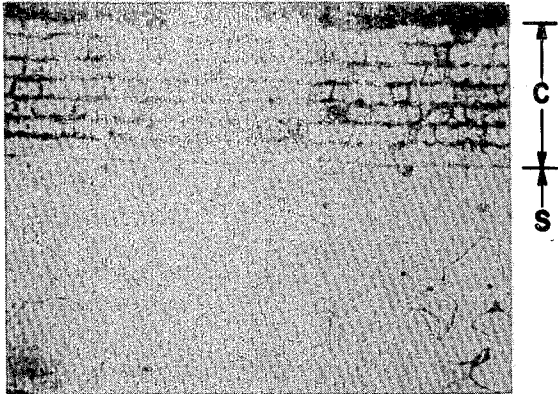


FIG. 1

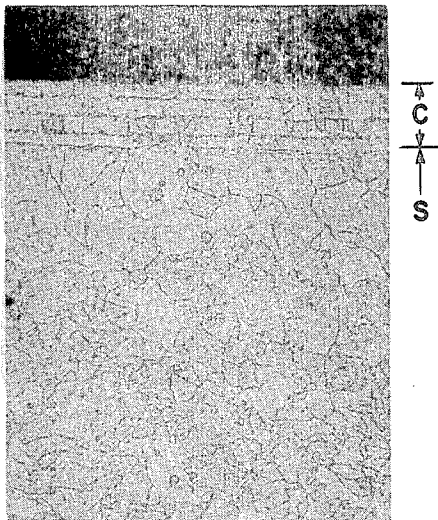


FIG. 2

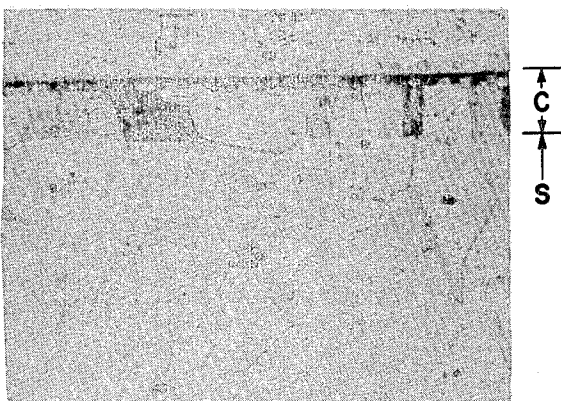


FIG. 3

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3 Sheets-Sheet 2

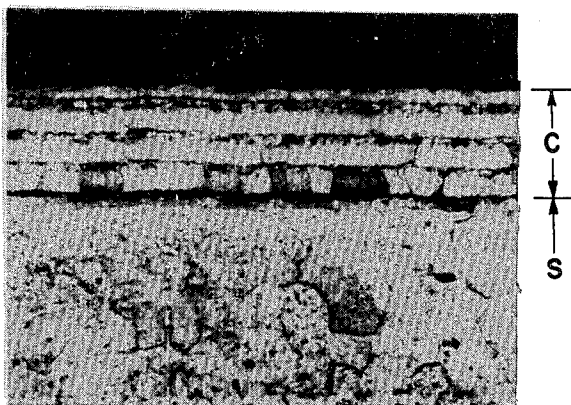


FIG. 4

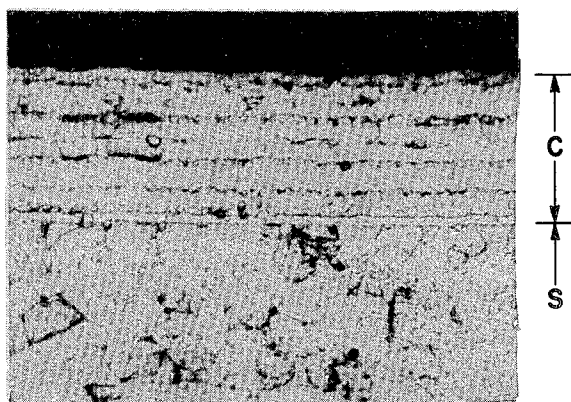


FIG. 5



FIG. 6

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3 Sheets-Sheet 3

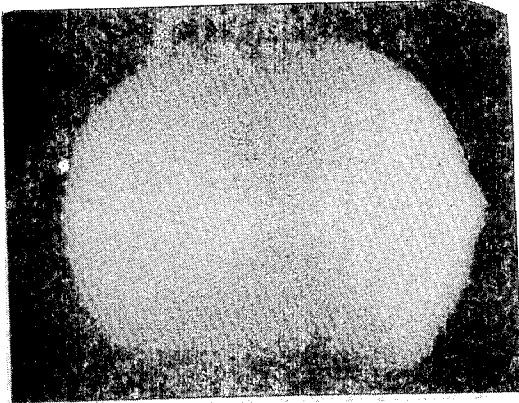


FIG. 7

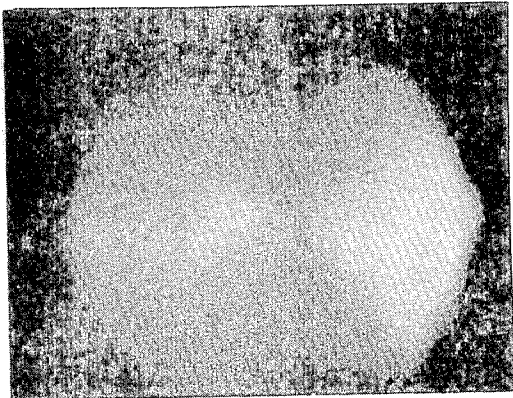


FIG. 8

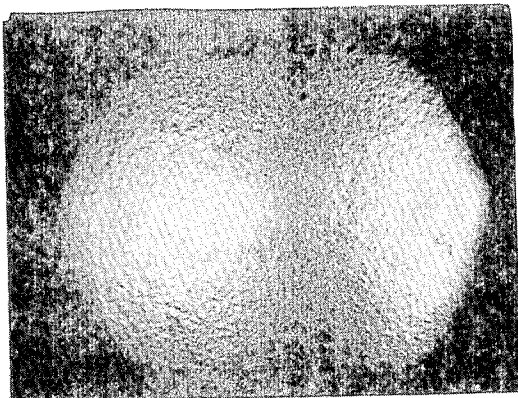


FIG. 9

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Cr-Fe DIFFUSION COATING FERROUS METAL SUBSTRATE

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Filed Sept. 24, 1963, Ser. No. 311,125

1 Claim. (Cl. 29—196.6)

This invention relates to a novel method of forming a diffusion coating of a chromium-iron alloy on a ferrous metal article and to novel articles of manufacture which can be prepared by said process. More particularly, the invention relates to a method of forming a diffusion coating of a chromium-iron alloy on a ferrous metal article by the electrolytic deposition of alternate thin layers of chromium and iron on the base metal followed by a short homogenizing anneal and to novel articles of manufacture prepared in this manner exhibiting a diffusion coating containing grains in a unique network whereby the dimension of each grain in said coating normal to the coating is substantially less than the thickness of said coating and wherein the grains are so disposed as to form a tortuous and indirect grain boundary path from the surface of said coating down to the base metal.

Metal coatings on dissimilar metal substrates are a known means of providing surface protection. It has been proposed in the past to form corrosion resistant coatings on ferrous metal articles by diffusion processes in which the element chromium is deposited on the ferrous metal surface and diffused inward by high temperature treatment of the article causing a diffusion coating of a chromium-iron (Cr-Fe) alloy to form that is highly integral with the base metal through a metallurgical bond. Such diffusion coatings are generally characterized by a concentration gradient of the diffusion element in the coating with the maximum concentration of the diffusing element being found at the outer surface and decreasing concentrations of the diffusing element being present down to the ferrous metal substrate.

