Jan. 10, 1933. L. H. MARSHALL 1,893,782

PRODUCTION OF COATED MALLEABLE IRON CASTINGS

Filed Jan. 2, 1930

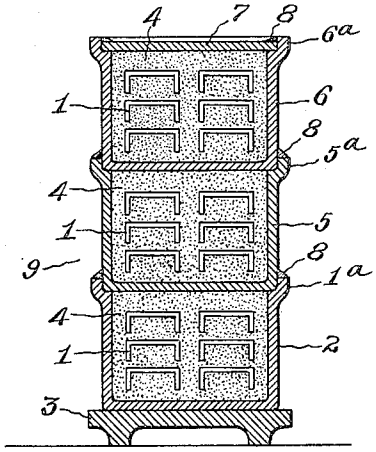


FIG. 1

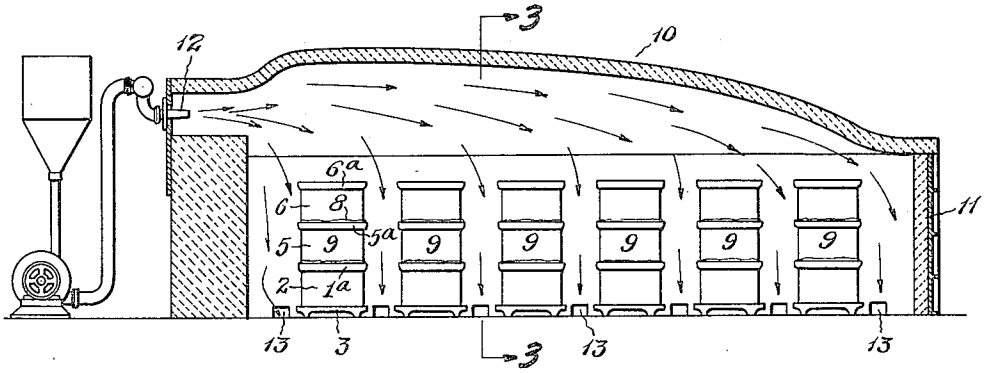


FIG. 2

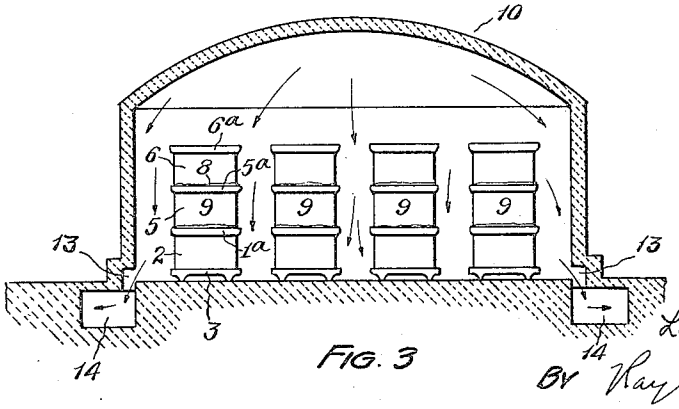


FIG. 3

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UNITED STATES PATENT OFFICE

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PRODUCTION OF COATED MALLEABLE IRON CASTINGS

Application filed January 2, 1930. Serial No. 417,978.

The invention relates to the production of alloy coatings on malleable cast iron.

A large proportion of the malleable cast iron produced at the present time is rust-proofed before going into service. This is usually accomplished by coating the castings with zinc by some one of the known methods, such as hot dip galvanizing and sherardizing. The production of the zinc coating has necessitated a separate process of manufacture and this, of course, makes the castings produced more expensive. Furthermore, under some conditions of service a harder or even more corrosion resistant surface than that afforded by zinc is desirable.

The present invention has for one of its chief objects the production of malleable cast iron having surfaces more highly resistant to corrosion than are produced by coating with zinc.

