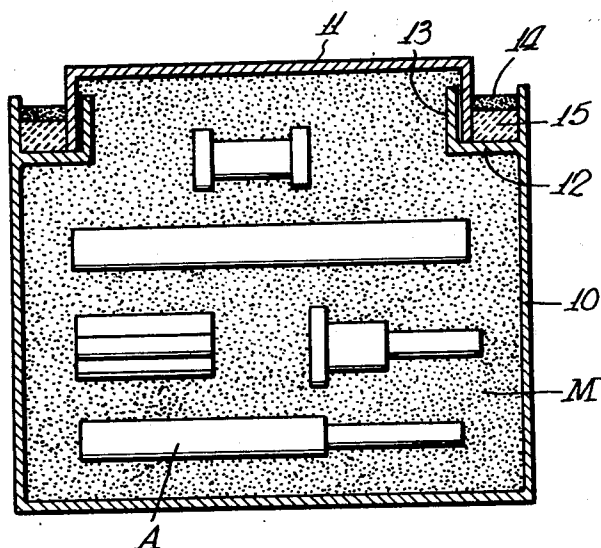


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R. L. SAMUEL
PROCESS OF COATING FERROUS METAL
AND HEAT PACK MIXTURE THEREFOR
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INVENTOR
Robert Lionel Samuel
BY
Dean Fairbank & Hirsch
ATTORNEYS

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PROCESS OF COATING FERROUS METAL
AND HEAT PACK MIXTURE THEREFORRobert Lionel Samuel, New Eltham, England, as-
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The present invention was developed more especially for the effective diffusion of chromium by heat treatment into the surface of articles of steel or other ferrous material embedded in a mass that serves as the source of chromium.

It is a general object of the invention to provide a heat treatment process which lends itself to the chromizing or chromium alloying by diffusion not only of low carbon steel but also of high carbon steel with diffusion of a substantial amount of chromium to a substantial depth into the surface of the steel or other ferrous article in a relatively short period of treatment, in order to afford a product that has a substantially continuous, non-porous skin of chromium-alloy that renders the article corrosion resistant, wear resistant, resistant to thermal oxidation or scaling on exposure even to temperatures such as are incurred in furnaces and heat engines, which process imparts improved non-galling properties substantially to preclude seizure and results in no noticeable change in the size or dimensions of the article as a consequence of the treatment; which process does not impair the ductility and cold workability of cold carbon steel sheets, though the effective diffusion layer be up to 0.10 inch deep; and as applied to high carbon steel and even to cast iron provides a surface which is hard and abrasion resistant and has a low coefficient of friction.

Where heat treatment for chromium diffusion into steel articles is performed in an atmosphere essentially of hydrogen in order to preclude oxidation, the reducing effect may be so intense as materially to decarbonize and thus impair the steel being treated, so that such process at best lends itself only to the treatment of low carbon steel. Moreover, the source of chromium in which the article to be treated is embedded would have to be granular rather than in powder form in order to afford an open path of flow for the hydrogen gas admitted into the gas-tight retort required for the purpose, and since such granular particles present a relatively small effective surface area as compared to the surface area of a powder, the efficiency of chromizing is relatively low.

Where such heat treatment of the steel article is conducted in a gaseous medium containing chlorine released from bleaching powder or the like, which bleaching powder, together with the ferro-chrome or other source of chromium embeds the article within the sealed pack to which the heat treatment is applied, the migration of chromium from the ferro-chrome to the surface

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being treated becomes inhibited, if not entirely arrested after but a relatively short period of heat treatment, since the ratio of ferrous chloride to chromous chloride progressively increases and correspondingly slows down the reaction according to the law of mass action, so that at best but a mild chromizing action of limited efficacy could be attained.

It is one of the objects of the invention to overcome the aforementioned objections to chromizing in the pack and this by resort to a new packing mixture which functions for sustained chromium diffusion into the ferrous article, substantially throughout the period of high temperature treatment and which diffusion is continued even during the ensuing cooling of the pack.

According to one feature of the invention the packing mixture used includes a substantial proportion of an adsorbent or absorbent clay, preferably unbaked, unvitirified kao'in which effectively absorbs or fixes the reaction-inhibiting ferrous halide vapor formed as the reaction product of the chromizing action, or fixes the ferrous element of such vapor and thus effectively removes the ferrous halide from the zone of action with resultant sustained and uninhibited chromizing action throughout the effective period of heat treatment.