A prior art diffusion method to form such a coating on ferrous metal articles involves electroplating a layer of chromium on the base metal and heating at high temperatures to cause a diffusion alloy coating to form. In accordance with such prior art means the presence of iron at the surface of the coating and the thickness of the Cr-Fe coating is dependent on the outward diffusion of iron from the ferrous metal substrate and the inward diffusion of chromium from the initial electroplated chromium layer so that for a given temperature the coating thickness is dependent on the well-known laws of solid-state diffusion for the two elements involved. Moreover, it has been found that the product resulting from such prior art diffusion method exhibits a diffusion coating in which the grains are commonly columnar from coating surface to the substrate metal and invariably contains a number of grains which have a dimension normal to the coating at least equal to the thickness of the coating. For many of these same grains the dimension normal to the coating is actually greater than the thickness of the coating since the grain extends appreciably into the base metal portion of the article. The columnar grains offer an undesirable grain network in the coating since they provide a direct grain boundary path from the surface of the coating to the substrate metal. This is particularly objectionable since corrosive attack most frequently occurs at the grain boundary and, if so, can progress directly to the ferrous metal substrate with the result that rust will soon appear at the surface of the coating. The presence of grains in the coating having a dimension normal to the coating equal to or greater than

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the thickness of the coating results in large grains forming in the coating inasmuch as during grain growth there is a strong tendency for grains to approach an equiaxed form and avoid a huge disparity in dimensions. Such large grains in a coating are highly objectionable because at deformed areas of the final article such grains are a principal factor in causing an undesirable surface texture that is detectable by the naked eye and often referred to in the art as "orange peel." The grain network and grain size described above for Cr-Fe alloy diffusion coatings on ferrous metal articles is not only associated with the prior art diffusion technique of electroplating and then high temperature heating but is also inherent in Cr-Fe alloy diffusion coatings formed on ferrous metal substrates by other diffusion methods known to the prior art such as by subjecting a ferrous metal article to the action of a chromium compound or compounds such as the chloride or fluoride of chromium in the gaseous state or the liquid state or by packing a ferrous metal article in powdered chromium material sometimes containing other constituents and heating. Attempts have been made in the past to refine grain size in the diffusion coating of these prior art products by recrystallizing techniques, such as cold working followed by thermal treatment. Although such attempts may reduce the average grain size in the coating to some slight extent, nevertheless, it is found that columnar grains are invariably present with some number of grains remaining in the coating which have a dimension normal to the coating that is either equal to or greater than the thickness of coating.

It is an object of the present invention to provide a diffusion method which offers a significant improvement in reducing the time for forming a Cr-Fe alloy diffusion coating on a ferrous metal substrate of specified thickness at a given diffusion temperature.

It is a further object of the present invention to form an article of manufacture comprising a ferrous metal substrate having a Cr-Fe alloy diffusion coating wherein said coating contains multiple layers of grains.

It is a further object of the present invention to form an article of manufacture comprising a ferrous metal substrate having a Cr-Fe alloy diffusion coating wherein on deformed areas objectionable "orange peel" is eliminated. It is still a further object to produce a pleasing smooth matte appearance on the surface of the above-described Cr-Fe alloy diffusion coating as formed in the diffusion process.

The above and other objects which will be obvious from the description hereinafter is accomplished in accordance with the present invention by a diffusion method which involves the electrodeposition of thin layers of iron alternately with thin layers of chromium followed by a short high temperature homogenizing anneal of the plated article. The novel products produced by this process comprise ferrous metal substrates having unique multiple layered Cr-Fe diffusion coatings. Each of the layers contains a brick-type network of grains. The dimensions of substantially all of the grains in a layer, measured normal to the coating, do not exceed the thickness of the layer containing the grains. The grain structure of the layers forms a tortuous and indirect grain boundary path from the surface of the coating to the substrate.

Embodiments of my invention and illustrations of certain prior art products are illustrated in the accompanying drawings in which:

FIGURES 1 and 2 are photomicrographs (500X) of etched cross sections of diffusion coated ferrous substrates of this invention,

FIGURE 3 is a photomicrograph (500X) of an etched cross section of a ferrous article coated by a prior art diffusion coating process,

FIGURES 4 and 5 are photomicrographs (750X) of etched cross sections of diffusion coated ferrous articles of this invention,

FIGURE 6 is a photomicrograph (750X) of an etched cross section of a ferrous article coated by a prior art diffusion coating process,

FIGURES 7 and 8 are photographs (7½X) of a deformed surface of the coatings of articles shown in FIGURES 4 and 5, respectively, and

FIGURE 9 is a photograph (7½X) of a prior art article showing a deformed surface of the coating of the article illustrated in FIGURE 6.

