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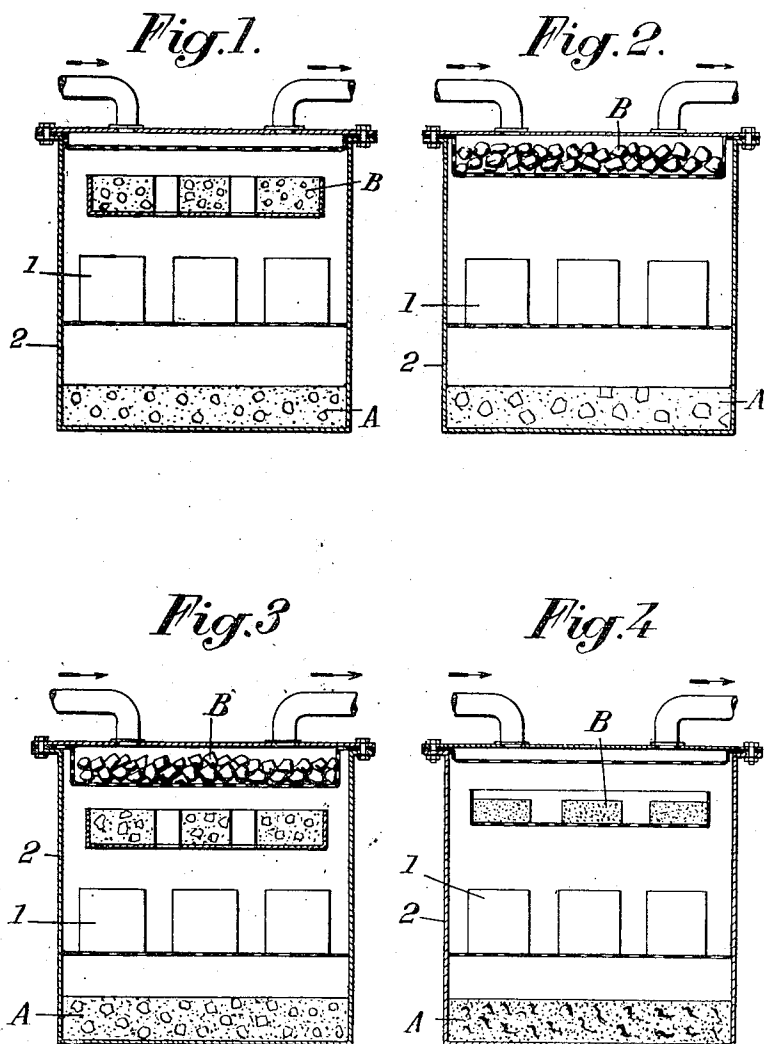
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2,801,187

METHODS FOR OBTAINING SUPERFICIAL DIFFUSION
ALLOYS, IN PARTICULAR CHROMIUM ALLOYS

Filed Nov. 28, 1951

2 Sheets-Sheet 1



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2 Sheets-Sheet 2

Fig. 5.

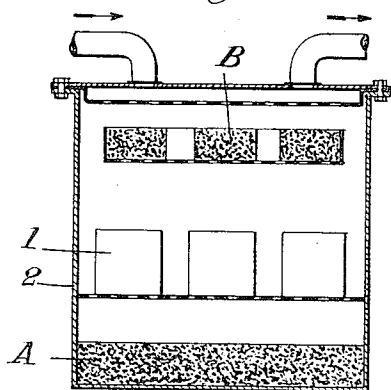


Fig. 6.

