

[54] **PROCESS OF FORMING A CARBIDE
LAYER OF VANADIUM, NIOBIUM OR
TANTALUM UPON A STEEL SURFACE**

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[57]

ABSTRACT

A process for the surface treatment of an iron or iron alloy stock comprising heating a mixture of boric acid or borate. A V-a group element of the periodic table consisting of vanadium, niobium and tantalum, or a substance containing the same, and carbon or a carbon containing substance to its fusing state in a bath vessel, and immersing the stock in the molten bath of said mixture, thereby forming a carbide layer of said element on the stock thus treated. The present invention can be performed without adding carbon to a mixture in the case when either said stock or said vessel includes carbon.

21 Claims, 7 Drawing Figures

FIG. 1

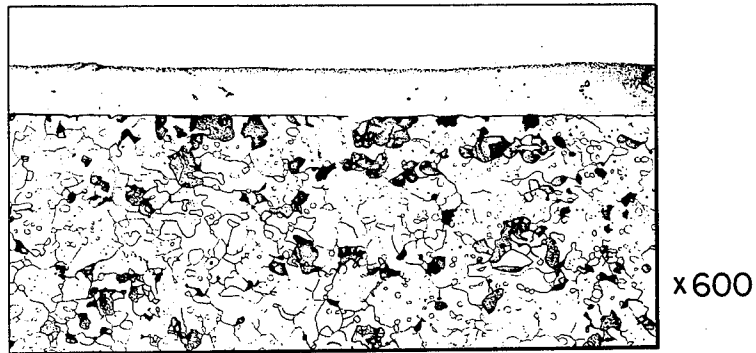
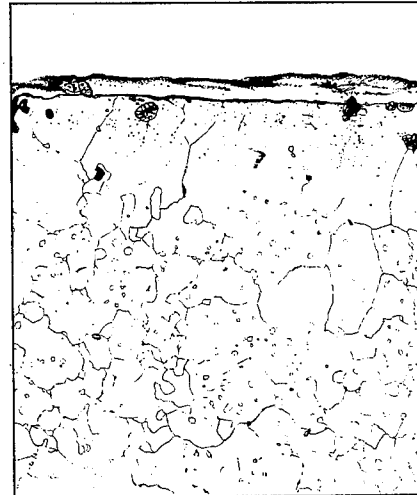