According to another feature, the chromium halide formed in the pack and which effects an interchange of iron for diffusion of metallic chromium into the surface of the article to be treated, is of character such as to become less rather than more stable as the pack is cooled and thus to decompose at such time, for release of further metallic chromium, much of which will diffuse into the said article, chromium diffusion thus taking place not only during the heating period in which the chromium halide gives up its halogen to the iron, but after such heating has been discontinued further chromium is released by decomposition of the remaining chromium halide.

Resort to any halogen that has an effective affinity of formation with chromium assures migration of the resultant chromium halide in vaporous form to the surface of the article to be chromized. This known fact suggests the use of the chloride and possibly the bromide or even the fluoride since these form stable chromous compounds. Iodine, however, as by far the least reactive of the halogens, would be ruled out as too unstable for the purpose, wholly aside from its greater cost as compared to chlorine.

The invention from one of its more important

aspects, is based on the discovery of the paradox that while chlorine, bromine and fluorine combine with chromium to form chromous halides that are stable, the reaction of chromium and iodine is quite different in being reversible, yet chromous iodide is found to be sufficiently stable for migration of its vapor as such to the surface to be chromized under the high temperatures at which the process is performed, but becomes unstable at lower temperatures and thus readily decomposes in the cooling operation for the desired further diffusion of chromium into the article to be chromized and the deposition of the iodine for further vaporization thereof in the next cycle of heat treatment.

Moreover, iodine which in absolute value is the weakest halogen in its inter-reaction with chromium, was found to be by far the strongest in relative value of inter-reaction to the equivalent ferrous halide for which reason iodine reacts much more readily than do the other halides for more efficient transfer thereof from chromium to iron during heat treatment.

Thus with the use of iodine there is not only a much more pronounced rate of migration and delivery of chromium for chromium diffusion into the articles being chromized, but chromizing is continued by decomposition of chromous iodide during cooling of the pack. If during heat treatment constant withdrawal of the iron iodide is also effected from the zone of action by resort to unbaked, unvitriified kaolin or the like in the manner above noted, the efficiency of chromium is further enhanced.

Aside from effecting the removal of all free oxygen from the pack before migration of chromium compound vapor to the surface to be treated, it was discovered that the chromium diffusion is retarded if the minute film of oxygen is not first removed, that almost invariably remains or forms upon the steel surface to be treated preparatory to introducing it into the pack, and regardless of the thoroughness with which it has been cleaned. To this end, according to one feature of the invention, the atmosphere in which the chromium diffusion is conducted should not merely be inert, but should be of somewhat reducing character.

According to the invention from one of its aspects, the desired expulsion of both free and combined oxygen from the pack is attained by vaporizing within the pack an ammonium salt and specifically ammonium iodide, which furnishes both the desired reducing atmosphere and iodine vapor for forming the chromium iodide above referred to. Ammonium iodide volatilizes readily at temperature as low as 200° C. and thus expels from the pack the air with its free oxygen. Beginning at about 300° C., the ammonium iodide decomposes into ammonia gas and hydriodic acid. Beginning at about 450° C. the ammonia gas breaks up into nitrogen and nascent hydrogen to afford an atmosphere of sufficient but not more than sufficient reducing effectiveness to remove objectionable oxide film from the articles to be chromized. This reducing effect is promoted by the inclusion in the packing mixture of a moderate proportion of silicon or potassium bichromate, each of which acts as a primer or starter or to activate the surface of the steel article to promote removal of the oxygen film and help to initiate and sustain the chromizing action.

Only after the reducing atmosphere has been created does the hydriodic acid effectively decompose in the pack at a temperature in the neigh-

borhood of 700° C. to release free iodine which combines with the chromium to produce the desired chromous iodide vapor. Hydrochloric and hydrobromic acids on the other hand are much more stable and do not effectively decompose at the required temperature to form an adequate source of halogen for purposes of the present invention, wholly aside from their corrosive effect as compared to iodine.

According to another feature, the ammonium iodide is incorporated into the compound in but a small proportion, not much more than that required to release the iodine needed for migration of the amount of chromium to be diffused into the steel during the cycle of operation.

While iodine by reason of its solidity at ordinary temperature, could easily be introduced into the pack as such to serve as the source of iodine vapor for carrying on the chromium diffusion process, its lack of reducing effect spells lowered efficiency in the absence of some source of reducing agent to be used concurrently therewith.

The use of ammonium iodide as the sole source of both iodine and nascent hydrogen, the latter to serve as the reducing agent, while feasible, does not ordinarily lead to optimum results, because where it is employed in amount adequate to afford the desired amount of iodine vapor, it might release too much nascent hydrogen with excessive reducing effect and consequent slight impairment in the chromium diffusion action.

