

[54] METHOD FOR FORMING AN  
IRON-MANGANESE CARBIDE LAYER ON  
THE SURFACE OF AN IRON BASE ALLOY  
ARTICLE CONTAINING CARBON

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[57] ABSTRACT

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117/118

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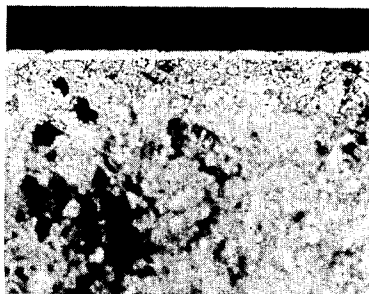
A method for forming an iron-manganese carbide layer on the surface of an iron base alloy article containing carbon in a powdery treating material comprising packing said article in the mixed powders of a tetrafluoroborate and a metal containing manganese and heating said article within said mixed powders, thereby forming a very hard iron-manganese carbide layer on the surface of said article. The method of this invention can be carried out without employing the non-oxidation atmosphere and can improve greatly the wear resistance of iron base alloy articles.

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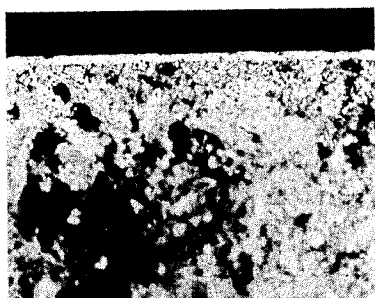
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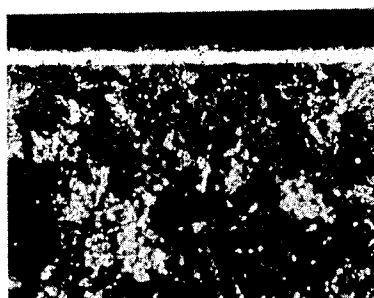
5 Claims, 7 Drawing Figures



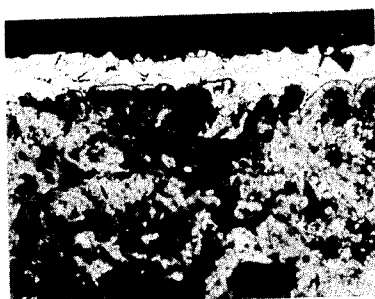
*FIG. 1*



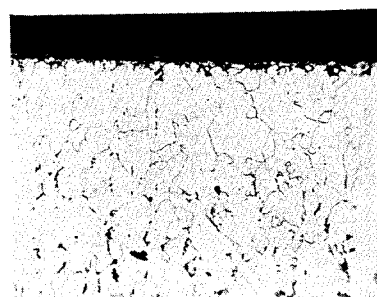
*FIG. 2*



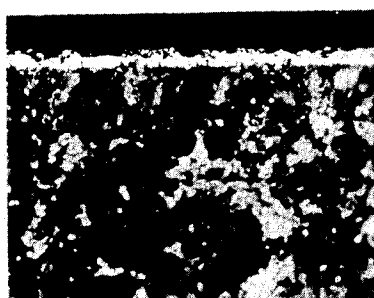
*FIG. 3*



*FIG. 5*



*FIG. 6*



*FIG. 7*

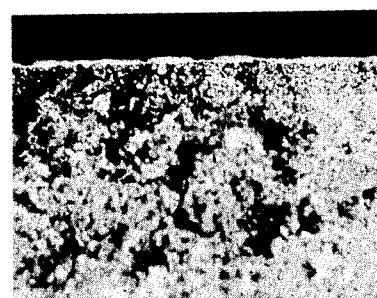
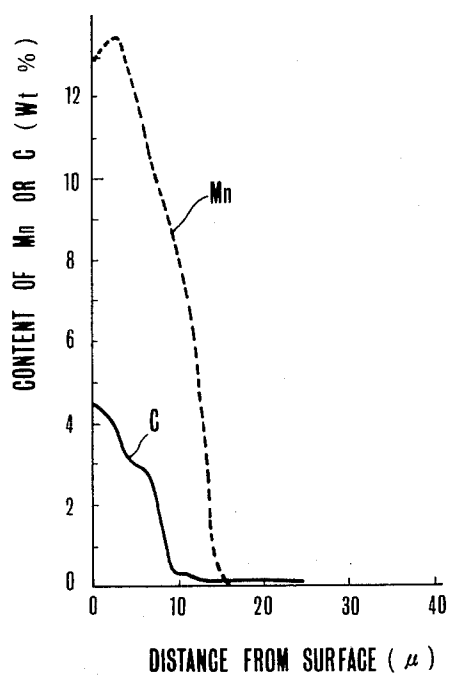


FIG. 4



# METHOD FOR FORMING AN IRON-MANGANESE CARBIDE LAYER ON THE SURFACE OF AN IRON BASE ALLOY ARTICLE CONTAINING CARBON

This invention relates to a method for forming an iron-manganese carbide layer on the surface of an iron base alloy article containing at least 0.1 percent by weight of carbon (hereinafter percent means percent by weight), and more particularly it relates to the formation of the carbide layer on the surface of the article in a powdery treating material. The iron base alloy article with the carbide layer formed thereon has a greatly improved hardness and wear resistance.

