

UNITED STATES PATENT OFFICE

2,269,601

PROCESS FOR THE MANUFACTURE OF
ARTICLES RESISTANT TO GASEOUS COR-
ROSION

René Perrin, Paris, France, assignor to Societe
d'Electrochimie d'Electro-Metallurgie et des
Acieries Electriques d'Ugine, Paris, France, a
corporation of France

No Drawing. Application April 22, 1939, Serial
No. 269,483. In France June 2, 1934

13 Claims. (Cl. 148—7)

This invention relates to a process for impart-
ing to articles of alloyed metal the property of
improved resistance to corrosion by a given gase-
ous substance especially at high temperatures. It is particularly adapted for rendering iron and
steel articles resistant to corrosion by gaseous
oxygen and sulphur compounds at high tempera-
tures.

The present application is a continuation-in-
part of my application, Serial No. 23,524, filed
May 25, 1935.

It is known that certain alloying elements,
such as aluminum, silicon, chromium and zir-
conium, when incorporated in suitable propor-
tions in alloyed metals (especially in alloyed iron
or steel) impart thereto a considerably increased
resistance to chemical corrosion when exposed
to gaseous substances such as oxygen or oxidiz-
ing mixtures (e. g. air, water vapor or carbon di-
oxide) or to gaseous sulphur compounds (e. g.
sulphur dioxide or hydrogen sulphide) especially
at high temperatures.

Protection against such gaseous corrosion is
generally ascribed to the formation upon the
surface of the alloyed metal, at the beginning of
its utilization, of a film or coating of a metallic
compound which is little or not at all attackable
by the atmosphere in which the said metal is
used; said film or coating serving to prevent said
alloyed metal from being appreciably attacked
subsequently by the corrosive constituents of said
gaseous body. Metallic compounds having the
properties required for this purpose are known
to those skilled in the art. It is known, for in-
stance, that a coating of alumina, formed upon
the surface of an article of aluminum, will pro-
tect the latter from attack by the oxygen of the
air, because, when adherent and of sufficient
thickness, it prevents the base metal from com-
ing into contact with the air. Such protective
coating may be constituted principally of chro-
mium oxide or aluminum oxide when the article
to be protected is made of an alloy of chromium
or aluminum and is to be subjected in use to an
atmosphere containing oxygen at high tempera-
ture. It is understood that the protection affor-
ded by such a film or coating is due not alone to the
chemical nature thereof, but also to its proper-
ties of adherence, compactness and thickness.
The term "base metal" is used herein to desig-
nate the chief component of the alloy (iron or
steel for example) from the alloying metal
(chromium or aluminum for example) which is
used to protect such chief constituent from cor-
rosion.

Heretofore a protective coating which fulfills
the stated conditions has been obtained only
by alloying with the base metal a very high pro-
portion of alloying elements; which, besides in-
volving excessive cost, has frequently the detri-
mental effect of imparting to the alloyed metal
properties at variance with those it should
possess. This occurs in the case of ferrous alloys
when it is necessary to add thereto a large pro-
portion (30% to 50%) of chromium or 10% or
more of aluminum in order to render them cor-
rosion-resistant to oxygen at high temperature,
say of the order of 1000° C. Hence it is very
difficult, and sometimes impossible, to regener-
ate such alloys (i. e. to subject them to a heat
treatment for the purpose of restoring thereto
properties which have deteriorated or disap-
peared in the course of mechanical operations,
such as forging or the like) and consequently
the range of application of such alloys is greatly
restricted. Such chrome alloys, moreover, when
maintained for a long time at high temperature,
are liable to become fragile by reason of the
growth of the grain of the ferrite.

It is obvious that, in the case of exposure to
oxygen it is possible with an alloy of iron and a
more readily oxidizable metal to form only the
oxide of the more readily oxidizable metal by sub-
jecting such alloy to a heating at high tempera-
ture at a partial pressure of oxygen of the order
of that corresponding to the dissociation of the
oxide of the more readily oxidizable metal at
that temperature, since under these conditions
the iron is practically not attacked. However,
the use industrially of such extremely small par-
tial pressures of oxygen involves difficulties so
serious as to make it impracticable.

