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FORMATION OF SILICON ALLOY COATINGS

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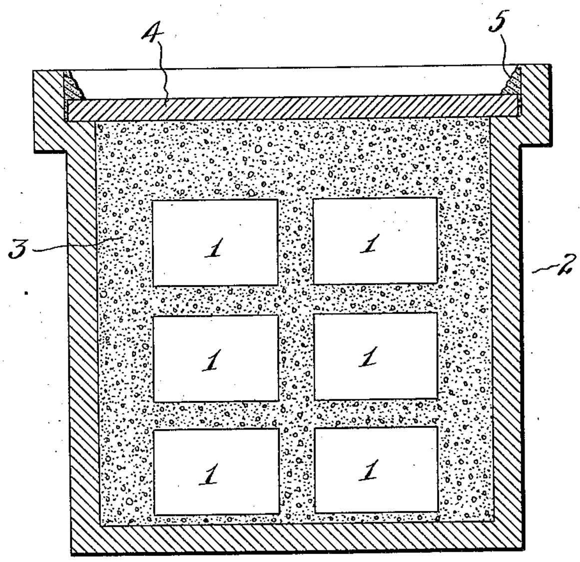

INVENTOR:
Leslie H. Marshall
BY Ray S. Ysler
ATTORNEY

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UNITED STATES PATENT OFFICE

LESLIE H. MARSHALL, OF COLUMBUS, OHIO, ASSIGNOR TO THE TECHNIMET COMPANY, OF COLUMBUS, OHIO, A CORPORATION OF OHIO

FORMATION OF SILICON ALLOY COATINGS

Application filed December 27, 1927. Serial No. 242,838.

The invention relates to the production of a silicon alloy coating or layer on the surface of articles to which it is desired to give superficially the characteristics of silicon or its alloys.

It has been known for some time that silicon alloys are remarkably resistant to many types of corrosion. Alloys containing up to 20% of silicon are marketed for use in the production of corrosion resisting articles, some of these alloys being known under trade names such as Duriron, Tantiron and Ironac. These alloys find wide use particularly in the chemical industry and have demonstrated their remarkable resistance to corrosion, especially sulphuric acid corrosion. These alloys, however, have to be cast to shape and are extremely hard and brittle and not susceptible of being machined. Also, even the heaviest sections are apt to fracture because of their brittleness. Accordingly the field of application of these alloys is limited. In view of these facts it has been proposed to form silicon alloy coatings on articles which it was desired to protect from corrosion; but, as far as I am aware, no successful method of carrying out this proposal has been found prior to my present invention, the coatings previously produced having been characterized by such hardness and brittleness as to render them unduly fragile. Furthermore, the relatively high temperatures involved in the treatments heretofore proposed have rendered it extremely difficult to avoid oxidation both of the silicon and of the surface to be coated or alloyed.

I have discovered that the brittleness and fragile character of the silicon alloy coatings heretofore produced is due to the relatively high temperatures of the treatments which have been employed. Accordingly one of the chief objects of the present invention is the provision of a process of forming silicon alloy coatings which involves the use of very moderate temperatures, with resultant production of relatively strong, tough coatings.

Another object of the invention is the provision of a process of forming silicon alloy coatings that is especially applicable to the coating of malleable iron castings.

A further object of the invention is the provision of a process of forming silicon alloy coatings which affords a non-oxidizing atmosphere under conditions readily maintained in commercial operation.

Another object of the invention is the provision of a process of forming silicon alloy coatings in which the surfaces of the article treated are rendered clean by positive fluxing action, with resultant uniform coating thereof.

Other objects more or less incidental or ancillary to those noted above will appear from the following description.

Speaking generally, my improved process involves enclosing the article to be given the silicon alloy coating with material which will when heated to a relatively moderate temperature provide (*a*) a non-oxidizing atmosphere capable of displacing air from the space surrounding the article before the temperature is high enough to cause substantial oxidation of the article to be coated, and/or (*b*) a fluxing action on the article to be coated insuring clean surfaces thereof, and (*c*) a compound of silicon adapted to vaporize by the time the moderate temperature of the treatment is attained and further adapted, while in the vapor state, to react or dissociate with resultant deposition of silicon on the article treated and the formation of a silicon alloy surface thereon.