A further object of the invention is the production of malleable cast iron with surfaces that are hard and wear resistant as well as being highly resistant to corrosion.

Another object of the invention is the provision of an inexpensive method of producing malleable cast iron with surfaces of the character above referred to.

Other objects of the invention more or less incidental or ancillary to the foregoing will be apparent from the following description.

In the production of malleable cast iron by the well known and established methods, the metal is first cast as white iron. In this condition the iron is hard and brittle and can be machined only by grinding. Such castings, with or without sand blasting or other definite cleaning operations, are then packed in the annealing pots in which they are usually surrounded by gravel or other packing. The gravel tends to reduce oxidation of the castings during annealing and also serves to support them and prevent distortion at the elevated temperatures. The annealing pots packed with the castings as described are charged into the annealing furnace and the latter is then closed and firing started. To properly anneal the castings a fairly definite heat treatment is required. That is they must be raised to and held at an elevated temperature, say 1400° F. to 1750° F., for a period of from two to five days. The higher the temperature the shorter the holding period. Then the temperature is allowed to fall, not faster than 10° F. per hour, until it has reached about 1000° F. The doors of the furnace can then be opened and the pots and their contents allowed to cool to room temperature. The total time of the commercial annealing cycle may vary, in different plants, from five to fourteen days. As is well known, the resulting castings are strong, ductile and easily machined as a result of the heat treatment.

My present invention is essentially characterized by the fact that the coating of the castings is carried out in such a manner that it can be effected during the annealing of the white iron castings, with a very great resultant saving of time and expense. This result has been made possible by my discovery of methods of forming alloy coatings with substances such as chromium and silicon which involve heat treatments within the temperature range permissible in the annealing of white iron castings and by procedures which lend themselves readily in other respects to malleableizing treatments under commercial conditions. My improved methods of forming alloy coatings are not limited to the coating of malleable iron. In fact my copending applications, Serial Nos. 242,837 and 242,838, both filed December 27, 1927, have as their subjects, respectively, the formation of chromium alloy coatings and the formation of silicon alloy coatings, of general application. Reference may be had to these latter applications for full detailed disclosures of the methods of chromium and silicon coating, and the description in the present application will be limited, so fas as the formation of the coatings is concerned, to such disclosure as is essential to the clear explanation and illustration of the present invention.

In carrying out my annealing and coating process, white iron castings, preferably after having been thoroughly cleaned, as by sand blasting, are introduced into a suitable chamber (such as an annealing pot) together with

material containing a substance (such as chromium or silicon) adapted to alloy with the iron of the castings and also containing a halogen compound adapted to evolve a non-oxidizing gas or vapor at temperatures below that at which the cast iron oxidizes materially say 700° F., and also adapted to react with the said substance to form a halide thereof which is vaporizable, at least in part, at temperatures below the maximum temperature employed for the annealing treatment of the castings. The castings and the material contained in the chamber therewith are then subjected to a heat treatment suitable to effect malleableizing of the castings. That is to say, the container and its contents are placed in a furnace and the temperature is gradually raised to some suitable temperature ranging from, say, 1400° F. to 1750° F. and there held for a period sufficient to effect the malleableizing of the castings, then slowly cooled to 1000° F., whereupon the furnace is opened and the treating container and its contents allowed to cool to room temperature.

Upon removing the cooled castings from the annealing pot they are found to have an alloy coating of the substance, (chromium or silicon, for example) introduced into the pot. During the annealing heat treatment as the temperature rises and while still below 700° F., or in other words the approximate minimum oxidizing temperature of iron, the halogen compound present in the annealing pot evolves a halogen or halide gas or vapor which is non-oxidizing and heavier than air, and it displaces any air present in the pot and prevents oxidation of the castings. Then, as the heating continues, a temperature is reached, at a point below or in the annealing range, at which the halogen or halide gas or vapor reacts with the coating substance (chromium, silicon or the like) to form a halide compound of that substance, which also, at some temperature in the annealing range, vaporizes to some extent and diffuses through the annealing pot and contacts with the iron of the castings. In contact with the iron the last mentioned vaporized compound reacts or dissociates with resulting deposition of the coating substance on the surface of the casting with the metal of which it alloys to form a coating.

