

[54] **METHOD FOR FORMING A CARBIDE LAYER OF AN ELEMENT SELECTED FROM THE GROUP CONSISTING OF V, NB, TA AND MIXTURES THEREOF ON THE SURFACE OF AN IRON, FERROUS ALLOY OR CEMENTED CARBIDE ARTICLE**

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[57] ABSTRACT

[21] Appl. No.: **355,283**

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June 8, 1972	Japan.....	47-56493

[52] U.S. Cl..... **204/39; 204/14 N**

[51] Int. Cl..... **C23b 5/00**

[58] Field of Search **204/39, 14 N; 148/15.5, 148/15**

A method for forming a carbide layer of an element selected from the group consisting of V, Nb, Ta on the surface of an iron, ferrous alloy or cemented carbide article in a treating molten bath, comprising preparing the treating molten bath composed of boron oxide and an element selected from the group consisting of V, Nb, Ta immersing the article in the treating molten bath and applying an electric current to the treating molten bath through said article being used as the cathode, thereby forming a very hard carbide layer of said element on the surface of said article. The method of this invention can form quickly a uniform and dense carbide layer on the surface of the article and can be carried out in the open air.

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14 Claims, 27 Drawing Figures

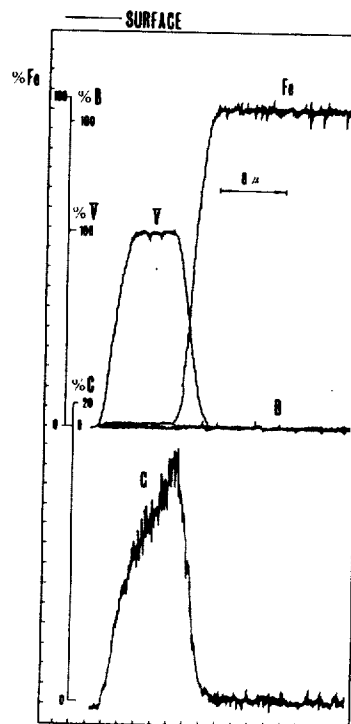
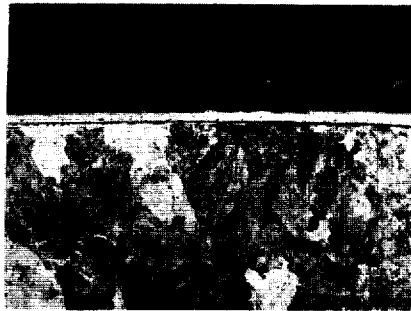


FIG. 1



($\times 400$)

FIG. 2



($\times 400$)

FIG. 3



($\times 400$)

FIG. 4



($\times 400$)

FIG. 9



($\times 400$)

FIG. 11



($\times 400$)