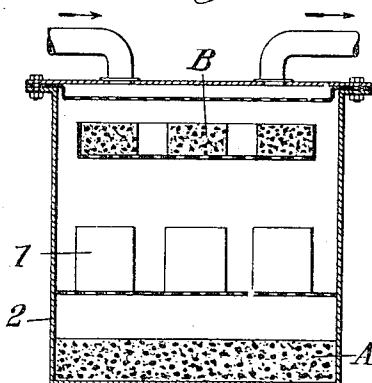
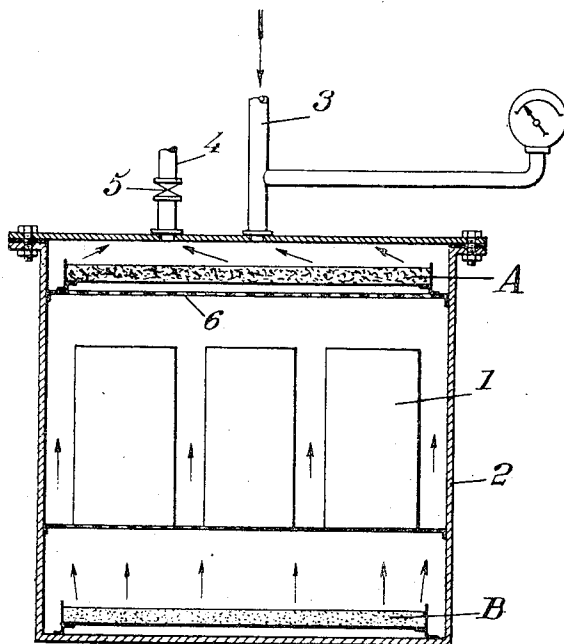


Fig. 7.



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METHODS FOR OBTAINING SUPERFICIAL DIFFUSION ALLOYS, IN PARTICULAR CHROMIUM ALLOYS

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6 Claims. (Cl. 117—50)

The present invention relates to methods for obtaining on metal pieces superficial diffusion alloys of the metal of said pieces with an addition metal, in particular chromium alloys.

It is known that superficial diffusion alloys can be obtained on metal pieces by the action on said pieces of a halide of the addition metal obtained from a cementing material containing either said addition metal halide in the solid or liquid form or the solid or liquid components necessary for forming said halide, said cementing material being placed in the treatment container out of contact with the piece to be treated and the whole being heated to a suitable temperature for disengagement of said halide.

However, whereas a cementing material, as above defined, is capable by itself and merely under the effect of heat, of giving off an addition metal halide, it is known that there are other possible sources of such a halide. For instance a mass of the addition metal, placed in a treatment container where halide vapors have already been produced by a cementing material, may be attacked by the vapors of a halogen acid resulting from the action of said halide vapors on the metal of the piece in treatment, to form a halide of the metal of said mass. In the following description and claims, such a source of an addition metal halide will be distinguished from a "cementing material" because it yields a halide only when placed, in a treatment container, in the presence of vapors of a halogen acid, whereas a "cementing material" only requires the action of heat to disengage an addition metal halide.

According to my invention, I make use, for obtaining superficial diffusion alloys on pieces in treatment, of two distinct halide sources capable of giving off under the effect of heat in the treatment container, at least two different halides, one of which is a fluoride, and these two sources are located in two distinct zones of said container, one of said zones being above the piece in treatment.

Preferred embodiments of my invention will be hereinafter described with reference to the accompanying drawing, given merely by way of example, and in which:

Figs. 1 to 6 are diagrammatic vertical sections of treatment ovens according to my invention, showing the arrangement of the pieces to be treated and the various materials used.

Fig. 7 is a similar view of a modification.

I will first consider the case where it is desired to obtain, in the superficial portion of a metal piece, a diffusion alloy of the metal of this piece with at least two metals.

According to my invention, the elements of formation of said halides are localized in at least two zones A and B of a treatment oven 2 (Figs. 1 to 6) in which the pieces 1 to be treated are so disposed as to have no contact whatever with the cementing material, at least one of these zones, for instance B, being located above zone A.

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The use of several sources of addition metal halides disposed as above indicated inside the treatment oven has several advantages:

The addition metal halides, which are located in the atmosphere of the oven already made homogeneous by thermal stirring due to the high temperature of treatment (from 800 to 1300° C.), are still more uniformly distributed.

It is possible, by distributing them in different zones, to make use of different halides for the different addition metals, without mutual soiling of the cementing materials by one another;

It is also possible to make use of different reactions to form the halides of the different metals which are to be diffused and thus to obtain, for metals having very different physical and chemical properties, a continuous and suitable production of the halides through which they are conveyed.

The reactions to be employed for forming the halides of the addition metals other than chromium vary according to the physical and thermo-dynamic constants of the metals in question and their halides (melting point and boiling point in particular).

Concerning the diffusion temperature, a distinction is to be made between the addition metal halides according to their volatility.

I will call "volatile halides" those having a boiling point lower than the temperature required for the treatment. These are in particular, when the pieces to be treated are made of ferrous metals, silicon, aluminium, titanium, molybdenum and tungsten halides.