Moreover, the problem under consideration is
not only to obtain at low cost a determined coat-
ing-composition, but also to produce a coating
having the required properties of homogeneity,
adhesiveness, compactness and thickness.

Contrary to previous practice and theory, the
present invention makes possible the manufac-
ture of corrosion resistant metallic articles of
various shapes made of alloyed metals, especially
ferrous alloys. This result is accomplished by
adding to the base metal relatively small pro-
portions of alloying elements and then treating
the alloyed metal articles by a heating treatment
under operating conditions that are thoroughly
practical and economical, as hereinafter more
fully described. The quantities of alloying ele-
ments required for accomplishing the above
stated result by the process of this invention are

relatively much smaller than required for the production of corrosion resistant alloys by methods heretofore used. For example, by the treatment of this invention a steel containing only 12% chromium is rendered resistant to the oxidizing action of air when the article is heated to 1,000° C., whereas a chrome steel which has not been so treated must contain at least about 30% chromium, in order to make it equally resistant to oxidation under these same conditions. The amount of alloying element added to the ferrous base metal will vary according to the conditions under which the articles are to be used. Thus where chromium is the alloying metal and iron or steel the base metal and the article is intended to resist oxidation at 800° C. it was previously necessary to provide a chromium content of about 12%. By the treatment according to the invention a steel containing only 5.5% chromium is rendered resistant to the same extent to oxidation at 800° C.

This invention has for its essential object to produce upon an article made of an alloyed metal containing one or several alloying constituents a coating which will afford effective protection against corrosion by exposure to a determined gaseous body at high temperature. In case the alloy to be treated contains more than one alloying constituent, the said protective coating may comprise several compounds, corresponding respectively to the several alloying constituents. In any case but a single protective coating is, or need be, formed.

The present invention consists essentially in subjecting the article to be rendered corrosion resistant to the action, at a sufficiently high temperature, of an atmosphere containing the gaseous substance which the article is intended to resist in actual use or of an atmosphere containing a gaseous substance which when combined with the alloying metal gives rise to a coating capable of resisting to the gaseous atmosphere in which the article is to be actually used. If the article is to be used in an atmosphere containing oxygen, it is given a heating treatment in an atmosphere containing oxygen. The heating treatment is carried out at a temperature sufficiently high to cause a combination of the gaseous substance and the alloying element of the alloyed metal until a sufficiently thick compact coating is obtained. The temperature of the heating treatment is preferably at or above the temperature to which the article is to be subjected in use. However, the temperature of the heating treatment need not be as high as the intended temperature of use but need be only sufficiently high to cause a combination of the gaseous heating treatment substance and the alloying element. The heating treatment is conducted in an atmosphere containing the gaseous substance at a partial pressure above the dissociation pressure of the compound of the gaseous substance and the alloying element but low enough to avoid the formation of such an amount of the corresponding compound of the base metal as would unduly impair the effectiveness of the coating. The alloying element of the alloyed metal which combines with said gaseous substance is such that the compound formed thereby has a dissociation pressure below that of the compound formed by the action of said gaseous substance upon the base metal; the treatment being carried out in such manner that an ad-

herent compact and homogeneous coating of sufficient thickness is obtained.