FIG. 3



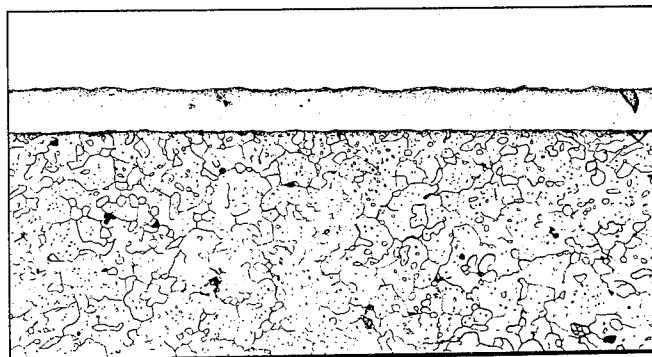
x600

FIG. 4



x600

FIG. 2



x600

FIG. 5



FIG. 6

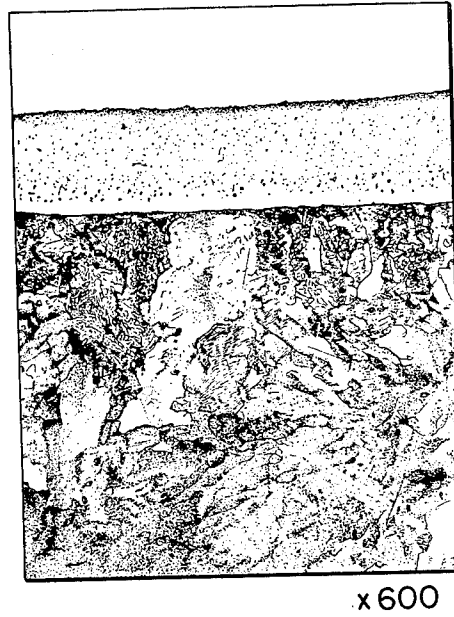
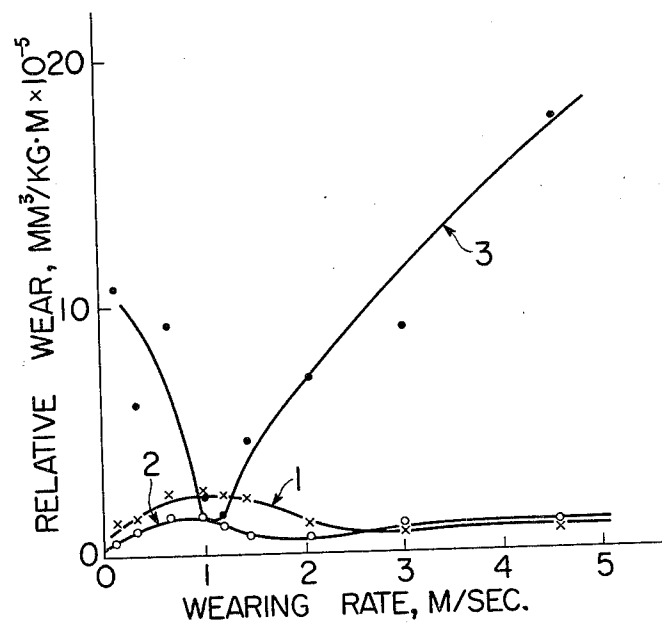


FIG. 7



PROCESS OF FORMING A CARBIDE LAYER OF VANADIUM, NIOBIUM OR TANTALUM UPON A STEEL SURFACE

This invention relates to a process for the surface treatment of an iron or ferrous alloy material so as to form thereon a carbide layer of a metal belonging to V-a group of the periodic table.

Various proposals have hitherto been made to coat a layer of a hard substance on the surface of iron or ferrous alloy material so as to improve its wear-resisting characteristics. The vapor phase coating, the cementation, the spraying, the discharge hardening and the like processes have been employed among others, for the formation of carbide or carbide-containing coatings on the ferrous products. Various drawbacks have been encountered such as by the very complexity of the apparatuses used for this purpose and/or troublesome and inconvenient operational procedures. In addition, defective and insufficient bonding of the coating to the mother material has frequently been encountered which is naturally a fatal drawback of this kind of prior art.

For carrying out the vapor phase coating, halides are employed as the coating material source, which necessitates the use of a specifically selected atmosphere furnace of rather complicated design. This kind of furnace, however, suffers appreciable corrosion caused by the attack of the gaseous halogens.

On the other hand, in the case of the cementation process, the surface of the stock to be coated is liable to become rather rough, and the coated layer consists of a mixed structure of the carbide and the stock material, representing thus a lower grade of surface hardness and anti-wearing performance than a layer exclusively composed of carbide.

In the case of the spraying process, the coating material is very high in price and the bonding of the coated layer with the mother stock is frequently and appreciable inferior.

In the case of the discharge hardening process, the coating procedure is highly tedious and time-consuming. In addition, the treated surface is rather rough, resulting in a substantial limitation of its usage.

The object of the present invention is to provide a substantially improved process for the surface treatment of iron and ferrous alloy stocks of the kind above referred to, capable of substantially obviating the aforementioned conventional drawbacks.

According to the novel teaching of the invention, an iron or ferrous alloy stock is immersed in a fused salt bath containing one or more V-a group elements of the periodic table in the presence of carbon. As a preferred method, the carbon may be admixed with the fused salt bath material. Or alternatively, the carbon may exist in the stock to be treated. It has been found upon carrying out a large number of practical experiments that in this way, a carbide layer of V-a group element or elements can be definitely formed on the surface of the stock. The thus formed carbide layer represents a high value of hardness and a superior resistance performance against wear. The process according to this invention is thus highly suitable for the surface treatment of dies, jigs and the like. It is highly productive, and it has been ascertained that the carbide layer thus obtained is strongly and tightly bonded to the surface of the

mother stock and has, in addition, a dense and continuous structure, thus obviating substantially the above mentioned various conventional drawbacks.