FIG. 5

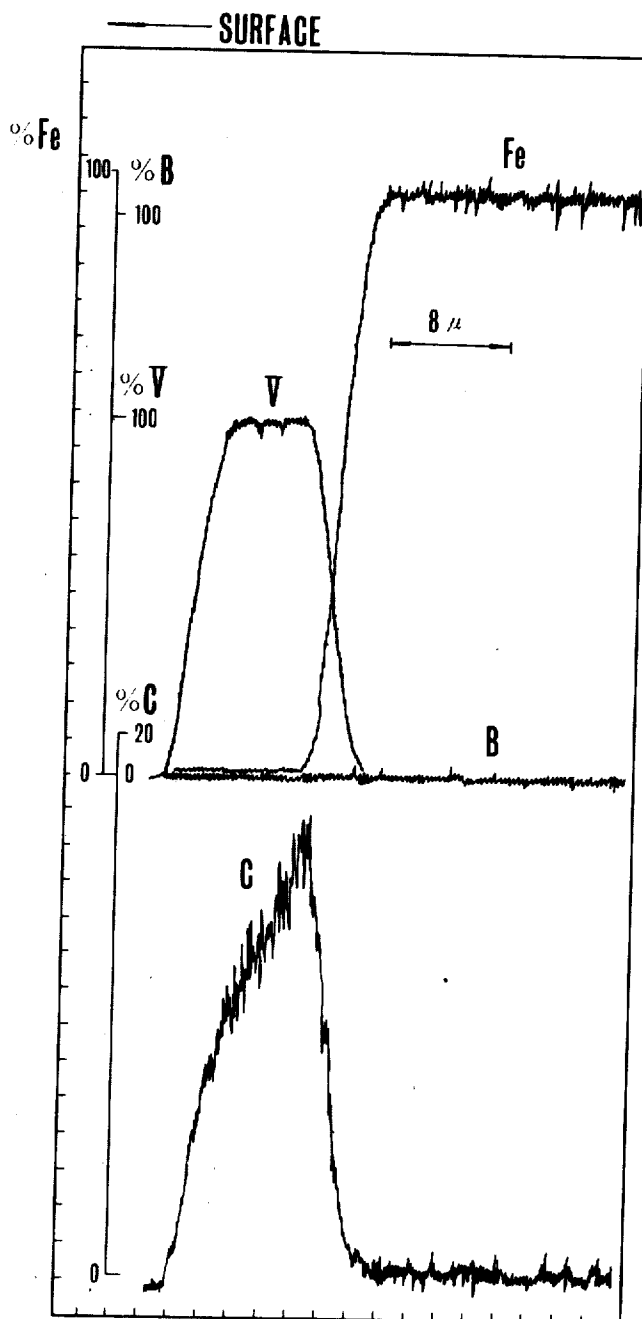


FIG. 6

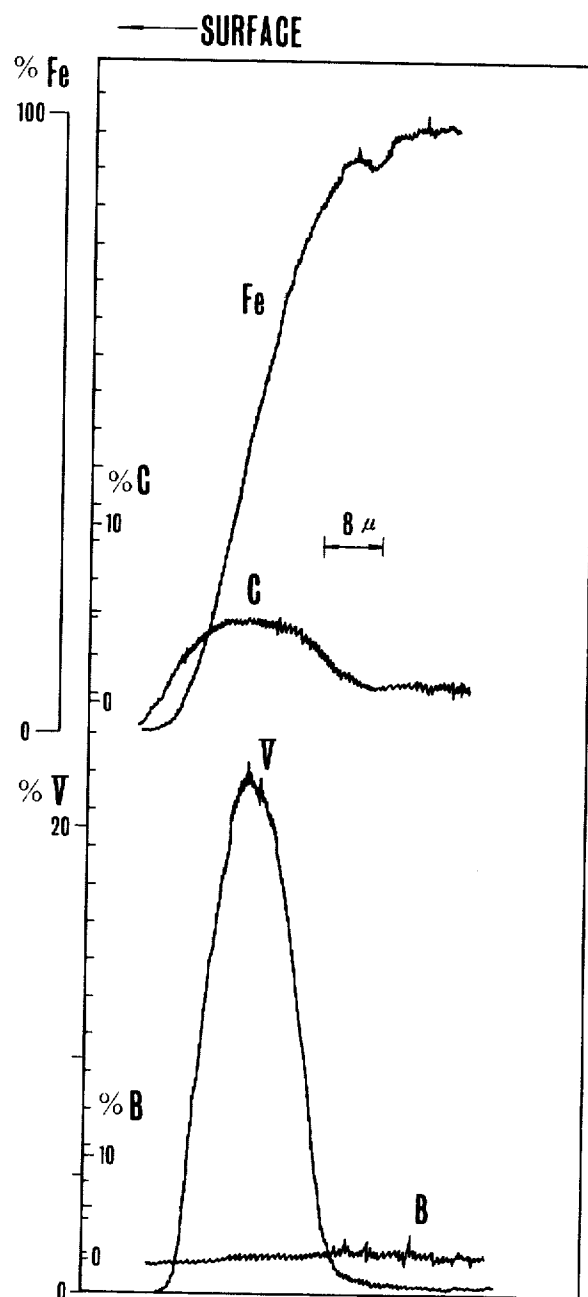


FIG. 7

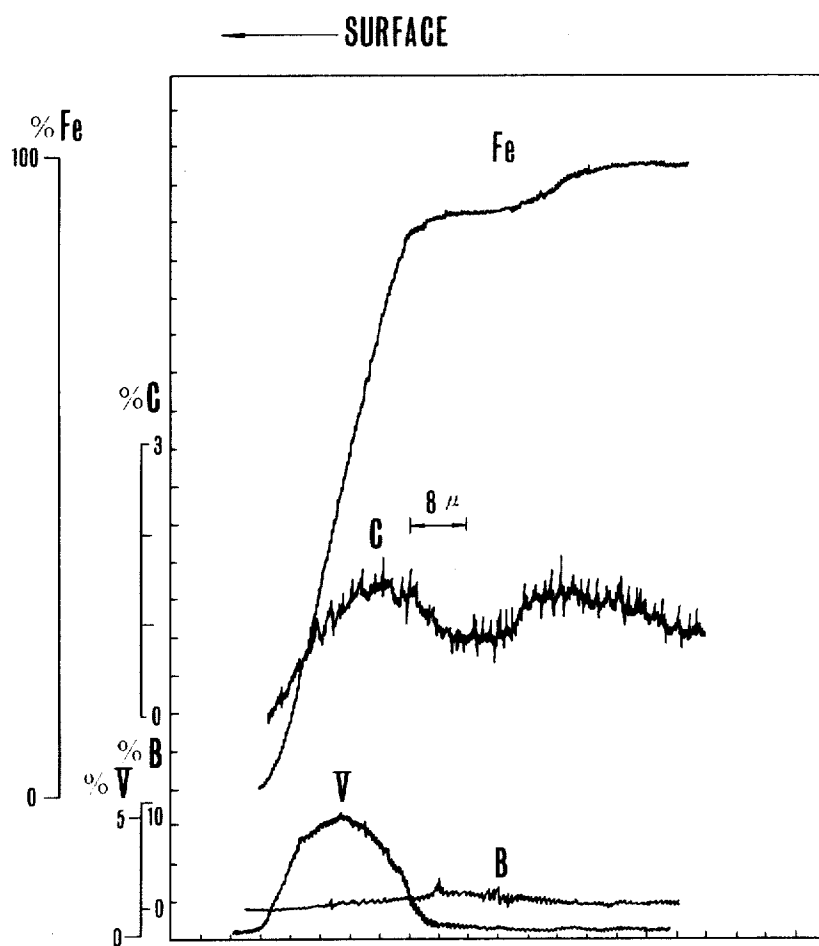


FIG. 8

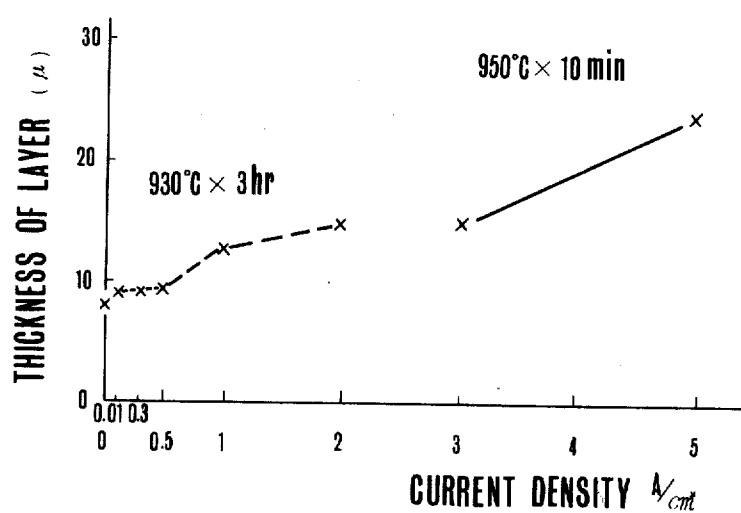


FIG. 10

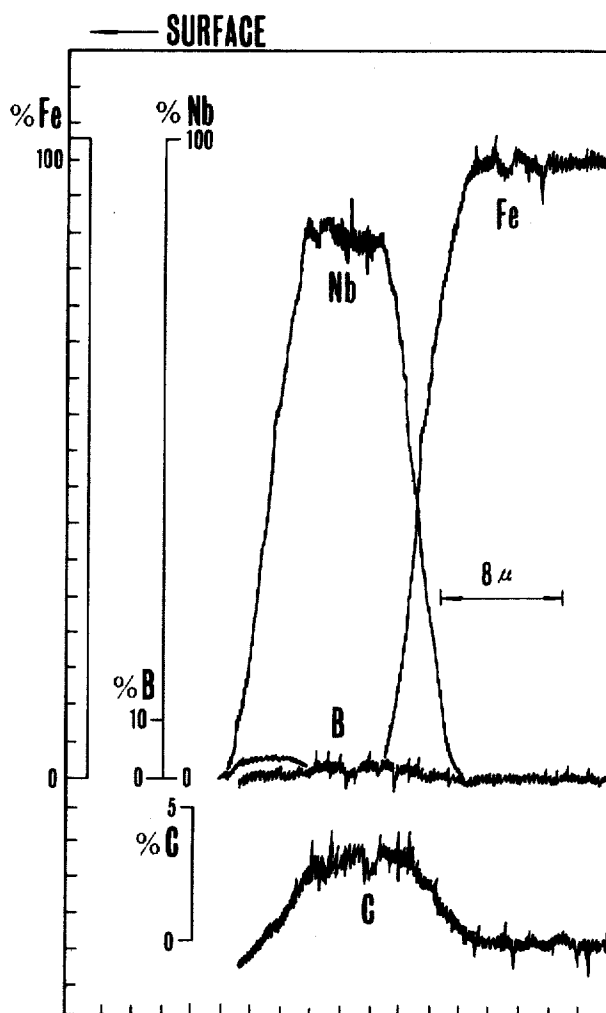


FIG. 12



($\times 400$)

FIG. 13



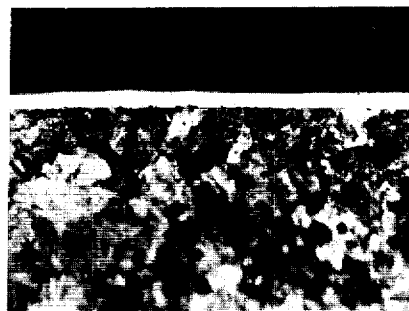
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FIG. 14



($\times 400$)

FIG. 17



($\times 400$)

FIG. 19



($\times 400$)

FIG. 20



($\times 400$)

FIG. 15

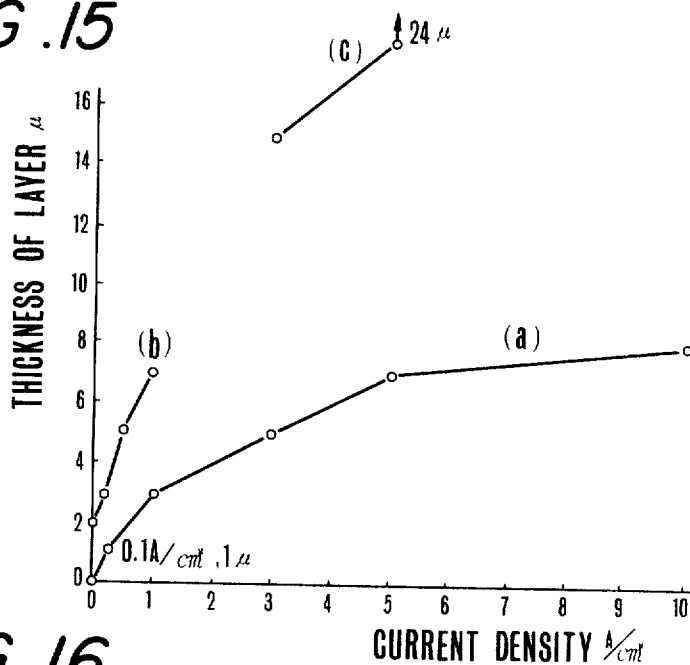
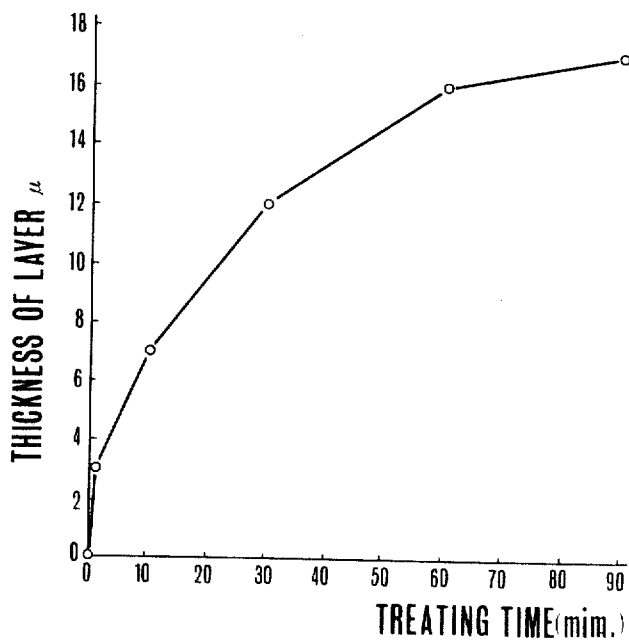