Thus in order to obtain an article of chrome steel which is resistant to oxidation at high temperature (e. g. 1,000° C.), the process may be carried out advantageously by starting with a chrome steel having a chromium content insufficient in practice to be resistant to corrosion by itself at that temperature (say a 12% content of chromium) and subjecting this steel to a temperature near 1,000° C. at a pressure of oxygen between a fraction of a millimeter and several millimeters of mercury, say between $\frac{1}{10}$ and 2 mm. of mercury for a sufficient time to produce a coating of chromium oxide thick enough to render the article corrosion resistant to oxygen at the temperatures and pressures under which it is intended to be used. The pressure of oxygen used during the heating treatment is kept insufficient to cause the formation of a coating rich in iron oxide, which coating would be permeable and would impair the effectiveness of the coating. If in the heating treatment just described the pressure of oxygen is $\frac{1}{2}$ mm. of mercury, it will ordinarily be sufficient to carry out the heating treatment for a period of about 90 hours to produce a sufficiently thick compact homogeneous and adherent protective coating which will withstand satisfactorily the oxidizing action of air when the heat treated article is intended for resisting oxidation by air at 1,000° C. The heating treatment described will produce a coating which is adherent and not detachable from the article. By examination by X rays it is found that this coating is constituted by Cr_2O_3 containing a small proportion of Fe_2O_3 . The thickness of this coating is less than $\frac{1}{16}$ mm.

The length of time required for forming a coating of proper thickness varies, of course, with varying conditions and depends also upon the particular use for which the article under treatment is destined. Therefore, in each case all details must be determined experimentally. This, however, is readily done. The maximum of oxygen pressure is likewise determined experimentally by a series of trials, in which the pressure is varied in a regular and progressive manner, as well understood by those skilled in the art.

In the treatment of an article of steel alloyed with say 4% of aluminum, the process may be carried out in a manner substantially similar to that described above. Obviously, in all cases the maximum pressure of oxygen at the determined temperature, to which the alloyed metal should be subjected during the heating treatment according to this invention, will depend upon the conditions attending the use for which the particular article is destined. Where, for example, chromium is the alloying metal, the protective coating may contain more oxide of iron (wherefore a higher partial pressure of oxygen at a determined temperature is permissible in the treatment according to this invention) when the article is intended for use at a lower temperature and with a lower pressure of oxygen. A protective coating may, for example, be formed at 1000° C. and with a partial oxygen pressure which is higher where the alloyed metal is to be used in air at 500° C. than when the same alloyed metal is to be used at 1000° C.

It should be observed that the protective coating will in fact contain not only the compound of the alloying metal (e. g. chromium oxide) but

also a small proportion of the corresponding compound of the base metal (e. g. iron oxide); in consequence whereof the corrosion resistance is, of course, correspondingly decreased. Therefore, the lower the temperature in which the article is to be used, the higher the permissible proportion of iron oxide.

The considerable importance of such a treatment as herein described is that it permits the utilization of articles made of alloys containing an alloying constituent in much smaller proportions than heretofore required, which alloys are, therefore, much less costly than those made heretofore for the same purpose, and which above all are more readily workable both in the hot and in the cold condition. Thus a steel with 12% of chromium is very easy to work and is easily heat treated to restore properties diminished by working while an iron alloy of 30% chromium is ferritic at all the range of temperatures, its properties cannot be restored by heat treatment and has moreover the disadvantage of becoming fragile by growth of the grain of ferrite during prolonged maintenance at a high temperature.

In order to improve the qualities of the protective coating and to accelerate its formation, the process according to the invention may be carried out by starting from a low pressure of treatment for the formation of the non-corrodible compound, for example of alumina and the pressure may be progressively increased after the first protective coating is formed. In this case one may even exceed without disadvantage, as soon as the protective coating is sufficiently thick, the pressure at which there is formed an appreciable proportion of the compound of the base metal, provided that this proportion is not so high as to unduly impair the effectiveness of the whole corrosion-resistant coating.

By increasing, during the treatment at a relatively high temperature according to this invention, the partial pressure of the gaseous substance, it is possible to cause the nature of the coating formed progressively to vary also. It is thus possible to use finally partial pressures of said gaseous substance which are relatively high and of the order of pressures to which the treated article is to be used under industrial conditions. Hence the final partial pressures to be employed in accordance with the invention are higher in the case of O and Fe, than the dissociation pressure of the oxide of the alloying element and that of FeO.