As the bath material, a mixture of boric acid (B_2O_3), and/or borate such as borax ($Na_2B_4O_7$), with V-a group element or elements is used. As is commonly known, the borate can fuse at a relatively low temperature, and acts as a kind of flux capable of keeping the stock surface in its clean and fresh state and suppressing the formation of oxide thereon. We found that a proper amount of V-a group element or elements can be fused in the molten state of borate. As the V-a group elements, one or more elements of vanadium (V), niobium (Nb) and tantalum (Ta), or in the form of its compound such as its ferro-alloy can be used, 5 percent by weight of V-a group element in the fused bath being sufficient. In practice, however, the V-a group element may be added to the fused salt bath in a quantity between about 1-70 wt. percent. With use of a lesser quantity of the V-a group element than 1 wt. percent, the speed of the formation of the carbide layer would be too slow to be accepted for the practical purpose. Too much addition of V-a group element (higher than 70 wt. percent) will increase the viscosity of the fused salt bath to such a high value that the dipping of the mother stock to be treated upon into the bath may become practically impossible. Even when the immersion is possible with only difficulty, the resulting carbide layer will become too much uneven to be accepted.

The carbon per se or its compound may be intentionally admixed with the molten salt bath material. Under circumstances, a graphite crucible or a bath vessel made of a predominantly carbon-containing substance may be used as the carbon source.

If the stock to be treated upon consists of a carbon-containing ferrous material, such as tool steel, structural alloy steel, cast iron or the like, the stock per se can be utilized as the carbon source.

Any combination of the aforementioned carbon sources may be naturally and under most cases preferably utilized for the purpose according to this invention.

As an example, when a high carbon steel stock was treated in a molten salt bath contained in a graphite vessel, a thick carbide layer was formed on the stock with superior results.

When low carbon stock such as of stainless steel, low carbon steel of a very low carbon content, is to be coated with a thick layer of carbide, it is highly preferable to case-harden in advance of the bath treatment, the stock so as to increase the carbon content in the surface thereof, in place of otherwise increasing of the treating temperature and/or prolongation of the treating period.

With use of a carbon or carbon containing vessel, it has been found that part of the carbon will be dissolved out of the material of the vessel into the molten salt bath and deposit on the stock in the form of a layer of carbide of the V-a group element.

In the case of utilization of a carbon-containing stock per se as the carbon source, it is believed that part of the contained carbon is drawn out from the interior of the stock to the surface thereof under the influence of the very presence of the V-a group element, resulting thus in the formation of a carbide layer.

Anyhow, the formation of a carbide of a V-a group element has been ascertained by the X-ray diffraction process.

When the carbon necessary for the formation of carbide layer is introduced intentionally into the molten salt bath, it may preferably amount to about 0.03 wt. percent or higher. When the carbon supply quantity should exceed its dissolving extremity in the molten salt bath, a carbonaceous layer will form on the free surface of the molten bath, thus taking no part in the formation of the desirous carbide layer, but it serves to interrupt positively communication of the ambient atmosphere with the bath material. Thus, especially in the case of bath treatment in the air atmosphere, an invasion of oxygen into the bath is positively prevented by the presence of the bath-covering carbonaceous layer, thereby a favorable effect being provided in the progress of the carbide formation on the stock under treatment.

The treating temperature may theoretically extend from the fusing point of the bath material to the melting point of the stock to be treated upon. In practice, however, it may preferably selected to about 800°–1,100°C, taking the forming velocity of the carbide layer and embrittlement caused by grain growth and the like into account.

When borax is used as the molten bath material, it may preferably be admixed with one or more compounds selected from the group comprising halides such as sodium chloride (NaCl), potassium chloride (KCl), sodium fluoride (NaF); oxides such as phosphorus oxide (P_2O_5) or the like; hydroxides such as sodium hydroxide (NaOH), potassium hydroxide (KOH); sulfates; carbonates; and nitrates, so as to lower the fusing temperature of the bath material, in consideration of the melting point of borax being about 740°C which lies above the transformation point of steel. In most steel stocks when treated at a bath temperature above the transformation point of steel for quicker formation of the carbide layer, distortion may be liable to occur by virtue of the transformation of steel and the distortion must be naturally be avoided by lowering the adopted higher bath temperature.

The treating time period depends upon the thickness of the carbide layer to be formed. The treatment shorter than an hour will, however, provide no practically acceptable formation of carbide layer, although the final determination of the treating period depends upon the treating temperature. With increase of the treating period, the thickness of carbide layer will be increased correspondingly. In practice, an acceptable thickness of carbide layer can be realized within 30 hours or shorter time period.

The process according to this invention can be carried into effect either under air atmosphere or inert gas atmosphere.

In the following, several preferred embodiments of the invention will be described by way of several numerical embodiments and by occasional reference to the accompanying drawings.

In the drawings:

FIGS. 1–6 are several micrographic representations reproduced, however, manually, for a more clearer showing of several samples of the carbide layer formed in accordance with the novel teaching of this invention.

