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FORMATION OF CHROMIUM ALLOY COATINGS

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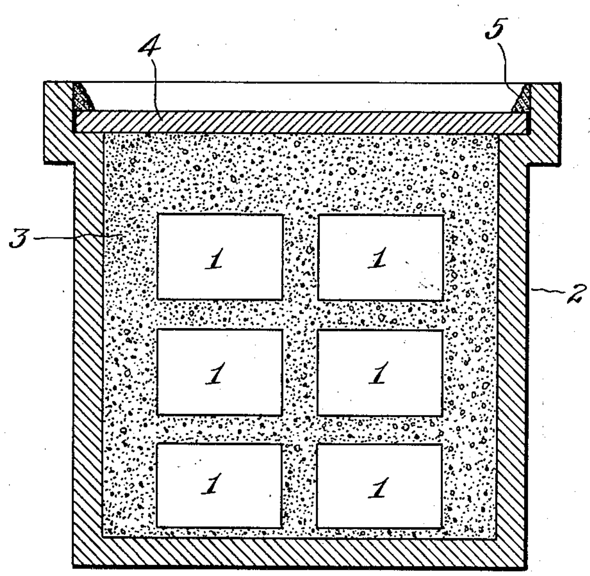

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FORMATION OF CHROMIUM ALLOY COATINGS

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

It is well recognized that chromium and many of its alloys have properties that are desirable, such as susceptibility of taking a high polish with resultant pleasing appearance, resistance to various kinds of corrosion, resistance to oxidation at high temperatures, and remarkable hardness. Articles made of chromium alloys have accordingly had a certain limited use. These alloys, however, are relatively expensive and somewhat difficult to form into more or less complicated shapes; and these considerations limit the commercial use of the chromium alloys. Where the purpose is to secure only the surface characteristics of chromium or its alloys, such as resistance to corrosion, pleasing appearance or superficial hardness, it has been realized that an alloy surface layer upon the article would serve the purpose practically as well as an article composed entirely of the alloy. It has, accordingly, been sought to give to articles superficial chromium alloy surfaces but, as far as I am aware, none of the proposals so far advanced have been susceptible of any considerable commercial application because of the relatively high temperatures involved in the treatments employed and the great difficulty of avoiding oxidation both of the chromium and of the surface to be coated or alloyed.

One of the principal objects of the present invention is the provision of a process for forming chromium alloy coatings which involves the use of moderate temperatures.

Another object of the invention is the provision of a process of forming chromium alloy coatings which affords a non-oxidizing atmosphere under conditions readily maintained on a commercial basis.

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

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

My improved process, generally considered, involves enclosing the article to be given the chromium alloy coating with material which will, when heat is applied thereto, 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, to the end above noted, and (*c*) a compound of chromium adapted to vaporize at least in part 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 chromium on the article treated and the formation of a chromium alloy surface thereon.

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

In order that my invention and the method of practicing the same may be clearly understood, concrete examples will now be given, 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.

Let it be assumed, for example, that the articles to be coated are formed of steel with carbon content of about 0.2%. These articles, designated by the numeral 1 in the drawing, after being thoroughly cleaned by sand blasting are introduced into a suitable container 2 and imbedded, as shown, in a packing 3 made up of a mixture of crushed ferro-chromium (70% chromium, 0.1% carbon), similarly crushed chrome ore to the amount of twice the volume of the crushed ferro-chromium and dry bleaching powder (chloride of lime) to the amount of 5% by weight of the entire packing. Preferably the ferro-chromium and chrome ore are crushed to pass a six mesh screen, being of varying particle sizes up to the maximum size capable of passing such a screen. As will be noted, the container has a tightly closed bottom so that vapors or gases cannot escape. Also, a layer of packing material of considerable thickness is covered over the topmost articles to be treated to protect them from gases that might enter through the top of the receptacle. However, the articles are further protected from the entrance of gases by the provision of a closely fitting cover 4, which is sealed at the edges by a luting 5 of 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 at high temperatures. The container and contents are now placed in a furnace and heated to 1900° F. and held at that temperature for twenty hours. The container is then removed from the furnace and allowed to cool to room temperature.