The determination of the grain network and grain size of the Cr-Fe alloy diffusion coatings, referred to herein and in the claim, is made from a photomicrograph, at least 500X, of the coating that clearly shows the outlines of the grains in a representative cross section taken generally normal to the surface of the coating. An illustrative technique and the technique employed for preparing the cross sections for the photomicrographs presented in the appended patent drawings involves the step of polishing the cross section and then etching the same with nital and glyceric acid solutions in sequence. The nital solution is composed of 3% concentrated nitric acid and 97% ethanol. The polished cross section is first contacted with this solution for 5-10 seconds. The section is then contacted with the glyceric acid solution composed of 10 parts concentrated nitric acid, 20-30 parts hydrochloric acid, 20-30 parts glycerine, balance water for 10-40 seconds.

The term "ferrous metal article" and "ferrous metal substrate" as used herein means a metallic substance in which the element iron is present in a predominate amount. Preferably, the metallic substance is iron or an alloy which contains at least 50% by weight iron.

Coating thickness as referred to herein and in the claim is determined by microscopic examination of cross sections of the coated article, after etching by 3% concentrated nitric acid, 97% ethanol for 30-60 seconds.

The method of the invention contemplates the use of at least three electroplate layers with the initial layer being of chromium. Any number of chromium and iron plates may be involved above three depending principally on the thickness of diffusion coating desired. The final plate may be of chromium or iron. It is found, however, that a better surface appearance after heat treating is obtained if the final plate is of iron and for this reason it is generally preferred to have a minimum of at least four plates in the coating in the sequence Cr-Fe-Cr-Fe. Usually it is desired to thoroughly clean the surface of the ferrous metal article before treatment by the method of the invention either by anodic cleaning means well known to the art or, alternatively, by degreasing, such as in trichlorethylene, followed by acid cleaning. It is also desirable to thoroughly rinse the treated article after each plate of the coating is applied.

A wide choice of chromium and iron plating baths are contemplated for the electrodeposition of alternate layers of chromium and iron, the plating baths currently employed industrially being fully suitable for the purposes of the invention. Since only the surface of the top layer in the coating is visible and since the subsequent heat treatment affects the appearance of the surface anyway, normally no special care need be exercised to deposit layers that have an attractive surface. For this reason, higher current densities and efficiencies may be obtained by operating the plating baths under conditions not normally used industrially. The operation of the chromium bath separate from the iron bath enables one to choose the most favorable set of conditions for each bath.

It has been found preferred for purposes of the invention to operate the iron plating bath at a pH level below that proposed in the past for such baths, namely, below a pH of 1 in order to avoid the formation of occasional blisters in the coating after heat treatment. The iron bath is preferably stirred vigorously during plating

in order to dislodge any hydrogen bubbles formed on the article treated which is operated as the cathode. This prevents formation of porosity due to lack of iron plating behind bubbles.

In the chromium plating bath, it is desirable that the current be turned off momentarily at the beginning of each cycle. This appears to result in a better chromium plate on the iron surface.

The thicknesses of the various chromium and iron electroplated layers may vary between wide limits depending upon the total number of layers used and the thickness of coating desired. However, it will be appreciated that thick layers, e.g., on the order of 0.5 to 1.0 mil tend to defeat the purpose of the method of the invention which is to obtain homogenization or inter-alloying of the layers in a relatively short time at a particular diffusion temperature. On the other hand, if the individual layers are too thin, e.g., less than 0.05 mil, too many separate plating steps are required to build up a coating of practical thickness for surface protection, e.g., 0.3 mil thickness. In view of these considerations, it is preferred that the individual layer thicknesses be in a range of from about 0.05 to 0.2 mil.

Knowing the current density and plating efficiencies of the plating baths and the size of the ferrous metal article to be treated, one can readily choose the correct plating times for obtaining the desired thicknesses of the chromium and iron layers and the particular laminate plated article to be formed.