It is, therefore, possible to produce a coating of such a nature (due to its chemical composition and to its adherence, its homogeneity, its thickness, and its compactness) that the alloyed metal, when subjected to action of atmospheres common in industry, shows an extraordinarily increased corrosion-resistance. Moreover, the remarkable quality of resistance to corrosion above described is attained with alloyed metals containing alloying elements (such as Al or Cr) in proportions very much lower than those required hitherto in order to obtain equally high corrosion-resistance.

For example, to obtain a sufficiently thick coating of oxide on an iron or steel alloy containing Al, the alloyed metal is first subjected to a relatively low pressure of oxygen, which nevertheless is very high with respect to the dissociation pressure of oxides such as Al_2O_3 (for example, 1.5-2 mm. of mercury); then, when the first coating is formed, the partial pressure of oxygen

may be increased slowly and progressively to 10 mm. of mercury. In this way, and without altering the resistance to corrosion of the coating, the thickness thereof may be increased in a relatively short time.

Inasmuch as the partial pressure of oxygen is very high relative to the dissociation pressure (at the temperature of the treatment) of the oxide of the alloying element added to the base metal, the formation of a compact coating of an oxide of sufficient thickness to be corrosion resistant to atmospheres now commonly used in industry may be effected in a comparatively short time. As has been already explained, the proper operating conditions (temperature, pressure, length of treatment, and the like) required for the production of a protective coating having the desired properties, are to be determined by suitable tests, regard being had in each case to the particular use for which the article under treatment is destined.

As a general rule, the following principles should be followed:

(1) The partial pressure of oxygen should be lower, the lower the proportion of alloying element added to the base metal.

(2) The treatment may be effected at higher partial pressure the lower the temperature of the treatment itself; thus temperature and pressure may be caused to vary inversely.

(3) The partial pressure of oxygen should be sufficiently high and the duration of the treatment should be sufficiently long so that a compact coating is obtained, which is thick enough to afford an efficacious protection against subsequent corrosion. It is not sufficient, in fact, to obtain a coating of a definite nature, it being also necessary that this coating be compact, adherent, and of sufficient thickness to insure corrosion-resistance. The partial pressure at which the treatment is carried out and the duration of the treatment will be, therefore, determined experimentally in each case.

When the coating is not sufficiently homogeneous (i. e. in a plane parallel to the outer surface of the coating), as explained below, the places at which a lack of such homogeneity exists will be manifested by the appearance of slits or cracks. When the coating is not sufficiently adherent, it has a tendency to separate from the base metal. When the coating is not sufficiently compact, there is liability of the formation of cracks under external influences and hence of corrosion. When the coating lacks the requisite thickness, there is a risk of its accidental removal.

It is to be understood in this connection that the "homogeneity" required for the purposes of this invention is not absolute or uniform homogeneity throughout the coating. What is required is that it should have a surface homogeneity; or, more precisely, the coating should be homogeneous in a plane which is parallel to the outer surface of the article. If, therefore, we consider two points of the coating, both being at the same depth from the external surface thereof, those points should show the same composition and structure.

Two examples of treatments with an indication of the results obtained will now be described.

In order to determine the oxidation resistance of an article of an iron aluminum alloy but not treated in accordance with the present invention, a cylindrical article of 50 mm. length and 8 mm.

diameter of iron aluminum alloy containing 4% aluminum was heated to 1000° C. for a period of eight hours in an atmosphere of pure dry oxygen under atmospheric pressure. It absorbed 270 cc. of oxygen calculated at 0° C. and 760 mm. of mercury.

A like article of the same dimensions of the same alloy was first subjected to a heating treatment according to the present invention, which consisted in maintaining the article for 72 hours at 1000° C. in an atmosphere of oxygen at a partial pressure of 2 mm. mercury. The article was then tested in the same manner as was the first article—namely, by heating it to 1000° C. for a period of 8 hours in an atmosphere of pure dry oxygen under atmospheric pressure. Under these conditions of test, it absorbed only 5 cc. of oxygen, that is only $\frac{1}{54}$ as much as the untreated article. Furthermore, the 5 cc. of oxygen absorbed also was less than that absorbed by another article identical in every way but made of steel containing 10% of aluminum but not treated according to the present invention, when tested under identical conditions.