Accordingly, it is another feature of the invention to use as the air expellant and as the required source of iodine and of hydrogen, a mixture of ammonium iodide and elemental iodine.

Another feature of the invention is to preclude the objectionable escape of the active volatile reagents from the pack during the chromium diffusion treatment without blocking escape of the air from the pack during the initial stages of heating and automatically to effect a hermetic seal of the pack upon cooling thus to preclude admission of air during the cooling period following the heat treatment and during which the gas pressure within the pack drops rapidly.

According to the invention, fusible silicate is deposited between the case and the rim of its cover of the pack which will not block the escape of air and gas in the low range of temperature when the ammonium iodide vaporizes. When such temperature has been reached as to fuse the silicate, a liquid seal is formed which sustains the small pressure evolved by the decomposition of the small amount of ammonium iodide and the vaporization of the iodine used. The silicate hardens during cooling of the closed pack and thereafter precludes entry of air. Refractory cement is placed under the fusible silicate to preclude flow of such silicate into the pack.

By reason of the great enhancement in intensity and duration of effective chromium diffusion effected by the invention during the period of heat treatment in the pack at heat treating temperature, by reason of the further chromium diffusion effected during cooling of the pack and by reason of the release of only enough hydrogen in the pack to promote the reaction and in amount insufficient to decarburize the steel being treated, the depth and integrity or continuity of the chromium diffused layer are greatly enhanced both in treating low carbon steel and in treating high carbon steel, the surface characteristics of which are greatly improved without in anywise impairing the steel structure. Instead of effective chromium diffusion to a depth of but 0.001

inch, diffusion is accomplished by the present invention to ten times that depth with low carbon steel of 0.10 percent carbon content, and this depth tapers off for higher carbon steels but even for steel of 1.0 percent carbon content, the effective depth of chromium diffusion is .002 inch. In usual practice, the chromium content at the exterior or skin of the article is as high as 50 percent and below the effective outer chromium layer, there is a region of comparable thickness with more diffuse chromium content.

With low carbon steels the chromium diffused layer produced by the present process is quite ductile and reasonably soft, so that sheets of low carbon content thus chromized can be bent, pressed and stamped with ease as well as cold rolled to considerable elongation. The chromized layer produced by the present process on high carbon steel is very hard, due apparently to alloying of chromium and carbon, is highly resistant to abrasion, has low coefficient of friction and is much less ductile than the layer on low carbon steel.

According to another feature, the presence of a small proportion of silicon in the packing mixture is effective to produce a barrier within the steel article by diffusion of the silicon before diffusion of the chromium and thereby to aid in producing a relatively uniform depth of chromium diffusion and a uniform outer layer or skin of chromium, devoid of porosity.

Since the process functions essentially by exchange of iron near the surface of the article being treated with chromium, the chromium diffused product is no different in dimensions from the original article before treatment. This feature is important especially in the treatment of such articles as shafts, pistons, gun barrels, screws, nuts and the like in which tolerances are held very close.

By the process set forth there is thus produced a steel article, the chromium layer or skin of which is substantially devoid of porosity, is corrosion resistant, wear resistant and resistant to thermal oxidation or scaling on exposure even to high temperature and has excellent non-galling properties that substantially preclude seizure.

The process is therefore applicable in a wide variety of fields which may roughly be divided into three main groups:

(a) Where corrosion resistance is required, such as for mudguards, bumpers, bolts and nuts for motor vehicles, tubes, blades and castings for steam turbines, water and steam pipes and fittings, cylinder blocks and heads and the water cooling system of the internal combustion engines;

(b) Where heat resistance is required such as for the exhaust manifolds of air cooled engines, valves and valve seats for internal combustion engines, blades for gas turbines and fittings for gas turbines and boilers;

(c) Where wear resistance is required alone or in addition to heat resistance, as for instance in gun barrels, especially for high speed projectiles and the like, cylinder blocks and cylinder linings for engines and the like.

The invention has an important application in the treatment of articles of stainless steel by the procedure herein set forth, in that it greatly improves the wear resistance and the galling or seizure characteristics of such articles and imparts thereto a surface of hardness far superior to that attained by ordinary heat treatment, and in fact

a hardness in the order of Vickers 1000 which corresponds to approximately Rockwell C70.

