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DIFFUSION PROCESS

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This application is a continuation-in-part of application Serial No. 139,369, filed September 20, 1961, now abandoned.

The present invention relates to the coating of ferrous metal articles by a novel liquid-to-solid transfer process. More particularly, the invention relates to the diffusion of various elements from a molten bath containing calcium as a transfer agent.

The primary purpose of metal coatings is for surface protection. Clad and coated metals are commonly used materials which have their surfaces protected against corrosion, oxidation, and wear. Most of these metal-to-metal materials commercially available are produced by electroplating, by hot dipping, or by cladding a sheet of one metal to a dissimilar metal. Such techniques provide a practical means for forming coatings of various metals to enrich the surface of a metal with certain elements which provide desirable properties not possessed by the base metal originally but are not operative or are impractical as a means of forming coatings including many other metals which also could be used to enrich or alloy the surface of more available and economical base metals. It is also known that coatings can be applied to ferrous metal surfaces through diffusion processes. Unfortunately, however, diffusion methods in the past have been found to be of limited commercial value due to apparatus limitations, inferiority of the coatings obtained, or economic reasons.

It is an object of the present invention to provide a practical method of diffusion-coating ferrous articles with one or more of the elements selected from the group consisting of molybdenum, zinc, titanium, niobium, vanadium, zirconium, yttrium, cerium, and gallium. The resulting articles have a coating containing one or more of the named diffusing elements alloyed with iron that provides utility in beneficiating the strength characteristics of the surface of the article or in making the surface of the article more resistant to corrosion or oxidation.

The above and other objects are accomplished in accordance with the present invention by immersing a ferrous metal article in a molten bath containing calcium as a transfer agent and having incorporated therein at least one diffusing element selected from the group consisting of molybdenum, zinc, titanium, niobium, vanadium, zirconium, yttrium, cerium, and gallium; wherein said contacting is carried out at a temperature between about 800° C. and the melting point of said article.

The diffusion method of the invention is applicable to any "ferrous metal article" which term as used herein means a metallic substance in which the element iron is present in a predominant amount. Preferably the ferrous metal article will be iron or an alloy which contains at least 50% by weight of iron. In addition to diffusing one or more of the diffusion elements onto a ferrous article, the process, if desired, can also be adapted to remove or decrease the amount of any of the named diffusing elements present in a ferrous article treated in order to alter its surface alloy composition.

Although it is not intended to limit the invention to any particular theory of operation, it is believed that the process of diffusing the named elements is best explained in terms of an isothermal liquid-to-solid transfer in which the molten calcium acts principally as a solvent and transfer medium to bring the diffusing elements in contact with the solid ferrous metal article accompanied by an isothermal, solid state diffusion process of coating growth. It is found that the greatest thermodynamic tendency for liquid-to-solid transfer to occur is when the molten calcium is saturated with the diffusing element and when the diffusing element is not present in the solid article, though capable of complete solution therein. The greatest tendency for liquid-to-solid transfer occurs, therefore, when the diffusion element exhibits a relatively low solubility in calcium and a high solubility in the ferrous metal article. In cases where the diffused element has a relatively high solubility in both calcium and the ferrous metal article, higher concentrations of diffusing element in the molten calcium are required in order to reach the greatest thermodynamic tendency for liquid-to-solid transfer to occur. Nevertheless, it has been observed that in the case of all the named diffusing elements only minor amounts of diffusing element need be present for significant liquid-to-solid transfer to occur even though such amount is less than what would effect the maximum transfer tendency possible.

Liquid-to-solid transfer results in the incorporation of the diffusing element into the substrate surface. At the high temperatures employed further inward diffusion of the element then causes coating growth. The rate of coating growth is dictated by the well-known laws of solid state diffusion and varies for the particular element involved.

It must be appreciated, therefore, that the liquid-to-solid transfer tendency will vary for the various different diffusing elements as will the rate of coating growth for the particular diffusing element involved. As a consequence, the rate of transfer for the elements and the obtainable concentration at the solid surface varies but, nevertheless, it has been observed that alloy coatings of each of the diffusing elements can be formed of appreciable thickness at practical rates containing useful and significant amounts of the diffusing element.

As illustrative of obtainable surface concentrations for alloy coatings of diffusing elements, suitable for the method of the invention, ferrous alloy coating may be prepared on a ferrous metal article containing up to about 10% by weight zinc, about 10% by weight yttrium, about 10% by weight gallium, about 7% by weight molybdenum, about 2% by weight cerium, and about 2% by weight titanium.