After the container and contents have cooled, the treated articles are removed from the container and packing and immediately washed in hot water and then boiled in a 10% sodium carbonate solution for one-half hour to neutralize and remove any salts that might remain on their surface, the chromium-iron alloys being susceptible to attack by the halide salts to some extent. The treated articles are then washed and dried.

The articles thus treated are found to have a coating bright in color and about 0.001 inch thick, the coating consisting of a high percentage of chromium at its outer surface with the percentage of chromium decreasing toward the inner part thereof.

The procedure above described may, within the scope of the present invention, be varied considerably with respect to materials employed, time of treatment, temperature of treatment and in other respects. Thus the material supplying the chromium may take various forms. For example, chromium metal (98% chromium) crushed to pass a two mesh screen and be retained on a twelve mesh screen, and mixed with 5% of its weight of bleaching powder, but not diluted with chrome ore or other diluent, will give a bright and shiny coating of chromium on low carbon steel articles after treatment at 1800° F. for five hours. Again, ferro-chromium (60% chromium, 0.1% carbon) crushed to pass a six mesh screen and mixed with 5% of its weight of bleaching powder but not otherwise diluted will give a good coating on low carbon steel articles after a treatment at 1800° F. for ten hours. Furthermore, diluents such as carbon, silicon, or other elements may be present in the chromium or ferro-chromium used. However, when a substantial amount of silicon or other element capable of reacting with the non-oxidizing gas or vapor and of alloying with the base metal and the chromium is present, the composition of the alloy coating formed will be modified accordingly. As indicated by the examples given above, the packing material may be otherwise diluted, with consequent decrease of the rate of coating. Examples of such other diluents in addition to chrome ore, are sand, alumina, magnesia and other refractory materials. These diluents, it may be noted, reduce a tendency of the packing material to cake around the articles treated, though in the case of sand, particularly when carbon is present, there may be some reduction of the sand with the resultant caking of the packing material. It is noted further that the particle size of the crushed chromium packing material is a matter of some practical importance. Pulverized material naturally presents a larger surface and yields a coating somewhat more quickly than the preferred six mesh material but the cost of pulverizing the material is relatively high and the increased expense is not warranted by the relatively small increase in the coating rate. Also, in the case of low carbon ferro-chromium in particular, the material, if finely divided, tends to stick to the surface of the article treated and gives a less attractive appearance. On the whole, the chromium or ferro-chromium when crushed to pass a six mesh screen, including the fine material that passes the screen along with the coarse, gives the preferable results for general purposes.

The material used as a flux and chromium carrier should be volatile at the temperature of treatment, and preferably, as previously indicated, it should volatilize at below the temperature at which either the packing material or the article to be coated oxidizes materially. I have found halogen compounds that volatilize or at least have an appreciable vapor pressure, below 700° F. to be satisfactory. Some of these compounds merely volatilize at temperatures below 700° F. and thus displace any air present in the container, the vapors being heavier than the air. Examples of halogen compounds that volatilize, at least in part, 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 chromium chloride. Others of the halogen compounds liberate halogens on heating and they are therefore particularly suitable. Examples of this latter class are gold (auric) chloride, ferric chloride, cupric chloride, phosphorous pentachloride, sulphur dichloride, sulphur tetrachloride and bleaching powder. Of the halogen compounds mentioned, bleaching powder, aluminum chloride and ferric chloride are probably most suitable for my process. Thus, in the foregoing specific example the bleaching powder can be replaced by a similar amount of ferric chloride (preferably though not necessarily anhydrous) or of aluminum 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 are operable in my process; thus 5% of anhydrous ferric bromide can be used in place of the bleaching powder given in the above example, though the bleaching powder is preferable because of its lower cost. Furthermore, the halogen compound employed need not be introduced as such into the treating container. Thus in the packing material there can be substituted for the 5% of ferric chloride, for example, 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.