If desired, a copper strike may be employed on the ferrous metal article before the laminate plating of chromium and iron to act as a barrier to the diffusion of carbon and nitrogen from the ferrous metal substrate which impurities in the coating in significant amounts can adversely affect the corrosion resistance and formability of the alloy diffusion coating. Usually, a layer of copper of approximately 0.1 mil will be sufficient to accomplish this objective.

It is also possible, if desired, to introduce other alloying elements into the coating such as nickel, cobalt, and others. This may be accomplished by plating alloy layers of Cr and Fe, such as Cr-Ni or Fe-Ni, rather than the pure elements themselves. Alternatively, one can introduce thin layers of a desired additional alloying element such as aluminum between the alternate layers of Cr and Fe.

The laminate plating of chromium and iron on the ferrous metal substrate is converted into a Cr-Fe alloy diffusion coating by a heat treatment step. The heat treatment should employ a combination of temperature and time which will interalloy the various layers with the layer(s) adjacent it and of course cause the initial chromium layer to form a diffusion layer with the ferrous metal substrate so that a continuous metallurgical bond is formed between coating and substrate. Typically, the number of individual layers of grains in the diffusion coating is one-half the number of electroplated layers plus one where a chromium plate is employed as the initial layer on the base metal and iron is the final plate. Also typical of the articles of the invention, the dimension of each grain in the diffusion coating in a direction normal to the coating does not exceed the thickness of the layer of grains which contains it so that this dimension is substantially less than the thickness of the coating. For example, in the case where the diffusion coating is formed from four electroplated layers of approximately equal thickness in the sequence Cr-Fe-Cr-Fe, the grains in the diffusion coating following heat treatment of the plated article will have a dimension normal to the coating of approximately one-third the thickness of the coating. It will be noted from FIGURES 1, 2, 4 and 5 that the grains which are disposed in side-by-side relationship form a mono-grain layer in which the grains have a substantially uniform thickness.

The temperature employed in the heat treatment may range between wide limits. However, in order to obtain the desired diffusion coating in shorter times in accordance with an object of the invention, the practical minimum temperature is approximately 800° C. and preferably the heat treatment will be employed in a temperature range of from 900 to 1100° C. The time of treatment obviously will depend on the temperature employed and the thickness of the individual plated layers. It is, of course, desirable to employ a combination of temperature and time in the heat treatment to achieve the grain network and grain size in the diffusion coating characteristic of the novel articles of manufacture of the invention. Selection of such conditions will be more apparent from working examples set forth hereinafter but as a guide to forming such coatings, heating periods of from 0.5 to 20 minutes should be employed where the thickness of the individual plated layers are in the preferred range of from 0.05 to 0.2 mil and the treating temperature is in the preferred range of from 900 to 1100° C. If the heat treatment significantly exceeds the limits set out above, columnar grains and a number of grains which have a dimension normal to the coating equivalent to or greater than the thickness of the coating are obtained and, hence, the final article is similar to products made by prior art diffusion techniques.

The environment during heat treatment must be selected with the end use of the diffusion coated article in mind. For non-decorative applications of the article where oxidation stains on the surface of the coating, which may be greenish or black in color, are not objectionable, the heat treatment may be conducted in the atmosphere. The article so prepared will exhibit good corrosion resistance per se. However, where oxidation stains resulting from heat treatment are objectionable, a non-oxidizing atmosphere is to be used and preferably an inert atmosphere such as argon, or a reducing atmosphere such as hydrogen. It is also possible to employ as the heating environment a molten metal or salt bath. A molten bath particularly suited for purposes of the invention is one containing calcium and chromium which as disclosed in my copending application S.N. 139,369 is a chromium diffusion medium in itself while at the same time serving as a medium to remove from the diffusion coating impurities such as carbon and nitrogen.

After heat treatment to cause substantially homogenization, the resulting article may be subjected to any of various post treatment steps. It is preferred to quench the article directly from the high temperature treatment. The articles may also be subjected to surface passivation, buffing, and cold working in accordance with techniques well known to the art.

A better understanding of the invention will be gained from the following examples and disclosure set forth below with reference to the patent drawings.

