

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

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3,713,993 1/1973 Mellors et al. 204/39 X
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[58] **Field of Search.** 117/113, 114 R, 118, 93; 204/39, 64 R

[57] ABSTRACT

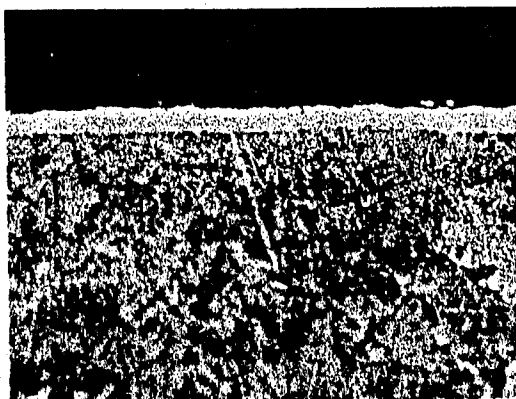
A method for forming a chromium carbide layer on the surface of an iron, ferrous alloy or cemented carbide article in a treating molten bath, comprising heating a boric acid or borate up to its molten state to form a molten bath, dipping a metal containing chromium into the molten bath, applying an electric current to the molten bath through said metal, which works as its anode, for anodically dissolving said metal into the molten bath to prepare the treating molten bath, and immersing the article in the treating molten bath, thereby forming a very hard chromium carbide layer on the surface of said article. The method of this invention can form a very smooth carbide layer on the surface of the article.

[56] References Cited

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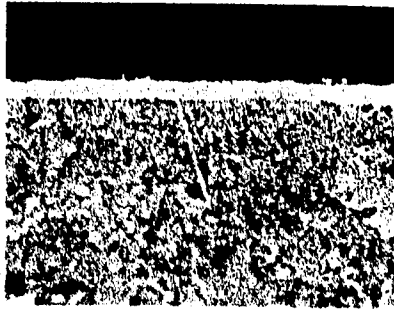
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9 Claims, 2 Drawing Figures



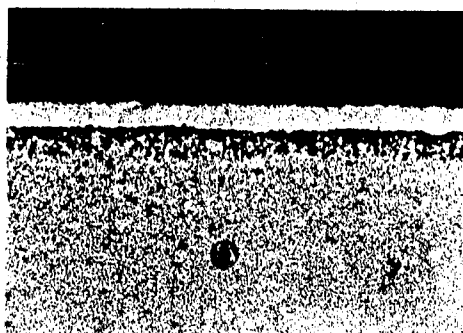
(X 400)

FIG. 1



(X 400)

FIG. 2



(X 400)

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

This invention relates to a method for forming a chromium carbide layer 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, oxidation resistance and corrosion resistance.

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 chromium carbide layer on the surface of metallic article in a treating molten bath consisting of boric acid or a borate and a metal powder containing chromium (U.S. Pat. No. 3,671,297). The method can form a uniform carbide layer and is highly productive and cheap. The chromium carbide has a very high hardness ranging from Hv 1800 to Hv 2000. 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 chromium carbide represents a greater resistance against oxidation and corrosion than the tungsten carbide forming cemented carbide does. Therefore, the formation of the chromium carbide layer on the surface of cemented carbide increases greatly the durability of the mold, jig and the like used in corrosion atmosphere or in high temperature.

The conventional method mentioned above, however, has a drawback. The method uses a treating molten bath containing metal particles. Said metal particles need relatively long time to dissolve into the bath, and undissolved metal particles happen to deposit into the carbide layer formed and make the surface of the article treated rough.

Therefore, it is the principal object of this invention to provide an improved method for forming a chromium carbide layer 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 a chromium carbide layer with denseness and uniformity and without any undissolved treating metal particles on the surface of the article.

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

It is a still further object of this invention to provide a treating molten bath which is capable of forming a chromium carbide layer having a smooth surface on the iron, ferrous alloy or cemented carbide article.

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 ad-

vantages therefore, 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 chromium carbide layer formed on the surface of a carbon tool steel according to Example 1;

FIG. 2 is a photomicrograph showing a chromium carbide layer formed on the surface of a cemented carbide according to Example 2.

Broadly, the present invention is directed to an improvement of the method for forming a chromium carbide layer on the surface of an iron, ferrous alloy or cemented carbide article in a treating molten bath and is characterized in that the treating molten bath is prepared by anodically dissolving chromium into the molten boric acid or borate. Namely, the method of the present invention comprises heating a boric acid or borate up to its molten state to form a molten bath, dipping a metal containing block chromium into the molten bath, anodically dissolving said metal into the molten bath to prepare the treating molten bath and immersing the article in the treating molten bath for forming a chromium carbide layer on the surface of said article. Said chromium carbide layer represents a superior resistance against oxidation and corrosion and a high value of hardness.