FIG. 7 is a chart illustrative of experimental wear-resisting tests performed on preferred samples of the carbide layer formed by the process according to this invention.

EXAMPLE 1

a 50 wt. percent; 50 wt. percent mixture, 150 grs., of borax and ferro-niobium (Fe-Nb) powder containing niobium 59 wt. percent and tantalum 3.6 wt. percent, was introduced into a graphite crucible and heated up to 900°C, and then a specimen, 5 mm thick, 12 mm wide and 70 mm long, made of a metal, JIS SKD1 (alloy tool steel, C : 1.80–2.40 wt. percent; Si : less than 0.40 wt. percent; Mn : less than 0.60 wt. percent; P : less than 0.030 wt. percent; S : less than 0.030 wt. percent; Cr : 12.00–15.00 wt. percent), was introduced into the fused bath and kept therein for 24 hours, taken out therefrom and air-cooled. Salts deposited were removed by dipping the treated specimen into a boiling water bath. Upon being micrographically observed, it was found that a layer of niobium carbide (NbC) as identified by X-ray diffraction method, the thickness being about 18 microns, was formed on the surface of the specimen. As manually reproduced in FIG. 1, the photomicrograph showed a smooth and pin-hole-free surface. By electron probe microanalysis on a cross-section of the thus coated specimen, niobium, tantalum and carbon were detected in the formed layer.

EXAMPLE 2

A powder mixture, 150 grs., consisting of 50 wt. percent of borax and 50 wt. percent of ferro-vanadium (including 52 wt. percent of vanadium) was introduced in a graphite crucible and a specimen consisting of a steel, JIS SKD1, was treated under the same treating conditions as in the foregoing Example 1.

The results are shown in FIG. 2 which was reproduced again manually.

The formed layer on the specimen amounted in its thickness to about 18 microns. It was smooth and pin-hole-free.

From X-ray diffraction tests, the layer consisted of vanadium carbide (VC). From an electron probe microanalysis, vanadium and carbon were detected.

TEST RESULTS

The treated specimens in the foregoing Examples 1 and 2 were tested on a Ohgoshi-type wear tester under final load 3.3 kg; friction stroke 600 mm; slider material : S45C—normalized.

For comparison, as a reference, a specimen of SKD1, quenched and tempered (oil-quenched from 975°C for 25 minutes and air-cooled from 200°C for 60 minutes) was tested under similar conditions.

The results are shown in FIG. 7, wherein curve 1 concerns with the first test specimen of Example 1. Curve 2 relates to the second test specimen of Example 2. Curve 3 relates to the specimen as a difference.

As is ascertained from Examples 1 and 2, as well as the foregoing "Test Results," when test specimens of SKD1-material are immersed in a molten salt bath containing borax and a V-a group element such as vanadium, niobium and tantalum placed within a bath vessel made of a material substantially including carbon, a layer of carbide of the V-a group element is formed.

While a reference specimen of SKD1 representing none of such carbide layer showed a high rate of sliding wear at a higher and a lower speed range defined at 1 m/sec. the coated specimens according to this invention showed a highly low and substantial constant rate of wear, irrespective of the sliding test speed. In this way, a remarkably improved wear-resisting characteristic could be realized.

EXAMPLE 3

A graphite crucible was used as in the foregoing Examples, and a fused salt bath mixture of borax or boric acid and V-a group element such as vanadium or a ferro-alloy such as ferro-niobium and ferro-vanadium was prepared in the crucible, and then ferrous specimens (each being 14 mm in diameter and 20 mm long) were treated as before.

The several test specimens, bath compositions, treating temperatures are shown in the following table:

TABLE

Spec. No.	Material of Specimen	Bath Composition (% by weight)	Treating Temperature & Time
1	JIS S45C	70% borax; 15% Fe-Nb(59% Nb; 3.6% Ta); 15% Fe-V(59% V);	1000°C × 8hrs
2	JIS SKD1	95% borax; 5% Fe-Nb(59% Nb; 3.6% Ta);	1100°C × 6hr
3	JIS S10C*	70% borax; 30% Fe-Nb(59% Nb; 3.6% Ta);	800°C × 24hr
	JIS S45C	42% borax; 30% V; 12% NaCl 16% KCl;	700°C × 24hr
5	SK2	70 % boron oxide; 30% V;	1000°C × 8hr

*(structural carbon steel, C:0.08-0.13 wt. %; Si:0.15-0.35 wt. %; Mn:0.30-0.60 wt. %; P:less than 0.03 wt. %; S:less than 0.035 wt. %)

Upon the specimen mentioned above, it was found in each case that a layer had been formed, the layer being of carbide of the respective element belonging to V-a group of the periodic table. The results of specimen No.1 are shown in FIG. 3; those of specimen No.2 in FIG. 4; those of specimen No. 3 in FIG. 5, respectively, in the form of manually reproduced photomicrographs.