It should be pointed out that chromium chloride has a low vapor pressure at the temperatures employed in my process and consequently in carrying out the process the chromium present in the treating chamber should be in correspondingly close proximity to the casting to insure contact of the chromium chloride with the casting.

The base metal on which the coating is produced, is not limited to iron and steel alone, but malleable cast iron, gray cast iron, and ferrous alloys can be coated; also other metals such as nickel, molybdenum, and tungsten can be coated. Thus nickel can be coated in the same way and under the same conditions as the low carbon steel objects cited above.

Similarly, the temperature of the treatment may be varied substantially. This variation depends both on the duration of the heat treatment and on the packing material used. The nature of the article to be coated also has some small effect, since iron very low in carbon coats at a slightly faster rate than does steel. Thus commercially pure iron (Armco iron) will coat in three-fourths the time required for 0.2% carbon steel. The relative effect of the packing material is indicated by the examples given above. If the time required for coating with chromium metal is taken as the unit, the 60% low carbon ferro-chromium will require about twice as long and the high carbon ferro-chromium (70% chromium, 5% carbon) about ten times as long.

The duration and temperature of the treatment are closely related and interdependent. Thus the undiluted low carbon 70% ferro-chromium will give a good coating on low carbon steel in eight hours at 1800° F.; but by extending the treatment to a period of sixty hours the temperature can be lowered to 1600° F., and if chromium metal is used in place of the ferro-chromium, the temperature for the sixty hours treatment can be reduced to about 1500° F. On the other hand, quite short periods of treatment are sufficient at a temperature of 2000° F., but the difficulties of working at this temperature increase the production cost and limit commercial use of such temperatures. Furthermore, it is to be noted that for steel articles or other ferrous articles containing 0.8% or more of carbon the temperature of treatment should be kept below 1800° F. to avoid danger of "burning" the steel, i. e. destroying its strength by incipient fusion. This danger is not present in the case of low carbon steel.

While I am unable to say with certainty precisely what goes on in the carrying out of my process, as at present advised I believe that the following actions occur. In the first stages of the heating, i. e. while the temperature is rising to say 700° F., the bleaching powder or other halogen compound employed vaporizes, dissociates with evolution of chlorine (or other halogen), or both of these actions occur. In any 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. Where chlorine or other halogen is evolved, there is the further advantage that even if some slight oxidation of the article being coated and of the chromium should occur, the fluxing action of the chlorine cleans the surfaces of the resulting oxide scale. As the heating continues the halogen compound in the vapor state, or the chlorine or other halogen evolved, reacts with the chromium to form chromium chloride. Thus, bleaching powder when heated evolves chlorine by dissociation as follows:

$$CaOCl_2 = CaO + Cl_2$$

The chlorine thus liberated reacts with the chromium as stated to form chromium chloride and the latter in the vapor state penetrating all parts of the space within the container reacts or dissociates in the presence of the article of iron or other material to be coated, and deposits metallic chromium thereon. The deposited chromium at the temperature of treatment penetrates the surface zone of the iron article and alloys therewith so that the coating becomes in effect an integral part of the article. The chlorine might, of course, in part react with the iron of the article being coated to yield ferrous chloride, but the latter would to some extent dissociate and thus make the chlorine again available for the continuation of the chromium coating process.