I will call "little volatile halides" those having a boiling point higher than the temperature of treatment, that is to say, in the case of pieces of ferrous metals, most of the nickel, chromium and cobalt halides.

In the case of volatile halides, it is necessary to achieve progressivity of their formation by the action on the diffusion metals of a compound formed in a slow and continuous manner in the course of the reaction.

I may obtain this result in different ways.

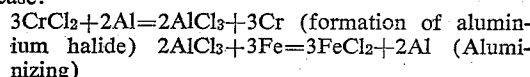
According to one of them, as known, I cause a chromium halide to act on the addition metal in a more or less divided state.

Another way consists, according to a feature of the present invention, in subjecting a reserve of the addition metals, located for instance at the upper part of a treatment oven, to the action of a halogen acid (preferably hydrofluoric acid) formed when chromium is diffused into the pieces to be treated.

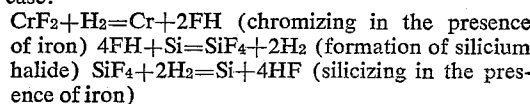
Still another way consists, according to another feature of my invention, in causing the alumina or zirconia which may be present in the cementing material to act upon the chromium fluoride.

In these three cases, metallizing is obtained with the following reactions:

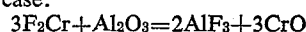
1st case:



2nd case:



3rd case:



These reactions may be produced in ovens as shown by Figs. 1 to 6.

The construction of Fig. 1 is suitable for a reaction of the kind of the first case. The cementing material is distributed at the lower part A and at the upper part B of the

oven. It contains uniformly a chromium cementing mixture, and a metal divided into pieces which may consist of silicon, molybdenum, aluminium-chromium, titanium and so on.

The arrangement of Fig. 2 corresponds to mixed reaction of the first and second cases. At the lower part A of the cementing oven is provided a chromium cementing mixture containing pieces of metal as in the preceding arrangement. At the upper part B of the cementation chamber, there is disposed a reserve of chromium accompanied with addition metals which may be silicon, molybdenum, titanium or aluminium-chromium.

The arrangement of Fig. 3 is also suitable for mixed reactions of the first and second cases. It is analogous to the preceding one, but a reserve of cementing material identical to that located at the lower part of the oven is disposed at the upper part below the reserve B of divided metals.

This kind of diffusion is advantageous to improve resistance to dry corrosion. For this purpose, for instance, mixed chromium-silicium or chromium-aluminium cementations will be produced, the diffusion layers possibly containing also tungsten (preferably to molybdenum) or zirconium.

Thus, by making use of the arrangement illustrated by Fig. 1 and making use of a chromium cementing material and a chromium reserve containing each 5 percent of silicium in pieces, I obtain in four hours at 1050° C. diffusion layers of a thickness of 0.25 mm. protecting the piece against prolonged dry oxidizing at temperatures up to about 900° C.

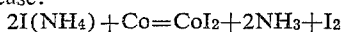
In the case of non-volatile halides, the halide concentration in the atmosphere of the oven is determined by the vapor tension of said halide at the temperature of the diffusion treatment.

These halides may be formed "in situ" through the action of an ammonium halide introduced into the cementing material, on one of the metals the diffusion of which is to be obtained, if the conditions of the reaction can be complied with.

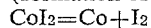
The halides may also be formed in a preceding operation and introduced as such into the cementing material, if the conditions of formation of these halides cannot be obtained in the diffusion oven.

Metallizing is obtained, in these two last mentioned cases, in accordance with the following reactions:

1st case:



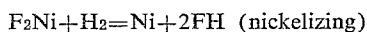
(formation of cobalt halide)



(cobaltizing in the presence of iron)

2nd case:

The formation of nickel fluoride took place in a preceding operation. This fluoride reacts upon hydrogen in the presence of iron as follows:



Several oven arrangements may be used.

The arrangement of Fig. 4 is suitable in the case of a reaction of the kind of the first case. At the lower part A of the diffusion oven 2, there is provided a chromium cementing mixture of the kind including ammonium fluoride, chromium and alumina. At the upper part of the diffusion oven there is disposed a cobalt cementing mixture of the kind including ammonium chloride, cobalt and alumina.