The temperature range of 1400° F. to 1750° F. above mentioned includes the temperatures more commonly employed in malleableizing, but there are special malleableizing processes that are carried out at other temperatures, in some cases below and in some cases above the said range, and these other temperatures are applicable for coating by my process to some, at least, of the coating metals referred to herein. Theoretically there is no definitely fixed lower limit of the range of malleableizing temperatures but, practically speaking, about 1200° F. may be considered the lower limit because at temperatures lower than that the increase in the necessary time of treatment with decrease in temperature is so great as to make such lower temperatures impractical. On the other hand, one or more special malleableizing processes have been proposed in which the treatment is carried out at temperatures ranging upward to the point of incipient fusion of the iron and with a temperature of 1000° C. recommended. However, I believe that approximately 1800° F. marks the upper limit of the range of practically useful malleableizing temperatures.

As is disclosed in my above mentioned copending applications Serial Nos. 242,837 and 242,838, my process of coating with chromium or chromium alloy can be carried out at temperatures ranging from 1500° F. to 2000° F. and my process of coating with silicon or silicon alloy can be carried out at temperatures ranging from 1000° F. to 1700° F.

Consequently, considering both the malleableizing and the coating aspects of my present combined process and the various coating metals to which it is applicable, it will be seen that the usefully operative temperatures of said process cover the entire malleableizing range of 1200° F. to 1800° F.

In order that my invention and the method of practicing it may be clearly understood I will now give specific examples pointing out the procedure in further detail. As has been noted, the methods employed to form the alloy coatings can be carried out under commercial conditions suitable for annealing of white iron castings and various known forms of apparatus suitable for such annealing can be employed in carrying out the present invention. In the interest of clearness I have shown in the accompanying drawing one or more forms of apparatus that is suitable.

In the drawing, Fig. 1 is a vertical section through a stack of annealing pots or boxes packed with castings to be annealed and coated.

Fig. 2 is a longitudinal vertical section through an annealing furnace with annealing pots therein.

Fig. 3 is a transverse section through the same furnace.

Chromium alloy coating.—White iron castings, designated by the numeral 1 in Fig. 1 of the drawing, preferably having first been thoroughly cleaned by sand blasting, are placed in a closed bottom annealing pot 2 resting on a suitable base 3, together with a packing 4 consisting of 97% by weight of ferro-chromium (70% chromium, 0.1% carbon) and 3% bleaching power (CaOCl), the packing material being crushed to pass a six mesh screen. Additional annealing

pots 5 and 6, similar to pot 2, are successively stacked upon the latter and filled with additional castings 1 and packing 4 as indicated. Thus arranged the pot 5 closes the upper end of pot 1 and pot 6 similarly closes the upper end of pot 5, each of the pots being preferably provided at its upper edge with an upwardly extending flange 1^a (or 5^a or 6^a, as the case may be). The upper pot 6 is then closed with a suitable cover plate 7 and the joints between the pots and the joint between the cover 7 and the pot 6 are further sealed by lutings 8 of moist clay or the like which serve to largely restrict the escape of gases from the tops of the annealing chambers.