It has been known that the iron-manganese carbide layer formed on the surface of an iron article is very hard and has a good wear resistance, and the formation of the iron-manganese carbide layers has been applied to the surfaces of metal moulds such as punches and die, tools such as pinchers and screwdrivers, and mechanical parts for the sake of the improvement of their wear resistance.

As the methods for forming the iron-manganese carbide layer on the surface of an iron alloy article, vapor plating, metal spraying, spark hardening and pack method has been known. However, these conventional methods have some defects. For example, the vapor plating uses halogen compounds as the source of the metal to be plated. Therefore it needs a complex apparatus such as a special atmospheric furnace and the halogen gases erode quickly the apparatus. The metal spraying needs a costly treating material and the bonding of the layer formed on the surface of an article is not so good. Spark hardening takes a long operation time for the treatment and the surface of the layer formed is not so smooth. Also the conventional pack method is to heat an article to be treated in the non-oxidation atmosphere or to heat a sealed container containing an article to be treated. Therefore the pack method necessitates a special atmospheric furnace or a special sealed container.

It is the principal object of this invention to provide a method for forming an iron-manganese carbide layer on the surface of an iron alloy article.

It is another object of this invention to provide a method for forming an iron-manganese 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 an iron-manganese 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 an iron-manganese carbide layer on the surface of an iron alloy article containing carbon 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 an iron-manganese carbide layer on carbon tool steel, which is formed according to Example 1;

FIG. 2 is a photomicrograph showing another iron-manganese carbide layer on carbon tool steel, which is formed according to Example 1;

FIG. 3 is a photomicrograph showing still another iron-manganese carbide layer formed on carbon tool steel according to Example 1;

FIG. 4 is a graph showing the relation between the contents of carbon and manganese included in the layer formed and the distance from the surface of the layer;

FIG. 5 is a photomicrograph showing an iron-manganese carbide layer formed on the surface of a structural carbon steel according to Example 2;

FIG. 6 is a photomicrograph showing an iron-manganese carbide layer formed on the surface of carbon tool steel according to Example 3;

FIG. 7 is a photomicrograph showing an iron-manganese carbide layer formed on the surface of carbon tool steel according to Example 4.

Broadly, the present invention is directed to a new pack method for forming an iron-manganese carbide layer on the surface of an iron base alloy article containing carbon by introducing manganese onto the surface of the article and combining said manganese with the carbon and iron included in the article, also the present invention can be carried out in the air or in an inert gas atmosphere and at a relatively low treating temperature. Namely, the method of the present invention comprises preparing the mixed powders composed of a tetrafluoroborate and metallic manganese or a metal containing manganese, packing the iron base alloy article containing at least 0.1 percent of carbon in said mixed powders and heating the article within said mixed powders so as to form the iron-manganese carbide layer on the surface of said article. It has been found upon carrying out a large number of experiments that the method of the invention can form the carbide layer in the air without a special container and at a relatively low temperature 700°C. Therefore, this method does not necessitate a special atmospheric furnace or container and is highly suitable for the surface treatment of tools, dies and parts for many kinds of equipments. Further, it is highly productive, and it has been recognized that the carbide layer thus obtained is strongly and tightly integrated to the surface of a mother article and has, in addition, a dense and uniform metallic phase. The Vickers hardness of the layer is about Hv 1400.

In order to prepare the powdery treating material, a tetrafluoroborate powder and the powder of the metal containing manganese are mixed together. As the tetrafluoroborate, potassium tetrafluoroborate ( $\text{KBF}_4$ ), sodium tetrafluoroborate ( $\text{NaBF}_4$ ), ammonium tetrafluoroborate ( $\text{NH}_4\text{BF}_4$ ) and the like can be used. In the powdery treating material, one or more than one kind of tetrafluoroborate can be used and these alkali tetrafluoroborates work as a promotor of this powdery treating material. As the metal containing manganese, metallic manganese and manganese alloys can be used and work as the principal ingredient of the treating material. Said alloys include the alloys with iron. Especially, the alloys with iron are suitable for the metal of the treating material because the alloys are cheap and easy to obtain. It is preferable that the tetrafluoroborate

