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3,108,013

METHOD OF CHROMIZING

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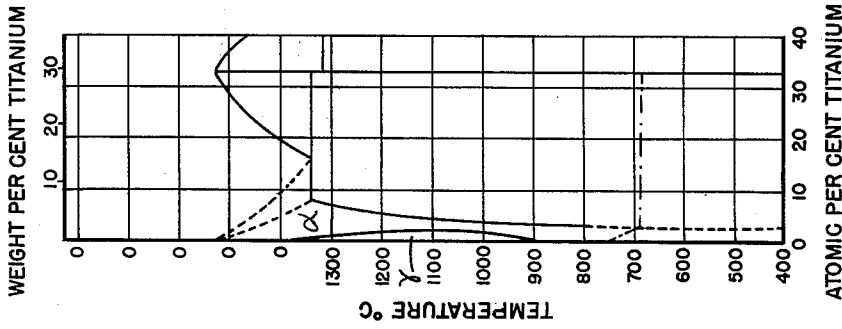


Fig. 3

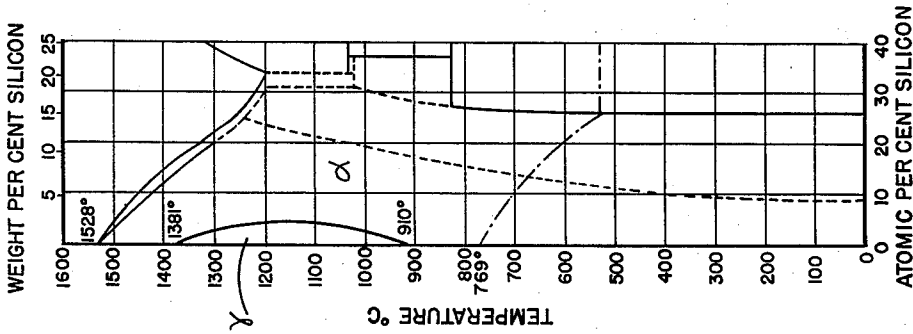


Fig. 2

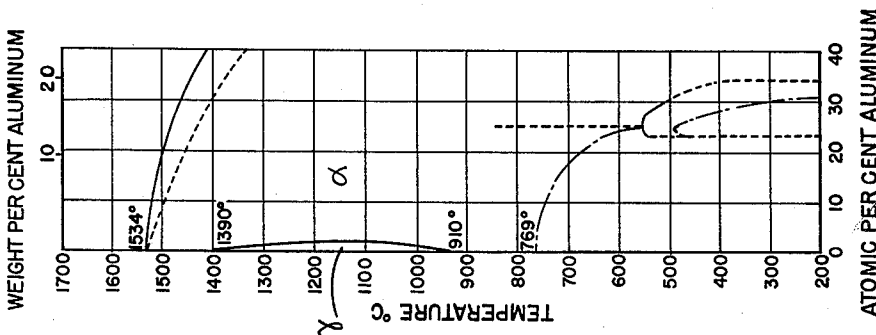


Fig. 1

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METHOD OF CHROMIZING

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2 Claims. (Cl. 117-107.2)

This invention relates to a method for coating metallic objects, and more especially to a process for depositing a coating of chromium or chromium rich alloys on the surface of base metal. In particular, this process relates to a process of depositing such coatings on ferrous substrates, one object of this invention being the production of more satisfactory coatings than has heretofore been possible.

The process of chromizing has been carried on in the past by several means. One of the more common means is the packing process wherein the object to be coated is placed in a closed container, the articles being embedded in a powdered material containing chromium either in the elementary or metallic form, in the form of chromium rich alloys, or in the form of a decomposable chromium compound, together with certain carrier and inert materials. The entire container is then heated in the absence of oxygen, and the chromium deposits on the surface of the article, and diffuses inwardly forming a coating of chromium rich ferrous alloy on the surface of the article to be coated.

Another well known means of producing such chromized coatings is by means of vapor plating. In the vapor plating process, the article to be coated is suspended in a chamber in a reducing or oxygen free atmosphere, and is subjected, at elevated temperatures, to a vaporized chromium compound such as the halogen or carbonyl compounds thereof. When these compounds come into contact with the heated surface of the object to be coated, decomposition or disproportionation reactions occur and the chromium is liberated at or near the surface of the object to be coated. This chromium similarly deposits on and diffuses into the ferrous substrate, producing a layer of chromium rich alloy.