In this manner a suitable number of annealing pots are packed with castings and these pots or stacks designated as entireties by 9 are then placed in a suitable annealing furnace which in the drawing is designated as an entirety by the numeral 10, the bases 3 serving to facilitate handling of the stacks of pots. The furnace at its front end has the usual charging door 11 and at its rear end is fitted with a powdered coal burner 12 which is arranged to deliver the hot products of combustion directly into the furnace chamber as indicated in Fig. 2. The side walls of the furnace are formed at points near the furnace floor with the side ducts 13, 13 which lead to flues 14 which in turn communicate with a stack or other suitable draft means. The filled annealing pots having been placed in the furnace as stated and the charging door 11 closed, the firing is started. The entering combustion gases sweep over and around the annealing pots and find exit through the ducts 13 and flues 14, as indicated in Figs. 2 and 3 of the drawing. With packing material of the character specified the furnace fire is regulated so that twenty-five hours time is consumed to bring the furnace chamber gradually to a temperature of 1650° F., after which the said temperature is held at temperatures ranging from 1600° F. to 1650° F, for a period of sixty hours, whereupon the furnace is allowed gradually to cool to a temperature of approximately 1000° F. over a period of eighty hours. The doors of the furnace are then thrown open and the pots allowed to cool to room temperature.

After removing the treated castings from the container and packing, they are immediately washed in hot water and then boiled in a saturated solution of sodium bicarbonate for one-half hour to remove or neutralize any salts that may remain on the surface of the castings. The castings are then washed in water and dried. The castings are thus cleansed to remove any halide salts that might adhere to them.

The castings thus treated are found to have, in addition to the usual qualities of high grade malleable castings, a coating of chromium or chromium alloy bright in color and of substantial thickness. The coating has an extreme outer layer fairly high in chromium and below this an alloy zone higher in iron. In a specific case of castings subjected to the last described treatment the compositon of the castings was approximately: carbon 2.70%, silicon 0.80%, manganese 0.32%, sulphur 0.06%, phosphorus 0.15%, and the coating formed on the castings was about 0.001″ thick, and the inner alloy layer of the coating contained a little combined carbon. In this connection, it will be understood that my invention is not limited to alloy coatings of any particular composition.

Castings with such chromium alloy coatings, in addition to the strength, durability and toughness of ordinary malleable castings have a bright or lustrous appearance that is very pleasing and have the marked advantage of great resistance to oxidation and dilute acid corrosion. Thus such castings withstand exposure to the weather and to such acid conditions as contact with mine water to a remarkable extent not equaled by other coatings which have heretofore been used for malleable castings. In addition the chromium alloy coating gives the casting a hard surface well adapting it for various mechanical uses such as clamps and the like.

While the foregoing detailed procedure is such as I consider suitable for the production of chromium coated malleable castings, the procedure can be varied widely within the scope of my invention. Thus the material supplying the chromium may be either higher or lower in chromium than the material specified above. For example, ferro-chromium containing 60% chromium or even less than 60% may be used. However, with the lower chromium content very thin coatings result. Again, carbon, silicon, aluminum or other alloying elements may be present in the chromium, and while they may slow down the coating process, a coating will nevertheless be formed. This fact makes it possible to utilize high carbon ferro-chromium, say 5% carbon, as the source of chromium, with the decided advantage that it is much lower in price and easier to crush than is the low carbon ferro-chromium. Also, the packing may be diluted with sand, alumina, magnesia, chrome ore or other refractory material but the coating rate is of course decreased by such dilutions. Then, particularly with carbon present, there may be some reduction of such diluents which causes the packing to cake and makes the removal of the treated articles somewhat difficult.

The temperatures employed in the heat treatment are variable with the composition of the packing material and the length of the treatment. Thus, if ferro-chromium less than 70% in chromium or containing carbon,

or otherwise slower acting than the ferro-chromium as specified in the above example, is used, only relatively high temperature anneals (about 1700° F.) will give a good coating. Even with the 70% chromium low carbon ferro-chromium, good results are difficult to attain with annealing temperatures much below 1600° F. However, by using commercial chromium (98.1% pure) I have produced chromium or chromium alloy coatings by treating at temperatures as low as 1500° F. In this latter case the chromium metal used was powdered to pass a 100 mesh screen and mixed with silica sand and anhydrous ferric chloride fine enough to pass a 30 mesh screen, in the following proportions:

	Per cent
Chromium metal	25
Silica sand	74
Ferric chloride	1

The castings, surrounded with this packing material in a well closed container, were heated to 1500° F. in 24 hours and held at that temperature for another 25 hours. With respect to the length of the heat treatment, the time required for the annealing treatmen itself is sufficient to produce a good coating, with other hereinmentioned conditions suitable. Exposure to the heat treatment for even longer periods than usual in the annealing operation do not affect the coating much, since when once formed the coating increases in thickness but slowly at the temperatures employed. In fact, an annealing temperature of 1700° F. for twenty-four hours or more is needed if the packing material consists of high carbon ferro-chromium (70% chromium, 5% carbon) crushed to pass a six mesh screen.

Halogen compounds other than bleaching powder can be used. Thus an equal amount of ferric chloride (preferably anhydrous) can be substituted for the bleaching powder, though it is to be observed that it tends to make the packing cake around the castings so that the latter are not so easily freed. Still other halogen compounds can be employed as has been pointed out in my copending application Serial No. 242,837, above referred to.

As illustrating the use of ferric chloride and at the same time a satisfactory manner of using a diluent in the packing, I have produced malleable castings with good chromium alloy coatings by using a packing consisting of about 87% sand blast sand (about six mesh size), 10% high carbon ferro-chromium (60% chromium, 5% carbon) crushed to pass a hundred mesh screen, and 3% ferric chloride (anhydrous). The sand, powdered ferro-chromium and the chloride are thoroughly mixed together, the last named material causing the powdered metal to adhere to the grains of sand. In this way the powdered metal is distributed over a large surface even though the mass of metal present is relatively small. The size of the sand grains is large enough to give a porous packing that permits the gases to circulate with relative ease. The castings themselves can also be mixed together with the packing materials, which tends to smear the castings with the powdered metal and the ferric chloride. Using this packing material in the malleableizing process with a treating temperature of 1650° F. to 1700° F. for 48 hours, I have secured good coatings on the malleableized castings, particularly on malleable iron containing about 2.6% carbon. With this packing material the cost of the ferro-chromium is reduced and the caking of the packing material, which tends to occur more or less when ferric chloride is employed, is minimized.

Silicon alloy coating.—When the castings annealed are to be coated with silicon or a silicon alloy, the procedure is much the same as in the case of the coating with chromium. However, in addition to substituting suitable silicon material for the chromium material, account must be taken of the fact that the silicon coating is formed more readily than the chromium coating. For instance, an over heavy and fragile coating of silicon would be formed under the same time and temperature conditions as would produce a good coating of chromium. For this reason either a lower annealing temperature should be used, with a correspondingly longer period of treatment, or the silicon content can be diluted and thus yield a coating of the desired character. To make the matter specific, the procedure specified above for the chromium coating can be followed throughout for the silicon coating if a packing is used consisting of 92% silica sand, 5% of ferro-silicon (50% silicon) and 3% of ferric chloride (preferably anhydrous). In coating with silicon I find that ferric chloride is preferable to bleaching powder. Also, I find that the annealing process is hastened somewhat when coating with silicon as some of the silicon is taken up by the iron and silicon increases the rate of graphitization. This addition of silicon tends to affect even the interior metal of the castings in the manner stated.

The castings that have been silicon coated by my process are bright in appearance and they also have increased resistance to weather and oxidation. However, as to these latter qualities, they are inferior to the chromium coated castings. The resistance of the silicon coatings to weather, oxidation and acid can be increased by making the coatings richer in silicon, but this is accomplished at the expense of decreased toughness and mechanical strength of the coatings.

Accordingly, the chromium coating is usually to be preferred.