roborate is selected to be 100 mesh or finer and the metal powder is 40 mesh or finer. The powdery tetrafluoroborate may be included in the treating material in a quantity between 1 and 40 percent. With use of less quantity of tetrafluoroborate than 1 percent, the formation of the carbide layer would not be uniform due to the instability as a result of the introduction of manganese onto the surface of the article. Too much addition of the tetrafluoroborate will make the treating material fused or sintered at a high treating temperature. Therefore, the treating material is solidified after the treating operation and it will be difficult to take the article treated out of the treating material and the treating material will be repeatedly unusable and besides the surface condition of the article will not be good. Preferably, the quantity of the tetrafluoroborate is between 2 and 30 percent. The remainder of the treating material is the powdery metal mentioned above. Said powdery metal may be mixed in a quantity between 60 and 99 percent and preferably in a quantity between 70 and 98 percent. In order to prevent the solidification of the treating material, inactive powdery substance having a high melting point such as alumina ( $\text{Al}_2\text{O}_3$ ), silica ( $\text{SiO}_2$ ), boron nitride (BN), chromic oxide ( $\text{Cr}_2\text{O}_3$ ) and the like can be added up to 80 percent of the treating material.

The heating temperature may be selected within the wide range from 650° to 1,200°C. At a heating temperature below 650°C, the adequate thick carbide layer cannot 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 be sintered and the article treated would be integrated with the treating material. At this time, the property of the iron base alloy article would be worsened. The preferable range of the heating temperature is 700° to 1,000°C. When iron base alloy articles are treated at a heating temperature above the  $\alpha = \gamma$  transformation point of the iron base alloys for quicker formation of the carbide, distortion may be liable to occur in most of the articles by virtue of the transformation of the iron base alloys, which distortion can be naturally avoided by lowering the heating temperature below 800°C for alloy steel and below 700°C for carbon steel. The present invention can be carried out at a lower temperature, 650°C. Therefore, the iron-manganese carbide layer can be formed without distortion.

The heating time depends upon the thickness of the carbide to be formed. Heating shorter than 1 hour 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 iron base alloy article must contain at least 0.1 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 manganese from the treating material to form the carbide on the surface of the article. The higher content of the carbon in the article is more preferable for forming the carbide layer. The iron base alloy article containing less than 0.1 percent of carbon may not be

formed with a uniform and thick carbide layer by the treatment. As long as the iron base alloy articles contain at least 0.1 percent of carbon, any kind of iron alloys such as iron alloys with chromium, tungsten, molybdenum or nickel can be used as the article of the present invention. Further, a pure iron article having 0.1 percent or more carbon in the portion near the surface, which carbon has been introduced from outside by casehardening, can also be used as the article of the present invention.

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

Hereinafter several examples will be shown to explain the invention in more detail. In the examples, small rods used as specimens are regarded to be the models of the pins of moulds and of the rod like parts of various apparatuses.

#### EXAMPLE 1

Several kinds of powdery treating materials composed of 60 to 98 percent of iron-manganese alloy (containing 76 percent of manganese) of -100 mesh and the balance of  $\text{KBF}_4$  of -200 mesh were introduced into each of alumina crucibles of 45 mm inner diameter and 60 mm height, and then specimens of 10 mm diameter and 5 mm height made of carbon tool steel (JIS SK4, containing 1.0 percent of carbon) were packed in each of said treating materials in said crucibles and were heated in an electric furnace under the air atmosphere at a temperature between 700° and 900°C for 4 hours, and then they were taken out of the furnace and cooled in the air. (Before the treatment, said specimens were treated to remove their rusts and rinsed to reveal their metallic surface.) During the heating the crucibles were not covered with any lid. 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/or by EPMA (Electro Probe Micro Analyzer).

The photomicrograph shown in FIG. 1 was taken from the specimen which was treated at 700°C for 4 hours in the powdery treating material composed of 20 percent of  $\text{KBF}_4$  and 80 percent of iron-manganese alloy. Also the photomicrographs shown in FIGS. 2 and 3 were taken from the specimens which were treated at 800°C in the treating material containing 2 percent of  $\text{KBF}_4$  and at 900°C in the treating material containing 30 percent of  $\text{KBF}_4$ , respectively. The photomicrographs indicate that an excellent layer is formed on the surface of each of the specimens. The other specimens treated in this Example were also observed to have an excellent (integral and dense) layer, which is similar to the layers shown in FIGS. 1 to 3. From the microscopic observation, it was found that the thickness of the layer formed is constant within the range from 2 to 40 percent of  $\text{KBF}_4$ . However, said thickness is greatly effected by the heating temperature and said thickness increases as the heating temperature increases. The EPMA tests revealed that the layers formed contain large amount of manganese and carbon. For example, one of the EPMA test results is shown in FIG. 4 with the relation of the contents of manganese and carbon included in the layer formed and the distance from the surface. The test layer was formed on carbon tool steel