While each of various features above recited may be used alone to the extent defined by the claims, it is preferred in practicing the invention to utilize most or all of said features in combination. The invention in a specific embodiment accordingly involves embedding the articles to be treated in a powder within a heat treatment pack such as shown in the drawings, said powder comprising a source of chromium such as ferro-chromium, a mass to fix and receive from the zone of reaction the ferrous halide or the ferrous element thereof produced in the chromizing reaction and consisting essentially of non-baked, non-vitrified kaolin or the like, a source of halogen (preferably iodine), and reducing agent to be generated in situ within the pack, the preferred such source being ammonium iodide preferably with some added elemental iodine, the ammonium iodide and iodine being present in but small proportion, to release little more iodine vapor than needed for producing that amount of chromium iodide that suffices for the desired chromium diffusion during heating and to release further chromium by decomposition of the remaining chromium iodide during cooling.

The present application is a continuation in part, of my co-pending application Serial No. 59,199, filed November 9, 1948, now abandoned.

Further to aid those skilled in the art to practice the invention, a few specific examples of applications of the process will now be set forth.

In the accompanying drawing the figure shows one embodiment of the chromizing pack.

A preferred packing mixture desirably used in powdered form to give greater surface of exposure and is feasible since the reactive atmosphere is formed in situ, is the following:

	Per cent
Ferro-chromium	65
Iodine	0.1
Ammonium iodide	0.25
Unbaked, unvitrified kaolin.....	Balance to 100

While a wide variety of the alloys generally known as ferro-chromium may be used, the best results are attained if that alloy contains 50 to 70 per cent and preferably about 65 per cent of chromium, 0.1 per cent of carbon and about 4 per cent of silicon, the rest being iron.

The presence of four (4) per cent of silicon in the ferro-chromium or about 2.7 per cent of silicon to the weight of the entire packing mixture powder is not critical but may be increased to 8 or 9 per cent of the weight of ferro-chromium or to from 5 to 6 per cent of the weight of the packing mixture. Any larger proportion of silicon is undesirable as leading to embrittlement. The silicon component apparently diffuses into the article before chromium diffusion commences and in some way, not clearly understood by me, improves the integrity of the chromium alloy skin formed and also forms a thin barrier within the structure that promotes uniformity in the depth of chromium alloy diffusion.

Where potassium bichromate is used instead of silicon to act as a primer or starter, it should be in amount not less than 2.5 per cent of the packing mixture, but if more than 5 per cent were used objectionable oxidation of the ferro-chromium might result.

The articles A to be treated are embedded in the powdered packing mixture M within a suitable refractory container 10. Desirably the container

has a flanged cover 11 resting on an inturned ledge 12 in the container flanged at 13 on which rests a mass of fusible silicate 14, which fills the space between the flange of the cover and the wall above the ledge 12 of the box.

As the box is heated in the furnace, the gases generated due to vaporization of the ammonium iodide cause expulsion of the air from the box and when a temperature in the order of 700 or 800° C. is reached, the fusible silicate melts and forms an effective liquid seal that sustains a pressure slightly above atmosphere and sustains the pressure evolved in the decomposition of the small amount of ammonium iodide and the vaporization of the small amount of elemental iodine when the latter is used.

When the box cools to below 700° C., the silicate freezes almost instantly and forms a non-porous barrier capable of withstanding the pressure differences between the atmosphere and the rapidly contracting gases in the box, so that no air can enter until the pack is opened.

Preferably the fusible silicate rests on a layer of refractory cement 15 therebelow which serves to prevent the flow of still liquid silicate into the box during the initial contraction of gases when the box is cooling off.

In practicing the process on low carbon steel structures, a heating period of as little as four to eight hours and a temperature in the range of 900° C. to 1300° C. being sufficient, the optimum temperature in general being 1050° C., the length of this period and the temperature used determining the depth of the desired chromium diffusion.

For high carbon steel of more than .4 per cent carbon and up to 1 percent carbon, the chrome diffusion is preferably conducted at a temperature from 30 to 40° lower than that specified above for low carbon steels, but otherwise the process is the same.

For chromium diffusion of cast iron articles with carbon content up to 4.5 per cent, the time of treatment is from 8 to 12 hours, the temperature range being from 800 to 1000° C., the optimum being about 900° C.

The packing mixture described may be used over and over again for chromizing a sequence of articles or batches of articles, provided that part of the used packing mixture be replaced after each operation with fresh mixture to the extent of about 10 per cent of the mass.

A modified packing mixture that effects considerable economy of ferro-chrome, may advantageously be employed but has the limitation of not admitting of re-use but would usually be discarded after but a single chromizing treatment.