It is seen from these photomicrographs that in each case, a tight and continuous layer of carbide was formed uniformly on the specimen.

EXAMPLE 4

A powder mixture, 100 grs, consisting of 70 wt. percent borax and 30 wt. percent of ferro-niobium powder (including 59 wt. percent of niobium and 3.6 wt. percent of tantalum) was charged in a stainless steel crucible and heated up to 1,000°C and then added with 5 grs of carbon powder.

Then, a pure iron specimen (5 mm in diameter; 15 mm long) was immersed in the molten bath and kept therein for 8 hours. Then, the specimen was taken out of the bath and deposited salts were removed in boiling water.

Upon being micrographically observed, it was found that a layer, about 2 microns thick, had been formed on the specimen. Upon X-ray diffraction NbC-diffraction was observed. By electron probe microanalysis on a cross-section of the specimen, niobium, tantalum and carbon were found on the specimen surface.

EXAMPLE 5

A powder mixture, 100 grs., consisting of 50 wt. percent borax, 30 wt. percent metallic vanadium (92 wt. percent vanadium) and 20 wt. percent sodium cyanate (NaCN), was charged in a stainless steel crucible and a same test specimen was used for the similar treatment.

Upon being microscopically observed the thus treated specimen, a layer, 2 microns thick, was observed. Upon X-ray diffraction test, VC-diffraction was seen. By electron probe microanalysis on a cross-section of the specimen, vanadium and carbon were found on the specimen surface.

From the foregoing Examples 4 and 5, it will be seen that when an iron specimen is immersed in a fused salt bath mixture including borax and niobium, vanadium or tantalum, added with carbon or a carbon-containing substance, a layer of carbide of V-a group element can be effectively formed.

EXAMPLE 6

A powder mixture, 80 grs., consisting of 70 wt. percent borax and 30 wt. percent of ferro-vanadium (52 wt. percent vanadium) was charged in a graphite crucible and heated up to 1,000°C. A pure iron specimen having the same dimensions as in the Example 4 was immersed in the fused salt bath and kept therein for 8 hours. Then, it was taken out of the bath and air-cooled. Salts deposited on the surface of the specimen were removed in a boiling water bath.

Upon being microscopically observed, a covering layer, 2 microns thick, was observed on the specimen. Upon X-ray diffraction test, VC-diffraction was found. By electron probe microanalysis, vanadium and carbon were found on the specimen surface.

It is seen from the foregoing that when an iron specimen is immersed in a fused salt bath including a borax and a vanadium containing substance charged in a vessel made substantially of carbon, vanadium carbide layer can be formed effectively on the specimen surface.

EXAMPLE 7

A powder mixture 100 grs., consisting of 70 wt. percent borax and 30 wt. percent ferro-niobium powder (59 wt. percent niobium and 3.6 wt. percent tantalum) was charged in a stainless steel crucible and heated up to 1,000°C. A test specimen of JIS SK2 (carbon tool steel, C:1.10-1.30 wt. %; Si:less than 0.35 wt. %; Mn: less than 0.50 wt. %; P:less than 0.03 wt. %; S: less than 0.03 wt. %) was introduced in the molten bath and kept therein for 8 hours, taken out therefrom and then air-cooled. Deposited salts were removed in a boiling water bath.

Upon microscopic observation on a cross-section of the thus treated specimen, a covering layer, 35 microns thick, was seen. Upon electron probe microanalysis on the cross-section, niobium, tantalum and carbon were

found in the layer. Upon X-ray diffraction, NbC-diffraction was seen. A photomicrograph of the formed layer is manually reproduced in FIG. 6. The surface of the formed carbide layer was smooth and pin-hole-free.

EXAMPLE 8

A powder mixture of 70 wt. percent borax and 30 wt. percent of ferro-vanadium (52 wt. percent vanadium) was used. Further treating conditions were same as in the foregoing Example 7. Test specimen was of JIS SK2. In this way, a carbide layer, about 35 microns thick, was formed on the specimen in an effective manner. VC-diffraction was observed.

