

1

2

3,342,628

**ALLOY DIFFUSION PROCESS**

John R. Sinclair, Vienna, W. Va., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware  
 No Drawing. Filed May 14, 1964, Ser. No. 367,577  
 2 Claims. (Cl. 117—114)

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 formation of platinum-iron alloy coatings on a ferrous metal substrate by means of a molten transfer agent.

The primary purpose of metal coatings is for surface protection. Dissimilar metal coatings offer a means by which to enrich the surface of a base metal with various elements which provide desirable properties not possessed by the base metal originally.

The present invention has as its primary object to provide a novel and practical method of diffusion-coating ferrous metal articles with the noble metal platinum. The resulting articles have a coating containing platinum alloyed with iron wherein the obtainable surface concentration of platinum for such alloy coatings may vary over a wide range to enhance the properties of the surface of the article, particularly with respect to improving its oxidation resistance.

The above and other objects are accomplished in accordance with the present invention by contacting a ferrous metal article with a molten bath containing an admixture of calcium and calcium chloride as a transfer medium and having platinum incorporated therein; wherein the amount of calcium is in the range of from about 0.5-50% by weight of said admixture and 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.

Although it is not intended to limit the invention to any particular theory of operation, it is believed that the method of diffusing platinum in accordance with the process of the invention is best explained in terms of an isothermal liquid-to-solid transfer in which the molten calcium-calcium chloride admixture acts principally as a transfer medium to bring platinum in contact with the solid ferrous metal article accompanied by an isothermal, solid state diffusion process of coating growth at a high temperature. A mixture of the IIA metal and the IIA metal salt has been found necessary to serve as the liquid transfer medium for the process of the invention. Platinum is not transferred to the metal substrate in a melt of calcium alone, in which it is completely miscible or in a melt of calcium chloride alone, in which it is insoluble. However, platinum is readily transferred to the ferrous metal substrate in a melt of an admixture of calcium and calcium chloride in which the amount of calcium in said admixture is present in an amount between about 0.5-50% by weight. The calcium in this admixture may be replaced by another IIA metal in which platinum is soluble. The calcium chloride component of the admixture serving as a transfer medium for the process of the invention may be replaced by any IIA metal halide in which platinum is substantially insoluble.

The molten transfer bath comprises calcium, calcium chloride, platinum, and other diffusing elements and diluent materials which may be present. The admixture of calcium and calcium chloride as the transfer medium may be replaced in part with various materials so as to re-

duce the amount of said admixture required for the diffusion process and to modify the melting temperature of the bath. Illustrative examples of such diluents are copper, lead, tin, and calcium nitride. To obtain high surface concentrations of platinum and generally for best results, it is preferred that the transfer bath contain at least 40% by weight of the calcium-calcium chloride mixture. Other diffusing elements such as those elements disclosed in co-pending application S.N. 330,540 which may be diffused onto a ferrous metal base by means of a IIA metal transfer agent may also be present in the bath. The bath may be completely in the molten state with platinum in solution or an excess of platinum may be present in solid form.

The molten bath can be prepared in a number of suitable ways. The bath may be formed by heating up a mixture of calcium, calcium chloride, and platinum together with any other desired constituents to process temperature. Alternatively, the diffusing element in selected concentration can be added to a molten charge of calcium and calcium chloride maintained at the process temperature. The diffusing element may be added periodically to replenish the bath or added continuously in controlled amounts to facilitate prolonged operation. The amount of the diffusing element in the bath does not appear to be critical. As little as a fraction of 1% by weight in the molten bath provides some coating. The optimum amount to be used can be readily determined and will, of course, depend on the concentration desired in the coating. The diffusing element may be added in almost any particle form but it is preferred that the form be as a finely divided powder. It is preferred to add platinum in its elemental form, the metal as commercially available being fully satisfactory. However, it is also possible to employ a platinum compound reducible by calcium to the metallic form of platinum as a source of the diffusing element, for example, the platinum halides, preferably platinum chloride, and platinum oxide. In general, platinum salts which are less stable than calcium chloride may be used.

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 platinum and any other diffusing elements which may be present and to maintain the calcium 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 calcium 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 1000-1200° 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 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 element migrates 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 element at its outer surface than are found in the interior.

A better understanding of the invention will be gained from the following illustrative example of a preferred mode of executing the invention.

#### Example

(a) A molten bath was formed in a carbon steel crucible from 10 grams calcium and 200 grams calcium chloride (5% by weight calcium based on the calcium-calcium chloride admixture) and 3 grams platinum in wire form. The bath was agitated and operated under an atmosphere of argon. A mild steel sample was treated in the bath for about one-half hour while the molten bath was maintained in a temperature range of 1050° C. The article recovered from the bath after this treating period had a Pt-Fe alloy coating having a surface concentration of about 65% Pt as determined by X-ray fluorescence. The coating was metallurgically bonded to the base metal and the surface of the article exhibited significantly improved oxidation resistance over the starting ferrous base metal.

(b) The procedure just described was repeated with the treatment in the bath being extended to 16 hours. The concentration of Pt on the surface was again found to be about 65%.

(c) Under conditions similar to the above run, a run was carried out in which only calcium was present as the transfer medium. In this run, no Pt-Fe alloy coating was formed.

(d) Under conditions similar to the first described run, a run was carried out in which only calcium chloride was present as the transfer medium. In this run, no Pt-Fe alloy coating was formed.

Runs under similar conditions to the first described run can be carried out with the calcium content of the calcium-calcium chloride mixture being in the range of from about 0.5-50% by weight to obtain a Pt-Fe alloy coating on a ferrous metal base wherein the surface of said coating will contain an amount of platinum sufficient to alter the properties of the starting base metal. In a preferred process, the calcium is present in a range from 5-25% by weight of the mixture.

The process of this invention may be used in fabricating articles which must withstand peculiar corrosive

conditions. Laboratory equipment, including spinnerets, as well as electrical contacts may be prepared. By treating thin ferrous metal substrates for an extended period of time, it is possible to obtain a platinum-iron article which has a relatively homogeneous structure. Intricately shaped articles may be prepared by selectively removing the ferrous base metal, leaving behind a thin platinum-iron shell. The desired composition of such articles and coatings on the ferrous substrates may be achieved by varying the concentration of the ingredients in the molten 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 the 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.

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 forming a Pt-Fe alloy diffusion coating on a ferrous metal article comprising contacting said article in a molten bath containing an admixture of calcium and calcium chloride and a source of platinum; wherein the amount of calcium is in the range of from 0.5-50% by weight of said admixture; and wherein said contacting is carried out at a temperature between about 800° C. and the melting point of said article.

2. A process for forming a Pt-Fe alloy diffusion coating on a ferrous metal article comprising immersing said article in a molten bath maintained at a temperature between 1000 and 1200° C. containing at least 40% by weight of an admixture of calcium and calcium chloride in which calcium is present in a range of from 5-25% by weight of said admixture, and platinum, and withdrawing the diffusion coated article from said bath.

#### References Cited

##### UNITED STATES PATENTS

3,184,292	5/1965	Argyriades et al.	-- 117-114	X
3,184,331	5/1965	Carter	----- 117-131	X
3,236,684	2/1966	Carter	----- 117-114	X
3,261,712	7/1966	Carter	----- 117-131	X
3,287,159	11/1966	Bellis et al.	----- 117-131	X

##### FOREIGN PATENTS

1,312,819 11/1962 France.

ALFRED L. LEAVITT, *Primary Examiner.*

R. S. KENDALL, *Examiner.*