Most of the chromizing processes in use today operate by the same general mechanism. In both these processes chromium is liberated at or near the surface of a heated article to be coated, and the chromium then diffuses inwardly to form the chromized shell on the substrate. However, it has been found that the processes heretofore in use have certain inherent limitations which limit the thickness and quality of the chromized coating produced. When the chromium is liberated at the surface of the substrate, it diffuses inwardly, alloying itself with the ferrous substrate, producing a chromium rich alloy. This finished coating consists of a very thin surface of chromium rich alloy covering a somewhat thicker layer of alloy becoming poorer in chromium as it penetrates the ferrous substrate.

The chromizing process heretofore in use has certain inherent limitations which affect both the thickness and quality of the coating produced. In the first place, it is difficult to produce a surface having any substantial thickness of chromium or an alloy rich in chromium, and thus the portion of the coating having the desired properties is necessarily very thin and discontinuous. For this reason, it is another object of this invention to overcome the inherent shortcomings of the processes now in use by producing a coating of substantially greater thickness than has heretofore been produced by known processes.

It has been found that by use of the conventional processes, it is very difficult to produce a chromized coating on ferrous substrates having a carbon content of greater

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than 0.10 percent. This appears to be due to the fact that during the diffusion coating process, the carbon in the ferrous substrate tends to diffuse outwardly and that the chromium preferentially tends to react with this carbon to form chromium carbide. The resulting layer of chromium carbide appears to act as a diffusion barrier, preventing the further inward diffusion of chromium thus limiting the thickness of coating that may be deposited by any of the known methods. For this reason, it is another object of this invention to overcome the inherent limitations of the known processes by providing a means whereby coatings of substantial thicknesses can be applied to ferrous substrates having substantial carbon content.

Another factor that has limited the effectiveness of the known chromizing processes is the fact that the diffusivity of chromium depends on the phase of the ferrous substrate through which the diffusion is taking place. It has been found that chromium will diffuse into and through iron in the alpha phase much more readily than it will diffuse through iron in the gamma phase. However, in order to have any diffusion at all, the whole system must be maintained at elevated temperatures which will give mobility to the atoms in the crystal structure to allow diffusion to take place. Once the iron is raised to the elevated temperature which will allow the reaction to occur, the iron undergoes a transformation at the so-called "transformation point" A_3 which is well known in the art, wherein the iron is converted from the alpha to the gamma phase, thereby reducing drastically the diffusivity of the chromium therein.

However, it has been found that certain additions, which are well known in the metallurgical art, have a profound effect on the temperature at which the transformation from alpha to gamma iron takes place. It has also been found that the addition of these elements to the coating composition will retard or even eliminate this transformation at or near the surface of the ferrous substrate, thereby permitting substantially increased diffusion of chromium therein. The provision of such transformation inhibiting elements in order to increase diffusivity of chromium is therefore another object of this invention.

A further object of this invention is to provide a process of the character provided for producing chromium diffusion coatings of a substantially greater thickness than heretofore possible.

Another object is the provision of a process wherein carbon eliminating or stabilizing neutralizing elements are provided to increase diffusivity of chromium.

It is another object of this invention to provide improved adherent uniform, evenly diffused continuous coatings having surfaces rich in chromium by means of increasing the diffusivity of the chromium and at the same time eliminating the adverse effects of carbon by the addition of certain alloying elements.

Other objects and advantages of this invention will be particularly set forth in the claims and will be apparent from the following description, when taken in connection with the accompanying drawings, in which:

FIG. 1 is a phase diagram of the iron aluminum system for the range between pure iron and an alloy containing 40 atomic percent aluminum showing the phases existing between 200° and 1700° C.;

FIG. 2 is a phase diagram similar to FIG. 1 showing the iron silicon system, and

FIG. 3 is a phase diagram similar to FIGS. 1 and 2 showing the iron titanium system.

In the chromizing process, it has been found that when the conventional processes are used on steel having more than $\frac{1}{10}$ of one percent of carbon, that the maximum coating that can be built up is generally limited to 1 or 2 mils in thickness. The limiting factor which effectively prevents further build up is the gradual decrease in rate

of diffusion of the chromium into the ferrous substrate as the process continues. This decrease appears to be due to two causes: the barrier effect of chromium carbides formed when the inwardly diffusing chromium reacts with the carbon in the ferrous substrate, and the poor diffusivity of chromium in iron in the gamma phase existing at temperatures above the critical point A_3 .