In such mixture the drastically reduced quantity of ferro-chromium is replaced by copper powder which acts as a catalyst to block the formation of ferrous iodide and therefore renders possible the use of less than the minimum of 30 per cent metallic chromium in the packing mixture heretofore found best.

An illustration of the modified formula is as follows:

	Per cent
Ferro-chromium	10 to 20
Copper powder	20 to 40
Ammonium iodide	0.25
Iodine	0.1
The balance of kaolin	

The copper powder having catalytic action only

with iodine, the mixture specified is not useful with any other halogen.

The ferro-chromium used in this packing mixture is preferably about 65 per cent chromium, 4 per cent silicon and 0.1 per cent carbon.

The process of the present invention is not limited in its applicability to the chromium treatment of ferrous articles, but is useful also for the treatment of other metals of the iron group such as nickel and cobalt and alloys thereof as well as to the treatment of such metals with other coating or protection metals of the chromium group, notably tungsten and molybdenum, and it is also useful in the treatment with other metal or mixture of metals including copper, aluminum, manganese, titanium or zirconium or mixtures of some or all of such metals. It is understood that for such other applications the ferro-chromium in the packing mixture would be replaced by metals including metal to be treated and the treating metal or metals.

An illustration of one specific compound that affords remarkable heat and oxidation resistance and effects simultaneously diffusion of chromium, silicon and aluminum, is of the following specifications:

	Per cent
Ferro-chromium { Chromium = 65 % Silicon = 4 % Carbon = 0.1 % Balance iron }	60
Silicon-aluminum { Silicon = 50 % Aluminum = 50 % }	12
Ferro-silicon { Silicon 75-80 % Balance iron }	8
Ammonium iodide	0.25
Iodine	0.10
Kaolin	Balance to 100

The proportions of components are not strictly critical but a variation of 2 to 3 per cent in the amounts of each of the components of the ferro-chromium and the silicon-aluminum is permissible and of 1 to 1.5 per cent in the component of the ferro-silicon.

With the mixture above set forth, the resulting coating is deeper than the normal chromium diffusion and in fact penetrations up to .030 inch are obtainable on any steel, low carbon or high carbon, which permits subsequent grinding to very close tolerances. Such coating shows the following average analysis:

	Per cent
Chromium	16
Silicon	8
Aluminum	3 to 4
Balance is iron	

As many changes could be made in the above process, and many apparently widely different embodiments of this invention could be made without departing from the scope of the claims, it is intended that all matter contained in the above description or shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense.

Having thus described my invention, what I claim as new and desire to secure by Letters Patent of the United States is:

1. A heat pack mixture powder for the chrome alloying of the surface of a ferrous structure, said powder comprising ferro-chrome of approximately 65 percent, ammonium iodide approximately 0.25 per cent, elemental iodine approximately 0.1 per cent and unbaked kaolin approximately 35 per cent.

2. In a process of applying a metal selected from the group consisting of chromium, tungsten

and molybdenum to a ferrous metal structure by the steps of embedding and enclosing said structure in powdered material, which material consists essentially of such metal, iron, a source of gaseous halogen and a refractory substance, and heat treating the embedded structure in an atmosphere substantially free from oxygen; the combination in which the refractory substance is unbaked, unvittrified kaolin, the source of gaseous halogen is selected from the group consisting of iodine and ammonium iodide, and the heating step is carried out at a temperature between 800° and 1300° C. for from 4 to 12 hours.

3. The process recited in claim 2 in which the source of gaseous halogen is ammonium iodide together with a small proportion of elemental iodine.

4. The combination recited in claim 2 in which the metal to be applied to the ferrous metal structure is chromium, the powdered material contains in the order of 50 to 65 per cent of ferro-chromium and the source of gaseous halogen is about 0.25 per cent of ammonium iodide and about 0.1 per cent of iodine.

5. The process recited in claim 2 in which the metal to be applied to the ferrous metal structure is chromium, in which the powdered material consists of approximately two parts by weight of ferro-chromium to one part by weight of unbaked, unvittrified kaolin and minor proportion of ammonium iodide.

6. The combination recited in claim 2 in which a primer, selected from the group consisting of silicon and potassium bichromate, is included in the powdered material.

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7. The process recited in claim 6 in which the primer component of the powdered material is 2.7 to 6 per cent of silicon.

8. The process recited in claim 6 in which the primer component of the powdered material is 2.5 to 5 per cent of potassium bichromate.

ROBERT LIONEL SAMUEL.

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