The arrangement of Fig. 5 is also adapted to a reaction of the kind of the first case. The same cementing mixture is disposed at the lower part A and at the upper part B of the cementing oven and it includes chromium, cobalt, alumina, ammonium chloride and ammonium fluoride.

The arrangement of Fig. 6 is suitable for reactions of the kind of the second case. The same cement is dis-

posed at the upper part and at the lower part of the oven. It includes in particular chromium, ammonium fluoride and nickel fluoride.

These diffusion methods may in particular be applied to improve the resistance of ferrous metals to nitric corrosion. For instance mixed layers of nickel and chromium containing a high percentage of nickel, will be formed, preferably with an arrangement as shown by Fig. 6. Layers obtained in six hours at a temperature of 1075° C. by means of a cementing mixture containing chromium, ammonium fluoride and nickel fluoride are perfectly bright and are not attacked after several hundreds of hours by boiling concentrated nitric acid.

The presence of nickel or cobalt is also advantageous to improve the resistance to local pitting under the effect of saline corrosion.

In some cases, for instance when use is made of cobalt and ammonium iodide, with arrangements such as those of Figs. 4 and 5, it is possible to obtain a kind of "cobaltizing" through thermal dissociation of cobalt iodide in contact with the metal treated. A deposit of cobalt is then superimposed on the diffusion alloy of cobalt with iron.

Thus, by making use of a cementing mixture consisting of powdered cobalt, alumina, ammonium iodide and ammonium chloride, it is possible to obtain in one hour at 1025° C. a uniform layer of a thickness of 0.2 mm.

I will now consider the problem of forming a diffusion alloy of a metal, and especially chromium and/or molybdenum, by making use, as agent for conveying this metal, of a halide thereof other than a fluoride.

It is known that when such a halide constitutes the only agent used for conveying the metal, serious difficulties are encountered. In particular, it is difficult correctly to recuperate the halide by means of an auxiliary reserve. On the other hand, dull surfaces of irregular aspects occur on the pieces treated.

These drawbacks may be avoided if the agent used for conveying the metal (which, for the sake of simplicity, will be hereinafter be supposed to be chromium) is the fluoride of this metal, i. e. chromium fluoride. However, in some cases, this solution cannot be adopted.

If the halide to be used cannot, for some reason, be the fluoride (if, in particular, it is the chloride) the drawbacks above mentioned can however be avoided, according to my invention, by maintaining on the piece to be treated, at least until the temperature of treatment has reached the value for which diffusion takes place, a protective layer of iron fluoride.

This process may be applied both when the diffusion action is exerted on a piece wholly out of contact with any solid or liquid substance (this being called the gaseous phase process) and when the piece to be treated is in contact with pieces of regenerating metal, a chromium cementing mixture being present in the oven but out of direct contact with the piece (this being called the semi-contact process).

According to an embodiment of my invention, the protective layer of iron fluoride may be obtained by causing chromium fluoride to cooperate with the halide or halides (other than fluoride) used for conveying chromium, it being well understood that the fluoride and the other halide or halides may be formed through any known method, either in the oven itself or in an auxiliary apparatus.

In particular, referring to Fig. 7, I may introduce simultaneously into the treatment oven 2 a chromium cementing mixture giving birth to a fluoride and a chromium cementing mixture giving birth to another halide or halides, in particular to a chloride and a bromide, since the high cost of iodine compounds and their corrosive action, especially on ferrous metals, generally prohibits the use of an iodide.

In this case, preferably, the two cementing mixtures

are not mixed together and are on the contrary located in distinct zones of oven 2, the cementing mixture A which is to supply the halogen compounds other than the fluoride being then placed in a zone close to the outlet orifice of the oven sweeping gases whereas the fluoride cementing mixture is on the opposite side.

In particular if the gas used for sweeping the oven is hydrogen introduced at the upper part of oven 1 with a slight overpressure through a conduit 3 and evacuated, during the treatment, also at the upper part through a conduit 4 provided with a valve 5, the cementing mixture A may be disposed at the top and the cementing mixture B at the bottom of the oven, pieces 1 being located between these two mixtures (and being possibly surrounded with pieces of chromium or ferro-chromium, in semi-contact processes).

Cementing mixture A may contain fluor compounds and cementing mixture B may be constituted by a mixture of chromium, alumina, ammonium fluoride and liquid hydrofluoric acid.