It is to be observed that while in the case of the chromium alloy coating the process operates most satisfactorily in the upper part of the temperature range of 1400° F. to 1750° F. most suitable for annealing, viz. in the part from 1600° F. to 1750° F., in the case of the silicon alloy coating it is preferable to avoid temperatures above about 1700° F., the remainder of the annealing range referred to, i. e. 1400° F. to 1700° F., being equally applicable to the silicon coating, however. It will be understood that the composition of the ferro-silicon employed or the amount of diluent used in compounding the packing material will depend upon the range of temperatures of the heat treatment and also upon the duration of the treatment, the more dilute silicon material being employed for the higher temperatures and the longer treatments.

The packing material, comprising the active coating materials and any inert material employed, can be used over and over again, if active coating materials are added in sufficient amounts to make up for the depletion. Indeed, I have found in practice that the process works more satisfactorily after the packing material has been used one or more times in this manner.

As my process is carried out under conditions generally considered to be most favorable for the proper annealing of the castings, the product secured has physical characteristics equaling the normal standard of good malleable castings and, in addition, has the above advantages of the coating of chromium or other substance.

I am unable to say with certainty precisely what goes on in the carrying out of my process of combined annealing and coating, but as at present advised I believe that in addition to the annealing affect upon the casting, the following actions occur. In the first stages of the heating, that is, while the temperature is rising to, say, 700° F. and before there has been any substantial oxidation of the casting due to the increase of temperature, the halogen compound constituting one of the constituents of the packing material 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 of the casting and of the coating material. In case chlorine or other halogen is evolved, even if some slight oxidation of the casting and of the coating material should occur, the fluxing or etching action of the chlorine cleanses the surface of the resulting oxide scale. As the heating continues with resultant rise of temperature, the halogen compound in the vapor state, or the chlorine or other halogen evolved, reacts with the coating material (chromium, silicon or the like) to form a halide thereof. Thus, in the coating with silicon by the use of ferric chloride, the 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 iron of the casting 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 some tendency to dissociate and thus reverse the last reaction, making available part of its chlorine to continue the coating process by forming silicon chloride. Thus, in any case, the chlorine acts as a carrier of silicon, permitting this element to pass through the vapor state at a lower temperature than would otherwise be possible.

As has been indicated, the halogen compound employed will, when the packing material is heated, either vaporize and thus displace any air present so as to maintain a non-oxidizing atmosphere, or the compound will dissociate with the evolution of halogen gas, the action that occurs being dependent upon the particular halogen compound employed, there being one group of these compounds which vaporizes as stated when heated and another group which dissociates with evolution of halogen gas. Among those in the former group are aluminum chloride, antimony chloride, arsenic chloride, mercuric chloride, phosphorous trichloride, carbon tetrachloride, sulphur monochloride, and bismuth chloride. Examples of the other class of halogen compounds are ferric chloride, bleaching powder, gold (auric) chloride, cupric chloride, sulphur dichloride, sulphur tetrachloride and phosphorous pentachlochloride. For the purpose of my invention I prefer to use members of the latter class of compounds since the halogen gas evolved not only displaces any air present and maintains a non-oxidizing atmosphere, but also has a positive cleansing or fluxing action on the

casting being coated. While I prefer to employ one of the chlorides mentioned, especially ferric chloride and bleaching powder, halogen compounds other than chlorides also can be used. Thus in the examples given there may be substituted for the bleaching powder or ferric chloride a similar amount of anhydrous ferric bromide. However, the cost of the chlorides is lower and their use is preferred. Furthermore, the halogen compound need not be introduced into the heating container as such. Thus where ferric chloride is desired a mixture of equal amounts by weight of powdered ferrous sulphate (preferably anhydrous) and powdered sodium chloride may be substituted for the ferric chloride. On heating the packing these two compounds react to give ferric chloride and sodium sulphate. Other known methods of forming ferric chloride, by reaction within the packing, might be used. However, I prefer to introduce the ferric chloride directly.

