ABSTRACT

A method for the chromizing of iron or ferrous alloy articles in powder treating material comprising packing said iron or ferrous alloy articles in the mixed powders of sodium potassium or ammonium tetrafluoroborate and metallic chromium or ferrochromium and heating said articles within said mixed powders, thereby forming iron-chromium solid solution layers or chromium carbide layers on the surfaces of said articles. The method of this invention can be performed without employing non-oxidative atmosphere.
**FIG. 2**

[Graph showing thickness of layer vs. content of KBF₄ (%).]

**FIG. 3**

[Graph showing thickness of layer vs. treating temperature (°C).]

**FIG. 4**

[Graph showing thickness of layer vs. treating time (hrs.).]
METHOD FOR THE CHROMIZING OF IRON OR FERROUS ALLOY ARTICLES

This invention relates to the chromizing of iron and ferrous alloys including iron, steel and alloy steels, and more particularly it relates to the chromizing of iron and ferrous alloys packed in powder treating material.

It has been widely realized to chromize the surface of iron and ferrous alloy in order to remarkably promote its corrosion resistance, its oxidation resistance and its wear resistance. And many different kinds of methods for the chromizing of iron and ferrous alloy have been suggested heretofore. The most commonly used method in practice is the so-called pack method by which iron and ferrous alloy to be treated is heated in powder treating material. In this pack method, the powder treating material is composed of chromium or ferrochromium powder and ammonium chloride powder, and iron or ferrous alloy to be treated is buried into the powder treating material, and then it is heated at a high temperature near 1,000°C in the hydrogen atmosphere or in the atmosphere of non-oxidation. The high temperature treatment is, however, objectionable in view of the deterioration of the properties of iron and ferrous alloy themselves and also the non-oxidation atmosphere makes the treatment complex and costly.

It is an object of this invention to provide an improved method for the chromizing of iron and ferrous alloy articles.

It is another object of this invention to provide a method for the chromizing, which is simple in practice and less expensive.

It is still another object of this invention to provide a powder treating material that is capable of the chromizing in the air and at a relatively low temperature.

It is a still further object of this invention to provide a powder treating material that forms a chromium carbide layer or iron-chromium solid solution layer on the surface of an iron or ferrous alloy article.

Other objects of the invention will appear hereinafter.

The novel features that are considered characteristic of the invention are set forth with particularity in the appended claims. The invention, itself, as to its method of operation, together with additional objects and advantages thereof, will best be understood from the following description of specific embodiments when read in connection with the accompanying drawings, in which:

FIG. 1 is a micro photographic representation showing a chromium carbide layer on medium carbon steel, which is formed according to Example 1;

FIGS. 2 to 4 are graphs obtained in Example 1 and showing the effects of the content of potassium tetrafluoroborate (KBF₄) in the treating material, the heating temperature and the heating time on the thickness of chromium carbide layer formed on the surface of medium carbon steel.

FIG. 5 is a graph obtained in Example 2 and showing conditions, i.e. treating temperature and the content of potassium tetrafluoroborate, for forming the chromium carbide layer on the surface of high carbon steel.

FIG. 6 is a micro photographic representation showing a chromium carbide layer on high carbon steel which is formed according to Example 2;

FIGS. 7 to 9 are graphs obtained in Example 3 and showing the effects of the content of KBF₄ in the treating material, the heating temperature and the heating time on the thickness of an iron-chromium solid solution layer formed on the surface of low carbon steel.

FIG. 10 is a micro photographic representation showing an iron-chromium solid solution layer on low carbon steel, which is formed according to Example 3;

FIGS. 11 and 12 are graphs obtained in Example 4 and showing the effects of the content of KBF₄ in the treating material and the heating temperature on the thickness of a layer formed on the surface of low carbon steel.

FIG. 13 is a micro photographic representation showing a chromium carbide layer on low carbon steel, which is formed according to Example 4;

FIG. 14 is a micro photographic representation showing a chromium carbide layer on pure iron is formed according to Example 5.

Broadly, the present invention is directed to an improved pack method for the chromizing of iron and ferrous alloys and is characterized to use the mixed powders of sodium potassium and ammonium tetrafluoroborate and metallic chromium or ferro-chromium as the treating material. Namely, the method of the present invention comprises preparing the mixed powders composed of said tetrafluoroborate and metallic chromium or ferrochromium, packing iron and ferrous alloy articles such as iron, steel or alloy steel articles in said mixed powders and heating the articles within said mixed powders so as to form chromium carbide layers or iron-chromium solid solution layer on the surfaces of the articles. It has been found upon carrying out a large number of practical experiments that in this way, a chromium carbide layer or an iron-chromium solid solution layer can be definitely formed on the surface of the article. The thus formed layer represent a high value of hardness and superior resistance performance against corrosion and oxidation. The method according to this invention is thus highly suitable for the surface treatment of tools, dies and parts for many kinds of equipments. It is highly productive, and it has been ascertained that the layer thus obtained is strongly and tightly bonded to the surface of mother material and, in addition, a dense and continuous structure, thus obviating substantially the above mentioned various conventional drawbacks.

As powdery treating material, mixed powders of tetrafluoroborate, i.e. potassium tetrafluoroborate (KBF₄), sodium tetrafluoroborate (NaBF₄) and ammonium tetrafluoroborate (NH₄BF₄) and metallic chromium or ferrochromium are used. Here the ferrochromium include low carbon ferrochromium and high carbon ferrochromium. One or more than one kind of sodium potassium or ammonium tetrafluoroborates can be used in the powdery treating material. Also both metallic chromium and ferrochromium can be added in the powdery treating material. It is preferable that these powders are selected to be 40 mesh or finer. The powdery tetrafluoroborate may be added to the treating material in a quantity between about 0.5 to 80 percent by weight (hereinafter percent means percent by weight). With use of less quantity of tetrafluoroborate than 0.5 percent, the formation of the chromium carbide layer or the like would not be uniform and would be too slow to be accepted for the practical purpose. Too much addition of the fluoroborate than 80 percent
will make the treating material fused or sintered. Therefore, the treating material is solidified after the treating process and it will be difficult to take the article treated out of the treating material and the treating material will be unusable repeatedly, and besides the surface condition of the article will not be well. Preferably, the quantity of the tetrafluoroborate is between 1 to 20 percent. The remainder of the treating material is powdery metallic chromium or ferrochromium, namely the metallic chromium or ferrochromium may be mixed in a quantity between 20 to 99.5 percent and preferably in a quantity between 80 to 99 percent. In order to prevent the solidification of the treating material inactive powdery substance having a high melting point such as alumina (Al₂O₃), silica (SiO₂), Boron nitride (BN), chromic oxide (Cr₂O₃) and the like can be added up to the same quantity as that of the treating material.

The heating temperature may be selected within the wide range from 550°F to 1200°F. At a heating temperature below 550°C, the adequate thick chromium carbide or the like layer can not be formed on the surface of the article treated, and in the case that a temperature over 1,200°C is selected, the powdery treating material would become to be sintered and the article treated would become one body with the treating material. At this time, the property of alloy forming the article would be worsened. The preferable range of the heating temperature is 700°C to 1000°C. When most of ferrous alloy is treated at a heating temperature above the transformation point of the ferrous alloy article for quicker formation of the carbide or the like layer, distortion may be liable to occur in the articles by virtue of the transformation of ferrous alloy, which distortion must naturally be avoided by lowering the adopted higher heating temperature below 800°C.

The heating time period depends upon the thickness of the carbide or the like layer to be formed. The heating shorter than 30 minutes will, however, provide no practically acceptable information of said layer, although the final determination of the heating time period depends upon the heating temperature. With increase of the heating time period, the thickness of said layer will be increased correspondingly. In practice, an acceptable thickness of the layer can be realized within 30 hours or shorter time period. The most preferable range of the heating time period will be 2 to 10 hours.

It is not necessary to carry out the method according to this invention in the atmosphere of hydrogen gas or in the atmosphere of non-oxidation gas, but the method can be carried into effect either under air atmosphere or inert gas atmosphere.

As the iron or ferrous alloy to be treated, iron, iron steel and alloy steels can be treated successfully. According to the method of the present invention, two kinds of layers, chromium carbide layer and iron-chromium solid solution layer are formed on the surfaces of iron and ferrous alloy. And each of said layers can be selectively formed by selectively using proper ferrous alloy and proper treating material. Generally, the kind of the layer depends on the content of carbon in the ferrous alloy to be treated and in the ferrochromium of the powdery treating material. In the case that ferrous alloy to be treated contains more than 0.1 percent carbon, the layer formed on the surface of said ferrous alloy would be chromium carbide. And if the ferrochromium of the powdery treating material contains more than 1 percent carbon, the layer formed may be chromium carbide. In other cases, iron or ferrous alloy contains not more than 0.1 percent of carbon and the ferrochromium of the powdery treating material contains not more than 1 percent of carbon, the layer formed would be iron-chromium solid solution.

The following table shows the combinations of the objects of the treatment, the kind of layer formed, the kind of metal in the powdery treating material and the kind of iron or ferrous alloy to be treated.

<table>
<thead>
<tr>
<th>Object of the treatment</th>
<th>Kind of layer to be formed</th>
<th>Chromium in powdery treating material</th>
<th>Iron or ferrous alloy to be treated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corrosion resistance</td>
<td>iron-chromium solid solution layer</td>
<td>low carbon ferrochromium or metallic chromium</td>
<td>pure iron</td>
</tr>
<tr>
<td>Oxidation resistance</td>
<td>chromium carbide layer</td>
<td>high carbon steel</td>
<td>low carbon steel</td>
</tr>
<tr>
<td>Wear oxidation</td>
<td>do.</td>
<td>high carbon steel</td>
<td>high carbon steel</td>
</tr>
</tbody>
</table>

**EXAMPLE**

Several kinds of powdery treating materials composed of 90 to 99 percent low carbon ferrochromium (65 percent chromium, 0.06 percent carbon and the balance of iron powder of -200 mesh and the balance of KBF₄ of -200 mesh were introduced into each of iron containers of 50 mm inner diameter and 40 mm height, and then specimens, 5 mm thick, 10 mm wide and 10 mm long, made of medium carbon steel (JIS S55C: C: 0.52 – 0.58 percent, Si: 0.15 – 0.35 percent, Mn: 0.60 – 0.90 percent, P: less than 0.030 percent, S : less than 0.035 percent, balance of iron) were packed in each of said treating material in said container and were heated in the air at a different temperature between 900°C and 1,050°C for 2 to 15 hours, then they were cooled in the air. All of the specimens were cut to be observed their cross sections by a microscope. A few of the specimens were also tested by X-ray diffraction. And it was recognized that a chromium carbide layer was formed on the surface of each of said specimens, and it was confirmed that said layer is composed of the chromium carbide such as Cr₂C₀ or Cr₃C₅. And also Vickers hardness of said layer was measured about
Hv 1,800, equal to the bulk of the chromium carbide.

The microphotograph shown in FIG. 1 was taken from the specimen which was treated at 950°C for 8 hours within the treating material composed of 3% KBF₄ and 97% percent low carbon ferrochromium. The microphotograph indicates that an excellent chromium carbide layer is formed within the surface of the specimen.

FIGS. 2 to 4 are graphs obtained in this Example and showing the effects of the content of KBF₄ in the treating material, the heating temperature and the heating time on the thickness of the chromium carbide layer formed on the surface of medium carbon steel. As shown in FIG. 2, the thickness of the chromium carbide layer formed does not change in the wide variances, from 1 to 10 percent in the content of KBF₄. However, as shown in FIGS. 2 and 3, said thickness gradually increases as each of the heating temperature and the heating time increases.

According to the embodiment described above, it is apparent that chromium carbide is formed by means of treating medium carbon steel in the mixed powder of low carbon ferrochromium and KBF₄, and the chromium layer of adequate thickness can be obtained by using a powder treating material containing 1 to 10 percent KBF₄.

EXAMPLE 2

By the same manner described in Example 1, specimens made of high carbon steel (JIS SK3, C: 1.00 – 1.10 percent, Si: less than 0.35 percent, Mn: less than 0.50 percent, P: less than 0.030 percent, S: less than 0.030 percent, balance of iron) were treated at a temperature between 600°C and 1050°C for 4 hours in the powder treating materials composed of 20 to 98 percent of low carbon ferrochromium and 2 to 80 percent of KBF₄. Then, all of the specimens treated were cut and observed by a microscope. The result of the observation, whether chromium carbide layer was formed or not, is shown in FIG. 5 with the relation of the treating conditions. In FIG. 5, the ordinate and the abscissa represent the heating temperature and the content of KBF₄ in the treating material respectively, and the dot marks indicate that the chromium carbide layer of a few microns for more in thickness was formed by the condition shown with each of said dot marks. As shown from the figure, in order to form an adequate thickness of the layer, the treating temperature may be 600°C or higher than 600°C.

The microphotograph shown in FIG. 6 was taken from the specimen which was treated at 700°C for 4 hours within the treating material composed of 80% KBF₄ and 20 percent low carbon ferrochromium. The microphotograph show the typical chromium carbide layer formed according to this Example.

EXAMPLE 3

By the same manner described in Example 1, specimens made of low carbon steel (carbon content is about 0.05 percent) were treated at a temperature ranging from 900°C to 1100°C for 2 to 15 hours in the powder treating materials composed of 0.5 to 15% KBF₄, and 85 to 99.5 percent low carbon ferrochromium. Then, all of the specimens treated were cut and observed by a microscope. A few of the specimens were also treated by X-ray diffraction, by an X-ray micro analyzer and by a Vickers hardness tester. And it was recognized that an iron-chromium solid solution layer was formed within each of said specimens. The content of chromium in said iron-chromium solid solution layer is 40 percent at the surface of said layer and decrease according to the distance from the surface. Also Hv 230 was measured on said layer. The typical non-chromium solid solution layer formed according to this Example is shown in FIG. 10. The microphotograph shown in FIG. 10 was taken from the specimen which was treated at 1,050°C for 8 hours within the treating material composed of 3% KBF₄, and 97 percent low carbon ferrochromium.

FIGS. 7 to 9 are graphs obtained in this Example and showing the effects of the content of KBF₄ in the treating material, the heating temperature and the heating time on the thickness of the iron-chromium solid solution layer formed on the surface of low carbon steel. As shown in FIG. 7, the thickness of the layer formed decreases from about 80 micron to 50 micron according to increasing the content of KBF₄ from 0.5 to 5 percent, the thickness of the layer becomes a constant value, 50 micron, in the higher content of KBF₄, than 5%. With regard to the heating temperature and the heating time, the thickness of the layer increases rapidly according to increasing each of the heating temperature and time as shown in FIGS. 8 and 9 respectively.

EXAMPLE 4

Specimens made of low carbon steel (carbon content is about 0.05 percent) were treated at a temperature between 900°C and 1150°C for 5 hours in the powder treating materials composed of 0.5 to 10% KBF₄, and 90 to 99.5 percent of high carbon ferrochromium (67 percent chromium, 4.9 percent carbon and the balance of iron) of −100 mesh. All the specimens were cut and tested as same as the specimens in the Examples 1 to 3. In this Example two kinds of layer, the iron-chromium solid solution layer and chromium carbide layer, were formed respectively. The powder treating material containing 1 percent or lower than 1% of the high carbon ferrochromium gave the iron chromium solid solution layer and the powder treating material containing 2 percent or higher than 2 percent of the high carbon ferrochromium gave the chromium carbide layer.

The effects of the content of KBF₄ in the treating material and of the heating temperature are shown in FIGS. 11 (obtained from the specimens treated at 1,000°C for 5 hours) and 12 (obtained from the specimens treated for 5 hours in the powder treating material containing 10% KBF₄).

As shown in FIG. 11, the thickness of the layer formed decreases rapidly from about 38 micron to about 10 micron, according to increasing the content of KBF₄ from 0.5 to 2 percent and becomes a constant value, about 5 micron, in the higher content of KBF₄ than 2 percent. With regard to the heating temperature, the thickness of the layer formed shows almost a constant value, about 5 micron at a temperature from 900°C to 1000°C and the thickness of the layer increases gradually according to increasing the heating temperature as shown in FIG. 12.

As a typical layer formed in this Example, a microphotograph is shown in FIG. 13, which was taken from the specimen treated at 1,050°C for 5 hours in the pow-
dery treating material composed of 10% KBF₄ and 90 percent of high carbon ferrochromium.

According to the results of this Example, when high carbon ferrochromium is employed as one of the essential elements of the treating material, the carbon of said ferrochromium is introduced together with chromium into the low carbon steel during the treatment, and then chromium carbide layer can be formed even though the low carbon steel does not contain equough carbon to form the carbide. However, the content of KBF₄ in the powdery treating material affects the formation of the carbide. Namely the low content of KBF₄ gives an iron-chromium solid solution layer, and the high content of KBF₄ gives the chromium carbide layer.

EXAMPLE 5

By the same manner described in Example 4, a specimen made of pure iron was treated at 1,150°C for 5 hours in the powdery treating material composed of 10% KBF₄ and high carbon ferrochromium. By this treatment, a layer shown in FIG. 14 was formed. And it was recognized that the layer is chromium carbide.

EXAMPLE 6

Specimens made of high carbon steel JIS SK3 (C:1.00–1.10 percent, Si: less than 0.35 percent, Mn: less than 0.50 percent, P: less than 0.030 percent, S: less than 0.030 percent) were treated at 1,000°C for 5 hours in each of the following powdery treating materials (a), (b) and (c).

a. treating material composed of 87 percent low carbon ferrochromium (65 percent chromium, 0.06 percent carbon and the balance of iron) of −100 mesh, of 3 percent of KBF₄ of −200 mesh and of 10 percent Al₂O₃ of −325 mesh;

b. treating material composed of 57 percent low carbon ferrochromium of −100 mesh, of 3 percent KBF₄ of −200 mesh and of 40% SiO₂ of −325 mesh;

c. treating material composed of 87 percent low carbon ferrochromium of −100 mesh, of 3% KBF₄ of −200 mesh and 10% BN of −325 mesh.

A specimen made of low carbon steel was treated at 1,050°C for 8 hours in the following treating material (d).

d. treating material composed of 87 percent low carbon ferrochromium of 100 mesh, of 3% KBF₄ of −200 mesh and of 10% Cr₂O₃ of −325 mesh.

The specimens treated in each of the treating material (a), (b) and (c) mentioned above were formed chromium carbide layers of 10 microns, of 10 microns and of 16 microns respectively, and the specimen treated in the treating material of (a) was formed an iron-chromium solid solution layer. And the all treating materials (a) to (d) were not solidified during their treatments.

According to the results of this Example, the addition of inactive powder substance having a high melting point such as Al₂O₃, SiO₂, BN and Cr₂O₃ into the powdery treating materials can effectively prevent the solidification of said treating materials without affecting badly the formation of the layers.

EXAMPLE 7

Specimens made of JIS SK3 were treated at 1,000°C for 5 hours in each of the following treating materials:

a. treating material composed of 97 percent metallic chromium of −100 mesh and of 3% KBF₄ of −200 mesh;

b. treating material composed of 97 percent metallic chromium of −100 mesh and of 3% NaBF₄ of −100 mesh;

c. treating material composed of 90 percent metallic chromium of −100 mesh and of 10% NaBF₄ of −100 mesh;

d. treating material composed of 90 percent metallic chromium of −100 mesh and of 10% NH₄BF₄ of −200 mesh;

e. treating material composed of 77 percent metallic chromium of −100 mesh, of 3% NaBF₄ of −100 mesh and of 20% Al₂O₃ of −325 mesh.

By the treatments described above, a chromium carbide layer of about 15 micron in thickness was formed on each of said specimens.

EXAMPLE 8

Specimens made of alloy steel (JIS SKD11: 1.5% C, 12% Cr, 1.0% Mo, 0.4% V, and the balance of iron) were treated under the following conditions:

a. treating material composed of 90 percent low carbon ferrochromium of −100 mesh and of 10% KBF₄ of −200 mesh, treating temperature and time being 1,050°C and 8 hours respectively;

b. treating material composed of 57 percent low carbon ferrochromium of −100 mesh, of 3% KBF₄ of −200 mesh and of 40% SiO₂ of −250 mesh, treating temperature and time being 1,000°C and 8 hours respectively.

The specimen treated under the treating condition of (a) was formed a chromium carbide layer of about 13 microns in thickness, and the specimen treated under the treating condition of (b) was formed a chromium carbide layer of about 15 microns in thickness.

What is claimed is:

1. A method for the chromizing of an iron or ferrous alloy article in powdery treating material, comprising the steps of packing said article in the powdery treating material consisting essentially of 0.5 to 80 percent by weight of one member selected from the group consisting of potassium tetrafluoroborate, sodium tetrafluoroborate, ammonium tetrafluoroborate and the mixture thereof and 20 to 99.5 percent by weight of one member selected from the group consisting of metallic chromium, ferrochromium and the mixture thereof, heating said ferrous metal article within said powdery treating material at a temperature between 550°C and 1,200°C for 1 to 30 hours, and taking said article out of said powdery treating material, thereby forming a chromized layer on the surface of said article.

2. A method according to claim 1, wherein an inactive powdery material selected from the group consisting of alumina, silica, boron nitride, chromium oxide and the mixture thereof is added to said powdery treating material.

3. A method according to claim 1, wherein said article is made of one selected from the group consisting of iron, steel and alloy steels.

4. A method according to claim 1, wherein said ferrochromium contains carbon.

5. A method according to claim 1, wherein said powdery treating material is of 40 mesh or finer.
6. A method according to claim 1, wherein said article is made of steel containing at least 0.1 percent by weight of carbon.

7. A method according to claim 1, wherein said ferrochromium contains more than 1 percent by weight of carbon.

8. A method according to claim 1, wherein said article is made of one member selected from the group consisting of pure iron and low carbon steel containing up to 0.1 percent by weight of carbon and said powdery treating material consisting essentially of 0.5 to 80 percent by weight of one member selected from the group consisting of potassium tetrafluoroborate, sodium tetrafluoroborate, ammonium tetrafluoroborate and the mixture thereof and 20 to 99.5 percent by weight of one member selected from the group consisting of metallic chromium, ferrochromium containing up to 1 percent of carbon and the mixture thereof.

* * * * *