Thus, at the beginning of the treatment, the hydrochloric and hydrobromic acids and the other chlorine and bromine compounds escape without being in contact with pieces 1 which are only subjected to the action of hydrofluoric acid and the fluorine compounds.

I may provide, between the portion of the oven containing pieces 1 and the cementing mixture B and the portion which contains the cementing mixture A, a porous or perforated partition 6 forming an obstacle between pieces 1 and vapors of hydrobromic or hydrochloric acid.

The sweeping gases are freely evacuated at the beginning of the operation through auxiliary outlet 4, which is closed when the chromium halides begin to have a substantial vapor tension.

The arrows of Fig. 7 represent the circulation of the gases in oven 2 during the heating period.

Of course, if the circulation of the gases through the oven were different, the location of cementing mixtures A and B would be different.

Besides, I may dispose, between cementing mixture A and/or pieces 1 and partition 6, a reserve of chromium or ferro-chromium in pieces.

But I might also, instead of separating cementing mixtures A and B, mix them together, in which case I preferably provide a substantial excess of fluoride in the mixture (more than 60%), whereby the equilibrium is constantly modified toward the formation of iron fluoride during the heating of the oven.

Another solution, for the obtainment of the protective layer of iron fluoride, consists in introducing into oven 2, for instance by mixing with the sweeping gases, an amount of gaseous hydrofluoric acid such that, in the presence of the other halogen acid or acids, the equilibrium tends toward the formation of iron fluoride on pieces 1.

It is then possible to make use of a cementing mixture constituted exclusively by chlorine and bromine compounds, the gaseous hydrofluoric acid being introduced into oven 2 together with the sweeping gas, during the period of heating of the oven.

For instance, an intensive sweeping may be performed while the temperature is still below 350° C. (at which temperature the halogen acids and the ammonium halides are substantially vaporized), after which a reduced sweeping may be maintained at temperatures ranging from 350 to 800° C.

Whatever be the solution that is adopted, it is found, in the case of cementation of ferrous pieces, that iron fluoride, which volatilizes only at temperatures close to 1100°, constitutes at the beginning of the treatment a very fine protective layer on pieces to be treated, whereas the other halogen compounds of iron would be volatile at low temperature (FeCl₃ at about 300° C.,

FeBr₂ at about 600°, FeI₂ at about 250°). In the absence of this protective layer, the action of the halogen acids other than hydrofluoric acid would not be limited at the beginning of the treatment. Now this action results, in vapor phase process, in particular in the case of the chloride and the iodide, in the formation of dull spots and pitting due to localized attacks. In the semi-contact process, pitting is not so intensive but often the addition metal sticks to the treated pieces. It is therefore obvious that the formation of the protective layer of iron fluoride, which makes it possible to avoid these defects, is of high interest.

Of course, the invention is not limited to the formation of iron and chromium alloys.

The pieces to be treated may be made, in particular, of special steels of the following metals: molybdenum, tungsten, nickel, cobalt, titanium and their alloys, and the addition metals, in addition to chromium and molybdenum, may be tungsten, nickel, cobalt, titanium, aluminum or silicon.

It should also be noted that the pieces to be treated may be of all kinds of dimensions and structures, the invention applying as well to cast or machined pieces as to calcined pieces and metallic powders.

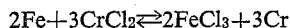
Anyway, the simultaneous utilization of a fluoride compound and of one or several halides, other than the fluoride, of the addition metal makes it possible, in particular owing to the use of chloride and bromide, to reduce the cost of the treatment.

The following advantages result from the method which has just been described.

The simultaneous presence of several halides makes it possible to increase the resultant vapor tension for the chromium halide, whereby, in particular, a better homogeneity can be obtained when the nature of the pieces imposes a relatively low diffusion temperature, for instance from 800 to 900° (case of some kinds of cast iron).

It becomes possible to form the halides according to different types of reaction, for instance by direct introduction or by action on the addition metals of the halogens, the halogen acids, the halides, ammonium and so on.