It is not necessary that the mixture constituting the packing material have the coating material distributed uniformly through it. Thus the castings to be coated may be dipped in a liquid in which is a heavy suspension of the material that is to form the coating. The sludge thus formed on the casting contains enough of the coating element to give an alloy deposit thereof on the casting when subjected to the annealing treatment in the presence of the halide gas, which latter may be introduced into the container by placing one of the suitable halogen compounds therein, as will be readily understood.

It should be pointed out in connection with the operation of coating with chromium that chromium chloride has a low vapor pressure at the temperatures suitable for malleableizing and consequently in carrying out my malleableizing and chromium coating process the chromium present in the treating chamber should be in correspondingly close proximity to the casting to insure contact of the chromium chloride vapor with the casting. In some instances it may be found feasible and preferable to support the chromium-containing material in such suitably close proximity to the casting without the use of inert packing material or without resorting to the use of a sludge coating on the casting.

It will be understood that the annealing pot and furnace equipment used may vary widely. Indeed practically any form of pots and furnace suitable for the annealing of castings can be employed, provided that the pots used have substantially gas tight bottom portions or bottom portions susceptible of being made gas tight. This is important since it is characteristic of my process that the halogen gas evolved during the process, being heavier than air, displaces air at first present in the annealing chambers upward and out through the incompletely sealed joints at the tops of said chambers and then maintains the desired atmosphere in the chambers through the remainder of the treatment. If the chambers did not have their bottom parts tightly closed the halogen gases would flow out and the effectiveness of the treatment be seriously reduced.

While chromium and silicon, particularly the former, are preferred as coating materials in carrying out my process, it is to be understood that the process in its broader aspects is not limited to these materials. Thus the process can be carried out with a suitable amount of zinc, or aluminum, or antimony, or tantalum (or ferro-tantalum) substituted for the ferro-chromium or ferro-silicon, the zinc, or other metal, being used preferably in a powdered or finely divided state. For example, a coating of zinc or zinc iron alloy can be formed by my process by proceeding as in the case of the chromium coating above described if a packing is used consisting of equal parts, by volume, of sand and zinc dust. A heavy zinc-iron coating or surface layer is formed on the castings. In coating with zinc the process is operable at various temperatures ranging from temperatures well below 1200° F., the lower limit of the useful malleableizing range, to 1700° F. Similarly, a coating of tantalum is formed by my process as described for chromium by using a packing of equal parts, by volume, of sand and ferro-tantalum (80% tantalum) crushed to 20 mesh and finer. In the case of antimony, I have produced a bright coating of antimony using a packing having only 8% by volume of powdered antimony (through 150 mesh screen) and the balance sand. The process is operable for coating with antimony or antimony alloy at temperatures ranging from 1500° F. to 1700° F. However, in all these cases the coating of zinc, or tantalum, or antimony has corrosion resisting qualities distinctly inferior to the coatings of chromium and of silicon. Malleable castings with coatings of aluminum also can be produced by my present process, using treating temperatures within the range of 1500° F. to 1700° F.

In characterizing herein the gas or vapor evolved in the annealing pots as "non-oxidizing", that term is of course used in its strict or limited sense indicating that the gas or vapor contains no oxygen capable of reacting to form oxides.

It will now be apparent that by means of my improved process of combined annealing and coating I am able to produce products of wide application in the arts and of great practical utility and that the process requires practically no more time than the standard processes of annealing alone and involves

little outlay for the materials required to form the coating. Furthermore, by reason of the fact that non-oxidizing atmospheres are secured and maintained in accordance with my process by the greatest ease under the normal working conditions under which castings are annealed commercially, the process lends itself especially well to commercial working.

While I have set forth specific materials and procedures suitable for the carrying out of my process, it is to be understood that I have done this for purposes of explanation and illustration and that the scope of the invention is indicated by the appended claims.