FIG. 16



SURFACE

FIG. 18

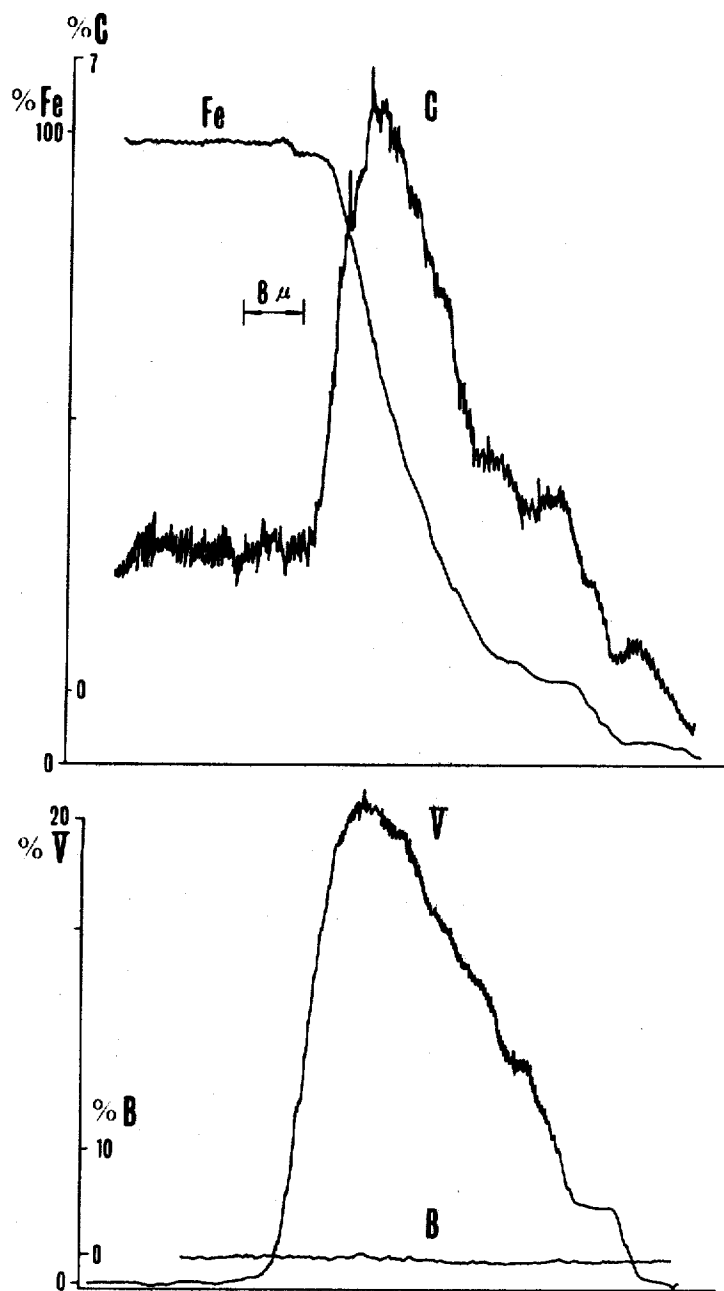
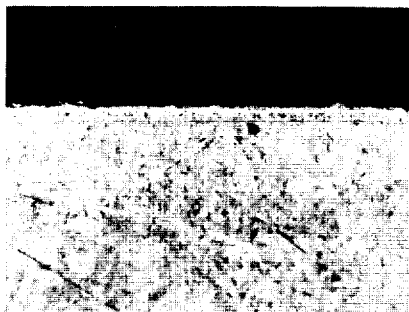


FIG. 21



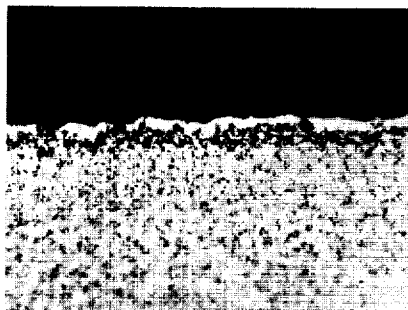
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FIG. 22



($\times 400$)

FIG. 24



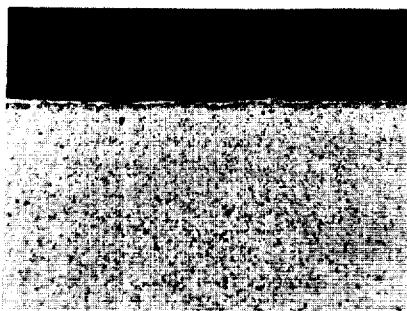
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FIG. 25



($\times 400$)

FIG. 26



($\times 400$)

FIG. 23

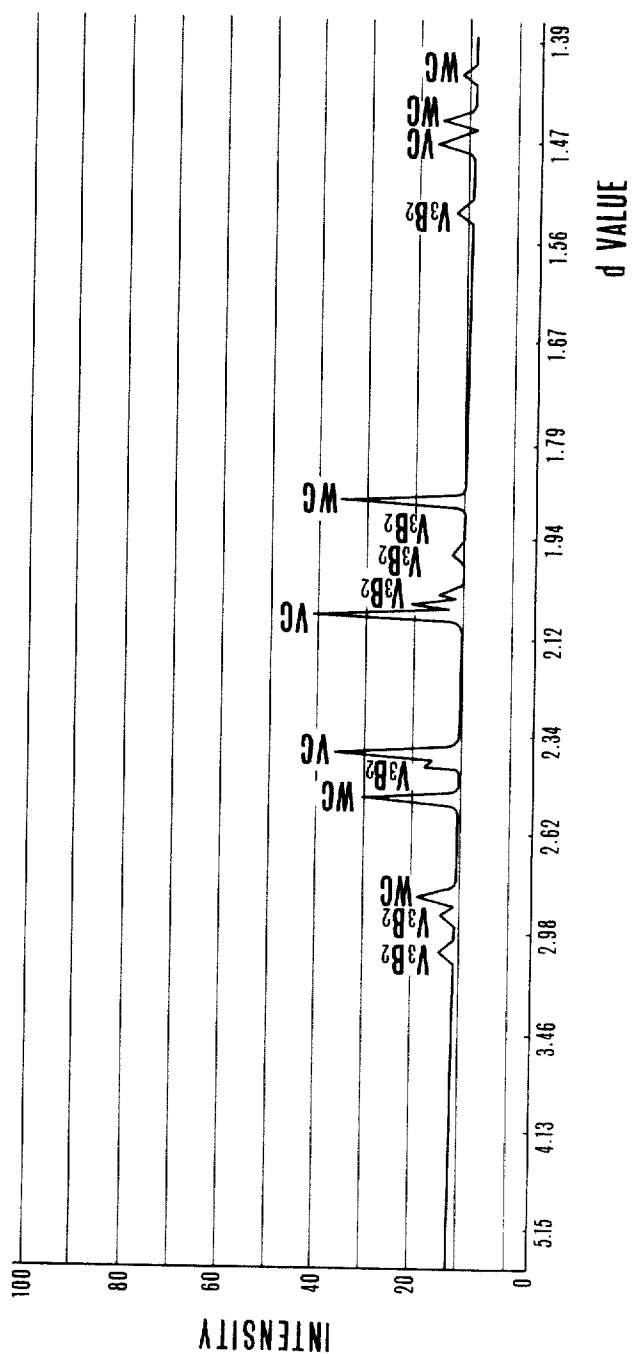
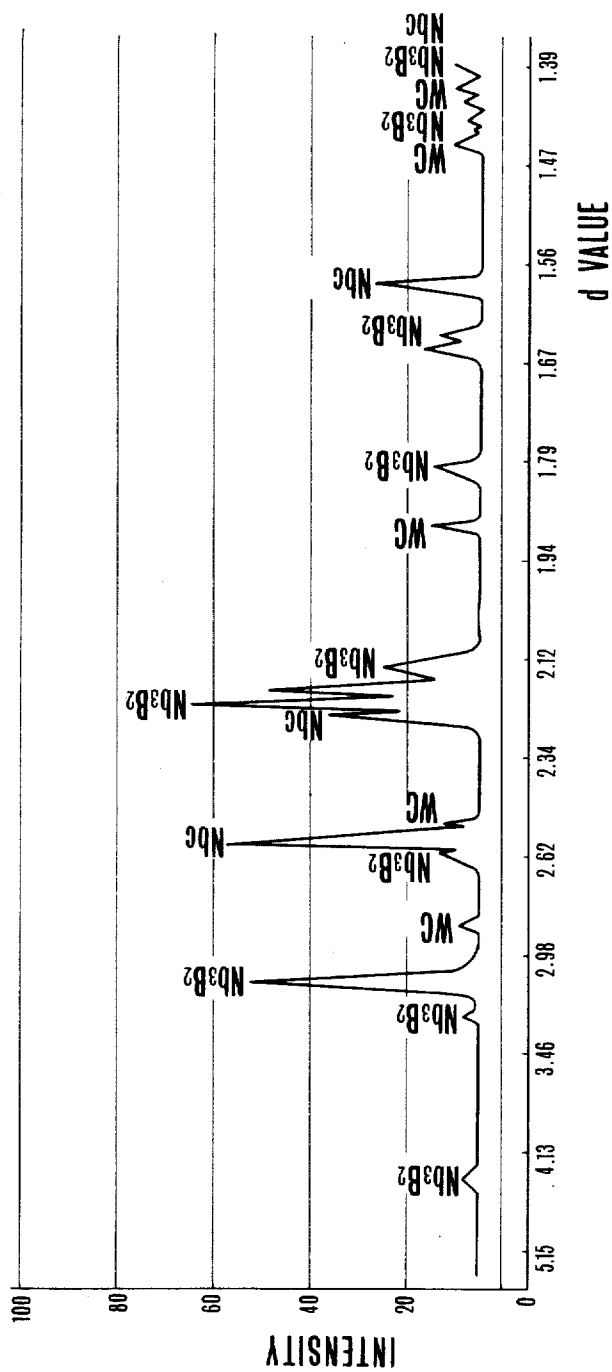


FIG. 27



**METHOD FOR FORMING A CARBIDE LAYER OF
AN ELEMENT SELECTED FROM THE GROUP
CONSISTING OF V, NB, TA AND MIXTURES
THEREOF ON THE SURFACE OF AN IRON,
FERROUS ALLOY OR CEMENTED CARBIDE
ARTICLE**

This invention relates to a method for forming a carbide layer of an element selected from the group consisting of V, Nb, Ta on the surface of an iron, ferrous alloy or cemented carbide article, and more particularly it relates to the formation of the carbide layer on the surface of the article immersed in a treating molten bath. The iron, ferrous alloy or cemented carbide article with the carbide layer formed thereon has a greatly improved hardness, wear resistance and machinability.