Upon intensive investigation of the mechanism for forming a layer on the surface of an article by diffusing chromium from the treating molten bath composed of a boric acid or borate and a metal powder containing chromium, it was found that the main source of the chromium forming the layer comes from the dissolved chromium in the treating molten bath rather than directly from the solid metal particle undissolved. Namely, the chromium contained within the metal powder is dissolved into the treating molten bath, and then said dissolved chromium reaches the surface of the article and diffuses into the article for forming the carbide layer with the carbon contained within the article. It is not necessary for the treating molten bath to contain the metal powder, and it is enough for the bath to contain chromium dissolved therein.

To solve the problem of dissolving the chromium into the treating molten bath for forming the carbide layer having a smooth surface, it was considered to dip a block of metal without contacting with the article to be treated instead of the metal powder mentioned above. However, the use of a block of metal instead of the metal powder reduces greatly the whole surface area of the metal so that the velocity of the dissolution of the chromium decreases remarkably. The metal block process may be worsened by the block reacting with oxygen in the air before dissolving enough chromium into the treating molten bath. By experiments, we found that said worsening of process using the metal block occurred when the metal block had a diameter of 2mm or larger than 2mm. In order to prevent this it was considered to use a thin film of the metal instead of the metal block or to employ an inert gas atmosphere for covering the treating molten-bath and preventing oxygen from being absorbed in the treating molten bath. However, in the former case, said thin film of the metal is not easily obtained and the later requires complicated and costly equipment and takes a long time to dissolve enough chromium for the treatment.

We have overcome the shortcomings mentioned above by anodically dissolving chromium from a large block of the metal containing chromium. Namely, using said large metal block as an anode in the molten bath, said boric acid or borate is electrolyzed by using the vessel of the bath as its cathode. By the anodic dissolution of chromium, the treating molten bath of the present invention is prepared. The chromium carbide layer can be formed by immersing an article in the treating molten bath. The formation of the carbide layer on the surface of an article may be carried out during the anodic dissolution of chromium into the treating molten bath.

As the substances constituting the bath, boric acid (B_2O_3) or borate, such as sodium borate (borax) ($Na_2B_4O_7$), potassium borate ($K_2B_4O_7$) and the like and mixtures 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 metal containing chromium, a block of pure metallic chromium or a block of the alloy containing chromium can be used. As the alloy, ferrochromium may be practical because it is relatively cheap and easily obtained. It is not preferable for said alloys to contain more than 10 percent by weight (hereinafter percent means percent by weight) of Ti, Zr, Hf, Mn, Si, Al, Mg, Cu or the rare earth element which reduce the boric acid or borate to metallic boron. In order to lower the viscosity of the treating molten bath, halogen compound such as sodium chloride, potassium chloride and sodium fluoride, oxide such as phosphoric oxide, hydroxide such as sodium hydroxide, sulphate, carbonate, nitride and the like can be added into the treating molten bath.

During the anodic dissolution of chromium, the practical current density may be selected within a range from 0.1 to 10 A/cm², the increase of the current density makes the necessary time short for dissolving a certain amount of chromium in the treating molten bath. The anodic dissolution of chromium can be carried out at a relatively low voltage at which the actual electrolysis of the boric acid or borate is not occurred. Although the necessary time for the anodic dissolution of chromium depends upon the current density, the volume of the treating molten bath, the size of the block as the anode and the compounds included in said block, the practical time of the anodic dissolution may be from 30 minutes to 5 hours.

As the quantity of the chromium dissolved in the treating molten bath, 1 percent of the chromium in the treating molten bath is sufficient. In practice, however, the chromium may be dissolved into the treating molten bath in a quantity between 2 and 20 percent.

The iron, ferrous alloy or cemented carbide to be treated must contain at least 0.06 percent of carbon, preferably contain 0.1 percent of carbon or higher. The carbon in the article enters into the 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 chromium 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 preferably for forming the carbide layer. The iron, ferrous alloy or cemented carbide article contain-

ing less than 0.06 percent of carbon may not be formed with a uniform and thick carbide layer by the treatment. Also, the article containing at least 0.06 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. Heating shorter than 10 minutes will, however, provide no practically accepted formation of said layer, although the final determination of the treating time depends on the treating temperature. 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 30 hours or shorter time. The preferable range of the treating time will be from 1 to 30 hours.

The vessel for keeping the treating molten bath of the present invention can be made of graphite, heat resistant steel, or ceramics such as metallic oxide and metallic nitride, each of which has a high melting point and a good resistivity against molten boric oxide or borate. In practice, a vessel made of heat resistant steel is sufficient.