What I claim is:

1. The process of forming coated malleable iron castings which includes the steps of enclosing a white iron casting in a chamber with material including a metal of the group consisting of chromium, silicon, zinc, aluminum and antimony and a halogen compound adapted, when said material and casting are heated, to evolve, before the casting becomes substantially oxidized, a non-oxidizing and etching gas or vapor heavier than air and capable of reacting with said metal to form a halide thereof vaporizable at least in part at temperatures below the maximum treating temperature of the process, heating the material and casting and meanwhile permitting the escape from the chamber of the air displaced upward by the heavier vapor formed; and continuing the heating at temperatures between 1200° F. and 1800° F. for a time adapted to malleableize the casting and simultaneously to form thereon an alloy coating of the said metal.

2. The process of forming coated malleable iron castings which includes the steps of enclosing a white iron casting in a chamber with material including a metal of the group consisting of chromium, silicon, zinc, aluminum and antimony and a halogen compound adapted, when said material and casting are heated, to evolve, before the casting becomes substantially oxidized, a non-oxidizing gas or vapor heavier than air and to react with said metal to form a halide thereof vaporizable at least in part at temperatures below the maximum operating temperature of the process; heating the material and casting and meanwhile permitting the escape from the chamber of the air displaced upward by the non-oxidizing vapor formed; and continuing the heating at temperatures between 1500° F. and 1700° F. for a time adapted to malleableize the casting and simultaneously to form thereon an alloy coating of the said metal.

3. The process of forming coated malleable iron castings which includes the steps of enclosing a white iron casting in a chamber with material containing chromium and a halogen compound adapted, when said material and casting are heated, to evolve, before the casting becomes substantially oxidized, a non-oxidizing gas or vapor and to react with the chromium to form a halide thereof vaporizable at least in part at temperatures below the maximum treating temperature of the process; and subjecting the material and casting to a heat treatment at temperatures between 1500° F. and 1800° F. for a time adapted to malleableize the casting and simultaneously to form on the casting an alloy coating chromium.

4. The process of forming coated malleable iron castings which includes the steps of enclosing a white iron casting in a chamber with material including chromium and a halogen compound adapted, when said material and casting are heated, to evolve, before the casting becomes substantially oxidized, a non-oxidizing and etching gas or vapor heavier than air and capable of reacting with the chromium to form a halide thereof vaporizable at least in part at temperatures below the maximum treating temperature of the process; heating the material and casting and meanwhile permitting the escape from the chamber of the air displaced upward by the heavier vapor formed; and continuing the heating at temperatures between 1600° F. and 1750° F. for a time adapted to malleableize the casting and simultaneously to form thereon an alloy coating of chromium.

5. The process of forming coated malleable iron castings which includes the steps of enclosing a white iron casting in a chamber with material containing silicon and a halogen compound adapted, when the material and casting are heated, to evolve, before the casting becomes substantially oxidized, a non-oxidizing gas or vapor heavier than air and to react with the silicon to form a halide thereof vaporizable at least in part at temperatures below the maximum treating temperature of the process; heating the material and casting and meanwhile permitting the escape from the chamber of the air displaced upward by the non-oxidizing vapor formed; and continuing the heating at temperatures between 1200° F. and 1700° F. and for a time adapted to malleableize the casting and simultaneously to form thereon an alloy coating of silicon.

6. The process of forming coated malleable iron castings which includes the steps of enclosing a white iron casting in a chamber with material containing zinc and a halogen compound adapted, when the material and casting are heated, to evolve, before the casting becomes substantially oxidized, a non-oxidizing gas or vapor heavier than air and to react with the zinc to form a halide thereof vaporizable at least in part at temperatures below the maximum treating temperature of the process; heating the material and casting and meanwhile permitting the escape from the chamber of the air displaced upward by

the non-oxidizing vapor formed; and continuing the heating at temperatures between 1200° F. and 1700° F. and for a time adapted to malleableize the casting and simultaneously to form thereon an alloy coating of zinc.

In testimony whereof, I hereunto affix my signature.

LESLIE H. MARSHALL.