More specifically, in my preferred procedure, the material with which the article to be treated is enclosed includes either silicon or an alloy or compound thereof, a substance capable of conversion to a non-oxidizing vapor or of evolving a non-oxidizing and fluxing gas below the temperatures at which silicon and the metal or other article to be treated oxidizes to any substantial extent, and also capable in the vapor or gaseous state of reacting with the silicon or its compound to form a silicon compound which in turn assumes the vapor state at the moderate temperature of the treatment and in that state reacts or dissociates with the resultant deposit of silicon upon the article to form an alloy coating thereon.

In order that my invention and the method of practicing it may be clearly understood, I will now give concrete examples, reference being had to the accompanying drawing which shows more or less diagrammatically a simple form of apparatus suitable for the carrying out of the process. The articles to be coated, for example, may be formed of commercially pure (Armco) iron. These articles, which are designated by the numeral 1 in the drawing, after being thoroughly cleaned by sand blasting or other means, are introduced into a suitable container 2 and imbedded, as shown, in a packing 3 composed of a mixture of crushed silicon (97% silicon) of a size to pass a six mesh screen and including fines, an equal volume of silica sand of about thirty mesh size, (Ottawa silica sand is suitable) and crushed ferric chloride, preferably but not necessarily anhydrous, to the amount of 5% by weight of the entire packing. The container 2 has a tightly closed bottom so that vapors or gases cannot escape. Also, a layer of the packing material of considerable thickness is covered over the topmost articles to be treated to protect them from any gases that might enter through the top of the receptacle. The articles, however, are further protected from gases by the provision of a closely fitting cover 4 which is sealed at the edges of a luting 5 of a refractory material such as powdered flint mixed with water to form a paste. The container 2 may preferably be made of low carbon, high chromium (25% chromium) iron, which is adapted to resist oxidation and deformation under the action of heat. The container and contents are now placed in a furnace and heated to temperatures from 1350° F. to 1400° F. and at such temperatures held for three hours. The container is then removed from the furnace and allowed to cool to room temperature. When the articles being treated have cooled they are removed from the container and packing and immediately washed in hot water and then boiled in a 10% sodium bicarbonate solution for one-half hour to neutralize and remove any salts remaining on their surfaces. Finally the treated articles are washed and dried.

The articles thus treated are found to be uniformly covered with a silicon alloy coating about five one-thousandths of an inch thick, the alloy of the coating being relatively high in silicon at its surface, with the percentage of silicon decreasing toward the interior and the coating being relatively strong and tough.

As further illustrating the application of my invention as well as indicating something of the possible range of variation of the various steps, I give the following additional example involving the coating of malleable iron castings. Following the general procedure described in connection with the first example, the malleable castings, having first been cleaned, as by sand blasting, are introduced into the treating container and imbedded in a packing of the following composition:

50% of 97% silicon, crushed to pass a six mesh screen, including the fines that pass.

45% of gravel, of a size to pass a six mesh screen and including fines that pass.

5% of anhydrous ferric chloride.

The containers thus packed are placed in the furnace and heated to temperatures ranging from 1300° F. to 1350° F. for a period of six hours. Thereafter the containers are removed from the furnace and after they have been allowed to cool the castings are removed from the packing and as in the first example cleansed of any halide salts adhering to their surfaces. The castings are found to have a satisfactory coating of silicon alloy as in the first instance. Special significance and value attaches to this last procedure because of the low temperatures employed. Thoroughly annealed cast iron can be heated as high as its critical temperature, that is around 1350° F., without altering its structure. As soon, however, as the temperature goes much above this point, say to 1400° F., the graphitized carbon begins to be reabsorbed by the iron which loses its softness and ductility. Such castings would have to be reannealed in order to be brought back to their desired condition. Such reannealing is avoided by the procedure last described above because the temperature is kept down to or below 1350° F. In many instances it would be desirable to apply silicon alloy coatings to malleable iron castings after they have been machined. The low temperature which characterizes my improved process makes it possible to do this without the necessity of reannealing the castings after the coating treatment.