There have been reported several kinds of methods for coating or forming a metallic carbide layer on the surface of metallic articles. We have developed a method for forming a carbide layer of V, Nb, Ta, and mixtures thereof on the surface of metallic article in a treating molten bath consisting of boron oxide such as boric acid or a borate and a metal powder containing said element or elements (Japanese Patent Application Ser. No. 44-87805). The method can form a uniform carbide layer and is highly productive and cheap. The carbide of V, Nb, Ta and the mixtures thereof, such as vanadium carbide (VC), niobium carbide (Nb) and tantalum carbide (TaC) has a very high hardness ranging from Hv 2000 to Hv 3000. Therefore, the carbide layer formed represents a high value of hardness and a superior resistance performance against wear and is thus highly suitable for the surface treatment of moulds such as dies and punches, tools such as pinchers and screwdrivers, parts for many kinds of tooling machines, automobile parts to be subjected to wear.

Further, the carbide of V, Nb, or Ta is much harder and less reactive with iron or steel at a high temperature than the tungsten carbide forming cemented carbide is. Therefore, the formation of the carbide layer of said element on the surface of a cutting tool made of cemented carbide increases greatly the durability of the tool.

The method mentioned above, however, takes a relatively long time for forming a practically acceptable thick carbide layer.

Therefore, it is the principal object of the present invention to provide an improved method for forming a carbide layer of an element selected from the group consisting of V, Nb and Ta on the surface of an iron, ferrous alloy or cemented carbide article in a treating molten bath.

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

It is still another object of this invention to provide a method for forming a metallic carbide layer on the surface of the article by applying an electric current to the article.

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

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 therefore, will best be understood from the following description of specific embodiments when read in connection with the accompanying drawings, in which:

FIGS. 1 to 4 are photomicrographs showing vanadium carbide layers on carbon tool steel, which are formed according to Example 1;

FIGS. 5 to 7 are graphs obtained in Example 1 by X-ray micro analyzer and showing the contents of the components forming the carbide layers;

FIG. 8 is a graph obtained in Example 1 and showing the effect of the current density applied to the article treated on the thickness of the layer formed;

FIG. 9 is a photomicrograph showing a niobium carbide layer on carbon tool steel, which is formed according to Example 2;

FIG. 10 is a graph obtained in Example 2 by X-ray micro analyzer and showing the contents of the components forming the niobium carbide layer;

FIGS. 11 to 13 are photomicrographs showing vanadium carbide layers on carbon tool steel, which are formed according to Example 3;

FIG. 14 is a photomicrograph showing a vanadium carbide layer formed on carbon tool steel according to Example 4;

FIGS. 15 and 16 are graphs obtained in Example 6 and showing the effect of the current density applied to the article treated on the thickness of the layer formed;

FIG. 17 is a photomicrograph showing a vanadium carbide layer formed on carbon tool steel according to Example 6;

FIG. 18 is a graph obtained in Example 6 by X-ray micro analyzer and showing the contents of the components forming the vanadium carbide layer;

FIG. 19 is a photomicrograph showing a vanadium carbide layer formed on carbon tool steel according to Example 7;

FIG. 20 is a photomicrograph showing a niobium carbide layer formed on carbon tool steel according to Example 9;

FIGS. 21 and 22 are photomicrographs showing vanadium carbide layers formed on carbon tool steel according to Example 11;

FIG. 23 is an X-ray diffraction chart of the vanadium carbide layer formed on cemented carbide according to Example 12;

FIG. 24 is a photomicrograph showing a vanadium carbide layer formed on cemented carbide according to Example 14;

FIG. 25 is a photomicrograph showing a niobium layer formed on cemented carbide according to Example 15;

FIG. 26 is a photomicrograph showing a niobium carbide layer formed on cemented carbide according to Example 16;

FIG. 27 is an X-ray diffraction chart on the niobium carbide layer formed on cemented carbide according to Example 16.

Broadly, the present invention is directed to an improvement of the method for forming a carbide layer of an iron, ferrous alloy or cemented carbide article in a treating molten bath and is characterized in that the treating bath is composed of a boric oxide and an element selected from the group consisting of V, Nb, and Ta dissolved therein and in that the article immersed in

the treating molten bath is applied with an electric current for depositing the element on the surface of the article. The element deposited reacts with the carbon contained within the article and forms the carbide layer of the element on the surface of the article. Namely, the method of the present invention comprises preparing a treating molten bath containing a molten boron oxide and an element selected from the group consisting of V, Nb, and Ta immersing an iron, ferrous alloy or cemented carbide article in the treating molten bath, applying an electric current to the treating molten bath through the article being used as the cathode for forming the carbide layer of the element on the surface of the article.

The electric current activates to deposit the element dissolved in the treating molten bath on the surface of the article and accelerates the formation of the carbide layer of the element on the surface of the article. The voltage of the electric current is relatively low. It is not necessary for said voltage to be enough high for electrolyzing the molten boron oxide in the treating molten bath. In order to accelerate the formation of the carbide layer of the element on the surface of the article, a relatively high voltage (in other words, a relatively large current density of the cathode) may be employed. In that case, large current density deposits a reduced boron on the surface of the article together with the element such as V, Nb, and Ta. Therefore, the carbide layer of the element comes to include a small amount of a boride of said element such as vanadium boride (VB_2), niobium boride (NbB_2) and tantalum boride (TaB_2), and in cases, the boride layer of said element is formed on the carbide of said element. Said boride of V, Nb, or Ta has been known to have a much higher hardness than that of the carbide of said V, Nb, and Ta. Also said boride has a good wear resistance and corrosion resistance against chemical reagent and molten metal. Therefore, the boride layer of said element formed and the carbide layer containing the boride work as well as the carbide layer of said element. However, with a too large current density, the deposition of boron is too much and prevents V, Nb, and Ta from depositing on the surface of the article. And said deposited boron forms boride such as iron boride and cobalt boride with metals of the mother material of the article. Therefore, a too large current density of the anode is not good.

The critical current density of the cathode composed of the article to be treated depends on the substance including V, Nb, or Ta in the treating molten bath. For example, in the treating molten bath containing the oxide of said element, a relatively large current density, 15 A/cm², can be applied for forming the carbide layer of said element on the surface of the article. In the treating molten bath containing the chloride of said element, the upper limit of the current density for forming the carbide layer of said element is 3 A/cm².

The practical lower limit of the current density of the cathode may be 0.01 A/cm². However, when the treating molten bath including the oxide of V, Nb, or Ta, more than 0.1 A/cm² is preferable.

The treating molten bath used in the present invention is composed of a molten boron oxide and a substance containing V, Nb, Ta or mixtures thereof. As said substance, the metals of said element, alloys containing said element, the oxide and chloride of said element such as V_2O_3 , V_2O_5 , $VOCl_2$, $NaVO_3$, Na_2VO_4 ,

NH_4VO_2 , Nb_2O_5 , Ta_2O_5 , VCl_3 , VCl_5 , $NbCl_4$, $TaCl_5$ can be used. In order to prepare the treating molten bath, the powder of said substance is introduced in the molten boron oxide, or the powder of said substance and the powder of said boron oxide are mixed together and then the mixture is heated up to its fusing state. By another method, a block of said metals or alloys immersed in the bath as the anode and is anodically dissolved in the molten boron oxide for preparing the treating molten bath.

As said boron oxide, boric acid (B_2O_3), borate such as sodium borate (borax) ($Na_2B_4O_7$), potassium borate and the like and the mixture thereof can be used. The boric acid and borate have a function to dissolve a metallic oxide and to keep the surface of the article to be treated clean, and also the boric acid and borate are not poisonous and hardly vaporize. Therefore, the method of the present invention can be carried out in the open air.