The deleterious effects of chromium carbide formed by the preferential combination of the chromium diffusing into the substrate and the carbon diffusing outwardly can be prevented either by removing the carbon from at least the surface layers of the substrate or by supplying a material in the coating composition having an affinity for carbon greater than that of the chromium itself. The carbon can be removed from the surface layers of the substrate by conventional decarburizing processes which consist of a heat treatment cycle in a reducing atmosphere such as deassociated ammonia (75% N_2 and 25% H_2) for a period ranging from approximately one-half hour to eight hours depending on the depth of decarburization desired, at a temperature of between approximately 1500° to 2260° F. These decarburizing heat treatment cycles are well known in the art and is not believed that further description thereof need be included in this place.

As stated above, it is equally effective to add a material to the coating composition having an affinity for carbon greater than that of chromium in order to tie up the carbon in non-reactive form so that it may not combine with the chromium to form the diffusion barrier described above. Such substances however must be so chosen that they have no adverse effect upon the process. For example, although oxygen or other oxidizing substances can be used for the removal of carbon from ferrous alloys in high temperatures, the oxides thus produced would seriously interfere with the deposition of a uniform, flaw free chromized case. For this reason, the substances used must be such that they and/or their reaction products must not form a film on the surface of the ferrous substrate which would interfere with the deposition of the chromium. Preferably the substances used should also diffuse inwardly so as to leave the surface of the coated material substantially pure ferro-chromium alloys.

It has been found that small quantities of metals such as aluminum, silicon and titanium will preferentially react with carbon forming metallic carbides which do not constitute a barrier to the diffusion of chromium. At the same time, these metallic carbides have very minor or no effect on the diffusion rates of chromium into the ferrous substrates, and do not form a coating which interferes with the deposition of a surface layer of chromium. These carbon eliminating elements need only be added in relatively small quantity since the amount of carbon present in even the carbon rich ferrous alloys amounts to considerably under one percent, and the carbon must be removed only from the surface layers where the actual inward diffusion of the chromium is taking place.

The second problem that must be solved for the production of thick chromized coatings is a prevention of the transformation of the iron from the alpha to the gamma phase at elevated temperatures. The effect of the phase of the iron on the diffusivity of chromium is substantial although no numerical data is available at the present time. However, Table I below covers the diffusivity of silicon in iron in the alpha and gamma phases respectively.

TABLE I

Composition Range of Silicon, Wt. Percent	Phase of Iron	Temp., ° C.	Diffusion Coefficient, Sq. cm. per sec.
0.0-1.0	Gamma	1,293	1.7×10^{-9}
2.3-3.7	Alpha	1,284	1.3×10^{-7}

As can be seen at substantially identical temperatures of 1284 and 1293° C., the diffusion coefficients of silicon

through iron in sq. centimeters per second, is 1.7×10^{-9} when the iron is in the gamma phase at 1.3×10^{-7} when the iron is in the alpha phase. Thus, it can be seen that the diffusivity of silicon through iron is almost 100 times greater when the iron is in the alpha phase than when the iron is in the gamma phase. The effect of the phase of the iron on the diffusivity of chromium is of the same order and thus is of the utmost importance in obtaining a thick chromized layer on the surface of ferrous substrates.

The transformation of the iron from the alpha to the gamma phase can be prevented by the addition of certain alloying elements including aluminum, silicon, titanium, molybdenum, columbium (niobium), phosphorus, tantalum, vanadium, tungsten and zirconium. However, it has been found that aluminum, silicon and titanium are the most satisfactory alloying agents for this purpose since they have no deleterious effects on the ferrous substrate. The effects of these alloying agents in the prevention of the transformation from the alpha to the gamma phase are clearly shown in the accompanying drawings. Referring to FIG. 1, this phase diagram shows that the gamma phase does not exist at all in alloys containing more than approximately 2 atomic percent of aluminum. FIG. 2 shows that the gamma phase does not exist in iron-silicon systems having more than $2\frac{1}{2}$ atomic percent of silicon. Similarly, FIG. 3 shows that the gamma phase does not exist in iron-titanium alloys having more than approximately 0.8 atomic percent of titanium. Thus, it is clear that the addition of very small amounts of these alloying elements completely prevents the existence of iron in the gamma phase which allows the diffusion of chromium into the ferrous substrate to take place at the high rate indicated in Table I above.

In order to produce chromized surfaces of substantial thickness on metal substrates by means of this invention, it is contemplated that both the prevention of the formation of chromium carbide and the transformation of iron from alpha to the gamma phase be achieved. There are many known substances that will react preferentially with carbon to form carbides, and it is contemplated that either the carbon will be removed by decarburization or that one or more of these substances will be added to the coating formulation. In addition to the above, it is contemplated that the coating formulation will contain one or more of the many known substances that will prevent the transformation of iron from the alpha to the gamma phase. However, it has been discovered that certain metals such as for example, aluminum, silicon and titanium will perform both functions in a satisfactory manner; and in such a case, only one additive will be included in the composition provided that this additive will accomplish both of the desired functions.