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 chromium or chromium alloy, so that the surface of the coated article takes on the characteristics of chromium and its susceptibility to taking a polish with resultant bright appearance or lustre, a high degree of resistance to various corrosive actions, a high degree of resistance to oxidation at high temperatures, and relatively great hardness. In other words, an article is thus produced adapted to many commercial uses. This result is secured, furthermore, with a process which lends itself in a remarkable degree to production on a commercial basis. In particular, the prevention of oxidation by the simple expedient of introducing into the treating chamber a substance adapted to vaporize or evolve a gas capable of displacing air from the treating space is accomplished with the greatest ease 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 chromium 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 chromium, both makes the process susceptible of operation under working conditions that can be maintained on a commercial basis without difficulty, and also renders the process available for work that could not be accomplished at higher temperatures. For example, such high temperatures are not feasible in the case of the high carbon steels, as above pointed out. Again, the moderate temperature which suffices in my process makes the process available for the coating of malleable iron castings, whereas the high temperatures which have characterized earlier proposals for chromium coating would destroy the qualities of such castings. In a separate application Serial No. 417,978, filed January 2, 1930, I set forth in detail the application of the present process to the combined malleableizing and coating of iron castings.

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 being 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 chromium which includes the steps of surrounding the article to be coated with a packing containing chromium or an alloy of chromium and the metal of which the said article is constituted; applying heat to the said article and packing; permeating the space surrounding the article with sufficient halogen or halogen compound gas or vapor before the temperature has been raised above the oxidizing temperature of the reacting metals present substantially to displace the air from said space and thereby prevent oxidation of the said metals; and thereafter continuing the heating of the packing and article to temperatures between 1500° F. and 2000° F. in the presence of halogen or halogen compound gas or vapor until a coating of chromium alloy is formed on the article.

2. The process of forming alloy coatings of chromium which includes the steps of surrounding the article to be coated with a packing containing chromium or an alloy of chromium and the metal of which the said article is constituted; applying heat to the said article and packing; permeating the space surrounding the article with sufficient halogen or halogen compound gas or vapor before the temperature has been raised above the oxidizing temperature of the reacting metals present substantially to displace the air from said space and thereby prevent oxidation of the said metals; and thereafter continuing the

heating of the packing and article to temperatures between 1500° F. and 2000° F. in the presence of halogen or halogen compound gas or vapor until the halogen or halogen compound gas or vapor reacts with the chromium to form a chromium compound and the latter reacts or dissociates in the presence of the article to form a coating of chromium alloy thereon.

3. The process of forming alloy coatings of chromium which includes the steps of surrounding the article to be coated with a packing containing chromium or an alloy of chromium 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 the oxidizing temperature of the reacting metals present; 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 said metals; and further heating the packing and article to temperatures between 1500° F. and 2000° F. in the presence of halogen or halogen compound gas or vapor until a coating of chromium alloy is formed on the article.

4. The process of forming alloy coatings of chromium which includes the steps of surrounding the article to be coated with a packing containing chromium or an alloy of chromium and the metal of which the said article is constituted and a material adapted to evolve a halogen gas at temperatures below the oxidizing temperature of the reacting metals present; 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 said metals; and further heating the packing and article to temperatures between 1500° F. and 2000° F. in the presence of halogen or halogen compound gas or vapor until a coating of chromium alloy is formed on the article.

5. The process of forming alloy coatings of chromium which includes the steps of surrounding the article to be coated with a packing containing chromium or an alloy of chromium and the metal of which the said article is constituted, an inert diluent and a halogen or halogen compound adapted to evolve non-oxidizing gas or vapor at temperatures below the oxidizing temperature of the reacting metals present; 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 said metals; and further heating the packing and article to temperatures between 1500° F. and 2000° F. in the presence of halogen or halogen compound gas or vapor until a coating of chromium alloy is formed on the article.

6. The process of forming alloy coatings of chromium which includes the steps of surrounding the article to be coated with a packing containing chromium or an alloy of chromium and the metal of which the said article is constituted; applying heat to the said article and packing; permeating the space surrounding the article with sufficient halogen or halogen compound gas or vapor before the temperature has been raised above the oxidizing temperature of the reacting metals present substantially to displace the air from said space and thereby prevent oxidation of the said metals; thereafter continuing the heating of the packing and article to temperatures between 1500° F. and 2000° F. in the presence of halogen or halogen compound gas or vapor until a coating of chromium 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 chromium which includes the steps of surrounding the article to be coated with a packing containing ferro-chromium and a halogen or halogen compound adapted to evolve a non-oxidizing gas or vapor at temperatures below the oxidizing temperature of the reacting metals present; heating the packing and contained article to cause such evolution or 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 said metals; and further heating the packing and article to temperatures between 1600° F. and 2000° F. in the presence of halogen or halogen compound gas or vapor until a coating of chromium alloy is formed on the article.