As the elements contained in the treating molten bath, one or more elements of vanadium (V), niobium (Nb) and tantalum (Ta) can be used, 1 percent by weight (hereinafter percent means percent by weight) of said element dissolved in the treating molten bath being sufficient. In practice, however, the element may be dissolved into the treating molten bath in a quantity between 1 and 20 percent. With use of less quantity of the element than 1%, the speed of formation of the carbide layer would be too slow to be accepted for the practical purpose. Too much addition of the element than 20 percent will increase the viscosity of the treating molten bath to such a high value that the dipping of the article to be treated upon into the bath may become practically impossible. Even when the immersion is possible with only difficulty, the resulted carbide layer will become too much uneven to be accepted.

The remainder of the treating molten bath is molten boron oxide.

When the powders of the metal of a V, Nb, or Ta or of the alloy containing said element such as ferrous alloys are used as the source, of the treating molten bath, the treating molten bath should be kept for a time for dissolving the element into the molten boron oxide before immersing the article to be treated into the treating molten bath. In case of preparing the treating molten bath by anodically dissolving the element, the range of the current density of the anode (the article) for forming the carbide layer on the surface of the article may be from 0.01 to 5 A/cm². When the formation of the layer is carried out by immersing the article as the cathode in the treating molten bath including the powder of the oxide of the element, the current density of the cathode may be selected within the range from 0.1 to 15 A/cm².

When the powder of the chloride of V, Nb, or Ta is used in the treating molten bath, the current density of the cathode (article to be treated) may be selected within the range from 0.01 to 3 A/cm². When the powder of the oxide or chloride of said element is used in the treating molten bath the ageing of the treating molten bath is not necessary because said oxide and chloride can be dissolved quickly into the molten boron oxide.

In case that the treating molten bath contains the chloride of V, Nb, or Ta or said element dissolved anodically, the surface of the carbide layer formed is very

smooth, and the layer does not contain any undissolved particles of the treating molten bath.

To form the carbide layer of V, Nb, Ta or mixtures thereof on the surface of the article, the article is immersed in the treating molten bath as the cathode, and a vessel containing the treating molten bath may be used as the anode. A metal plate or rod dipped in the treating molten bath can be used as the anode. In cases, V, Nb or Ta metal block containing a can be used in the anode. Said metal block is anodically dissolved into the treating molten bath during the formation of the carbide layer.

The iron, ferrous alloy or cemented carbide to be treated must contain at least 0.05 percent of carbon, preferably contain 0.1 percent of carbon or higher. 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 molten bath 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, ferrous alloy or cemented carbide article containing less than 0.05 percent of carbon may not be formed with a uniform and thick carbide layer by the treatment. Also, the article containing at least 0.05 percent of carbon only in the surface portion thereof can be treated to form a carbide layer on the surface of the article. For example, a pure iron article, which is case-hardened to increase the carbon content in the surface portion thereof, can be used as the article of the present invention.

Here, iron means iron containing carbon and case-hardened iron, ferrous alloy means carbon steel and alloy steel, and cemented carbide means a sintered tungsten carbide containing cobalt. Said cemented carbide may include a small amount of titanium carbide, niobium carbide, tantalum carbide and the like.

In some cases, the carbon contained in the treating molten bath can be used as the source of the carbon for forming the carbide layer on the surface of the article. However, the formation of the carbide layer is not stable and the use of the carbon in the treating molten bath is not practical.

Before the treatment, it is important to purify the surface of the article for forming a good carbide layer by washing out the rust and oil from the surface of the article with acidic aqueous solution or another liquid.

The treating temperature may be selected within the wide range from the melting point of boric acid or borate to the melting point of the article to be treated. Preferably, the treating temperature may be selected within the range from 800° to 1100°C. With lowering of the treating temperature, the viscosity of the treating molten bath increases gradually and the thickness of the carbide layer formed decreases. However, at a relatively high treating temperature, the treating molten bath is worsened rapidly. Also the quality of the material forming the article is worsened by increasing the crystal grain sizes of said material. The treating time depends upon the thickness of the carbide layer to be formed treating temperature and the current density of the anode. Heating shorter than 2 minutes will, however, provide no practically accepted formation of said layer. With the increase of the treating time, the thickness of the carbide layer will be increased correspondingly. In practice, an acceptable thickness of the layer

can be realized within 5 hours or shorter time. The preferable range of the treating time will be from 2 minutes to 5 hours.

The vessel for keeping the treating molten bath of the present invention can be made of graphite or heat resistant steel.

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

EXAMPLE 1

700 grams of borax was introduced into each of two graphite crucibles having a 65mm innerdiameter and heated in an electric furnace under the air. One of the crucibles was heated upto 930°C and the other to 950°C. Then, each of the crucibles were introduced by 117 grams of ferrovanadium (containing of 59 percent of vanadium) powder of less than 100 mesh, mixed together and kept for 1 hour. Thus, two kinds of the treating molten bath were prepared. By using the treating molten bath kept at 930°C, each of one group of the specimens having a 7mm diameter and made of carbon tool steel (JIS SK4) was immersed down to 40mm from the surface of the treating molten bath and applied with an electric current for 3 hours as using said specimen as the cathode. The current density of the cathode applied was within the range from 0 to 2 A/cm². In the same manner as mentioned above by using the other treating molten bath kept at 950°C, each of the other group of the specimens having a 7mm diameter and made of carbon tool steel was treated for 10 minutes with a current density of the cathod within the range from 3 to 5 A/cm². After taking the specimens out of each of the treating molten bathes, all the specimens treated were cooled in the air, washed with hot water and examined. The specimens were cut vertically and the cross sections were polished and microscopically observed. The photomicrographs shown in FIGS. 1 to 4 were taken from the specimens treated respectively with a current density of 0.01 A/cm², 0.3 A/cm², 1.0 A/cm² and 5.0 A/cm². From the results by X-ray micro analyzer, the layers formed with a current density of 0.05 A/cm² or lower than 0.05 A/cm² were vanadium carbide composed of vanadium and carbon. FIG. 5 shows the distribution of the contents of vanadium, iron, carbon and boron contained in the surface portion of the specimen treated with a current density of 0.01 A/cm². The layers formed with a current density higher than 0.1 A/cm² were recognized to be the carbide containing boron. Also a boride layer composed of Fe₂B or FeBC and Fe₂B was recognized between said carbide layer and the mother material. Further, it was recognized that the thickness of the boride layer increases as the increase of the current density. FIGS. 6 and 7 shows each of the distribution of vanadium, iron, carbon and boron contained in the layer formed respectively with a current density of 2 A/cm² and 5 A/cm².

FIG. 8 shows the effect of the current density on the thickness of the layers formed. The thickness of the layers formed increases as the increase of the current density. However, the layers formed with a current density of 3 A/cm² or higher than 3 A/cm² consists mainly of FeB and Fe₂B and the thickness of the vanadium carbide layer formed on the layer composed of FeB and Fe₂B does not increase. Therefore, it is not always good

to employ a large current density. However, at a relatively small current density, a higher current density is preferable to form a thicker layer of vanadium carbide or of the vanadium carbide containing boron. In the layers formed with a current density above 0.1 A/cm², boron was clearly identified. Although in the layers formed with a current density of 0.1 A/cm² or lower than 0.1 A/cm², boron was not identified, said layers may possibly include boron.

From this example, it was recognized that the application of an electric current to the specimen treated increased the thickness of the layers formed on the specimen.

EXAMPLE 2

In the same manner as described in Example 1, a treating molten bath composed of 80 percent of borate and 20 percent of ferroniobium (containing 59 percent of niobium and 3.9 percent of tantalum) powder of 100 mesh or finer than 100 mesh was prepared. And each of the specimens made of carbon tool steel (JIS SK4) was treated respectively at 950°C under each of the conditions. Specimen 2-1 was treated with a current density of 0.03 A/cm² for 3 hours, Specimens 2-2 and 2-3 were treated respectively with 0.3 A/cm² for 3 hours and with 3 A/cm² for 10 minutes. As the comparison, Specimen 2-A was treated for 3 hours at 950°C without applying an electric current.

All the specimens were examined by a microscope, X-ray micro analyzer and by X-ray diffraction method. The layer formed on Specimen 2-1 is shown in FIG. 9. The layer had a thickness of 13 microns and a uniform and smooth surface. FIG. 10 shows the distributions of the contents of niobium, iron, carbon and boron contained in the surface portion of Specimen 2-1, which were obtained by X-ray micro analyzer. From the results of said X-ray micro analyzer and X-ray diffraction method, the layer formed was identified to be the niobium carbide containing boron.

Specimen 2-2 was found to have a layer which was similar with the layer formed on Specimen 2-1.

Specimen 2-3 was found to have a niobium carbide layer of about 9 microns thick and a layer composed of iron boride (Fe₂B) between said niobium carbide and its mother material.

Specimen 2-A was found to have a niobium carbide layer of 11 microns thick and the layer was recognized to contain a small amount of tantalum.