at 900°C in the treating material containing 30 percent of KBF<sub>4</sub>. In FIG. 4, the ordinate and the abscissa represent the contents (percent) of each manganese and carbon and the distance or depth (micron) from the surface of the specimen, respectively. In the range to 2 or 3 microns from the surface, about 12 percent of manganese is included and as the distance increases, the content of manganese decreases rapidly and the content becomes about zero at the distance of 13 - 14 microns. On the other hand, the content of the carbon is 4.5 - 4.7 percent near the surface and becomes to be about 3 percent at the distance of 4 - 6 microns, and at the distance of 8 microns the content of carbon becomes 1 percent which is the same as the carbon content of the mother steel.

The layer tested by the EPMA and mentioned above was also tested by the X-ray diffraction method and it was revealed that the layer is composed of iron-manganese carbide. Also the upper portion of the mother material includes manganese in the form of the solid solution of manganese in iron. In some specimens treated were observed a second layer between the iron-manganese carbide layer and mother material. The second layer was recognized to be the solid solution of iron.

According to the Example described above, it is apparent that the manganese of the treating material is introduced into the surface of a carbon tool alloy article and forms iron-manganese carbide with the carbon and iron included in the article by using a powdery treating material including KBF<sub>4</sub> in a wide range.

#### EXAMPLE 2

Specimens of 10 mm diameter and 5 mm height made of structural carbon steel (JIS S10C, containing 0.1 percent of carbon) with their rust removed were treated under the same conditions of Example 1. All the specimens treated were observed by a micro scope and a few of them were tested by an X-ray diffraction method and/or EPMA. From the micro scopic observation, all the specimens treated were formed with a thin layer. As one example, the layer treated at 800°C for 4 hours in the powdery treating material containing 2 percent of KBF<sub>4</sub> are shown in FIG. 5. From the results of X-ray diffraction and EPMA, the layer is revealed to be iron-manganese carbide, (Fe,Mn)<sub>3</sub>C and the upper portion of the mother material includes an iron solid solution with manganese.

#### EXAMPLE 3

NaBF<sub>4</sub> of 200 mesh or finer was used as the promotor in place of the KBF<sub>4</sub> in the treating materials used in Example 1. Specimens of 10 mm diameter and 5 mm height made of carbon tool 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 with the same conditions of Example 1 except their promotor mentioned above. All the specimens treated were observed by a micro-scope and a few of them were tested

by an X-ray diffraction method and/or EPMA. From the micro-scopic observation, all the specimens treated were formed with a layer. As one example, the photomicrograph taken from the specimen treated at 800°C for 4 hours in the treating material containing 10 percent of NaBF<sub>4</sub> are shown in FIG. 6, and the layer was recognized to be iron-manganese carbide (Fe,Mn)<sub>3</sub>C.

According to the example, it is apparent that NaBF<sub>4</sub> works as the promotor of this treating material.

#### EXAMPLE 4

NH<sub>4</sub>BF<sub>4</sub> of 200 mesh or finer was used as the promotor of the KBF<sub>4</sub> in the treating materials used in Example 1. Specimens made of carbon tool steel which is the same as the steel used in Example 1 were treated at a temperature between 700° and 900°C for 4 hours in the powdery treating material containing 30 percent of NH<sub>4</sub>BF<sub>4</sub>. All the specimens treated were observed by a microscope and a few of them were tested by an X-ray diffraction method and/or EPMA. From the micro-scopic observation, all the specimens treated were formed with a layer. As one example, the photomicrograph taken from the specimen treated at 700°C are shown in FIG. 7. Also the layer was recognized to be iron-manganese carbide, (Fe,Mn)<sub>3</sub>C.

What is claimed is:

1. A method for forming an iron-manganese carbide layer on the surface of an iron base alloy article containing at least 0.1 percent carbon in a powdery treating material, comprising the steps of preparing the powdery treating material consisting essentially of 1 to 40 percent of at least one member selected from the group consisting of potassium tetrafluoroborate, sodium tetrafluoroborate and ammonium tetrafluoroborate and mixtures thereof and 60 to 99% of a member selected from the group consisting of metallic manganese and iron-manganese alloys, packing the iron base alloy article in said powdery treating material, heating said article within said powdery treating material at a temperature of between 650°C and 1,200°C for 1 to 30 hours, and taking said article out of said powdery treating material, thereby forming an iron-manganese carbide layer on the surface of said article.

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

3. A method according to claim 1, wherein said article is casehardened for increasing the content of carbon in the portion near the surface of the article before the heating step.

4. A method according to claim 1, wherein said powdery treating material has a particle size less than 40 mesh.

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 in amounts up to 80% to said powdery treating material.

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