EXAMPLE 1

A 1008 aluminum killed steel strip, 20 mils thick was alternately electroplated on one side with a layer of chromium and a layer of iron until a laminate plate coating containing six layers of chromium, each having a thickness in the range of from 0.05 mil to 0.10 mil and six layers of iron, each about 0.2 mil thick, was formed. The chromium and iron plating baths used had the following compositions and operating conditions:

Cr bath:	Fe bath
250 g./l. of CrO_3 -----	300 g./l. of $\text{FeCl}_2 \cdot \text{H}_2\text{O}$.
2.5 g./l. of H_2SO_4 -----	335 g./l. of CaCl_2 .
30 to 35° C. -----	pH < 1.
500 amps./ft. ² -----	85 to 90° C.
35-40% current efficiency -	120 amps./ft. ² .
	approximately 95% current efficiency.

The plated article was immersed in a molten bath of calcium containing about 10% by weight chromium maintained at a temperature of 1100° C. for 2 minutes. At the end of this period, the article was removed from the Ca-Cr bath and rapidly quenched in an oil bath. The article was removed from the bath and thoroughly cleaned by immersion in a degreasing bath containing trichloroethylene and dried.

FIGURE 1 is a photomicrograph (500X) of a nital and glyceric acid etched cross section through the Cr-Fe alloy diffusion coating (C) and a portion of the ferrous metal substrate (S) of the article prepared above which is representative of the novel article of manufacture of the invention. It will be noted that there are multiple layers of grains with the grains being so disposed in these layers as to form a tortuous and indirect grain boundary path from the surface of the coating to the substrate metal. Furthermore, it is to be noted that the dimension of each grain in the coating normal to the coating is substantially less than the thickness of the coating. Very small discrete particles may be noted at the interface of the chromium layers. It is believed that these particles are chromium oxide which usually form in electroplate chromium layers especially when the plating is carried out at relatively low temperatures. The presence of these chromium oxide particles may assist in impeding the grain growth in the laminate coating thereby maintaining the brick-type network of grains in the coating that is characteristic of the articles of the invention.

The concentration of chromium at the surface of the coating was determined by X-ray fluorescence to be about 39% by weight. The sample exhibited excellent corrosion resistance when subject to the copper acetic acid salt spray (CASS) test 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 strip was also subjected to a 300 mil Olsen cup deformation and no objectionable "orange peel" was noted.

EXAMPLE 2

Using the same plating baths of Example 1, a 1008 aluminum killed steel strip, 20 mils thick, was alternately electroplated on one side with a layer of chromium and a layer of iron until a laminate plate coating containing three layers of chromium ranging from about 0.05 to 0.2 mil thick and three layers of iron, each about 0.2 mil thick, was formed. The plated article was immersed in a molten bath of calcium containing 10% by weight chromium maintained at a temperature of 1100° C. for 1 minute. The article was then removed from the Ca-Cr bath and quenched in an oil bath. The article was then cleaned and dried as explained in Example 1.

FIGURE 2 is a photomicrograph (500X) of a nital and glyceric acid etched cross section through the Cr-Fe alloy diffusion coating (C) and a portion of the ferrous metal substrate (S) of the article. Again it is to be noted that the grains are in multiple layers of a brick-type network whereby the dimension of each grain in said coating is substantially less than the thickness of the coating. The coating thickness was determined to be 1 mil. The concentration of chromium at the surface of the coating was determined by X-ray fluorescence to be about 35% by weight.

In order to offer a comparison of the novel article of manufacture of the invention with products of similar nature obtained by prior art diffusion process, a sample of Bethnamel (approximately 0.002% C) iron, 20 mils thick, was electroplated with a 0.25 mil layer of pure chromium. This plated article was then immersed in a molten bath of calcium containing chromium maintained at a temperature of 1100° C. for 10 minutes in

order to obtain a diffusion coating of comparable thickness of the article of the invention prepared in this example.