EXAMPLE 3

1000 grams of borax was introduced into a graphite crucible and heated up to 900°C for melting the borax in an electric furnace and then a metallic plate, 6 × 40 × 50 mm, made of ferro-vanadium (containing 53.7 percent of vanadium) was dipped in the molten borax. With use of the metallic plate and the crucible as an anode and cathode respectively, said metallic plate was anodically dissolved into the molten borax by applying a direct current for 2 hours at a current density of 2 A/cm² of the anode. Thus a treating molten bath containing 9.8 percent of said ferrovanadium was prepared.

Next, Specimens 3-1 to 3-6 having a diameter of 7mm and made of carbon tool steel (JIS SK4) were respectively immersed into the treating molten bath and were treated at 900°C under respective conditions. Specimen 3-1 was treated for 2 hours and with a cur-

rent density of 0.03 A/cm², Specimens 3-2 to 3-6 were treated respectively for 2 hours and with 0.1 A/cm², for 2 hours with 0.3 A/cm², for 1 hour with 0.7 A/cm², for 10 minutes with 1.0 A/cm², and for 10 minutes with 3.0 A/cm².

All Specimens 3-1 to 3-6 were examined by a microscope, X-ray micro analyzer and by X-ray diffraction method. Specimens 3-1 to 3-6 were formed with a layer or layers having a respective thickness of 9 microns, 9 microns, 11 microns, 37 microns, 5 microns and 47 microns. Only one layer was formed on Specimen 3-1 and Specimens 3-2 to 3-6 were formed with each two layers. FIG. 11 shows a microphotograph of the layer formed on Specimen 3-1. FIGS. 12 and 13 show respectively microphotographs of the layers formed on Specimens 3-3 and 3-6. By the result of X-ray micro analyzer and X-ray diffraction method, the layer formed on Specimen 3-1 was identified to be vanadium carbide and the two layers formed on Specimens 3-2 to 3-6 were identified respectively to be the vanadium carbide containing boron (V(C,B)) and to be iron boride (FeB or Fe₂B) composed of boron and iron which is the main component of the mother material. All the surfaces of the Specimen 3-1 to 3-6 were very smooth.

From this example, it was recognized that the treating molten bath prepared by anodic dissolution gives a very smooth surface of the specimen treated without depositing any small particles to the surface of the article.

EXAMPLE 4

In the same manner as described in Example 3, the molten borax was prepared and then a metallic plate, 50 × 45 × 6mm, made of ferrovanadium (containing 53.7 percent of vanadium) and a specimen, 40 × 33 × 9mm, made of carbon tool steel (JIS SK5) were dipped in the molten borax with keeping a distance of 15mm from each other. With use of said metallic plate as the anode and the specimen as the cathode, an electric current was applied to the molten borax for 4 hours at a cathodic current density of 0.3 A/cm². By the treatment, the specimen was formed with a layer of about 9 microns. The layer formed is shown in FIG. 14. Also, the layer was identified to be the vanadium carbide containing boron.

EXAMPLE 5

In the same manner as described in Example 4, a metal plate, 50 × 40 × 6mm, made of ferroniobium (containing 58.9 percent of niobium and 3.6 percent of tantalum) was anodically dissolved into a molten borax at 900°C. Thus, a treating molten bath containing about 8.5 percent of said ferrovanadium was prepared. Next, a specimen having a diameter of 7mm and made of carbon tool steel (JIS SK4) was dipped into the treating molten bath as the cathode. With use of the vessel keeping said treating molten bath, said specimens was treated for 3 hours with a current density of 0.03 A/cm². By microscopic observation, a layer of 14 microns was formed on the surface of the specimen. And said layer was identified to be the niobium carbide containing a small amount of boron and tantalum by X-ray micro analyzer and by X-ray diffraction method.

EXAMPLE 6

90 grams of borax was introduced into a graphite crucible having a 35mm innerdiameter and heated up to

950°C for melting the borax in an electric furnace under the air, then 17 grams of vanadium oxide (V_2O_5) powder was gradually introduced into the molten borax and mixed with the molten borax for preparing a treating molten bath (which contains 16 percent of vanadium oxide). In said treating molten bath, several specimens having a 7mm diameter and made of carbon tool steel (JIS SK4) were respectively treated at 950°C for a time ranging from 1 to 90 minutes with a current density ranging from 0 to 15 A/cm² in the same manner as described in Example 1. All the specimens treated were take out of the treating molten bath, cooled in the air, washed with hot water for dissolving the treating material adhered to the specimens. The specimens were cut vertically and the cross sections were polished and examined by a microscope and X-ray micro analyzer and by X-ray diffraction method. The photomicrograph in FIG. 17 is shown as one of the examples of the layers formed in this example. From a group of the specimens treated for 10 minutes with a current density ranging from 0 to 15 A/cm², line (a), in FIG. 15, was obtained. Line (a) shows the effect of the current density applied to a specimen on the thickness of the vanadium carbide layer formed on the specimen. In order to show the difference between the vanadium oxide powder used in this Example and the ferrovanadium powder used in Example 1, lines (b) and (c) are shown together with line (a) in FIG. 15. Line (b) was obtained from the specimens treated in the treating molten bath containing 20 percent of ferrovanadium powder instead of vanadium oxide powder for 30 minutes with a current density ranging from 0 to 1 A/cm². Line (c) was obtained from the specimens treated in said treating molten bath containing 20 percent of ferrovanadium for 10 minutes with a current density ranging from 3 to 5 A/cm². Although, the treating molten bath containing said ferrovanadium powder can form a vanadium carbide layer on the surface of a specimen without applying an electric current, the treating molten bath containing the vanadium oxide powder can not form a vanadium carbide layer on the surface of a specimen without applying an electric current. Therefore, it is necessary for the treating molten bath composed of molten borax and vanadium oxide powder to apply at least 0.1 A/cm² an electric current to the specimen to be treated for forming a vanadium carbide layer on the surface of the specimen (with use of a current density of 0.1 A/cm², a layer of 1 micron was formed on the surface of the article treated). The difference between the vanadium oxide powder in this Example and ferrovanadium powder in Example 1 is supposed to be contributed that the vanadium oxide must be reduced to metallic vanadium for forming a vanadium carbide layer on the surface of the specimen by an electric current.

The other difference between the vanadium oxide powder and ferrovanadium powder is that the treating molten bath containing the vanadium oxide can form a carbide layer with a relatively large current density at which the treating molten bath containing the ferrovanadium can not form a carbide layer on the surface of the specimen treated.

One of the example, FIG. 18 shows the distributions of the contents of vanadium carbon, iron and borax forming the surface portion of the specimen treated in the treating molten bath containing vanadium oxide with a current density of 3 A/cm². From the distribu-

tions and the result of the X-ray diffraction, the surface portion of the specimen is known to vanadium carbide containing little boron. Also the layer formed with a current density of 10 A/cm² was found to contain a little boron. The layers formed on the surface treated in the treating molten bath containing the ferrovanadium with a relatively large current density were explained in Example 1.

From a group of the specimens treated for a time ranging 1 to 90 minutes with a current density of 5 A/cm², the graph shown in FIG. 16 was obtained. The graph shows the effect of the treating time on the thickness of the carbide layer formed on the surface of the specimen treated.

As the oxide of vanadium, V_2O_5 was used in this Example. However, the following oxides and compounds containing vanadium can be used as the oxide of vanadium; VO, VO_2 , C_2O_3 , Na_3VO_4 , NH_4CO_3 , $VOCl_2$, $VOCl_4$ and the like.

EXAMPLE 7

In the same manner as described in Example 6, a treating molten bath composed of 87 percent of borax and 13 percent of vanadium oxide, V_2O_5 , was prepared. Next a specimen having a 7mm diameter and made of carbon tool steel (JIS SK4) was treated in the treating molten bath at 900°C for 10 minutes with a current density of 3 A/cm². By the treatment, a layer of about 4 microns in thickness was formed on the surface of the specimen. The surface condition of the layer was very smooth. The photomicrograph taken from the cross section of the specimen is shown in FIG. 19. And the layer was identified to be vanadium carbide (VC) by X-ray diffraction method.

EXAMPLE 8

In the same manner as described in Example 6, two kinds of treating molten bathes were prepared. One was made of 86percent of borax and 14 percent of $NaVO_3$ and the other was made of 70 percent of borax and 30 percent of $NaVO_4 \cdot H_2O$. Specimen 8-1 having a 7mm diameter and made of carbon tool steel (JIS SK4) was treated at 900°C in the treating molten bath containing $NaVO_3$ for 30 minutes with a current density of 0.1 A/cm². Specimen 8-2 having the same size and made of the same steel as Specimen 8-1 was treated at 900°C in the treating molten bath containing $NaVO_4 \cdot H_2O$ for 10 minutes with a current density of 1.0 A/cm². By the treatments, on the surface of Specimen 8-1 was formed a vanadium carbide (VC) layer of about 5 microns in thickness and on the surface of Specimen 8-2 was formed a vanadium carbide layer of about 4 microns in thickness.