This invention will now be described further with reference to specific examples illustrating the process including specific examples of coating compositions which result in the provision of chromium alloy coatings of thickness up to 20 mils on ferrous substrates under the given conditions.

Example 1

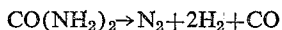
The object to be coated is embedded in a mixture consisting of reactive and inert ingredients in an airtight, heat resistant reaction chamber. The ingredients consist of the following:

	Percent
Chromium powder	15 to 30
Silicon powder	1.5 to 9
Ammonium halides	2.5 to 10
Urea	0.5 to 5
Inert filler material	45 to 80

The ingredients are evenly mixed and charged into a heat resistant alloy chamber and the object to be coated is properly embedded in the mixture, care being taken to assure contact of the mixture with all surfaces to be

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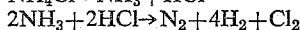
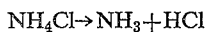
coated. The reaction chamber is then sealed with sealing materials as described below, and the chamber is heated to initiate the reaction. As the chamber is heated past the temperature of 132.7 degrees centigrade, the urea melts and upon further heating vaporizes and decomposes to form nitrogen, hydrogen, and carbon monoxide according to the following equation:



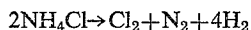
The evolved gases expell the air from within the reaction chamber, and fill it with inert and reducing gases which effectively prevent any oxidation from taking place within the chamber. Excess gases can escape through the sealing materials as the latter become molten when the reaction chamber is heated to operating temperature.

The sealing material preferably comprises mixtures of chromium oxide, iron oxide, carbon and glass powders, adjusted to melt at a temperature between 1400 and 1600 degrees Fahrenheit, which is slightly lower than the reaction temperature maintained during this process. For this reason, the seal is molten during the reaction process, and therefore the evolved gases are held under pressure greater than atmospheric but the excess gas can escape during the coating process. However, when the coating process has been completed, the chamber is allowed to cool, the seal solidifies preventing the entrance of oxygen during the cooling period, thereby preventing any oxidation from occurring at any time during the cycle.

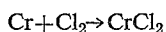
As the reaction chamber is further heated the ammonium chloride decomposes to form chlorine, nitrogen, and hydrogen according to the following equations:



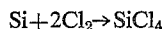
or



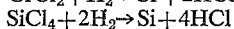
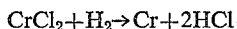
The chlorine, in gaseous form, then reacts with the chromium powder in the pack to form chromous chloride according to the following equation:



Similarly, the gaseous chlorine at elevated temperature reacts with the silicon metal in the pack to form silicon chloride according to the following equation:



As the heating continues to about 1750 to 2250 degrees Fahrenheit, the silicon and chromium chlorides which have been formed in the pack adjacent to the metallic surface of the object to be coated come in contact with the surface. Since these halogen compounds of chromium and silicon are unstable, they will be reduced upon contact with the hot surface of the object to be coated in an atmosphere containing hydrogen according to the following equations:

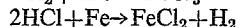
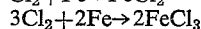
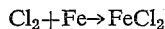


Thus, it may be seen that both metallic chromium and silicon are liberated at or adjacent to the surface of the object being coated. Since both chromium and silicon are soluble in and reactive with iron, these elements will diffuse into the ferrous substrate forming solid solutions, and intermetallic compounds depending upon the local temperature and concentration existing. As the silicon diffuses inwardly in the iron, it preferentially combines with the carbon which, at these temperatures, is diffusing outwardly, forming carbides which will not interfere with the inward diffusion of the chromium. At the same time, the presence of silicon at or near the surface raises the critical point A_3 and therefore prevents the transformation of iron from the alpha to the gamma phase at or adjacent to the surface, further promoting the inward diffusion of chromium to form a thick case of chromium rich alloy at the surface of the substrate.

At the same time the above reactions are occurring, the

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chlorine liberated by the thermal decomposition of the chromium chloride and the silicon chloride and ammonium chloride will tend to react with the iron according to the following equations:



The ferrous and ferric chlorides formed by the above reactions are gaseous at the existing temperatures, and tends to pass off with the hydrogen, nitrogen, and other gases formed during this reaction.