It is also possible, for the manufacture of precision pieces, to combine halides so as to obtain a good state of surface without substantially modifying the dimensions of the pieces to be treated. This is due to the fact that the addition of chromium by means of the fluoride achieves a perfect surface, but, under certain conditions of sweeping, chromium is added without iron being eliminated. The iron fluoride which tends to form is immediately dissociated under the action of the sweeping hydrogen into iron and hydrofluoric acid. On the contrary, the addition of chromium by means of chloride and bromides takes place without any material modification of the dimensions of the pieces, the corresponding iron halide being eliminated according to the reaction:



Thus, a suitable combination of various halides, one of which is a fluoride, makes it possible considerably to reduce the variations of dimension which occur as compared to those which take place when the fluoride is used alone.

What I claim is:

1. The process of forming on a metal body having iron as a principal component a superficial diffusion alloy with an addition metal selected from the group consisting of chromium, molybdenum, tungsten, nickel, cobalt, titanium, aluminum and silicon which comprises raising the temperature of said iron body to the temperature at which said addition metal is capable of diffusing into said iron body, forming a protective layer of iron fluoride on the surface of said iron body while raising its temperature, and bringing vapors of an addition metal halide other than fluoride into contact with said iron body after

said diffusing temperature has been reached to cause diffusion of said addition metal into said iron body.

2. The process of forming on a metal body having iron as a principal component a superficial diffusion alloy with chromium which comprises raising the temperature of said iron body to the temperature at which chromium is capable of diffusing into said iron body, exposing said iron body to vapors of chromium fluoride while raising said temperature to form a protective layer of iron fluoride on the surface of said iron body, and bringing a chromium halide other than fluoride into contact with said iron body after said diffusing temperature has been reached to cause diffusion of chromium into said iron body.

3. The process of forming on a metal body having iron as a principal component a superficial diffusion alloy with chromium which comprises raising the temperature of said iron body to the temperature at which chromium is capable of diffusing into said iron body, exposing said iron body to vapors of hydrofluoric acid while raising its temperature to form a protective layer of iron fluoride on the surface of said iron body, and bringing vapors of a chromium halide other than fluoride into contact with said iron body after said diffusing temperature has been reached to cause diffusion of chromium into said iron body.

4. The process of forming on a metal body having iron as a principal component a superficial diffusion alloy with chromium which comprises positioning said metal body in a container, positioning in said container at a point spaced above said iron body a first cementation mixture capable on heating of evolving vapors of a chromium halide other than fluoride, positioning in said container at a point spaced below said iron body a second cementation mixture capable on heating of evolving vapors of chromium fluoride, raising the temperature of said container to the temperature at which chromium is capable of diffusing into said iron body, allowing said chromium halide evolved from said first cementation mixture to escape from the top of said container as long as the temperature is below said diffusing temperature, whereby practically only said chromium fluoride vapors evolved from said second cementation mixture contact said iron body at temperatures below said diffusing temperature and form a protective layer of iron fluoride on said iron body, and retaining in said container said chromium halide vapors evolved from said first cementation mixture after said diffusing temperature has been reached which will then contact said iron body and cause diffusion of said chromium therein.

5. The process of forming on a metal body having iron as a principal component a superficial diffusion alloy with chromium which comprises positioning said metal body in a container, positioning in said container at a point spaced from said iron body a cementation mixture capable on heating of evolving vapors of a chromium halide other than fluoride, raising the temperature of said container to the temperature at which chromium is capable of diffusing into said iron body, introducing gaseous hydrofluoric acid into said container only as long as the temperature is below said diffusing temperature sufficient to form a protective layer of iron fluoride on said iron body at temperatures below said diffusing temperatures whereby said chromium halide vapors evolved from said cementation mixture after said diffusing temperature has been reached will then cause diffusion of said chromium into said iron body.

6. The process of forming on a metal body having iron as a principal component a superficial diffusion alloy with chromium which comprises positioning said metal body in a container, positioning in said container at a point spaced from said iron body a cementation mixture capable on heating of evolving vapors of chromium fluoride and of a chromium halide other than fluoride, said cementation mixture being such that the evolved vapors are more than 60 percent chromium fluoride, and raising the temperature of said container to the temperature at which chromium is capable of diffusing into said iron body, whereby said chromium fluoride vapors form a protective layer of iron fluoride on the surface of said iron body while raising its temperature before vapors of the other chromium halide have been able appreciably to attack said surface at temperatures below that at which chromium is capable of diffusing into said body, and said iron fluoride is decomposed when said chromium diffusion temperature is reached so as to enable said other chromium halide then to contact said iron body to cause diffusion of chromium into said body.

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