EXAMPLE 9

In the manner as described in Example 6, a treating molten bath made of 93 percent of borax and 7 percent of Nb_2O_5 was prepared. Next, a specimen made of carbon tool steel (JIS SK4) was treated in the treating molten bath at 900°C for 60 minutes with a current density of 3 A/cm². By the treatment, a niobium carbide layer shown in FIG. 20 was formed on the surface of the specimen.

EXAMPLE 10

100 grams of borate was introduced into a graphite crucible and heated up to 900°C for melting said borate

in an electric furnace under the air, and then 16 grams of vanadium chloride (VCl_3) powder was added into the molten borax and mixed together. Thus, a treating molten bath was prepared. Next, Specimens 10-1 to 10-6 having a 7mm diameter and 40mm long and made of carbon tool steel (JIS SK4 containing 1.0 percent of carbon) were respectively treated in the treating molten bath at 900°C for a time ranging 10 minutes to 60 minutes with a current density ranging from 0.01 to 3.0 A/cm². After each of the treatments, each of the Specimens was taken out from the treating molten bath, cooled in the air and washed out the treating material adhered to the Specimen with hot water. Specimens 10-1 to 10-6 were cut vertically and examined by a microscope, X-ray micro analyzer and X-ray diffraction method. On the surface of Specimen 10-1 treated for 60 minutes with 0.01 A/cm² was formed a vanadium carbide (VC) layer of about 9 microns in thickness. Specimen 10-2, which was treated for 60 minutes with 0.05 A/cm², was formed with a vanadium carbide layer of about 9 microns in thickness. The photomicrograph taken from Specimen 10-1 is shown in FIG. 21. Specimens 10-3 and 10-4 treated respectively for 30 minutes with a current density of 0.1 A/cm² and 0.5 A/cm² were formed with a layer thereon. The thickness of the layer on Specimen 10-3 was about 4 microns and the thickness of the layer on Specimen 10-4 was about 8 microns. Said two layers were identified to consist of the upper portion composed of the vanadium carbide containing boron and of the lower portion composed of iron boride (Fe_2B). On the surfaces of Specimens 10-5 and 10-6 which were treated for 10 minutes with a current density of 1.0 A/cm² and 3.0 A/cm² respectively, a layer of about 10 microns and a layer of about 16 microns were formed respectively. And said two layers were identified to consist of the upper portion composed of the vanadium carbide (VC) containing boron and the lower portion composed or iron boride (Fe_2B). The photomicrograph taken from Specimen 10-5 shown in FIG. 22.

EXAMPLE 11

A treating molten bath made of 700 grams of borax and 120 grams of niobium chloride powder was prepared in a graphite crucible. Next, specimens having a 8mm diameter and 40mm long and made of tool alloy steel (JIS SKD61 containing 0.45 percent of carbon) were respectively treated in the treating molten bath at 950°C with use of each of the specimens as the cathode and of the graphite crucible as the anode. On the surface of the specimen treated for 60 minutes with a current density of 0.01 A/cm², a niobium carbide (NbC) layer of about 4 microns was formed. The specimen treated for 30 minutes with 0.1 A/cm² was formed with a niobium carbide layer of about 5 microns. From said two niobium carbide layers, any boron was not detected. The specimen treated for 30 minutes with 0.5 A/cm² was formed with a 7 microns layer thereon, which consisted of the upper portion composed of the niobium carbide containing boron and of the lower portion composed of iron boride (Fe_2B). On the surface of the specimen treated for 10 minutes with 1.0 A/cm², a layer of about 9 microns in thickness was formed thereon. The layer was identified to consist of the upper portion composed of the niobium carbide containing boron and of the lower portion composed of iron boride (Fe_2B).

EXAMPLE 12

90 grams of borax was introduced into a graphite crucible having a 35mm innerdiameter and heated up to 1000°C for melting the borax in an electric furnace under the air, and then 31 grams of vanadium chloride (VCl_3) powder was gradually introduced and mixed into the molten borax. Thus, a treating molten bath was prepared. Next, Specimens 12-1 to 12-5, 40 × 5.5 × 1.0mm, made of cemented carbide composed of 9 percent of cobalt and 91 percent of tungsten carbide (WC) were treated respectively in the treating molten bath under each of the conditions shown in Table 1.

Table 1

Specimen	12-1	12-2	12-3	12-4	12-5
current density (A/cm ²)	0.03	0.3	1.0	5.0	10
treating time (hour)	5hr.	5hr.	2hr.	10min.	1min.

On the surface of Specimen 12-1, a layer of about 7 microns was formed. The layer was identified to be vanadium carbide by X-ray diffraction method. Specimens 12-2 and 12-3 were formed respectively with a layer of about 12 microns and of 5 microns. The two layers were recognized to consist of vanadium boride (V_3B_2) (at the upper portion) and vanadium carbide (at the lower portion). The layer formed on the surface of Specimen 12-5 was identified to be tungsten boride (W_2B_5). By the result of X-ray micro analyzer of Specimen 12-2, the layer was found to contain about 78 percent of vanadium and a large amount of boron. Also, the X-ray diffraction chart of the layer is shown in FIG. 23. Also the hardness of the layer of Specimen 12-1 was measured to be about Hv 3000. The hardness of the layer of Specimen 12-4 was about Hv 3250. By the way, the hardness of the mother material of Specimens were measured to be about Hv 1525.

EXAMPLE 13

500 grams of borax was introduced into a graphite crucible having a 65mm innerdiameter and heated up to 1000°C, and then 125 grams of ferrovanadium (containing 92 percent of vanadium) powder was added and mixed into the borate. Thus, a treating molten bath was prepared. Next two specimens having the same size and made of the same cemented carbide as the specimens used in Example 12 were respectively treated in the treating molten bath with use of each of the specimens as the cathode and of the crucible as the anode. The specimen treated for 13 hours with a current density of 0.01 A/cm² was formed with a layer of about 15 microns thereon, and the specimen treated for 1 hour with 5 A/cm² was formed with a layer of about 7 microns thereon. By X-ray micro analyzer and X-ray diffraction method, the layer formed under the condition of 0.01 A/cm² was identified to be vanadium carbide (VC) and the layer formed under the condition of 5 A/cm² was identified to consist of vanadium boride (V_3B_2) (at the upper portion) and vanadium carbide (VC)(at the lower portion). The hardness of the layer formed under the conditions of 0.01 A/cm² was measured to be about Hv 3014.

EXAMPLE 14

In the same manner as described in Example 6, a treating molten bath was made of 500 grams of borax and 100 grams of V_2O_5 powder. Specimens 14-1 to 14-7 having the same size and made of the same cemented carbide were treated respectively in the treating molten bath at 1000°C under the conditions shown in Table 2.

Table 2

Specimen	14-1	14-2	14-3	14-4	14-5	14-6	14-7
current density (A/cm ²)	0.1	0.5	1.0	5.0	10	20	30
treating time	9hr.	16hr.	5hr.	1hr.	10min.	3min.	1min.

Each of Specimens 14-2 to 14-7 was formed with a layer thereon. However, Specimen 14-1 was not formed with any layer thereon. The layers formed on Specimens 14-2 to 14-4 were of about 8 microns, 12 microns and 11 microns respectively and were identified to be vanadium carbide (VC). The layers formed on Specimens 14-5 and 14-6 were of about 6 microns and 4 microns respectively and were recognized to be a composite layer composed of vanadium carbide (VC) and vanadium boride (V_3B_2). However, on the surface of Specimen 14-7, no vanadium was detected. The layers of Specimen 14-4 and 14-5 were measured to contain respectively 70 percent and 94 percent of vanadium. From the layer of Specimen 14-4, no boron was detected. But the layer of Specimen 14-5 was found to have a relatively large amount of boron. The photomicrograph taken from Specimen 14-5 is shown in FIG. 24. The hardness of each of the layers formed on Specimens 14-2 and 14-5 was about Hv 2960 and Hv 3200 respectively.

EXAMPLE 15

In the same manner as described in Example 3, the 500 grams of molten borax was prepared, and then a metallic plate, 40 × 35 × 4mm, made of electrolytic niobium was anodically dissolved into the molten borax at 1000°C for 2 hours with a current density of 1 A/cm². Thus, a treating molten bath containing about 9.4 percent of niobium was prepared. Next, Specimens 15-1 to 15-9 having the same size and made of the same cemented carbide as the Specimens used in Example 12 were treated respectively in the treating molten bath at 1000°C under the conditions shown in Table 3.

Table 3

Specimen	15-1	15-2	15-3	15-4	15-5	15-6	15-7	15-8	15-9
current density (A/cm ²)	0.01	0.05	0.1	0.5	1.0	3.0	5.0	10.0	20
treating time	16hr.	15hr.	15hr.	10hr.	4hr.	1hr.	1hr.	3min.	1min.

Table 4

Specimen	16-1	16-2	16-3	15-4	16-5	16-6	16-7	16-8	16-9
current density (A/cm ²)	0.01	0.03	0.05	0.1	0.5	1.0	3.0	5.0	10
treating time	14hr.	15hr.	10hr.	5hr.	13hr.	5hr.	3min.	1hr.	10min.

