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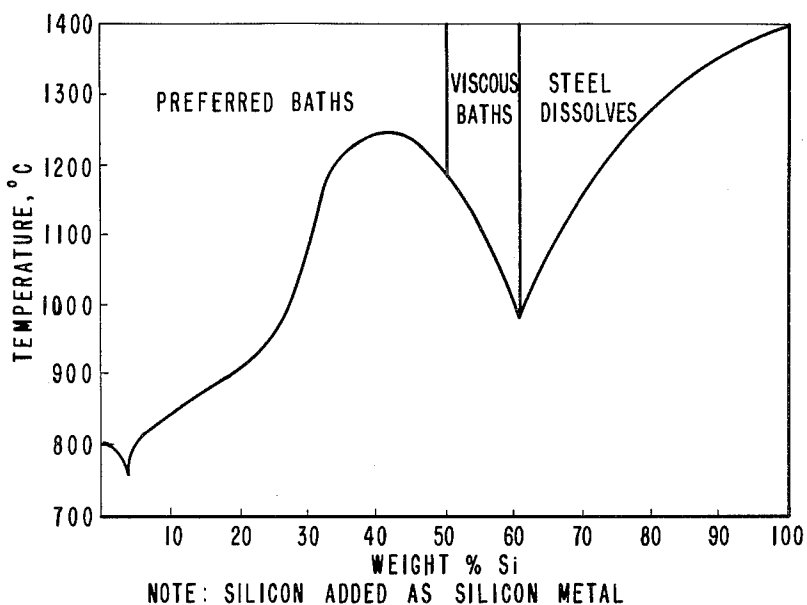
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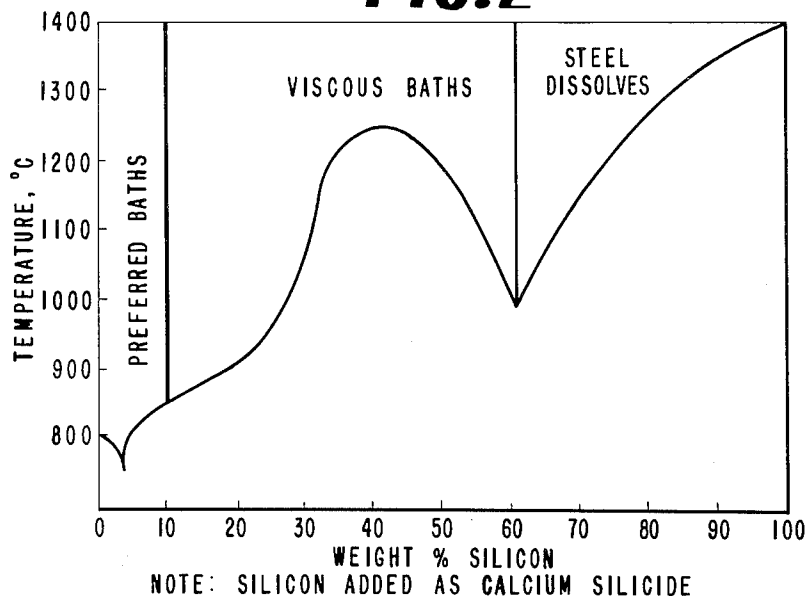
ALLOY DIFFUSION COATING PROCESS

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**FIG. 1**



**FIG. 2**



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## ALLOY DIFFUSION COATING PROCESS

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4 Claims. (Cl. 117—135.1)

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

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 silicon and iron on a ferrous metal substrate by using a molten metal transfer agent.

Preparation of bulk alloys of iron and silicon are well known. However, such alloys have been commonly limited to those containing about 4% silicon due to the increasing brittleness which makes fabrication difficult at higher silicon concentrations. While higher concentrations have been attained, such products have had only limited utility.

It is an object of this invention to provide a process for preparing iron-silicon diffusion coated articles which exhibit improved properties. 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 silicon and a Group IIA metal selected from the class consisting of calcium, barium, and strontium, which are hereinafter referred to as transfer agents.

In practicing this invention, a mixture containing at least about 5% by weight of one or more of the transfer agents and a controlled amount of silicon is heated to a temperature above about 800° C. and the ferrous metal article to be coated is immersed in the resulting molten bath. After a preselected period of time which may extend from a few minutes to an hour or more, depending on the coating characteristics desired, the article is removed from the bath, quenched if desired, and then cleaned to remove the quenching medium and adherent bath. Caution should be exercised in any treatment of calcium-silicon residues where the spontaneously flammable silane gas may form by reaction with acid. In a preferred process, a blanket of inert gas surrounds the molten bath; however, this is not essential since the bath may be operated under carefully controlled conditions in the ambient atmosphere. The bath can be agitated to maintain a uniform composition.

As previously indicated, the amount of silicon in the bath must be controlled. The amount will vary, depending on the silicon source used, but in all cases should be less than 60% by weight. This is best illustrated by reference to the drawings, in which

FIGURE 1 is a diagram which depicts some of the bath characteristics when the source of silicon is silicon metal, and

FIGURE 2 is a diagram which depicts some of the bath characteristics when the source of silicon is calcium silicide.

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In preparing both diagrams, the transfer agent used was calcium; however, one or more of the other transfer agents may be substituted for calcium.

Referring to FIG. 1, the area above the curve depicts bath which are completely liquid. Three zones are illustrated. In the zone labeled "Preferred Baths," ferrous metal articles can be immersed in the liquid without difficulty. As the concentration of silicon in the bath is increased above 50%, the viscosity of the bath increases. This zone is labeled "Viscous Baths" and in the lower concentrations within this zone difficulty is experienced in immersing the ferrous article in the bath. With concentrations approaching 60%, the bath becomes so viscous that it is impossible to immerse the article. At about 60% concentration, the ferrous metal or steel article dissolves. Operable baths do exist in the area below the curve when temperatures above about 800° C. are used. These baths must contain less than 60% silicon. While some solids may exist, the baths may be characterized as being essentially molten.