An article of an iron chromium alloy containing 12% of chromium was tested for corrosion resistance with pure dry oxygen under atmospheric pressure at 1000° C. for a period of 8 hours. It absorbed 420 cc. of oxygen. A like article of the same dimensions of the same composition was given a heating treatment according to the present invention which consisted in maintaining the article for 72 hours at 1000° C. in an atmosphere of oxygen at a partial pressure of 2 mm. of mercury and was then tested by heating it to 1000° C. for a period of 8 hours in pure dry oxygen under atmospheric pressure. It absorbed only 10 cc. of oxygen in this test—that is to say only $\frac{1}{42}$ as much as the untreated alloy. The 10 cc. of oxygen which was absorbed was less than that absorbed by a like article identical in every way but made of an alloy containing 30% of chromium when tested under the same conditions but untreated according to the present invention.

Amongst its industrial applications for the production of articles intended to resist high temperatures without being rapidly destroyed by the gases of the atmosphere to which they are exposed, may be mentioned for example furnace elements, pyrometers, wires for electrical resistances, a. s. o.

As previously pointed out, it is practically impossible, within reasonable limits of a specification, to set forth the exact conditions under which the heating treatment should be carried out to render an article corrosion resistant under every condition to which it may be subjected in actual use. One skilled in the art will have no difficulty in determining the optimum conditions of heating treatment for any particular intended use of the article. However, in order to set forth the invention as clearly as possible within reasonable limits of a specification, the following further explanation is given.

I have specifically referred to the use of chromium, aluminum, silicon and zirconium as alloying elements. The invention is not limited to these particular alloying elements but is applicable to other alloying elements which form corrosion resistant compounds when subjected to gaseous atmospheres, which corrosion resistant compounds have dissociation pressures lower than that of the corresponding compound of the base

metal and will form a sufficiently thick compact homogeneous and adherent protective coating on the article to protect it effectively from the attack of the gaseous atmosphere to which the article is to be subjected in use. Another alloying element which I may use in addition to aluminum, chromium, silicon, and zirconium previously mentioned is beryllium.

The amounts of alloying elements used will depend, among other factors, on the composition and temperature of the gaseous atmosphere in which the article is to be used. It also depends upon the amount of the particular alloying element which may be added to the particular base metal without unduly adversely affecting its physical properties and its ability to be worked into the desired shape. Considering chromium as the alloying element and iron or steel as the base metal for the production of articles intended to resist oxidation of air at atmospheric pressure and at temperatures of about 1000° C., the amount of chromium is preferably about 12%. The amount of chromium may be reduced, if the temperature of use is lowered or the partial pressure of the oxygen in the air is reduced or the degree of corrosion resistance required for the article is less than that ordinarily encountered. The resistance to corrosion of a ferrous alloy containing chromium in any appreciable amount, say as low as 3%, is increased by treatment according to the present invention. As a general statement, I shall use for most purposes not less than 12% of chromium in ferrous alloys intended for use in air under atmospheric pressure. The upper limit of chromium for ferrous alloys will probably not be above 30%, because to increase the chromium beyond this would be uneconomical or would adversely affect its fabricating properties too greatly. The range of chromium which will be used most generally in ferrous alloys is between about 12% and 17%.

With regard to aluminum as the alloying element, the preferred percentage for ferrous alloys is about 4%. I prefer to use not less than 1.5% in most cases and not over 6%. The silicon may be as low as 2% or as high as 7% but is preferably between 3% and 4%. The other alloying elements, if used, may be employed in percentages substantially less than are required to produce the desired protection where the article is not subjected to a previous heating treatment in accordance with the present invention. Thus, as a general statement, it may be said that $\frac{1}{2}$ or $\frac{1}{3}$ of the usual amount of alloying element is required according to the present invention.