By each of the treatments, on the surface of Specimen 15-2, a vanadium carbide (VC) layer of about 13 microns was formed. The photomicrograph of the layer is shown in FIG. 25. On each of Specimens 15-4 and 15-5, a composite layer of about 15 microns and 6 microns respectively was formed. From the layer, niobium carbide (NbC) and the niobium boride (Nb_3B_2) were clearly detected. The niobium boride was contained in the upper portion of the layer and the niobium

carbide was contained in the lower portion of the layer. On Specimen 15-7, a composite layer of about 25 microns was formed. The layer was found to consist of Nb_3B_2 at its upper portion, NbC at its middle and W_2B_5 at its lower portion. On Specimens 14-8 and 15-9, composite layers of about 10 microns and 13 microns were formed. The composite layer of Specimen 15-8 was found to consist of Nb_3B_2 at its upper portion, NbC at its middle and Co_3B at its lower portion. The thickness of the layers composed of Nb_3B_2 and NbC was decreased as the increase of the current density applied. By X-ray micro analyzer, the layer formed on Specimen 15-8 was contained about 60 percent of niobium. However the layer formed on Specimen 15-9 was not detected any niobium. A large amount of boron was detected from both of said layers. However, the layer formed with a higher current density was found to contain a higher content of boron. The hardness of each of the layers formed on Specimens 15-2 and 15-4 was measured to be about Hv 2920 and Hv 3190.

EXAMPLE 16

In the same manner as described in Example 6, a treating molten bath composed of 500 grams of borax and 80 grams of Nb_2O_5 powder was prepared. Next, Specimen 16-1 to 16-9 having the same size and made of the same cemented carbide as the Specimens used in Example 12 were treated respectively in the treating molten bath at 1000°C under the conditions shown in Table 4.

By each of the treatment, Specimen 16-1 was not formed with any layer thereon, however, on the surface of each of Specimens 16-2 to 16-9 a layer having a thickness ranging from 3 to 15 microns was formed. The layers formed on Specimens 16-2 and 16-3 were identified to be NbC and the layers formed on Specimens 16-4 to 16-8 were recognized to contain NbC and Nb₃B₂. The layer formed on Specimen 16-9 was identified to be W₂B₅. As the example, an X-ray diffraction chart taken from the layer of Specimen 16-6 is shown in FIG. 27. By X-ray micro analyzer, the layers formed on Specimens 16-4 and 16-7 were measured to contain about 67 percent and 57 percent of niobium respectively. It was difficult to measure the content of boron in each of the layers of Specimens 16-2 and 16-6 was measured to be about Hv 2980 and Hv 3230 respectively.

EXAMPLE 17

In the same manner as described in Example 10, a treating molten bath composed of 115 grams of borax and 25 grams of NbCl₅ powder was prepared. Next, Specimens 17-1 to 17-7 having the same size and made of the same cemented carbide as the Specimens used in Example 12 were treated respectively in the treating molten bath at 1000°C under the conditions shown in Table 5.

Table 5

Specimen	17-1	17-2	17-3	17-4	17-5	17-6	17-7
current density (A/cm ²)	0.05	0.1	0.5	1.0	5.0	15	20
treating time	14hr.	10hr.	8hr.	5hr.	1hr.	10min.	1min.

By each of the treatments, on the surface of each of Specimens 17-1 to 17-7 was formed a layer. The thickness of the layer of each of Specimens 17-1 to 17-6 was about 25, 27, 30, 20, 18 and 8 microns respectively. Each of said layers were recognized to consist of a NbC portion and a W₂B₅ portion. The thickness of said NbC portion was decreased as the increase of the current density applied. The layer of Specimen 17-7 was composed of only W₂B. The hardness of the layer formed on Specimen 17-2 was about Hv 3000.

EXAMPLE 18

In the same manner as described in Example 3, and 500 grams of molten borax was prepared, and then a metallic plate, 50 × 40 × 4mm, made of electrolytic tantalum was anodically dissolved into the molten borax at 1000°C for 1 hour with a current density of 1 A/cm². Thus, a treating molten bath containing about 11.2 percent of tantalum was prepared. Next, Specimens 18-1 to 18-5 having the same size and made of the same cemented carbide as the Specimens used in Example 12 were treated respectively in the treating molten bath at 1000°C under the conditions shown in Table 6.

Table 6

Specimen	18-1	18-2	18-3	18-4	18-5
current density (A/cm ²)	0.01	0.05	0.5	1.0	10
treating time	16hr.	14hr.	12hr.	1hr.	5min.

By each of the treatment, all the Specimens 18-1 to 18-5 were formed with a layer thereon. The thickness of the layer of each of Specimens 18-1 to 18-5 was about 20, 23, 25, 13 and 5 microns respectively. By the X-ray diffraction method, the layers formed on Specimens 18-1 to 18-3 were identified to be tantalum carbide (TaC). The layers formed on Specimen 18-4 was recognized to be composed of TaC and W₂B₅. The layer formed on Specimen 18-5 was identified to be W₂B₅. Also by X-ray micro analyzer, the layers of Specimens 18-1 to 18-3 were recognized to contain boron within the TaC.

What is claimed is:

1. A method for forming a carbide layer of an element selected from the group consisting of V, Nb, Ta and mixtures thereof on the surface of an iron, ferrous alloy or cemented carbide article, said article containing at least 0.05 percent by weight of iron, comprising the steps of preparing a treating molten bath composed of molten boron oxide and a substance containing an element selected from the group consisting of V, Nb, Ta and mixtures thereof in a vessel, immersing said article into the treating molten bath, applying an electric current to the treating molten bath, through said article being used as the cathode for depositing the element on

the surface of the article and for forming the carbide layer of said element, with the carbon contained within said article, on the surface of said article, and removing the article from the treating molten bath.

2. A method according to claim 1, wherein said boron oxide is selected from the group consisting of boric acid and borate.

3. A method according to claim 2, wherein said borate is selected from the group consisting of sodium borate and potassium borate.

4. A method according to claim 1, wherein said substance is a metallic powder containing said element and the current density of the cathode is selected within the range from 0.01 to 5 A/cm².

5. A method according to claim 4, wherein said metallic powder is of the element selected from the group consisting of V, Nb, Ta and mixtures thereof.

6. A method according to claim 4, wherein said metallic powder is of an alloy containing the element selected from the group consisting of V, Nb, Ta and mixtures thereof.

7. A method according to claim 6, wherein said alloy is a ferrous alloy.

8. A method according to claim 1, wherein said substance is an oxide of the element selected from the group consisting of V, Nb, Ta and mixtures thereof and the current density of the cathode is selected within the range from 0.1 to 15 A/cm².

9. A method according to claim 1, wherein said substance is a chloride of the element selected from the group consisting of V, Nb, Ta and mixtures thereof and

the current density of the cathode is selected within the range from 0.01 to 3 A/cm².

10. A method according to claim 1, wherein the step of preparing the treating molten bath comprises heating a boron oxide in the vessel, dipping a metallic block containing the element selected from the group consisting of V, Nb, Ta and mixtures thereof and anodically dissolving said metallic block into the molten boron oxide, the current density of the cathode, in the step of applying an electric current, is selected within a range from 0.01 to 5 A/cm².

11. A method for forming a carbide layer of an element selected from the group consisting of V, Nb, Ta and mixtures thereof on the surface of an iron or ferrous alloy article, said article containing at least 0.05 percent by weight of iron, comprising the steps of preparing a treating molten bath composed of molten boron oxide and a substance containing an element selected from the group consisting of V, Nb, Ta and mixtures thereof in a vessel, immersing said article into the treating molten bath, applying an electric current of a cathodic current density within the range from 0.01 to 5 A/cm² to the treating molten bath through said article being used as the cathode for depositing the element on the surface of the article and for forming the carbide layer of said element, with the carbon contained within said article, on the surface of said article and removing

the article from the treating molten bath.

12. A method for forming a carbide layer of an element selected from the group consisting of V, Nb, Ta and mixtures thereof on the surface of a cemented carbide article, said article containing at least 0.05 percent by weight of carbon, comprising the steps of preparing a treating molten bath composed of molten boron oxide and a substance containing an element selected from the group consisting of V, Nb, Ta and mixtures thereof in a vessel, immersing the cemented carbide article into the treating molten bath, applying an electric current of a cathodic current density within the range from 0.01 to 15 A/cm² to the treating molten bath through said article being used as the cathode for depositing the element on the surface of the article and for forming the carbide layer of said element, with the carbon contained within said article, on the surface of said article and removing the article from the treating molten bath.

13. A method according to claim 1, wherein said treating molten bath is composed to molten boron oxide and 1 to 20 percent by weight of said substance dissolved in said molten boron oxide.

14. A method according to claim 13, wherein said treating molten bath is kept at a temperature within a range from 800° to 1100°C.

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