Without giving further specific examples in detail, it may be noted that the procedure first described above may, within the scope of the present invention, be varied considerably with respect to materials employed, the time of treatment, temperatures of treatment, and in other respects. Thus various materials may be used to supply the silicon. For example, in the procedure described ferro-silicon containing 50% silicon may be substituted for the 97% silicon specified if the temperature of treatment for three hours is raised to 1500° F. Furthermore, ferro-silicon with still lower percentages of silicon can be employed if still higher temperatures are employed. Coatings may be secured using as high as 99% of the sand or other refractory constituent, though in such cases the coating secured is not quite as thick as that secured with the preferred proportions first described. If the sand or other diluent is omitted the reacting materials, if they contact with the article being coated, tend to sinter on it and render the surface of the coating somewhat porous so that the surface has a tendency to retain moisture and promote corrosion when the coated article is put into use. This difficulty is likely to be serious if there is less than 30% of the diluent in the packing. By the use of a suitable amount of diluent material it is feasible to work up to temperatures of about 1700° F. On the other hand, I have found that thin alloy coatings can be produced at treating temperatures as low as 1000° F. if undiluted 97% silicon crushed to pass a six mesh screen be used as the packing and the heating be continued for thirty hours or more. However, the procedure first described is preferred both because it gives a denser coating more resistant to corrosion than do the treatments at the lowest and highest temperatures mentioned, and because the operations can be carried on with sufficient ease at the intermediate temperatures. Carbon, aluminum or other alloying elements may be present in the silicon or ferro-silicon used, but such diluents may slow up the process of the coating. Diluents other than sand, such as alumina, magnesia or other refractory materials may be used. It is noted further that the particle size of the crushed silicon packing material is a matter of some practical importance. Pulverized material of course presents a larger surface and yields a coating somewhat more quickly than the six mesh material specified, but the sintering of the packing on the article coated is more pronounced when the packing material is powdered. On the other hand larger particle size than the six mesh size can be used, but such material tends to correspondingly slow up the coating action. Generally speaking, the silicon or ferro-silicon crushed to pass a six mesh screen (and including such fine material as passes the screen along with the coarse), gives the best results.

The material used as a flux and silicon carrier should be volatile at the temperature of treatment, and preferably, as has been indicated, it should volatilize below the temperature at which either the packing material or the article to be coated oxidizes materially. I have found halogen compounds that vaporize or at least have an appreciable vapor pressure or evolve halogen gas, below about 700° F. to be satisfactory. Some of such compounds merely vaporize, wholly or in part, at temperature below 700° F. and thus displace any air present in the container with a non-oxidizing atmosphere, the vapors being heavier than the air. Examples of halogen compounds that vaporize below 700° F. are aluminum chloride, antimony chloride, arsenic chloride, mercuric chloride, phosphorous trichloride, carbon tetrachloride, sulphur monochloride and bismuth chloride. Ammonium chloride also vaporizes below 700° F. and within the same temperature range dissociates with formation of ammonia and hydrochloric acid, both of which are gaseous and adapted to displace air from the treating container. Also, the hydrochloric acid has an etching effect on iron and gives a clean surface, and at the higher temperatures of the coating treatment it dissociates to permit some chlorine to react to form silicon chloride. Others of the halogen compounds liberate halogens on heating and they are therefore particularly suitable because the halogen not only displaces the air and is non-oxidizing but also has a fluxing or etching action on the article being treated. Examples of these latter compounds, in addition to ferric chloride are gold (auric) chloride, cupric chloride, sulphur dichloride, sulphur tetrachloride and phosphorous pentachloride. In the foregoing specific examples the ferric chloride can be replaced, for example, by a similar amount of cupric chloride. The ammonium chloride is not so desirable for my purposes because the ammonia evolved tends to react objectionably with iron being coated. Halogen compounds other than chlorides also serve my purpose. Thus 5% of anhydrous ferric bromide can be used in place of the ferric chloride given in the above example though the ferric chloride is preferable because of its lower cost. Furthermore, the ferric chloride need not be introduced into the treating container as such. Thus in the packing material there may be substituted for the 5% of ferric chloride, 10% (by weight) of a mixture of equal amounts by weight of powdered ferrous sulphate (preferably anhydrous) and powdered sodium chloride. On heating the packing, these two compounds react to give ferric chloride and sodium sulphate. Any other known method of forming ferric chloride, by reaction within the packing, might be used. However, this method of introducing the ferric chloride usually contaminates the packing as with the sodium sulphate in the example just given, and this is ordinarily undesirable.