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

1000 Grams of borax was introduced into a graphite crucible and heated up to 900°C for melting the borax in an electric furnace under the air, and then a metallic plate, 5 × 40 × 50mm, made of ferro-chromium (containing 66.8 percent of chromium) was dipped in the middle of 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 3 hours at an electric current density of 1 A/cm² of the anode. Thus a treating molten bath containing 9 per-

cent chromium was prepared.
Next, a polished specimen of 7mm diameter and 80mm long made of carbon tool steel (JIS SK3; containing 1.1 percent of carbon) was immersed into the treating molten bath and kept therein for 2 hours, taken out therefrom and air cooled. The treating material adhered to the surface of the specimen was removed by washing with hot water and then the specimen treated was investigated. The surface of the specimen was very smooth. After cutting and polishing the specimen, the specimen was micrographically observed, and it was found that a uniform layer shown in FIG. 1 was formed. The thickness of the layer was about 8 microns. And the layer was identified to be chromium carbide (Cr₂₃C₆, Cr₇C₃) by X-ray diffraction method and by an X-ray microanalyzer. Also it was identified that iron was dissolved into said chromium carbide layer as a solid solution.

EXAMPLE 2

500 Grams of borax was introduced into a graphite crucible and heated up to 1000°C for melting the borax in an electric furnace, and then an electrolytic chromium plate, 10 × 10 × 5mm was anodically dissolved into the molten borax by applying a direct current for 8 hours at an electric current density of 1 A/cm² of the surface of the anode. By calculating the loss of the weight of the plate, a treating molten bath containing about 4.2 percent of chromium dissolved was prepared.

Next, a specimen, 1mm thick, 5.5mm wide and 30mm long, made of cemented carbide composed of 91 percent of tungsten carbide and 9 percent of cobalt was immersed into the treating molten bath and kept therein for 15 hours, taken out there from and air-cooled. Treating material adhering to the surface of the specimen was removed by dipping the specimen into hot water. The surface of the specimen treated was smooth. After cutting and polishing the specimen, the cross section of the specimen was micrographically observed and tested by X-ray diffraction method and by X-ray microanalyzer. By the observation, a layer having a uniform and dense structure and a 18 micron thickness was found. Said layer was shown in FIG. 2. By X-ray diffraction method, strong chromium carbide (Cr₇C₃) diffraction lines were detected from the layer. By X-ray microanalyzer, the layer was found to contain a large amount of chromium.

Next, in order to evaluate the treatment, specimens treated by the same way mentioned above were subjected to either an oxidation test and a corrosion test. As references, non-treated specimens were also tested. The oxidation test was to heat a specimen in open-air at 800°C for 1 hour and then to measure the weight gain of the specimen due to the oxidation of the specimen. The corrosion test was to dip a specimen into an aqueous solution of nitric acid (HNO₃) for 50 hours and then to measure the weight loss of the specimen due to the dissolution of the specimen. The oxidation gain of the non-treated specimen was 61.87 mg/cm².

Also the dissolved weight loss of the specimen treated was 2.65 mg/cm². In comparison, the dissolved weight loss of the non-treated specimen was 23.07 mg/cm².

It is apparent from the results that the cemented carbide having a chromium carbide layer thereon has great oxidation and corrosion resistance.

What is claimed is:

1. In a method for forming a chromium carbide layer on the surface of an iron, ferrous alloy or sintered tungsten carbide containing cobalt article, the surfaces of which articles contain at least 0.06 percent by weight of carbon, which comprises preparing a molten treating bath consisting essentially of boric acid or a borate and metallic chromium dissolved therein,

immersing said article into said molten treating bath, maintaining said article in said molten treating bath to form the chromium carbide layer on the surface of said article, and

removing said article from said molten treating bath, the improvement wherein said molten treating bath is prepared by the method which comprises, heating a boric acid or a borate selected from the group consisting of sodium borate and potassium borate to its molten state to form a molten bath, dipping a metal block of chromium or a chromium alloy containing not greater than 10 percent by weight of Ti, Zr, Hf, Mn, Si, Al, Mg, Ca or the rare earth elements which reduce boric acid or borate to metallic form into the molten bath and applying an electric current to the molten bath through said metal block as anode and an electric conductive material, which is in contact with the molten bath, as cathode to anodically dissolve said metal block.

2. A method according to claim 1, wherein said metallic chromium alloy is a ferrous alloy.

3. A method according to claim 1, wherein said article to be layered is made of one selected from the group consisting of carbon steel and alloy steel containing at least 0.06 percent of carbon.

4. A method according to claim 1, wherein said molten treating bath contains at least 1 percent by weight of chromium dissolved therein.

5. A method according to claim 1, wherein the electric current density of the anode is selected in a range from 0.1 to 10 A/cm² and said metal block is anodically dissolved for a time ranging from 30 minutes to 5 hours.

6. A method according to claim 1, wherein a vessel containing the molten bath is used as the cathode during the step of applying the electric current.

7. A method according to claim 1, wherein during the step of maintaining the article in the treating molten bath, said metal block is again anodically dissolved for supplying chromium into the molten treating bath.

8. A method according to claim 1, wherein said article to be layered is kept in the treating molten bath for 1 to 30 hours at a temperature ranging from 800° to 1100°C.

9. A method according to claim 1, wherein said molten treating bath contains chloride or fluoride of alkali metal for lowering the viscosity of the molten treating bath.

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