The molten metal transfer bath comprises calcium, the diffusing element or elements, and any diluent materials which may be present. Calcium may be replaced in part with various diluent materials so as to reduce the amount of calcium required for the diffusion process and to modify the transfer properties of the diffusing elements. Illustrative examples of such diluents are copper, lead, tin, and calcium nitride. For effective results in the process, calcium must be present in such amounts to constitute at least 10% by weight of the bath and preferably about 40% by weight of the bath. The bath may be completely in the molten state with the diffusing elements in solution in the calcium. However, in cases where the diffusing element has but a limited solubility in calcuim and excess of the solid diffusing element may be present in solid form.

The molten bath for the method of the invention can be prepared in a number of suitable ways. The bath may be formed by heating up a mixture of calcium and one or more of the diffusing elements together with any desired diluents to process temperature. Alternatively, one or more of the diffusing elements in selected concentration can be prepared and added to a molten charge of calcium

maintained at process temperature. The diffusing elements may be added periodically to replenish the bath or added continuously in controlled amounts to facilitate prolonged coating operation. The diffusing elements may be added in almost any particle form. It has been found, however, at least in the instance of those diffusing elements that are only slightly soluble in calcium, such as molybdenum, that improved results are obtained if the diffusing element is added in the form of a finely divided powder. The diffusing elements are generally introduced to the diffusing bath in their elemental form, the metals as commercially available being fully satisfactory in the process. Sources of the diffusing elements other than the elemental form of the metal may also be used, such as, for example, an alloy formed from two of the desired diffusing elements or formed from iron and one or more of the diffusing elements or formed from one or more of the diffusing elements with a metal that acts as a diluent in the molten bath. In addition, compounds which are reducible by calcium to the metallic form of the diffusing element may be employed as a source of the diffusing element.

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 open atmosphere. It is preferred to agitate the bath during operation by mechanical or some other means but this again is not essential.

The operating temperature of the bath for the process is selected to favorably affect the rate of diffusion of the elements and to maintain the calcium present in the bath in the molten state. Generally temperatures less than about 900° C. are not considered practical for metal diffusion because the rate of diffusion is too slow, although in the case of zinc, the minimum practical temperature for diffusion may be considered to be as low as 800° C. A preferred operating temperature for the process is from about 1000–1200° C. for all the diffusing elements with the exception of zinc. If such temperatures are employed in the diffusion of zinc, it is desirable to operate with a closed system in order to prevent zinc from distilling off from the bath. The maximum practical operating temperature may be considered to be the normal boiling point of calcium but in any event the temperature of operation must be maintained below the normal melting point of the solid ferrous metal article treated.

The residence time of the ferrous article in the molten bath for diffusing in any particular diffusing element 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 of a particular diffusing element or combination thereof, 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 batch-wise 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 elements migrate into the solid surface of the ferrous articles and thus alter the characteristics of the articles. For the usual treating times, ranging from approximately 5 minutes to several hours, the coating is characterized by different concentrations of the diffusing elements at its outer surface than are found in the interior.

A better understanding of the invention will be gained from the following illustrative examples of preferred modes of executing the invention. Throughout the examples, the amounts of the various ingredients are given in terms of percent by weight unless otherwise indicated. The concentrations of the diffusing elements reported in the coatings represent a measure of their average concentration in approximately the top 0.3 mil of the coating as determined by X-ray fluorescence. The thicknesses of the coatings reported were determined by microscopic examination of cross sections of the coated articles, after etching by 3% concentrated nitric acid, 97% ethanol in 30–60 seconds. It is to be understood, however, that due to the nature of diffusion coatings, significant concentrations of the diffusing elements can be present in layers of the coated article deeper than the etch test indicates.

Example 1

A molten bath was formed in a carbon steel crucible from 40 g. calcium and 106 g. zinc. The bath was agitated and operated under argon. A mild steel sample was treated in the bath for about 2 hours at 800° C. The article recovered from the bath had a coating one mil thick, having a surface concentration of 6% zinc. The coating was metallurgically bonded to the substrate and the surface of the article exhibited improved corrosion resistance over the unmodified ferrous base metal.

Example 2

In a molybdenum crucible, a molten bath was formed of 6 g. calcium and 10 g. of molybdenum powder. A sample of iron (0.0025% C) was treated in this bath at 1100° C. for 15 minutes. The article recovered from the bath had a coating thickness of approximately 0.4 mil, having a surface concentration of approximately 1% molybdenum. The surface of the article when exposed to an oxidizing atmosphere showed less tendency to develop a tightly adherent scale than the unmodified base metal. This free-scaling characteristic is a recognized advantage in forging operations and in hardening operations. The article formed by this example also exhibits improved resistance to attack by chlorides over the unmodified ferrous base metal.