8. The process of forming alloy coatings of chromium which includes the steps of surrounding the article to be coated with a packing containing chromium or an alloy of chromium and the metal of which the said article is constituted and bleaching powder; heating the packing and contained article to evolve chlorine from the bleaching powder in an amount sufficient substantially to displace air from the space surrounding the article and thereby prevent oxidation of the said metals; and further heating the packing and article to temperatures between 1500° F. and 2000° F. in the presence of halogen or halogen compound gas or vapor until a coating of chromium alloy is formed on the article.

9. The process of forming alloy coatings of chromium which includes the steps of surrounding the article to be coated with a packing containing chromium or an alloy of chromium and the metal of which the said article is constituted and a halogen or halogen com-

pound adapted to evolve a non-oxidizing gas or vapor at temperatures below the oxidizing temperature of the reacting metals present, 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 an amount sufficient substantially to displace air from the space surrounding the article and thereby prevent oxidation of the said metals; and further heating the packing and article to temperatures between 1500° F. and 2000° F. in the presence of halogen or halogen compound gas or vapor until a coating of chromium alloy is formed on the said article.

10. The process of forming alloy coatings of chromium which includes the steps of surrounding the article to be coated with a packing containing chromium or an alloy of chromium 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 an amount sufficient substantially to displace the air from the space surrounding the article and thereby prevent oxidation of the reacting metals present; and further heating the packing and article to higher temperatures in the presence of halogen or halogen compound gas or vapor until a coating of chromium alloy is formed on the article.

11. The process of forming alloy coatings of chromium which includes the steps of surrounding the article to be coated with a packing containing chromium or an alloy of chromium 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 the oxidizing temperature of the reacting metals present; heating the packing and contained article to cause such evolution of gas or vapor in an amount sufficiently substantially to displace the air from the space around the article and thereby prevent oxidation of the said metals; and further heating the packing and article to temperatures above the oxidizing temperature of the metals present to cause (*a*) reaction between the gas or vapor evolved by the halogen compound and the chromium to form a halide of chromium, (*b*) some vaporization of the said halide of chromium and (*c*) reaction or dissociation of the halide of chromium with the resultant deposition of chromium on the article to be coated.

12. The process of forming alloy coatings of chromium which includes the steps of surrounding the article to be coated with a packing containing chromium or an alloy of chromium and the metal of which the said article is constituted and a halide adapted to evolve a halogen gas at temperatures below the oxidizing temperature of the reacting metals present; heating the packing and contained article to cause such evolution of gas in an amount sufficient substantially to displace the air from the space around the article and thereby prevent oxidation of the said metal; and further heating the packing and article to temperatures between 1500° F. and 2000° F. in the presence of halogen or halogen compound gas or vapor until a coating of chromium alloy is formed on the article.

13. The process of forming chromium alloy coatings on articles of steel containing 0.8% or upwards of carbon, which process includes the steps of surrounding the article to be coated with a packing containing chromium or ferro-chromium and a halogen or halogen compound adapted to evolve a non-oxidizing gas or vapor at temperatures below the oxidizing temperature of the reacting metals present; heating the packing and contained article to cause such evolution of gas or vapor in an amount sufficient substantially to displace the air from the space around the article and thereby prevent oxidation of the said metals; and further heating the packing and article in the presence of halogen or halogen compound gas or vapor to higher temperatures, but not to exceed 1800° F. in the case of the article, until a coating of chromium alloy is formed on the article.