The temperature of the heating treatment for producing the protective coating is preferably at or near the temperature of intended use of the article. This temperature, however, may be materially less than the temperature of intended use of the article, so long as the heat treating temperature is high enough to form the corrosion resistant compound of the alloying element. This temperature, as previously pointed out, will depend on the pressure of the gaseous substance in the heat treating atmosphere which causes corrosion. As a general statement, it may be said that if the chromium ferrous article is to be used for resisting oxidation of air at atmospheric pressure and at 1000° C., the temperature of the oxygen containing heating atmosphere will not be less than 600° C. nor higher than 1100° C.

The heating treatment temperature for aluminum containing ferrous alloy articles for use at temperatures of about 1000° C. in air at atmospheric pressure may be between 800° C. and 1200° C.

The time of the heating treatment for a ferrous alloy containing 4% of aluminum, in order to produce an article intended for use in air at atmospheric pressure and at a temperature of 1000° C. is generally between 10 and 100 hours where the partial pressure of oxygen in the heating atmosphere is 1 mm. of mercury. Generally the time of heating will be of the order of 80 hours. For a chromium containing ferrous alloy to be used under the same conditions, the time of heating treatment is generally also between 10 and 100 hours.

The partial pressure of oxygen in the heating atmosphere may be as low as $\frac{1}{50}$ mm. of mercury or as high as 3 mm. of mercury, depending upon the heating treatment temperature, the proportion of alloying element and the intended use of the article.

It is to be emphasized again that the values which have been given are merely for illustrative purposes and it is not intended to limit the invention thereto.

The word "article" as used herein includes not only articles which have reached their final form but also articles which have not reached their final form.

The invention is not limited to the particular examples or to the preferred embodiments but may be otherwise embodied or practiced within the scope of the following claims.

I claim:

1. A process for improving the resistance of a metal to corrosion by a given gaseous substance, which comprises alloying with the said metal an alloying element which combines at high temperature with the gaseous substance to form a corrosion resistant compound having a dissociation pressure lower than that of the compounds of the base metal with said gaseous substance which are formed under the same heating conditions, and subjecting the alloyed metal to a heating pretreatment in an atmosphere containing the said gaseous substance at a partial pressure above the dissociation pressure of the said compound of the gaseous substance and the alloying element but below that at which the corresponding compound of the base metal forms in amount to materially impair the effectiveness of the coating wanted for the contemplated use of the alloy and below the partial pressure of said gaseous substance to which the alloyed metal is to be subjected in actual use, and at a temperature at which the alloying element combines with the gaseous substance to form the above said corrosion resistance compound, the heating being prolonged until a compact homogeneous and adherent protective coating of substantial thickness is obtained on the alloyed metal.

2. A process for improving the resistance of a metal to corrosion by a given gaseous substance, which comprises alloying with the said metal an alloying element which combines at high temperature with the gaseous substance to form a corrosion resistant compound having dissociation pressure lower than that of the compounds of the base metal with said gaseous substance which is formed under the same heating conditions, said alloying element being added in an amount insufficient to give by itself satisfactory resist-

ance to corrosion by the said gaseous substance under the intended conditions of use, and subjecting the alloyed metal to a heating pretreatment in an atmosphere containing said gaseous substance at a partial pressure above the dissociation pressure of the said compound of the gaseous substance and the alloying element but below that at which the corresponding compound of the base metal forms in amount to materially impair the effectiveness of the coating and below the partial pressure of said gaseous substance to which the alloyed metal is to be subjected in actual use and at an elevated temperature at which the alloying element combines with the gaseous substance to form the above said corrosion resistant compound, the heating being prolonged until a compact homogeneous and adherent protective coating of substantial thickness is obtained on the alloyed metal.