The base metal on which the coating is produced may vary widely. For example, satisfactory coatings can be made on articles of malleable cast iron, gray cast iron, ferrous alloys and steel. The coatings on low carbon steel, that is to say, steel with up to about 0.2% carbon, are somewhat more tenacious than those on high carbon steels. Obviously articles made of higher carbon steel can be coated with perhaps better effect, if the articles are first superficially decarbonized by known methods. Also other metals such as copper, brass, bronze, nickel, molybdenum, chromium and tungsten can be coated. Thus articles of copper can be coated as were the iron articles in the example first given above, using a temperature of 1300° F.

What has been said above sufficiently indicates the considerable range of temperatures which can be employed under the varying conditions stated, the temperature suitable for any given time of treatment being determined largely by the concentration of the silicon, the amount of inert diluent employed and the character of the base material coated. The treatment temperatures which I have found useful range from 1000° F. to 1700° F. In this connection it is to be observed that the packing material itself need not be heated to the full treating temperatures herein specified since the silicon halide (or halides) is formed and volatilized at lower temperatures, in fact well below 700° F. in the case of the chlorides. Thus where the article to be coated can be heated by passing an electric current through it, it will suffice if said article is thus brought to the treating temperature though the packing material surrounding the article does not attain that temperature.

The duration of the treatment is more or less variable, depending upon the temperature and the composition of the packing material. This also is apparent from the foregoing description.

I am not able to say with certainty precisely what goes on in the carrying out of my process, but as at present advised I believe that the following actions occur. In the first stages of the heating, that is while the temperature is rising to say 700° F., the ferric chloride or other halogen compound employed either vaporizes or dissociates with evolution of chlorine (or other halogen). In either case, the vapor or halogen gas formed displaces any air present in the treating container and thus obviates or at least minimizes oxidation both of the article to be coated and of the coating material. In case chlorine or other halogen is evolved, even if some slight oxidation of the article being coated and of the silicon should occur, the fluxing action of the chlorine cleanses the surface of the resulting oxide scale. The halogen compound in the vapor state, or the chlorine or other halogen evolved, reacts with the silicon to form silicon halide which also vaporizes. These latter actions occur at moderate temperatures and, as above noted, at temperatures well below 700° F. in the case of the silicon chlorides. Hence the silicon halide, as well as the original halide, may provide non-oxidizing and fluxing conditions before oxidizing temperatures are reached and maintain said conditions as the temperature rises. Taking a concrete case, ferric chloride when heated evolves chlorine by dissociation as follows:

$$2FeCl_3 = 2FeCl_2 + Cl_2$$

The chlorine thus liberated may react with the silicon thus:

$$Si + 2Cl_2 = SiCl_4$$

This reaction is reversible and in the presence of the article to be coated, the silicon chloride would dissociate to form silicon and chlorine. The silicon would immediately alloy with the metal (iron for example) of the article being treated at the temperature of the treatment and the halogen compound would continue to dissociate. The chlorine freed by the dissociation of the silicon chloride would then react with more silicon at points more remote from the iron article and the deposition of silicon would thus continue.

Possibly some of the chlorine evolved may react with the iron of the article being coated thus:

$$Cl_2 + Fe = FeCl_2$$

This ferrous chloride would have an appreciable vapor pressure at the temperature of the treatment. The dissociation of this vapor in the neighborhood of the packing material would permit the latter to alloy with the iron of the vapor and the chlorine thus liberated would react to form silicon chloride. Thus, in any case, the chlorine acts as a carrier of silicon, permitting this element to pass through the vapor stage at a lower temperature than would otherwise be possible.

Whatever the precise actions may be that go on during the process, the result is the formation of a complete and highly uniform coating of silicon or silicon alloy on the article treated, so that the surface of the coated article takes on the characteristics of the silicon alloys, especially a bright appearance, great resistance to weathering, acid corrosion (particularly that of sulphuric acid solution), soil corrosion and high temperature oxidation up to 2000° F. Furthermore, the coating secured is relatively tough and durable. Thus by my improved process an article is produced adapted to many commercial uses. This result, furthermore, is secured with a process which lends itself readily to production under commercial conditions. In particular, the prevention of oxidation by the simple expedient of introducing into the packing material a substance adapted to form a vapor or gas capable of displacing air from the treating space is easily accomplished under working conditions readily attainable. The articles to be coated are packed in the treating container under ordinary conditions without exclusion of air, difficulties that would be incident to the introduction into the treating container of a non-oxidizing gas as such are avoided, approximately atmospheric pressure is used throughout the process, and where the halide of the metal to be coated is used as the flux or carrier further advantage is attained. Again, the conversion of the silicon into a compound vaporizable at moderate temperatures and capable of reacting or dissociating in the presence of the article to be coated with resultant deposition of silicon both makes the process susceptible of operation under working conditions that can easily be maintained in commercial operation and also renders the process available for work that could not be accomplished at higher temperatures, such for example as the silicon coating of malleable iron castings without the necessity of subsequent malleabilizing treatments.