14. The process of forming alloy coatings of chromium on ferrous articles containing 0.8% or upwards of carbon, which process includes the steps of surrounding the article to be coated with a packing containing chromium or ferro-chromium and a halogen or halogen compound adapted to evolve a non-oxidizing gas or vapor at temperatures below the oxidizing temperature of the reacting metals present; heating the packing and contained article to cause such evolution of gas or vapor in an amount sufficient substantially to displace the air from the space around the article and thereby prevent oxidation of the said metals; and further heating the packing and article in the presence of halogen or halogen compound gas or vapor to temperatures above the oxidizing temperature of the said metals, but not to exceed 1800° F. in the case of the article, until a coating of chromium alloy is formed on the article.

15. The process of forming alloy coatings of chromium which includes the steps of surrounding the article to be coated with a packing containing chromium or an alloy of chromium and the metal of which the article is constituted and a halide adapted to evolve a halogen gas at temperatures below the oxidizing temperature of the reacting metals present; heating the packing and contained article to cause such evolution of gas in an amount sufficient substantially to displace the air from the space around the article and thereby prevent oxidation of the said metals;

and further heating the packing and article in the presence of halogen or halogen compound gas or vapor to temperatures above the oxidizing temperature of the said metals until a coating of chromium alloy is formed on the article.

16. The process of forming alloy coatings of chromium on ferrous articles which includes the steps of surrounding the ferrous article to be coated with a packing containing chromium or ferro-chromium 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 gas in an amount sufficient substantially to displace the air from the space around the article and thereby prevent oxidation of the reacting metals present; and further heating the packing and article in the presence of halogen or halogen compound gas or vapor to temperatures above the oxidizing temperature of the said metals until a coating of chromium alloy is formed on the article.

17. The process of forming alloy coatings of chromium which includes the steps of enclosing in a treating chamber the article to be coated together with material including chromium or an alloy of chromium and the metal of which the said article is constituted and with the chromium or chromium alloy in close proximity to the article; applying heat to the said article and material; permeating the space surrounding the article with sufficient halogen or halogen compound gas or vapor before the temperature has been raised above the oxidizing temperature of the reacting metals present substantially to displace the air from said space and thereby prevent oxidation of the said metals; and thereafter continuing the heating of the article and the said material to temperatures between 1500° F. and 2000° F. in the presence of halogen or halogen compound gas or vapor until a coating of chromium alloy is formed on the article.

18. The process of forming alloy coatings of chromium which includes the steps of enclosing in a treating chamber the article to be coated together with material including chromium or an alloy of chromium and the metal of which the said article is constituted and with the chromium or chromium alloy in close proximity to the article; applying heat to the said article and material; permeating the space surrounding the article with sufficient halogen or halogen compound gas or vapor before the temperature has been raised above the oxidizing temperature of the reacting metals present substantially to displace the air from said space and thereby prevent oxidation of the said metals; and thereafter continuing the heating of the said material and article to temperatures between 1500° F. and 2000° F. in the presence of halogen or halogen compound gas or vapor until the halogen or halogen compound gas or vapor reacts with the chromium to form a chromium compound and the latter reacts or dissociates in the presence of the article to form a coating of chromium alloy thereon.

19. The process of forming alloy coatings of chromium which includes the steps of enclosing in a treating chamber the article to be coated together with materials including chromium or an alloy of chromium and the metal of which the said article is constituted and with the chromium or chromium alloy in close proximity to the article; applying heat to the said article and material; permeating the space surrounding the article with sufficient halogen or halogen compound gas or vapor before the temperature has been raised above the oxidizing temperature of the reacting metals present substantially to displace the air from said space and thereby prevent oxidation of the said metals; thereafter continuing the heating of the said material and article to temperatures between 1500° F. and 2000° F. in the presence of halogen or halogen compound gas or vapor until a coating of chromium alloy is formed on the article; and removing from the surface of the article adherent halide salts.

In testimony whereof, I hereunto affix my signature.

LESLIE H. MARSHALL.