FIGURE 3 is a photomicrograph (500X) of a nital and glyceresia etched cross section through the Cr-Fe alloy diffusion coating (C) and a portion of the ferrous metal substrate (S) of this article. It will be noted that the grains are not all in multiple layers, some being columnar from the surface of the coating down to the base metal. Moreover, a number of grains are present which have a dimension normal to the coating which is either nearly equal to or greater than the thickness of the coating. The coating of FIGURE 3 is not only characteristic of the particular prior art diffusion method illustrated in this example but from other investigations conducted is typical of Cr-Fe alloy diffusion article produced by other known prior art diffusion methods.

FIGURES 4-9 illustrate the significance of the grain microstructure of the coating of the novel articles of the invention with respect to surface texture or the phenomenon referred to as "orange peel."

FIGURE 4 is a photomicrograph (750X) of a nital and glyceresia etched cross section through a Cr-Fe alloy diffusion coating (C) and a portion of the ferrous metal substrate (S) of an article of the invention made in accordance with the general procedure of the first run reported hereinabove under Example 2. As typical of these coatings, in the coating there are multiple layers of grains and the dimension of each grain normal to the coating is substantially less than the thickness of the coating. A portion of this article was subjected to a 300 mil Olsen cup deformation. No objectionable "orange peel" was visible to the naked eye at the deformed surface of the coating. FIGURE 7 is a photograph (7½X) of the deformed surface of the coating which shows a smooth surface texture.

FIGURE 5 is a photomicrograph (750X) of a nital and glyceresia etched cross section through a Cr-Fe alloy diffusion coating (C) and a portion of the ferrous metal substrate (S) of an article of the invention made in accordance with the general procedure of the run reported in Example 1 above. In the coating, there are multiple layers of grains and, again, the dimension of each grain normal to the coating is substantially less than the thickness of the coating. A portion of this article was subjected to a 300 mil Olsen cup deformation. No objectionable "orange peel" was visible to the naked eye at the deformed surface of the coating. FIGURE 8 is a photograph (7½X) of the deformed surface of the coating which shows a smooth surface texture.

By contrast, FIGURE 6 is a photomicrograph (750X) of a nital and glyceresia etched cross section through a Cr-Fe alloy diffusion coating (C) and a portion of the ferrous metal substrate (S) of an article formed by a prior art diffusion process employing a base metal comparable to the base metal employed in the preparation of articles of the invention as illustrated in FIGURES 4 and 5. The grain are largely columnar from the surface of the coating down to the base metal providing a direct path for corrosive attack and many grains have a dimension normal to the coating that is either equal to or greater than the thickness of the coating. A sample of this article was given a 300 mil Olsen cup deformation. Objectionable "orange peel" was apparent to the naked eye at the deformed surface of the coating. FIGURE 9 is a photograph (7½X) of the deformed surface of the coating which shows a coarse and rough surface texture.

EXAMPLE 3

As stated hereinabove, various environments are suitable for the heat treatment step of the method of the invention. Actually, it has been found that the use of a hydrogen environment during heat treatment leads to better "orange peel" ratings, all other variables being the same, than a Ca-Cr bath environment. The following run is illustrative of using a hydrogen environment during the

heat treatment in the diffusion method hereof to form articles of the invention.

A 1008 aluminum killed steel strip, 20 mils thick, was alternately plated on one side with a layer of chromium and a layer of iron, using the same plating baths of Example 1, until a laminate plate coating containing 4 layers of chromium ranging from 0.05 to 0.1 mil thick and 4 layers of iron, each about 0.2 mil thick, was formed. The plated article was heated in a hydrogen furnace having a purification train to convert oxygen impurities to water and trap the water so produced in liquid nitrogen. The heating step was carried out at a temperature of 925° C. for 10 minutes. The treated article was then removed from the furnace and rapidly quenched in a blast of cool hydrogen gas.

A nital and glyceresia etched cross section was made of the coating and the grain microstructure was observed to be similar to FIGURE 1 and characteristic of the coatings of novel articles of the invention. A sample of the article was found to exhibit outstanding corrosion resistance on the CASS test. Another sample of the article was subjected to an Olsen cup test (300 mils) with no objectionable "orange peel" being noted.