3. A process for improving the resistance of a metal to corrosion by a given gaseous substance, which comprises alloying with the said metal an alloying element which combines at high temperature with the gaseous substance to form a corrosion resistant compound having dissociation pressure lower than that of the compounds of the base metal with said gaseous substance which are formed under the same heating conditions, and subjecting the alloyed metal to a heating pretreatment in an atmosphere containing the said gaseous substance at a partial pressure above the dissociation pressure of the said compound of the gaseous substance and the alloying element but below that at which the corresponding compound of the base metal forms in amount to materially impair the effectiveness of the coating and below the partial pressure of said gaseous substance to which the alloyed metal is to be subjected in actual use and at a temperature at which the alloying element combines with the gaseous substance to form the above said corrosion resistance compound, the heating being prolonged until a compact homogeneous and adherent protective coating of substantial thickness is obtained on the alloyed metal, and progressively increasing the partial pressure as the heat treatment is continued.

4. A process for improving the resistance of iron and steel to corrosion by oxidizing and sulphurous gases, which comprises alloying with a ferrous base metal an alloying element of the class consisting of chromium and aluminum, and subjecting the ferrous alloy to a heating pretreatment in an atmosphere containing the gas at a partial pressure above the dissociation pressure of any compound which forms by the reaction of the gas and the alloying element but below that at which the corresponding compound of the ferrous metal forms in amount to materially impair the effectiveness of the coating wanted for the contemplated use of the alloy and below the partial pressure of said gaseous substance to which the iron or steel is to be subjected in actual use and at a temperature at which the alloying element combines with the gas to form the above said corrosion resistant compound, the heating being prolonged until a compact, homogeneous and adherent protective coating of substantial thickness is obtained on the ferrous alloy.

5. A process for improving the resistance of iron and steel to corrosion by oxidizing and sulphurous gases, which comprises alloying with a ferrous base metal an alloying element of the

class consisting of chromium and aluminum in an amount insufficient to render the alloy resistant to corrosion by oxidizing and sulphurous gases under the intended conditions of use, and subjecting the ferrous alloy to a heating pretreatment in an atmosphere containing the gas at a partial pressure above the dissociation pressure of any corrosion resistant compound which forms by a reaction of the gas and the alloying element but below that at which the corresponding compound of the ferrous metal forms in amount to materially impair the effectiveness of the coating and below the partial pressure of said gaseous substance to which the iron or steel is to be subjected in actual use and at a temperature at which the alloying element combines with the gas to form the above said corrosion resistant compound, the heating being prolonged until a compact, homogeneous and adherent protective coating of substantial thickness is obtained on the ferrous alloy.

6. A process for improving the resistance of iron and steel to oxidation, which comprises alloying with the ferrous base, chromium in an amount insufficient to render the alloy resistant to oxidation under the intended conditions of use, and subjecting the ferrous alloy to a heating pretreatment in an atmosphere containing oxygen at a partial pressure above the dissociation pressure of chromium oxide but below that at which iron oxide forms in amount to materially impair the effectiveness of the coating and below the partial pressure of oxygen in the atmosphere to which the iron or steel is to be subjected in actual use and at a temperature at which chromium combines with oxygen, the heating being prolonged until a compact homogeneous and adherent protective coating high in chromium oxide and low in iron oxide and of substantial thickness is obtained on the ferrous alloy.

7. A process for improving the resistance of iron and steel to oxidation, which comprises alloying with the ferrous base, aluminum in an amount insufficient to render the ferrous base resistant to oxidation under the intended conditions of use, and subjecting the ferrous alloy to a heating pretreatment in an atmosphere containing oxygen, at a partial pressure above the dissociation pressure of aluminum oxide but below that at which iron oxide forms in amount to materially impair the effectiveness of the coating and below the partial pressure of oxygen in the atmosphere to which the iron or steel is to be subjected in actual use and at a temperature at which aluminum combines with oxygen, the heating being prolonged until a compact homogeneous and adherent protective coating high in aluminum oxide and low in iron oxide and of substantial thickness is obtained on the ferrous alloy.