The advantages attaching to the use of a packing or treating material that evolves a non-oxidizing gas or vapor, and particularly a halogen gas, are not limited to the forming of silicon or silicon alloy coatings but can be realized in forming alloy coatings of other substances. Thus, for example, I am able to employ this same feature in forming chromium alloy coatings, as set forth in my copending application Serial No. 242,837, filed December 27, 1927. In the said chromium coating process, as preferably practiced, the article to be coated, which may for example be formed of low carbon steel, is enclosed with a packing including metallic chromium, or an alloy or compound thereof, and a substance, such for example as ferric chloride, capable of conversion to a non-oxidizing vapor or of evolving a non-oxidizing and fluxing gas at temperatures below 700° F. Heat is then applied to cause such vaporization or evolution of gas; and the packing and article are then further heated to temperatures between 1500° F. and 2000° F., until a coating of chromium alloy is formed on the article. At the latter temperatures the halogen gas or vapor reacts with the chromium to form chromium chloride which in turn reacts or dissociates with the resultant deposit of chromium on the article to be coated.

In characterizing herein the gas or vapor in the treating container as "non-oxidizing", that term is, of course, used in its strict or limited sense indicating that the gas or vapor is of such a nature that it will not form a film of metallic oxides on the article to be coated.

While I have set forth some of the variations of materials, temperatures and times of treatment which may be used in the carrying out of my invention, it should be understood that I have not attempted to point out all variations of this character but that the invention comprehends all modifications within the scope of the appended claims.

What I claim is:

1. The process of forming alloy coatings of silicon which includes the steps of enclosings the article to be coated with a packing containing silicon or an alloy of silicon and the metal of which the said article is constituted; applying heat to the said article and packing; permeating the space around the article with sufficient halogen or halogen compound gas or vapor before the temperature of the article has been raised above 700° F. to displace the air from said space and thereby prevent oxidation of the reacting metals present; and thereafter continuing the heating of the packing and article to hold said article at temperatures between 1000° F. and 1700° F. in the presence of halogen or halogen compound gas or vapor until a coating of silicon alloy is formed on the article.

2. The process of forming alloy coatings of silicon which includes the steps of enclosing the article to be coated with a packing containing silicon or an alloy of silicon and the metal of which the said article is constituted; applying heat to the said article and packing; permeating the space around the article with sufficient halogen or halogen compound gas or vapor before the temperature of the article has been raised above 700° F. to displace the air from said space and thereby prevent oxidation of the reacting metals present; and thereafter continuing the heating of the packing and article to hold said article at temperatures between 1000° F. and 1700° F. in the presence of halogen or halogen compound gas or vapor until the latter reacts with the silicon to form a silicon halide and the latter reacts or dissociates in the presence of the article to form a coating of silicon alloy on the article.

3. The process of forming alloy coatings of silicon which includes the steps of enclosing the article to be coated with a packing containing sicilon or an alloy of silicon and the metal of which the said article is constituted and a halogen or halogen compound adapted to evolve a non-oxidizing gas or vapor at temperatures below 700° F.; heating the packing and contained article to cause such evolution of gas or vapor in sufficient amount to permeate the space surrounding the article, substantially displace the air from said space and thereby prevent oxidation of the reacting metals present; and further heating the packing and article to hold said article at temperatures between 1000° F. and 1700° F. in the presence of halogen or halogen compound gas or vapor until a coating of silicon alloy is formed on the article.

4. The process of forming alloy coatings of silicon which includes the steps of enclosing the article to be coated with a packing containing silicon or an alloy of silicon and the metal of which the said article is constituted and a material adapted to evolve a halogen gas at temperatures below 700° F.; heating the packing and contained article to cause such evolution of gas in sufficient amount to permeate the space surrounding the article, substantially displace the air from said space and thereby prevent oxidation of the reacting metals present; and further heating the packing and article to hold said article at temperatures between 1000° F. and 1700° F. in the presence of halogen or halogen compound gas or vapor until a coating of silicon alloy is formed on the article.