It will be seen thus from the foregoing Examples 7 and 8 that when borax and a substance containing a V-a group element are charged in a stainless steel crucible and heated up to a proper temperature, an iron specimen of a carbon-containing substance such as SK2 is immersed in the thus fused salt bath, even with no intentional addition of carbon, a carbide layer of the V-a group element can be effectively formed on an iron stock.

According to the novel teaching of the present invention, the process for the formation of a carbide of an element selected from the V-a group on an iron stock can be brought into effect, when necessary, without use of a specific inert gas atmosphere.

It will be further definitely seen that the present invention provides a perfectly unique process for the formation of carbide layer of V-a group element on an iron or iron alloy stock only immersing the latter in a molten salt bath containing the Va-series element, wherein the supply of the necessary carbon constituent can be performed by an intentional introduction thereof from outside of the bath into the latter or reliance made upon the bath vessel per se for this purpose when the latter has been made of carbon or carbon-containing substance. As was referred to hereinbefore, the stock per se can be utilized as such carbon source, when it contains a reasonable amount of carbon.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for the surface treatment of an iron or iron alloy stock, comprising the steps of heating a mixture consisting essentially of boric acid or a borate, at least one element of group V-a of the Periodic table consisting of vanadium, niobium and tantalum or a substance containing the same, and carbon or a carbon-containing substance to its fusing state in a bath vessel, and immersing the stock in the molten bath of said mixture, thereby forming a carbide layer of said element on the stock thus treated.

2. A process according to claim 1, wherein borax is used as said borate.

3. A process according to claim 1, wherein said substance containing V-a group element is a ferro-alloy thereof.

4. A process according to claim 1, wherein 1 to 70 percent by weight of V-a group element is included in said mixture.

5. A process according to claim 1, wherein at least 0.03 percent by weight of carbon is included in said mixture.

6. A process according to claim 1, wherein said heating step is performed within the range of 800°C to 1,100°C.

7. A process according to claim 1, wherein at least one member selected from the group consisting of a hydroxide or halide of sodium or potassium and a phosphorus oxide is added to said mixture.

8. A process according to claim 1, wherein 42 to 95 percent by weight of said boric acid or borate is included in said mixture.

9. A process according to claim 6, wherein said stock is immersed in said mixture for a period of time of from 1 to 30 hours.

10. A process for the surface treatment of an iron or iron alloy stock, comprising the steps of heating a mixture consisting essentially of boric acid or a borate and at least one element of Group V-a of the Periodic table consisting of vanadium, niobium and tantalum or a substance containing the same, to its fusing state in a vessel containing carbon as its main ingredient, and immersing the stock in the molten bath of said mixture, thereby forming a carbide layer of said element on the stock thus treated.

11. A process according to claim 10, wherein said vessel is made of graphite.

12. A process for the surface treatment of an iron or iron alloy stock, comprising the steps of heating a mixture consisting essentially of boric acid or a borate, at least one element of Group V-a of the Periodic table consisting of vanadium, niobium and tantalum or a substance containing the same to its fusing state in the vessel, and immersing an iron or iron alloy stock containing carbon in the molten bath of said mixture, thereby forming a carbide layer of said element on the stock thus treated.

13. A process according to claim 12, wherein said substance containing a group V-a element of the Periodic table is a ferro-alloy containing a group V-a element.

14. A process according to claim 12, wherein said stock is selected from the group consisting of high-carbon steel, high-carbon alloy steel and cast iron.

15. A process according to claim 12, wherein said stock is a low-carbon stock and is case-hardened prior to said immersing step to increase the carbon content on the surface thereof.

16. A process according to claim 12, wherein borax is used as said borate.

17. A process according to claim 12, wherein 1 to 70 percent by weight of said V-a group element is included in said mixture.

18. A process according to claim 12, wherein said heating step is performed within the range of 800°C to 1,100°C.

19. A process according to claim 12, wherein at least one member selected from the group consisting of a hydroxide or halide of sodium or potassium and a phosphorus oxide is added to said mixture.

20. A process according to claim 12, wherein 42 to 95 percent by weight of said boric acid or borate is included in said mixture.

21. A process according to claim 18, wherein said stock is immersed in said mixture for a period of time of from 1 to 30 hours.