8. A process for improving the resistance of iron and steel to oxidation, which comprises alloying with a ferrous base metal from 3% to 30% of chromium, and subjecting the ferrous alloy to a heating pretreatment in an atmosphere containing oxygen at a partial pressure above the dissociation pressure of chromium oxide but below that at which iron oxide forms in amount to materially impair the effectiveness of the coating and below the partial pressure of oxygen in the atmosphere to which the iron or steel is to be subjected in actual use, and at a temperature at which the chromium combines with oxy-

gen, the heating being prolonged until a compact homogeneous and adherent protective coating of chromium oxide of substantial thickness is obtained on the ferrous alloy.

9. A process for improving the resistance of iron and steel to oxidation, which comprises alloying with a ferrous base metal from 3% to 30% of chromium, and subjecting the so formed ferrous alloy to a heating pretreatment at a temperature between about 600 and 1100° C. in an atmosphere containing oxygen at a partial pressure above the dissociation pressure of chromium oxide but below that at which iron oxide forms in amount to materially impair the effectiveness of the coating and below the partial pressure of oxygen in the atmosphere to which the iron and steel is to be subjected in actual use, the heating being prolonged until a compact homogeneous and adherent protective coating of chromium oxide of substantial thickness is obtained on the ferrous alloy.

10. A process for improving the resistance of iron and steel to oxidation at high temperatures, which comprises alloying with a ferrous base metal from 1.5 to 6% of aluminum, and subjecting the so formed ferrous alloy to a heating pretreatment at a temperature of between 800° and 1200° C. in an atmosphere containing oxygen at a partial pressure above the dissociation pressure of aluminum oxide but below that at which iron oxide forms in amount to materially impair the effectiveness of the coating and below the partial pressure of oxygen in the atmosphere to which the iron or steel is to be subjected in actual use, the heating being prolonged until a compact, homogeneous and adherent protective coating of aluminum oxide of substantial thickness is obtained on the ferrous alloy.

11. A process for improving the resistance of iron and steel to oxidation at high temperatures, which comprises alloying with a ferrous base metal about 3% to 30% of chromium, and subjecting the so formed ferrous alloy to a heating pretreatment at a temperature between about 600° and 1100° C. for 10 to 100 hours in an atmosphere containing oxygen at a partial pressure above the dissociation pressure of chromium oxide but below that at which iron oxide forms in amount to materially impair the effectiveness of the coating, the partial pressure of the oxygen in the heating pretreatment atmosphere being between $\frac{1}{10}$ mm. and 3 mm. of mercury, the heating being prolonged until a compact homogeneous and adherent protective coating of chromium oxide of substantial thickness is obtained on the ferrous alloy.

12. A process for making steel containing about 12 to 17% chromium resistant to oxidation at temperatures of the order of about 1000° C., which comprises subjecting the steel to a heating pretreatment at about 600 to 1100° C. in an atmosphere containing oxygen at a partial pressure of about .02 to 3 millimeters of mercury and above the dissociation pressure of chromium oxide but below that at which iron oxide forms in amount to materially impair the effectiveness of the protective coating which is formed and continuing such heat treatment until a compact homogeneous and adherent protective coating high in chromium oxide and low in iron oxide and of substantial thickness is formed on the surface of the steel.

13. A process for making steel containing about 1.5 to 6% aluminum resistant to oxidation at

temperatures of the order of about 1000° C., which comprises subjecting the steel to a heating pretreatment at about 800 to 1200° C. in an atmosphere containing oxygen at a partial pressure of about .02 to 3 millimeters of mercury and above the dissociation pressure of aluminum oxide but below that at which iron oxide forms in an amount materially to impair the effectiveness of

the protective coating which is formed and continuing such heat treatment until a compact homogeneous and adherent protective coating high in aluminum oxide and low in iron oxide and of substantial thickness is formed on the surface of the steel.

RENÉ PERRIN.