Example 3

In an iron container, a bath was formed containing 500 g. calcium and 50 g. titanium powder. A sample of iron (0.0025% C) was immersed in this bath for one hour at 1100° C. The article withdrawn from the bath had a coating 0.6 mil thick, having a surface concentration of 0.2% titanium.

Example 4

A molten bath was formed in a steel crucible from 500 g. calcium and 50 g. niobium powder. A sample of iron (0.0025% C) was immersed in this bath for one hour at 1100° C. The article withdrawn from the bath had a coating one mil thick, having a surface concentration of 0.2% niobium.

The above run was repeated separately for vanadium and zirconium wherein vanadium and zirconium powder were substituted for the niobium powder of the run described. It was found that coatings of comparable thicknesses were formed in which similar surface concentrations of vanadium and zirconium, respectively, were obtained.

Although the surface concentration of titanium, niobium, vanadium, and zirconium obtainable by the diffusion method of the invention is usually small, these small amounts are sufficient to beneficially alter the properties of an iron or steel and are actually equal to the small amounts often used in known commercial steels to improve the strength properties of the unmodified steels. Moreover, since these diffusing elements have a strong

tendency to form carbides and nitrides, their presence at the surface in the coating in the amounts obtainable by the method of the invention greatly facilitates the ability to carburize or nitride the surface of the articles in subsequent treating operations to form articles which exhibit highly improved resistance to wear.

Example 5

A molten bath was formed in an iron container from 100 g. calcium and 5 g. cerium oxide (CeO_2). A mild steel sample was treated in this bath for 2 hours at 1100° C. A coating 0.5 mil thick was obtained having a surface concentration of approximately 2% cerium.

Example 6

A molten bath was formed in a carbon steel crucible from 50 g. calcium and 3 g. gallium. The bath was agitated and operated under a blanket of argon gas. A mild steel sample was treated in this bath for 2 hours at 1100° C. A coating 0.5 mil thick was obtained having a surface concentration of approximately 0.3% gallium. The foregoing run was repeated in which yttrium was substituted for gallium. A coating of comparable thickness was obtained having a surface concentration of approximately 0.25% yttrium.

It has been found that the concentration of various of the named diffusing elements, particularly molybdenum, titanium, niobium, vanadium, zirconium, and yttrium, can be increased markedly in the coating over that which is possible when any of said elements is present as the single diffusing element in the bath if another diffusing element such as chromium, nickel, or aluminum is present in the molten bath during formation of the coating. The following example illustrates this result.

Example 8

A bath was formed in a carbon steel container from 51 g. calcium, 17 g. aluminum, and 4 g. yttrium. The bath was agitated and operated under argon. A mild steel sample was treated in this bath for 2 hours at 1100° C. The diffusion article removed from the bath exhibited a coating 0.6 mil thick having a surface concentration of 15% aluminum and 10% yttrium.

It is, of course, to be appreciated that many well-known treatments can be employed to improve the surface appearance of a 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 also may be subjected to subsequent thermal treatments in order to beneficiate the physical properties such as quenching or annealing.

While other modifications of this invention which may be employed within the scope of the invention have not been described, the invention is intended to include all such as may be comprised within the following claims.

I claim:

1. A process for diffusion-coating a ferrous metal article comprising immersing said article in a molten bath containing at least 10% by weight calcium and having incorporated therein at least one diffusing element selected from the group consisting of molybdenum, zinc, titanium, niobium, vanadium, zirconium, yttrium, cerium, and gallium, said bath being maintained at a temperature between 800° C. and the melting point of said article and withdrawing the diffusion coated article from said bath.

2. The process of claim 1 in which the diffusing element is zinc.

3. A process for the diffusion coating of a ferrous metal article comprising immersing said article in a molten bath containing at least 10% by weight calcium and a source of at least one diffusing element selected from the group consisting of molybdenum, zinc, titanium, niobium, vanadium, zirconium, yttrium, cerium, and gallium, said bath being maintained at a temperature between 1000–1200° C. and withdrawing the diffusion coated article from said bath.

4. The process of claim 3 in which the diffusing element is molybdenum.

5. The process of claim 3 in which the diffusing element is zinc.

6. The process of claim 3 in which the diffusing element is titanium.

7. The process of claim 3 in which the diffusing element is niobium.

8. The process of claim 3 in which the diffusing element is zirconium.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,184,330 May 18, 196

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 59, for "about 40%" read -- above 40% --.

Signed and sealed this 5th day of October 1965.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents