United States Patent [19]

Arai et al.

[11] **3,874,909**

[45] **Apr. 1, 1975**

[54] **METHOD FOR FORMING A CARBIDE LAYER ON THE SURFACE OF AN IRON OR FERROUS ALLOY ARTICLE**

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[22] Filed: **Dec. 19, 1972**

[21] Appl. No.: **316,502**

[30] **Foreign Application Priority Data**

Dec. 20, 1972	Japan	46-102629
Dec. 20, 1971	Japan	46-102630
Dec. 20, 1971	Japan	46-102631

[52] **U.S. Cl.** .... **117/106 C,** 117/107.2 P, 117/118

[51] **Int. Cl.** **C23c**

[58] **Field of Search** .... 117/107.2 P, 106 C, 118

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Primary Examiner—Leon D. Rosdol
Assistant Examiner—Harris A. Pitlick
Attorney, Agent, or Firm—Wenderoth, Lind & Ponack

[57] **ABSTRACT**

A method for forming a carbide layer of a metal selected from Ti, Zr, Hf, V, Nb, Ta, Mo or and or mixtures thereof on the surface of an iron or ferrous alloy article in a powdery treating material comprising packing said article in the mixed powders of a tetrafluoroborate and said metal and heating said article within said mixed powders, thereby forming a very hard carbide layer of said metal on the surface of said article. The method of this invention can be carried out without employing a non-oxidation atmosphere and can improve greatly the wear resistance of iron and ferrous alloy articles.

11 Claims, 19 Drawing Figures

(X 400)

FIG. 1

(×400)

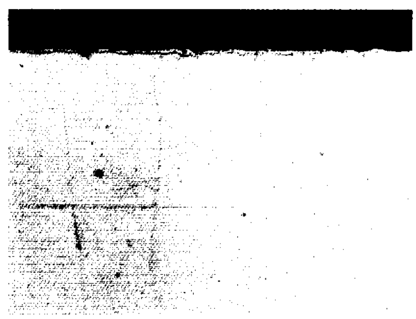
FIG. 4

(×400)

FIG. 5

(×400)

FIG. 6



(×400)

FIG. 7

(×400)

FIG. 11

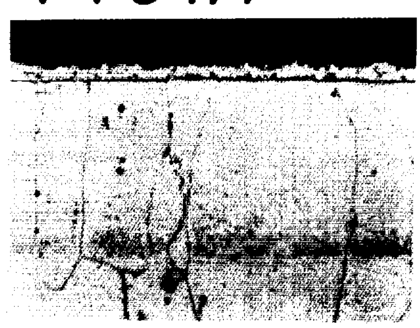


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FIG. 2

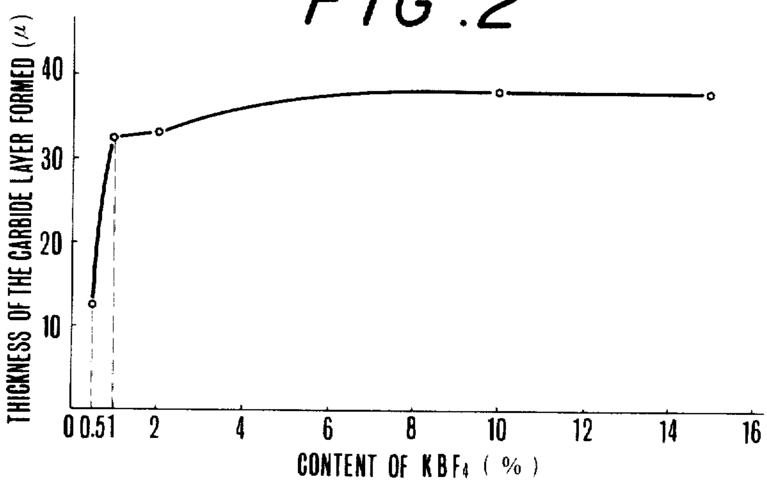


FIG. 3

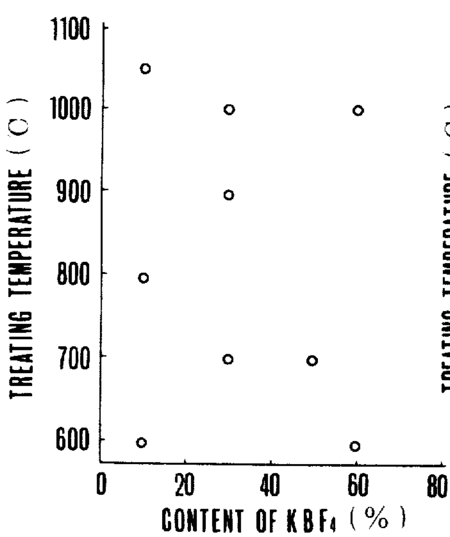


FIG. 12

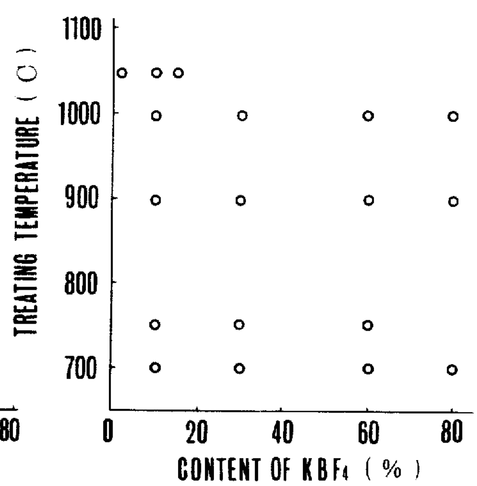


FIG. 8

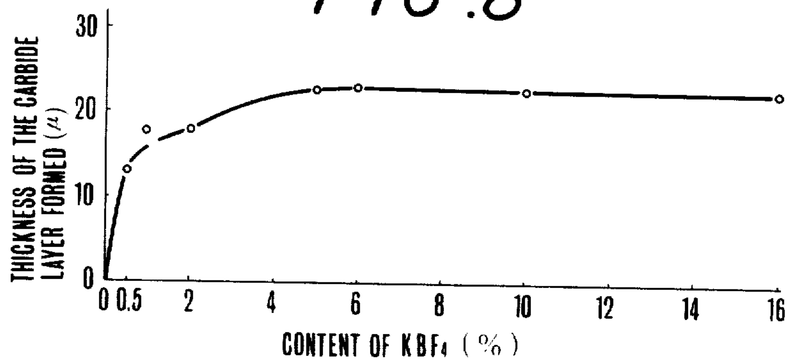


FIG. 9

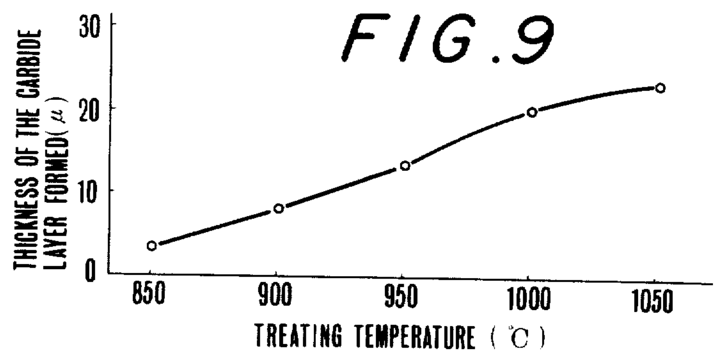


FIG. 10

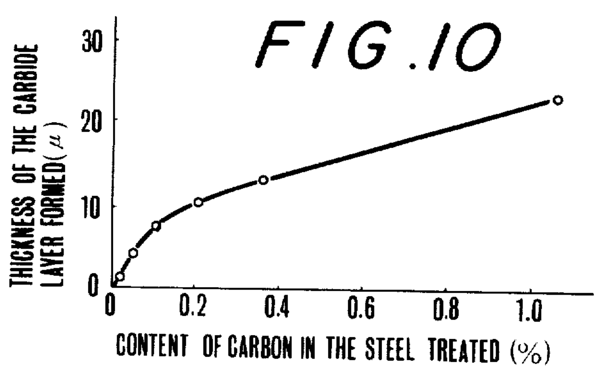


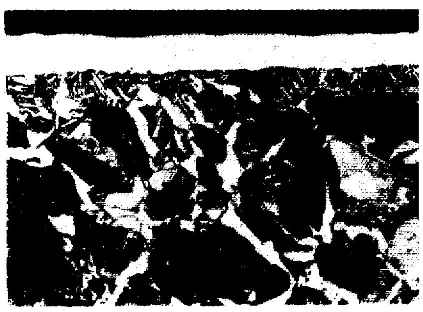
FIG. 13

(×400)

FIG. 14

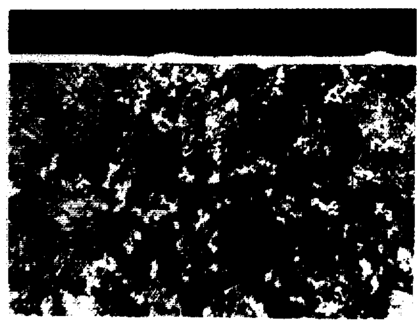
(×400)

FIG. 15



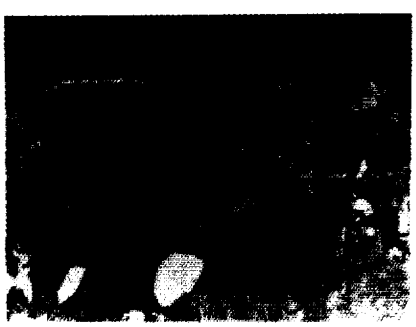
(×400)

FIG. 18



(×400)

FIG. 19



(×400)

FIG. 16

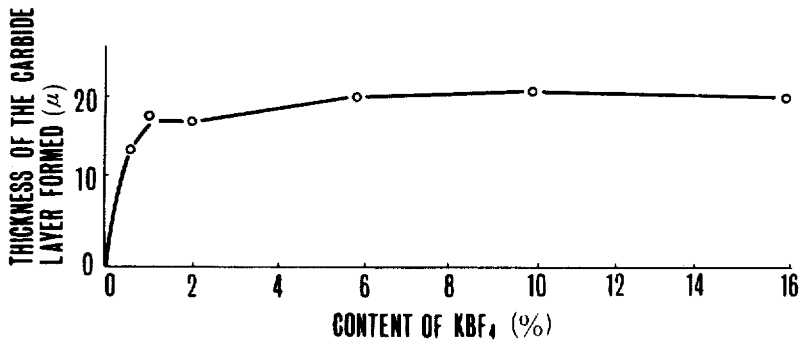
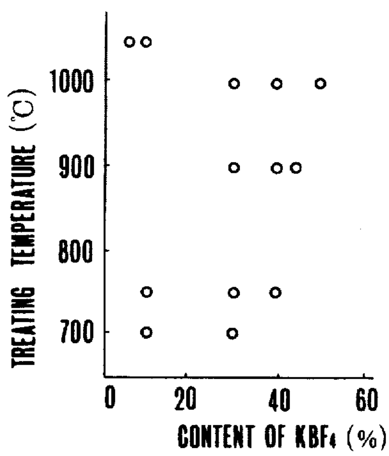

THICKNESS OF THE CARBIDE LAYER FORMED (μ)
0
10
20
0
2
4
6
8
10
12
14
16
CONTENT OF KBF_4 (%)

FIG. 17


TREATING TEMPERATURE (℃)
700
800
900
1000
0
20
40
60
CONTENT OF KBF_4 (%)

METHOD FOR FORMING A CARBIDE LAYER ON THE SURFACE OF AN IRON OR FERROUS ALLOY ARTICLE

This invention relates to a method for forming a carbide layer of Ti, Zr, Hf, V, Nb, Ta, Mo or W on the surface of an iron or ferrous alloy article, and more particularly it relates to the formation of the carbide layer on the surface of the article packed in powdery treating material. The iron or ferrous alloy article with the carbide layer formed thereon has a greatly improved hardness and wear resistance.

There have been reported several kinds of methods for coating or forming a metallic carbide layer on the surface of metallic articles. Among them, a powdery pack method for forming a metallic carbide on the metallic article has been realized because of its easiness in practice and its good operability. Said pack method, however, is not used in practice except for forming a chromium carbide layer.

Therefore, it is the principal object of this invention to provide a method for forming a carbide layer of Ti, Cr, Zr, Hf, V, Nb, Ta, Mo, W or mixture thereof on the surface of an iron or ferrous alloy article.

It is another object of this invention to provide a method for forming a metallic carbide layer of a denseness and uniformity on the surface of the article.

It is still another object of this invention to provide a method for forming a carbide layer, which is simple in practice and less expensive.

It is a still further object of this invention to provide a powdery treating material that is capable of the formation of a carbide layer on the surface of an iron or ferrous alloy in the air and at a relatively low temperature.

Other objects of this 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 photomicrograph showing a titanium carbide layer on high carbon steel, which is formed according to Example 1;

FIG. 2 is a graph obtained in Example 1 and showing the effect of the content of potassium tetrafluoroborate (KBF_4) in the treating material on the thickness of the titanium carbide layer;

FIG. 3 is a graph showing the conditions of treatments employed in Example 1;

FIG. 4 is a photomicrograph showing a titanium carbide layer formed according to Example 3(c);

FIG. 5 is a photomicrograph showing a hafnium carbide layer formed at 1050°C in Example 4;

FIG. 6 is a photomicrograph showing a titanium carbide layer formed according to Example 5;

FIG. 7 is a photomicrograph showing a vanadium carbide layer on high carbon steel formed at 1050°C for 8 hours in the treating material containing 10 percent of KBF_4;

FIGS. 8 and 9 are graphs obtained in Example 6 and showing the effects of the content of KBF_4 in the treating material and the heating temperature on the thickness of the vanadium carbide layer;

FIG. 10 is a graph obtained in Example 7 and showing the effect of the content of carbon included in the steel to be treated on the thickness of the vanadium carbide layer;

FIG. 11 is a photomicrograph showing a niobium carbide layer formed on the steel containing 0.1 percent of carbon;

FIG. 12 is a graph showing the conditions of the treatments employed in Example 8(c);

FIG. 13 is a photomicrograph showing a vanadium carbide layer formed according to Example 9(c);

FIG. 14 is a photomicrograph showing a niobium carbide layer formed according to Example 10(a);

FIG. 15 is a photomicrograph showing a tungsten carbide layer formed according to Example 11;

FIG. 16 is a graph obtained in Example 11 and showing the effect of the content of KBF_4 in the treating material of the thickness of the tungsten carbide layer;

FIG. 17 is a graph showing the conditions of treatments employed in Example 12;

FIG. 18 is a photomicrograph showing a tungsten carbide layer formed according to Example 13(b);

FIG. 19 is a photomicrograph showing a molybdenumcarbide layer formed according to Example 14(a).

Broadly, the present invention is directed to a new pack method for forming a carbide layer of Ti, Zr, Hf, V, Nb, Ta, Mo, or W on the surface of an iron or ferrous alloy article and is characterized in that the treating material is composed of a tetrafluoroborate and a metal containing a IV-b, V-b u VI-b group element of the periodic table and in that the iron or ferrous alloy article to be treated contains at least 0.05 percent of carbon (hereinafter percent means percent by weight). Namely, the method of the present invention comprises preparing the mixed powders composed of a tetrafluoroborate and a metal containing Ti, Zr, Hf, V, Nb, Ta, Mo or W, packing the iron or ferrous alloy article containing at least 0.02 percent of carbon in said mixed powders and heating the article within said mixed powders so as to form the carbide layer such as a titanium carbide layer or the like on the surface of said article. It has been found upon carrying out a large number of practical experiments that the carbide layers formed in this way represent a high value of hardness and superior resistance performance against wear. 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 carbide layers thus obtained is strongly and tightly integrated to the surface of a mother article and has, in addition, a dense and uniform phase.

In order to prepare the powdery treating material; a tetrafluoroborate powder and the powder of the metal containing titanium (Ti), zirconium (Zr), hafnium (Hf), vanadium (V), niobium (Nb), tantalum (Ta), molybdium (Mo) or tungsten (W) are mixed together. As the alkali tetrafluoroborate, potassium tetrafluoroborate (KBF_4), sodium tetrafluoroborate ($NaBF_4$) and ammonium tetrafluoroborate (NH_4BF_4) and the like can be used. In the powdery treating material, one or more than one kind of tetrafluoroborate can be used and these tetrafluoroborates work as a promotor of this treatment. As the metal containing Ti or the like, metallic Ti, Zr, Hf, V, Nb, Mo, W and the alloys thereof can be used and work as the principal ingredient of the treating material. Said alloys include the alloys with iron, nickel, cobalt, manganese, aluminium or the like. Especially, the alloys with iron, i.e. ferrous alloys, are suitable for the metal of the treating material because most of the ferrous alloys are cheap and easy to obtain. It is preferable that the tetrafluoroborate and metal powders are selected to be 40 mesh or finer. The powdery tetrafluoroborate may be included in the treating material in a quantity between about 0.5 to 80 percent by weight. With use of less quantity of tetrafluoroborate than 0.5 percent, the formation of the carbide layer would not be uniform and would be too slow to be accepted for the practical purpose. Too much addition of the tatrafluoroborate 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 good. However, under special conditions such as treating at a low temperature, the tetrafluoroborate can be included as much as 80 percent in the treating material. Preferably, the quantity of the tetrafluoroborate is between 1 to 30 percent.

The remainder of the treating material is the powdery metal mentioned above. Said powdery metal may be mixed in a quantity between 20 to 99.5 percent, and preferably in a quantity between 70 to 99 percent. In order to prevent the solidification of the treating material, an inactive powdery substance having a high melting point such as alumina (Al_2O_3), silica (SiO_2), boron nitride (BN), chromic oxide (Cr_2O_3) and mixture thereof and the like can be added up to the same quantity as that of the treating material.

The iron of ferrous alloy article must contain at least 0.02 percent of carbon. The carbon in the article becomes to be a composition of the carbide during the treatment. Namely it is supposed that the carbon in the article diffuses to the surface thereof and reacts with the metal from the treating material to form the carbide on the surface of the articles. The higher content of the carbon in the article is more preferably for forming the carbide layer. The iron or ferrous alloy article containing less than 0.05 percent of carbon may not be formed with a uniform and thick carbide layer by the treatment. As long as the iron or ferrous alloy articles contain at least 0.02 percent of carbon, any kind of iron or ferrous alloy article can be used as the article of the present invention.

The heating temperature may be selected within the wide range from 600 to 1200°C. At a heating temperature below 600°C, the adequate thick carbide layer can not be formed on the surface of the article treated and in the case that a temperature over 1200°C is selected, the powdery treating material would become to be sintered and the article treated would be integrated with the treating material. At this time, the property of the iron or ferrous alloy article would be worsened. The preferable range of the heating temperature is 700 to 1000°C. When ferrous alloys are treated at a heating temperature above the transformation point of the ferrous alloy articles for quicker formation of the carbide, distortion may be liable to occur in most of the articles by virtue of the transformation of the ferrous alloy articles, which distortion can be naturally avoided by lowering the heating temperature below 800°C.

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

The treating conditions of the present invention were generally mentioned above. However, the conditions may be varied a little depending on the kind of the carbide layer to be formed.

When a carbide layer of a IV-b group element, such as a titanium carbide layer, a zirconium carbide layer and the like, is desired, the iron of ferrous alloy article to be treated should contain at least 0.5 percent of carbon and preferably 0.1 percent of carbon or more. The treating temperature should be in range from 600° to 1200°C and preferably in a range from 700° and 1000°C. And the powdery treating material should be composed of 0.5 percent to 60 percent of tetrafluoroborate and 40 percent to 99.5 percent of a metal containing a IV-b group element.

When a carbide layer of a V-b group element, such as a vanadium carbide layer, a niobium carbide layer and the like, is desired, the iron or ferrous alloy article to be treated should contain at least 0.02 percent of carbon and preferably 0.05 percent of carbon or more. The treating temperature should be in a range from 650° to 1200°C and preferably in a range from 750° to 1000°C. And the powdery treating material should be composed of 0.5 percent to 80 percent of tetrafluoroborate and 20 percent to 99.5 percent of a metal containing a V-b group element.

When a molybdenum carbide layer of tungsten carbide layer is desired, the iron of ferrous alloy article to be treated should contain at least 0.5 percent of carbon and preferably 0.1 percent of carbon or more. The treating temperature should be in a range from 650° to 1200°C and preferably in a range from 750° to 1000°C. And the powdery treating material should be composed of 0.5 to 45% of tetrafluoroborate and 55 to 99.5% of a metal containing molybdenum or tungsten.

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

Example 1

Several kinds of powdery treating materials composed of 85 to 99.5 percent ferrotitanium (42 percent titanium, 0.04 percent carbon and the balance of iron) powder of -100 mesh and the balance of KBF_4 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 wide and 10 mm long, made of high carbon tool steel (JIS SK3, containing 1.00 to 1.10 percent of carbon) were packed in each of said treating materials in said containers and were heated in the air at 1050°C for 8 hours, and then they were cooled in the air. All of the specimens were cut to be observed on their cross section by a microscope. A few of the specimens were also tested by a X-ray diffraction method. And it was recognized that a titanium carbide layer wad formed on the surface of each of said specimens. Also the carbide layer was confirmed to be composed of the crystals of the titanium carbide TiC. And also Vickers hardness of said layer was measured about Hv 2900.

The photomicrograph shown in FIG. **1** was taken from the specimen which was treated at 1050°C for 8 hours in the powdery treating material composed to 10 percent of KBF_4 and 90 percent of ferrotitanium. The photomicrograph indicates that an excellent titanium carbide layer is formed on the surface of the specimen.

FIG. **2** is a graph obtained in this example and showing the effect of the content of KBF_4 in the treating material on the thickness of the carbide layer formed on the high carbon tool steel. As shown in FIG. **2,** the thickness of the carbide layer formed is rapidly increased from about 12 microns to over 30 microns according to the increase of the content of KBF_4 from 0.5 to 1 percent, then the thickness of the layer becomes nearly constant, i.e. about 30 to 40 microns, although the content of KBF_4 is increased.

According to this example, it is apparent that the excellent titanium carbide layer can be formed in the treating material containing at least 0.5 percent of KBF_4.

Example 2

In the same manner as described in Example 1, specimens made of high carbon tool steel (JIS SK3) were treated at a temperature between 600° and 1050°C for 4 hours in the powdery treating materials composed of 10 to 80 percent of KBF_4 and the balance of ferrotitanium. Then, all of the specimens treated were cut and observed by a microscope. The results of the observations, whether the titanium carbide layer was formed or not, are shown in FIG. **3** with the treating conditions. In FIG. **3,** the ordinate and the abscissa represent the treating temperature and the content of KBF_4 in the treating material, respectively, and the white round marks indicate that the titanium carbide layer is formed under the condition shown with each of said marks. The specimens treated in the treating material containing 60 percent of KBF_4 were formed partially with the two layers, i.e. the titanium carbide layer and boron compound layer.

According to this example, it is apparent that the titanium carbide layer can be formed at a relatively low temperature such as at 600°C.

Example 3

In the same manner as described in Example 1, specimens made of high carbon tool steel (JIS SK3) were treated at 1000°C for 4 hours in each of the following powdery treating materials (a), (b) and (c).

a. treating material composed of 90 percent of ferrotitanium of -100 mesh and 10 percent of $NaBF_4$ of -100 mesh;

b. treating material composed of 70 percent of ferrotitanium of -100 mesh and 30 percent of $NaBF_4$ of -100 mesh;

c. treating material composed of 90 percent of ferrotitanium of -100 mesh and 10 percent of $NaBF_4$ of -200 mesh.

The specimens treated in each of the treating materials (a), (b) and (c) mentioned above were formed with the titanium carbide layers of 25 microns, 20 microns and 25 microns, respectively.

As one of the examples, the photomicrograph taken from the specimen which was treated in the treating material (c) is shown in FIG. **4.**

Example 4

The specimens made of high carbon tool steel (JIS SK3) were treated at 600° or 1050°C for 4 hours in the treating material composed of 90 percent of ferrozirconium (80 percent of zirconium and hafnium and the balance of iron) powder of -100 mesh and 10 percent of KBF_4 powder of -200 mesh. The specimens treated were formed with the carbide layer of 3 microns at 600°C or the carbide layer of 20 microns at 1050°C. The carbide layers formed were recognized to be composed of zirconium carbide by X-ray diffraction. Also said layers were recognized to include hafnium by an electro prove microanalyzer (EPMA).

FIG. **5** shows the photomicrograph taken from the specimen treated at 1050°C.

Example 5

The specimens, 2 mm thick, 10 mm wide and 10 mm long, made of low carbon steel (containing 0.05 percent of carbon were treated at 1000°C for 4 hours in the treating material composed of 70 percent of ferrotitanium powder of -100 mesh and 30 percent of KBF_4 powder of -200 mesh. The specimens treated were formed with two, upper and middle, layers. Said upper layer was about 3 microns in thickness and was recognized to be composed of titanium carbide. And said middle layer was about 70 microns in thickness and was recognized to be composed of a solid solution of titanium in iron. The photomicrograph taken from the specimen obtained in this example is shown in FIG. **6.**

Example 6

Several kinds of powdery treating materials composed of 84 to 99.5 percent of ferrovanadium (52 percent of vanadium, 0.09 percent of carbon and the balance of iron) powder of -100 mesh and 0.5 to 16 percent of KBF_4 powder of -200 mesh were introduced into each of iron containers, and then specimens, 5 mm thick, 10 mm wide and 10 mm long, made of high carbon tool steel (JIS SK3) were packed in each of said treating materials in said containers and were heated in the air at a temperature between 850° and 1050°C for 8 hours in an electronic furnace. The specimens treated were tested in the same manner as explained in Example 1. And it was recognized that a vanadium carbide layer shown in FIG. **7** was formed on the surface of each of the specimens. The photomicrograph shown in FIG. **7** was taken from the specimen treated at 1050°C for 8 hours in the treating material containing 10 percent of KBF_4.

FIGS. **8** and **9** are graphs obtained in this Example and showing the effects of the content of KBF_4 in the treating material, and the treating temperature on the thickness of the vanadium carbide layer formed on high carbon tool steel. As shown in FIG. **8,** the thickness of the vanadium carbide layer formed is rapidly increased to about 15 microns as the content of KBF_4 increases to 0.5 percent, then the thickness of the layer is slowly increased from about 15 microns to about 23 microns according to the increase of the content of KBF_4 from

0.5 to 5 percent. In the case that the content of KBF_4 is over 5 percent, the thickness of the carbide layer becomes constant, i.e. about 23 microns. With respect to the treating temperature, the thickness of the carbide layer formed gradually increases from about 3 microns to about 25 microns according to the increase of the treating temperature from 850° to 1050°C.

One of the carbide layers formed was tested by a X-ray diffraction method and it was confirmed that the layer was composed of the crystals of vanadium carbide. Also the carbide layer formed at 1050°C for 8 hours in the treating material containing 10 percent of KBF_4 was measured by a Vickers hardness tester and Hv 2800 was measured.

Example 7

Specimens made of several kinds of carbon steel (respective carbon content being 0.02, 0.05, 0.1, 0.2 and 0.35 percent) were treated at 1050°C for 8 hours in the treating material containing 10 percent of KBF_4 in the same manner as described in Example 6. The results obtained in this Example are shown in FIG. **10** with the thickness of the carbide layer formed and the content of the steel treated. As shown in FIG. **10**, the thickness of the carbide layer formed increases according to the increase of the carbon content in the steel.

The photomicrograph shown in FIG. **11** was taken from the specimen made of the steel containing 0.1 percent of carbon. The two layers i.e. upper and middle layers, are seen on the photomicrograph, the upper layer was confirmed to be a vanadium carbide layer of about 5.6 microns in thickness and the middle layer to be about 80 microns in thickness and to be a layer of solid solution of vanadium in iron.

According to this Example, it is apparent that thicker carbide layers can be formed from the steel having a higher content of carbon.

Example 8

In the same manner as described in Example 6, specimens made of high carbon tool steel were respectively treated at a temperature between 700° and 1050°C for 4 hours in a treating material containing 2 to 80 percent of KBF_4. The treating conditions under which the vanadium carbide layer was formed on the specimen are shown in FIG. **12.** The white round marks indicate the treating conditions, the treating temperature and the content of KBF_4 in the treating material. From this example, it is apparent that the carbide layer can be formed at a temperature in the wide range from 700° to 1050°C and in the treating material containing 2 to 80 percent of KBF_4. And also it was observed that the thicker carbide layer was formed at a higher treating temperature.

Example 9

In the same manner as described in Example 6, specimens made of high carbon tool steel (JIS SK3) were treated at 1000°C (in the treating materials (d) and (f)) or at 750°C (in the treating material (e)) for **4** hours in each of the following treating materials (d), (e) and (f).

d. treating material composed of 90 percent of ferrovanadium powder of −100 mesh and 10 percent of $NaBF_4$ powder of −100 mesh;

e. treating material composed of 70 percent of ferrovanadium powder of −100 mesh and 30 percent of $NaBF_4$ powder of −100 mesh;

f. treating material composed of 90 percent of ferrovanadium powder of −100 mesh and 10 percent of NH_4BF_4 powder of −200 mesh.

The specimens treated in each of the treating materials (d), (e) and (f) mentioned above were formed with the vanadium carbide layers of about 8 microns, 3 microns and 12 microns, respectively.

As one of the examples, the photomicrograph taken from the specimen treated in the treating material (c) is shown in FIG. **13.**

Example 10

In the same manner as described in Example 6, specimens made of high carbon tool steel (JIS SK3) were treated in each of the following treated materials (g) and (h).

g. treating material composed of 90 percent of ferroniobium (containing 53.2 percent of Nb, 8 percent of Ta, 0.06 percent of carbon and the balance of iron) powder of −100 mesh and 10 percent of KBF_4 powder of −200 mesh;

h. treating material composed of 40 percent of ferroniobium powder of −100 mesh and 60 percent of KBF_4 powder of −200 mesh.

The specimen treated at 1050°C for 8 hours in the treating material (g) was formed with the niobium carbide layer of 25 microns in thickness. And the specimen treated at 1000°C for 4 hours in the treating material (h) was formed with the niobium carbide layer of 15 microns in thickness.

The photomicrograph shown in FIG. **14** was taken from the specimen treated in the treating material (g).

Example 11

Several kinds of powdery treating materials composed of 84 to 99.5 percent of ferrotungsten (containing 78.7 percent of W, 0.17 percent of carbon and the balance of iron) powder of −100 mesh and 0.5 to 16 percent of KBF_4 powder of −200 mesh were introduced in each of iron containers, and then specimens, of 5×10×10 mm, made of high carbon tool steel (JIS SK3) were packed in each of said treating materials in said containers and were heated at 1050°C for 8 hours in an electronic furnace. The specimens treated were tested in the same manner as explained in Example **1.** And it was recognized that a tungsten carbide layer shown in FIG. **15** was formed on the surface of each of the specimens. The photomicrograph shown in FIG. **15** was taken from the specimen treated in the powdery treating material containing 10 percent of KBF_4. The carbide layers formed were recognized to be composed of the tungsten carbide $(Fe, W)_6C$ by a X-ray diffraction method.

FIG. **16** is a graph obtained in this Example and showing the effect of the content of KBF_4 in the treating material on the thickness of the tungsten carbide layer formed on high carbon tool steel.

Example 12

In the same manner as described in Example 11, specimens made of high carbon tool steel were treated in each of the treating materials composed of 55 to 90 percent of ferrotungsten powder of −100 mesh and 10 to 45 percent of KBF_4 powder of −200 mesh at a temperature between 700°C and 1050°C for 4 hours. The treating conditions are shown with the white round marks in FIG. **17.** All the specimens treated were formed with the tungsten carbide layers on the surfaces thereof. And the specimens, treated in the treating materials containing at least 40 percent of KBF_4, were formed with the tungsten carbide layers containing a small amount of iron boride.

Example 13

In the same manner as described in Example 11, specimens made of high carbon tool steel (JIS SK3) were treated at 750°C for 4 hours in each of the following treating materials (i) and (j).

i. treating material composed of 55 percent of ferrotungsten powder of −100 mesh and 45 percent of $NaBF_4$ powder of −100 mesh;
j. treating material composed of 90 percent of ferrotungsten powder of −100 mesh and 10 percent of NH_4BF_4 of −200 mesh.

The specimens treated in one of said treating materials (i) and (j) were formed with the tungsten carbide layers of about 6 microns in thickness.