The above reaction can be continued until a chromium rich coating of approximately 20 mils of thickness has been deposited on the substrate. During this entire time, the glassy reaction chamber seal will be in the liquid phase, and the various gases formed by the above reactions, including nitrogen, hydrogen, chlorine, carbon monoxide and others, will be partially removed from the reaction scene by bubbling through the molten seal.

After this sufficient coating has been completed, the reaction chamber is allowed to cool. As soon as the temperature of the reaction chamber drops, the seal will solidify preventing the entrance of air or oxygen into the reaction chamber, thereby preventing oxidation of the reactants of the chamber at elevated temperatures. After the entire chamber has cooled to room temperature, the seal may be broken and the coated object removed from the pack. After the object has been cleaned by brushing, sandblasting, or other suitable means, it will be found that it is completely covered with an adherent, coherent chromium rich case of high uniformity and integrity, which is greatly superior to any chromized case which has been heretofore obtained by previous methods.

Example II

The object to be coated is embedded in the reaction chamber in a mixture of the following composition:

	Percent
Chromium powder	15 to 30
Aluminum powder	2 to 10
Ammonium halides	0.5 to 6.0
Urea	0.5 to 5.0
Inert filler material	50 to 80

The chamber is then heated to the temperature given above and as described in Example 1. This results in a chromium-silicon-iron alloy coating approximately 20 mils in thickness.

Example III

The object to be coated is embedded in a mixture consisting of:

	Percent
Chromium powder	15 to 30
Titanium hydride powder	2 to 10
Iodine	1/2 to 6
Urea	1/2 to 5
Inert filler material	50 to 80

The procedure as given in Example I is followed: This results in a chromium-titanium-iron coating of approximately 20 mils in thickness.

While the above examples have been given in terms of the packing process, the formulae given above are equally useful when applied to the so-called "vapor plating" process. In this case, the same formulae would be used, with the omission of the inert filler material. The object to be coated is placed inside a closed heat-resistant reaction chamber, together with a quantity of the reactive material or the reactive material can be introduced into the reaction chamber from an outside generator and the chamber sealed as described above. As the temperature of the chamber is raised toward the reaction temperatures, the volatile components of the reaction mixture break down, forming inert gas, flushing out the air contained in the chamber as described above. As the temperature nears

the reaction temperature, the chromium bearing compounds decompose and fill the reaction chamber with reactive vapor which decomposes on the surface of the object to be coated, building up the chromium alloy coating. In all other respects, the vapor plating process will be carried out in a manner identical to that described above.

The results of the coatings of this process produce chromium alloy coatings which are thicker, more uniform and in other ways more satisfactory than the coatings heretofore produced by the known methods. For example, Table II, reproduced below, shows the results of coatings of several samples of steel with pure chromium by the pure unalloyed chromium by the methods heretofore used, compared to samples of the same steels coated with chromium alloys as described by the above process.

TABLE II

Substrates	Coating Thickness in Mils			
	Chromium	Chromium-Aluminum	Chromium-Silicon	Chromium-Titanium
AISI 1020-----	0.5	22.0	12.0	18.0
AISI 304-----	3.0	10.0	4.0	9.0
AISI 310-----	2.0	6.0	3.5	5.0
AISI 430-----	2.0	25.0	30.0	15.0

It thus may be seen that although AISI 1020 steel can be coated with a maximum of approximately 0.5 mil of chromium by the known processes, the addition of aluminum increases the thickness of the chromium coating to 22 mils, the addition of silicon increases the coating to 12 mils, and the addition of titanium increases the coating to a thickness of 18 mils. It is clear that thicker and more satisfactory coatings can be applied by the process embodying this invention.

While there has been shown and described the pre-

ferred form of mechanism of this invention it will be apparent that various modifications and changes may be made therein, particularly in the form and relation of parts, without departing from the spirit of this invention as set forth in the appended claims.

We claim:

1. The process of coating a ferrous metal object comprising the steps of heating said object in a reducing atmosphere in contact with a volatile compound of chromium and a volatile reactive compound of titanium, said volatile reactive compound of titanium being present in a quantity sufficient to combine with the carbon in the surface layer of said object and to leave an excess of at least 2.0%.

2. The process of coating a ferrous metal object comprising, in combination, the method steps of embedding said object in a mixture of metallic chromium, metallic titanium, said titanium being present in a quantity sufficient to combine with the carbon in the surface layer of said object and to leave an excess of at least 2.0%, a volatile halide and an inert filler in a closed reaction chamber, sealing said chamber and heating the same to a temperature of from between 1700 to 2300 degrees Fahrenheit.

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