5. The process of forming alloy coatings of silicon which includes the steps of enclos-

ing the article to be coated with a packing containing silicon or an alloy of silicon and the metal of which the said article is constituted, an inert diluent and a halogen or halogen compound adapted to evolve a non-oxidizing gas or vapor at temperatures below 700° F.; heating the packing and contained article to cause such evolution of gas or vapor in sufficient amount to permeate the space around the article, substantially displace the air from said space and thereby prevent oxidation of the reacting metals present; and further heating the packing and article to hold said article at temperatures between 1000° F. and 1700° F. in the presence of halogen or halogen compound gas or vapor until a coating of silicon alloy is formed on the article.

6. The process of forming alloy coatings of silicon which includes the steps of enclosing the article to be coated with a packing containing silicon or an alloy of silicon and the metal of which the said article is constituted; applying heat to the said article and packing; permeating the space around the article with sufficient halogen or halogen compound gas or vapor before the temperature of the article has been raised above 700° F. to displace the air from said space and thereby prevent oxidation of the reacting metals present; and thereafter continuing the heating of the packing and article to hold said article at temperatures between 1000° F. and 1700° F. in the presence of halogen or halogen compound gas or vapor until a coating of silicon alloy is formed on the article; removing the article from the packing; and removing from the surface of the article adherent halide salts.

7. The process of forming alloy coatings of silicon which includes the steps of enclosing the article to be coated with a packing containing material consisting of upwards of 90% silicon, an inert diluent and a halogen or halogen compound adapted to evolve a non-oxidizing gas or vapor at temperatures below 700° F.; heating the packing and contained article to cause such evolution of gas or vapor in an amount sufficient to permeate the space surrounding the article, substantially displace the air from said space and thereby prevent oxidation of the reacting metals present; and further heating the packing and article to hold said article at temperatures between 1350° F. and 1500° F. in the presence of halogen or halogen compound gas or vapor until a coating of silicon alloy is formed on the article.

8. The process of forming alloy coatings of silicon which includes the steps of enclosing the article to be coated with a packing containing silicon or an alloy of silicon and the metal of which the said article is constituted and a halide adapted to evolve a halogen gas at temperatures below 700° F.; heating the packing and contained article to cause such evolution of halogen gas in sufficient amount to permeate the space surrounding the article, substantially displace the air from said space and thereby prevent oxidation of the reacting metals present; and further heating the packing and article to hold said article at temperatures between 1000° F. and 1700° F. in the presence of halogen or halogen compound gas or vapor until a coating of silicon alloy is formed on the article.

9. The process of forming alloy coatings of silicon on oxidizable or corrodible metallic articles which includes the steps of enclosing the article to be coated with a packing containing silicon or an alloy of silicon and the metal of which the article is constituted and a halide of the metal to be coated which is adapted to evolve a halogen gas at temperatures below 700° F.; heating the packing and contained article to cause such evolution of halogen gas in sufficient amount to permeate the space surrounding the article, substantially displace the air from said space and thereby prevent oxidation of the reacting metals present; and further heating the packing and article to hold said article at temperatures between 1000° F. and 1700° F. in the presence of halogen or halogen compound gas or vapor until a coating of silicon alloy is formed on the article.

10. The process of forming alloy coatings of silicon which includes the steps of enclosing the article to be coated with a packing containing ferro-silicon and a halogen or halogen compound adapted to evolve a non-oxidizing gas or vapor at temperatures below 700° F.; heating the packing and contained article to cause such evolution of gas or vapor in sufficient amount to permeate the space surrounding the article, substantially displace the air from said space and thereby prevent oxidation of the reacting metals present; and further heating the packing and article to hold said article at temperatures between 1000° F. and 1700° F. in the presence of halogen or halogen compound gas or vapor until a coating of silicon alloy is formed on the article.

11. The process of forming alloy coatings of silicon which includes the steps of enclosing the article to be coated with a packing containing the silicon or an alloy of silicon and the metal of which the said article is constituted and ferric chloride; heating the packing and contained article to evolve chlorine from the ferric chloride in sufficient amount to permeate the space surrounding the article, substantially displace the air from said space and thereby prevent oxidation of the reacting metals present; and further heating the packing and article to hold said article at temperatures between 1000° F. and 1700° F. in the presence of halogen or halogen com-

pound gas or vapor until a coating of silicon alloy is formed on the article.