The procedure described above was repeated for various other ferrous metal substrates with similar results. It was observed in this series of testing that the choice of the ferrous metal has an influence on the surface texture or "orange peel" rating. For example, 1008 aluminum killed steel appeared to offer the best rating. Mild steel as the base metal (e.g., 0.04%-0.06% C.) gives slightly poorer ratings. Stabilized steels such as titanium containing steels are almost equivalent to mild steel while low carbon content irons such as Bethlehem (0.002% C) gave the poorest ratings. Nevertheless, for any given base metal, articles of the invention with coatings having multiple layers of grains whereby the dimension of each grain in said coating normal to coating was substantially less than the thickness of the coating offered better ratings than prior art articles with alloy diffusion coatings containing grains having a dimension normal to the coating equal to or greater than the thickness of the coating.

EXAMPLE 4

The following run illustrates the use of an environment involving an inert atmosphere for the heat treatment of laminate plated articles.

Using the plating baths of Example 1, a 1008 aluminum killed steel strip, 20 mils thick was alternatively electroplated with Cr and Fe layers until four layers of chromium ranging from 0.05 to 0.1 mil thick and four layers of iron, each 0.2 mil thick, were formed on one side of the base metal. The plated article was heated in an argon furnace substantially free of oxygen at a temperature of 1000° C. for 7 minutes. The treated article was removed and quenched in a cool blast of helium.

A nital glyceresia etched cross section was made of the coating and found to be characteristic of grain structure and size of the coating of the articles of the invention. The chromium concentration at the surface of the coating was determined by X-ray fluorescence to be approximately 35% by weight. A sample of the article subjected to a 300 mil Olsen cup exhibited no objectionable "orange peel." The foregoing run was repeated without the quench step and with the quench step carried out in oil or water instead of a helium blast with similar results in "orange peel" rating.

The above runs were repeated for different ferrous metal substrates and varying numbers of alternate chromium and iron layers. All the resulting articles exhibited smooth attractive surfaces as coated which could be readily buffed to a mirror-like finish. The articles in which iron was the final plate exhibited particularly outstanding surface appearance as coated.

As may be noted from the foregoing examples, high chromium concentrations are obtainable at the surface

of the diffusion coating. It is possible due to the flexibility of the diffusion method hereof in which the various individual plated layers may be of varying thicknesses to obtain any chromium concentration desired at the surface of the coating up to about 60% by weight. Since the principal object of such coatings is to provide surface protection against corrosion, it is preferable to have the chromium concentration at the surface at least about 12% by weight to impart a stainless steel-like quality to the coating. However, lower chromium concentrations at the surface are obviously possible, if desired. A distinctly novel feature of the diffusion method hereof permits one to arrive at almost any desired chromium concentration gradient within the coating. It is, therefore, possible to obtain a coating in which the chromium concentration is the highest at the surface in the coating typical of prior art coatings or a coating in which the chromium concentration is nearly the same throughout the coating or a chromium gradient in the coating wherein the highest chromium concentration is in the interior of coating. The latter, for example, would be very desirable if the coated article is to be buffed wherein for a 1 mil coating the top 20 to 30% of the coating may be removed.

A representative article contemplated for the invention would contain an average chromium concentration of about 25% by weight in the coating. For such a concentration, if a coating thickness of 1 mil is desired, the total iron plates would add up to 0.75 mil and the chromium plates would add up to 0.25 mil. The thickness and placement of the layers in forming the laminate plate before heat treatment will determine the chromium concentration gradient in the coating.

While other modifications of this invention which may be employed within the scope of the invention have not been described, the invention is to include all such modifi-

cations which may be comprised within the following claim.

I claim:

An article of manufacture comprising a ferrous metal substrate having a diffusion coating consisting essentially of Cr-Fe thereon, said coating having from about 12 to 60% by weight of chromium and being comprised of at least three layers of diffused alloy, the layers being substantially parallel to the surface of the base metal, each layer having grains the dimension of which measured normally to the coating is no thicker than the thickness of each layer, said grains being disposed in side-by-side relationship in a mono-grain brick-type network in which the grains have a substantially uniform thickness, the grains in the different layers forming a tortuous and indirect grain boundary path from the surface of said coating to said substrate.

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HYLAND BIZOT, *Primary Examiner*.