As one of the Examples of the layer formed, the photomicrograph taken from the specimen which was treated in the treating material (j) is shown in FIG. **18.**

Example 14

In the same manner as described in Example 11, specimens made of high carbon tool steel (JIS SK3) were treated at 900° or 1050°C for 4 hours in each of the following treating materials (k) and (l).

k. treating material composed of 90 percent of ferromolybdenum (containing 61.66 percent of Mo, 0.05 percent of carbon and the balance of iron) powder of −100 mesh and 10 percent of KBF_4 powder of −200 mesh;
l. treating material composed of 40 percent of ferromolybdenum powder of −100 mesh and 60 percent of KBF_4 powder of −200 mesh.

The specimen treated at 1050°C in the treating material (k) is formed the molybdenum carbide layer of 3 microns in thickness, and the specimen treated at 900°C in the treating material (l) was formed with the molybdenum carbide layer of 1 micron in thickness. Said molybdenum carbide layers were confirmed to be composed of the molybdenum carbide $(Fe,Mo)_3C$.

The photomicrograph shown in FIG. **19** was taken from the specimen treated in the treating material (k).

What is claimed is:

1. A method for forming a carbide layer on the surface of iron or a ferrous alloy article in a powdery treating material, said article containing at least 0.02 percent of carbon, comprising the steps of preparing 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 mixtures thereof and 20 to 99.5 percent by weight of one member selected from the group consisting of metallic Ti, Zr, Hf, V, Nb, Ta, Mo, W, ferrous alloys thereof, and mixtures thereof packing the article in said powdery treating material, heating said article within said powdery treating material at a temperature between 600° and 1200°C for 1 to 30 hours; taking said article out of said powdery treating material, and thereby forming the carbide layer of Ti, Zr, Hf, V, Nb, Ta, Mo, W of mixtures thereof on the surface of said article.

2. A method according to claim **1,** wherein said article contains at least 0.05 percent of carbon and is heated at a temperature between 700° and 1000°C in the powdery treating material consisting essentially of 1 to 30 percent of said tetrafluoroborate and 70 to 99 percent of said metal.

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

4. A method according to claim **1,** wherein said powdery treating material is less than 40 mesh inclusive.

5. A method according to claim **1,** wherein an inactive powdery material selected from the group consisting of alumina silica, boron nitride, chromium oxide and mixtures thereof is added up to the same quantity as that of said treating material.

6. A method for forming a carbide layer of a IV-*b* group element on the surface of iron or a ferrous alloy article in a powdery treating material, said article containing at least 0.05 percent of carbon comprising the steps of preparing the powdery treating material consisting essentially of 0.5 to 60 percent by weight of one member selected from the group consisting of potassium tetrafluoroborate, sodium tetrafluoroborate, ammonium tetrafluoroborate and mixtures thereof and 40 to 99.5 percent by weight of a IV-*b* group metal powder selected from the group consisting of Ti, Zr, Hf, ferrous alloys thereof and mixtures thereof, packing the article in said powdery treating material, heating said article within said powdery treating material at a temperature between 600° and 1200°C, taking said article out of said powdery treating material, and thereby forming the carbide layer of said IV-*b* group element on the surface of said article.

7. A method according to claim **8,** wherein said article contains at least 0.1 percent of carbon and is heated at a temperature between 700° and 1000°C.

8. A method for forming a carbide layer of a V-*b* group element on the surface of iron or a ferrous alloy article in a powdery treating material, said article containing at least 0.02 percent carbon, comprising the steps of preparing 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 mixtures thereof and 20 to 99.5 percent of a V-*b* group metal powder selected from the group consisting of V, Nb, Ta, ferrous alloys thereof and mixtures thereof, packing the article in said powdery treating material, heating said article within said powdery treating material at a temperature between 650° and 1200°C, taking said article out of said powdery treating material, and thereby forming the carbide layer of said V-*b* group element on the surface of said article.

9. A method according to claim **8,** wherein said article contains at least 0.05 percent of carbon and is heated at a temperature between 750° and 1000°C.

10. A method for forming a carbide layer of Mo or W on the surface of iron or a ferrous alloy article in a powdery treating material, said article containing at least 0.05 percent carbon, comprising the steps of preparing the powdery treating material consisting essentially of 0.5 to 45 percent by weight of one member selected from the group consisting of potassium tetrafluoroborate, sodium tetrafluoroborate, ammonium tetrafluoroborate and the mixtures thereof and 55 to 99.5 percent of a metal powder selected from the group consisting of Mo, W, ferrous alloys thereof and mixtures thereof, packing the article in said powdery treating material, heating said article within said powdery treating material at a temperature between 650° and 1200°C, taking said article out of said powdery treating material, and thereby forming the carbide layer of Mo or W on the surface of said article.

11. A method according to claim **10**, wherein said article contains at least 0.1 percent of carbon and is heated at a temperature between 750° and 1000°C.

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