12. The process of forming alloy coatings of silicon which includes the steps of enclosing the article to be coated in a packing containing silicon or an alloy of silicon and the metal of which the said article is constituted and a halogen or halogen compound adapted to evolve a non-oxidizing gas or vapor at temperatures below 700° F., said packing being held in a container with tight side and bottom walls; heating the packing and contained article to cause such evolution of gas or vapor in sufficient amount to permeate the space around the article, substantially displace the air from said space and thereby prevent oxidation of the reacting metals present; and further heating the packing and article to hold said article at temperatures between 1000° F. and 1700° F. in the presence of halogen or halogen compound gas or vapor until a coating of silicon alloy is formed on the article.

13. The process of forming on oxidizable or corrodible metallic articles coatings of material adapted to alloy with the base material of the article, which process includes the steps of enclosing the article to be coated with a packing containing a coating material; applying heat to the said article and packing; permeating the space surrounding the article with a halogen or halogen compound gas or vapor before the temperature of the article has been raised above its oxidation point to displace the air from said space and thereby prevent oxidation of the reacting metals present; and thereafter continuing the heating of the packing and article to temperatures above said oxidation point in the presence of halogen or halogen compound gas or vapor until the desired coating is formed on the article.

14. The process of forming on oxidizable or corrodible metallic articles coatings of material adapted to alloy with the base material of the article, which process includes the steps of enclosing the article to be coated with a packing containing the coating material and a halogen or halogen compound adapted to evolve a non-oxidizing gas or vapor at temperatures below 700° F.; heating the packing and contained article to cause such evolution of gas or vapor in sufficient amount to permeate the space around the article, substantially displace the air from said space and thereby prevent oxidation of the reacting metals present; and thereafter continuing the heating of the packing and article to hold said article at temperatures above 700° F. in the presence of halogen or halogen compound gas or vapor until the desired coating is formed on the article.

15. The process of forming on oxidizable or corrodible metallic articles coatings of material adapted to alloy with the base material of the article, which process includes the steps of enclosing the article to be coated with a packing containing the coating material and a material adapted to evolve a halogen gas or vapor at temperatures below 700° F.; heating the packing and contained article to cause such evolution of gas or vapor in sufficient amount to permeate the space around the article, substantially displace air from the said space and thereby prevent oxidation of the reacting metals present; and thereafter continuing the heating of the packing and article to hold said article at temperatures above 700° F. in the presence of halogen or halogen compound gas or vapor until the desired coating is formed on the article.

16. The process of forming alloy coatings of silicon which includes the steps of enclosing in a treating chamber the article to be coated together with material including silicon or an alloy of silicon and the metal of which the said article is constituted; applying heat to the said article and material; permeating the space around the article with sufficient halogen or halogen compound gas or vapor before the temperature of the article has been raised above 700° F. to displace the air from said space and thereby prevent oxidation of the reacting metals present; and thereafter continuing the heating of the said material and article to hold said article at temperatures between 1000° F. and 1700° F. in the presence of halogen or halogen compound gas or vapor until a coating of silicon alloy is formed on the article.

17. The process of forming alloy coatings of silicon which includes the steps of enclosing in a treating chamber the article to be coated together with material including silicon or an alloy of silicon and the metal of which the said article is constituted; applying heat to the said article and material; permeating the space around the article with sufficient halogen or halogen compound gas or vapor before the temperature of the article has been raised above 700° F. to displace the air from said space and thereby prevent oxidation of the reacting metals present; and thereafter continuing the heating of the said material and article to hold said article at temperatures between 1000° F. and 1700° F. in the presence of halogen or halogen compound gas or vapor until a coating of silicon alloy is formed on the article; and removing from the surface of the article adherent halide salts.

18. The process of forming an oxidizable or corrodible metallic articles coatings of material adapted to alloy with the base material of the article, which process includes the steps of enclosing in a treating chamber the article to be coated together with material including a coating substance; applying heat to the said article and material; permeating the space surrounding the article with a halogen or halogen compound gas or vapor before the

temperature of the article has been raised above its oxidation temperature to displace the air from said space and thereby prevent oxidation of the reacting metals present; and thereafter continuing the heating of the said material and article to temperatures above said oxidation point in the presence of halogen or halogen compound gas or vapor until the desired coating is formed on the article.

In testimony whereof, I hereunto affix my signature.

LESLIE H. MARSHALL.