Similar zones are depicted in FIG. 2. When the silicon source is calcium silicide, the bath becomes viscous at low concentrations. The preferred operable area is therefore restricted to concentrations below about 10%. As in FIG. 1, the area below the curve depicts a zone in which the ingredients do not constitute a completely molten bath at the temperature indicated.

The lower limit for silicon in the bath is not critical. The amount used will depend on the characteristics desired in the coated article as well as the treating time and temperature of the bath. It is generally preferred that an amount between about 1% and 10% be used to provide concentrations of silicon up to about 10% in the coating. The silicon will, of course, be present in the gradient which decreases from the surface toward the interior of the coated article. Coatings having a thickness in the range from a fraction of a mil to 10 mils or more are provided by this process.

As indicated in the foregoing discussion the amount of silicon in the bath is restricted to less than 60% by weight. Accordingly, when using a transfer agent alone, an amount greater than 40% by weight of the transfer agent is used. It is a preferred embodiment, from about 90% to about 99% by weight of the transfer agent is used. This amount 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 any 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, tin, and calcium nitride.

The operating temperature of the bath for the process is selected to favorably affect the rate of diffusion of silicon 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

A bath containing 500 grams of calcium and 87 grams of calcium silicide was heated at 1060° C. in an atmosphere of argon. A mild steel coupon, 3 inches by ½ inch by 0.040 inch, containing 0.06% carbon, gained 17 mg. in thirty minutes of treatment. The surface of the sample contained more than 1% silicon. Higher concentrations of silicon were obtained on mild steel coupons treated for more than thirty minutes.

#### Example II

A bath was prepared by adding 300 grams of silicon to 1200 grams of calcium. The bath was heated to 1100° C. at which time a steel panel, weighing 10.5 grams, was immersed in the molten liquid for a period of thirty minutes. The panel was removed and weighed. It was found to have gained 0.077 grams in weight which indicated that diffusion of silicon into the sample occurred.

A second bath was prepared in which 1200 grams of silicon were added to 1200 grams of calcium. The viscosity of the bath was so high that it was difficult to immerse a steel panel in it.

#### Example III

A bath was prepared containing 1200 grams of calcium to which was added 90 grams of a commercial grade calcium silicide (Analysis: about 63% by weight silicon and 27% by weight calcium.), thereby giving a concentration of about 60 grams or 5% by weight of silicon in the bath.

A steel sample, weighing 10.5 grams, was immersed for fifteen minutes in the molten liquid bath which was heated to 1100° C. Upon removal from the bath, the sample was found to have gained 0.034 gram, indicating silicon diffusion into the steel.

A second bath was prepared into which 180 grams of calcium silicide having the analysis mentioned above was added. This bath which contained about 120 grams (about 10% by weight) of silicon, when heated to 1100° C., was almost solid. It was not possible to immerse a steel sample in it.

#### Example IV

This example illustrates the necessity for maintaining the composition of the bath within limits previously specified.

A bath was prepared containing 2000 grams of calcium silicide (Analysis: 63% by weight silicon and 27% by weight calcium.) in a 110-mil thick, 310 grade stainless steel pot having a 60-mil thick, steel liner. The bath was heated to a temperature between 1000° and 1010° C., at which time the constituents melted, providing a viscous liquid. The temperature was raised to 1150° C. and a mild steel sample was immersed in the bath under a protective argon atmosphere. The steel sample dissolved in the bath as did portions of the steel liner and stainless steel pot. The experiment was repeated using a fresh bath at 1100° C. The same dissolution of the steel occurred.

Minor amounts of various metals in addition to silicon will be present in the coated articles prepared by this process. If desired, the intentional addition of small amounts of such metals as, for example, manganese, nickel, and cobalt may be included 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 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 fabricating electrical apparatus. Surface enrichment of an electrical iron with silicon 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. The products prepared by following the instant process may also be used in applications where corrosion, heat, or wear are problems, e.g., automotive water pump, shafts, cylinder liners, and valve guides, as well as in tubes, nails, screws, and bolts.

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 be limited to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. A process for forming a silicon-iron alloy diffusion coating on a ferrous metal article comprising contacting said article with a molten bath containing an admixture of a Group IIA metal selected from the class consisting of calcium, barium, and strontium and a source of silicon, said bath containing at least about 5% by weight of said Group IIA metal and less than about 60% silicon by weight, the temperature of said bath being maintained between about 800° C. and the melting point of said article, said article being maintained in contact with said bath for a time sufficient to provide a silicon/iron alloy diffusion coating thereon.

2. A process for forming a silicon/iron alloy diffusion coating on a ferrous metal article comprising immersing said article in a molten bath containing an admixture of calcium and a source of silicon wherein calcium is present in said admixture in an amount from at least about 5% to about 99% by weight and said silicon is present in an amount less than 60% by weight of said bath, the temperature of said bath being maintained between about 800° C. and the melting point of said article, said article

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being maintained in said bath for a time sufficient to provide a silicon/iron alloy diffusion coating thereon.

3. The process of claim 2 wherein said source of silicon is silicon metal and the temperature and amount of silicon is maintained within the limits defined by the area above the curve designated "Preferred Baths" in the diagram of FIGURE 1 of the drawing.

4. The process of claim 2 wherein said source of silicon is calcium silicide and the temperature and amount of calcium silicide is maintained within the limits defined by the area above the curve designated "Preferred Baths" in the diagram of FIGURE 2 of the drawing.

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