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### PROCESS FOR BORIDING STEEL

Harald Krzyminski, Konigstein, Germany, assignor to Deutsche Gold- und Silber-Scheideanstalt vormals Roessler, Frankfurt, Germany  
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### ABSTRACT OF THE DISCLOSURE

Steel is borided by employing a composition including a boriding agent, an activator, a diluent and free carbon. The use of the free carbon produces pore free boride layers of normal thickness.

Several processes of boriding are known for the production of hard surface layers on steels and other metals. The process differs essentially according to the type of boron imparting agent.

The treatment of the metals in boron imparting salt melts is known according to two variants. Variant 1 takes place without electrolysis. In Variant 2 the deposition of boron is assisted electrolytically wherein the part to be borided is the cathode while the crucible wall or a special electrode is used as the anode. The anode can also consist of a boron containing material.

Besides there have been tried experiments to boride steel by high frequency heating in aqueous boron containing solutions. For this purpose there were preferably used aqueous solutions of borax or boric anhydride.

Further experiments have extended to the addition of gaseous boriding agents. For this purpose there are used as boron supplying gases boron halides, diborane and various organic boron compounds. A special place between the liquid and gaseous boriding processes is occupied by the so-called "drop gas boriding." In this process liquid boriding agents, for example boron tribromide, boron trichloride and triethyl boron are added dropwise into the preheated oven chamber and vaporized.

Finally there have been tried experiments with boriding pastes in which a paste of a boron containing agent, a fluid agent and a binding agent are applied to the work-piece. The named processes until now have only been tried and employed on a laboratory scale. A practical use has not been attained with any of the processes.

Attempts to employ the boriding in large scale have only led to success to a certain extent with powdered boriding agent. In the treatment the boriding with powders corresponds to the long known powder carburizing. The part to be treated is embedded with the boriding powder in boxes and subjected to an annealing treatment for several hours in the temperature range of 800 to 1100° C. The boxes normally consist of steel plate and are closed with a cover of the same material. The boriding powder includes the boron containing material and in many cases a diluent and activating addition. As boron containing material there can be used amorphous boron, crystalline boron, ferroboron, boron carbide and borax as well as mixtures of these materials. As activating additives there can be added the following compounds: potassium chloride, sodium chloride, ammonium chloride, calcium chloride and barium chloride as well as various fluorides, especially barium fluoride and magnesium fluoride. Thus ammonium alkali metal and alkaline earth metal chlorides and fluorides can be used as activating agents.

Very hard layers are produced on the parts by the treatment. In the case of iron work pieces these consist of the compounds FeB and Fe<sub>2</sub>B. The boron rich compound FeB is formed only if the boriding activity of the agent is sufficiently strong. Since the FeB phase is only insig-

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nificantly harder than the Fe<sub>2</sub>B phase but is essentially more brittle, one is frequently content with a weaker boriding activity and strives for a boriding layer which is constructed only of the compound Fe<sub>2</sub>B. These layers possess a very high resistance to wear which is why the processes today are employed in the industry to an increasing extent for various high load prefabricated parts and tools.

A serious deficiency of the boriding powders is that the outer zones of boriding layers produced with them are permeated more or less strongly with pores and oxidized inclusions. Inclusions are due to the fact that the powder structure contains oxygen or oxygen containing gases which have an oxidizing effect on the prefabricated parts. On the other hand experiments have shown that the presence of oxygen or oxygen containing gases is indispensable for the production of thicker layers. If the treatment takes place in completely sealed boxes or in a vacuum, the strength of the layer is reduced by about one half.

It has now been found unexpectedly that these deficiencies, namely either the formation of layers with oxide inclusions or the formation of thinner layers, can be eliminated if the product added for boriding contains free carbon in addition to the boron supplying substance, as for example boron carbide. If there is used this type of mixture the layers formed are pore free but still have the same thickness as the previously known borided layers, e.g. 220 to 240  $\mu\text{m}$  after a treating time of 5 hours at 900° C.\* Likewise their structure is the equal to that which can be produced by the customary boriding powders, which means that the improvement of the properties is not reduced by the diffusion of carbon.

As boron containing materials there can be used amorphous boron, crystalline boron, ferroboron, boron carbide, borax, boric anhydride and mixtures of these materials in any proportions. These are mixed as is customary in the art with activating materials. Thus there can be used the activating materials set forth previously, e.g. ammonium, alkali metal and alkaline earth metal halides, e.g. ammonium chloride, potassium chloride, sodium chloride, calcium chloride, barium chloride, potassium fluoride, barium fluoride, magnesium fluoride, sodium bromide, sodium fluoride and calcium bromide as well as mixtures thereof.

The composition can also contain the customary diluents such as graphite, silicon carbide, aluminium oxide, and other stable compounds.

The novelty of the invention is based primarily upon the inclusion in the mixture of free carbon, for example in the form of finely ground charcoal or carbon black, or activated carbon. It has been found that the action of the mixture is best if the content of free carbon is between 2 and 40%, preferably between 5 and 15%. The amount of activating agent is usually between 2 and 10%, preferably 4%. The amount of boron containing material is usually at least 10% of the composition and can be as much as 96%. When a diluent is employed it is used in an amount of 5 to 88%.

Unless otherwise indicated all parts and percentages are by weight.

If the amount of free carbon is less than 2% there is no guarantee of the formation of pore free layers while, if the amount of free carbon is above 40%, then the boriding activity is noticeably diminished.

The invention is primarily adapted to the boriding of steel but can also be used to boride other metals such as iron powder material parts, all kinds of cast iron, nickel and molybdenum. The boriding can be accomplished at conventional boriding temperatures, e.g. temperatures of 80 to 1100° C.

\*  $\mu\text{m}$  1/1000 mm.

## EXAMPLE 1 (COMPARISON)

A sample of steel Ck 15, normalized, was treated for 5 hours at 900° C. in a boriding powder composed of 74% boron carbide (B<sub>4</sub>C), 16% borax and 10% potassium fluoride.

Then it was determined by metallographic examination that there was formed a boride layer having a thickness of 220 to 240 millimicrons. The outer part of this layer, however, was strongly porous and contained coarse oxidic inclusions up to a depth of about 60 millimicrons.

## EXAMPLE 2

Another experiment was carried out with a mixture of 66% boron carbide, 16% borax, 10% potassium fluoride and 8% carbon, the latter in the form of finely ground charcoal. Again a sample of the steel Ck 15 was borided for 5 hours at 900° C.

The metallographically ascertained boride layer had a thickness of 220 to 250 millimicrons. The entire layer was pore free.

## EXAMPLE 3

A further experiment was carried out with a mixture of 54% boron carbide, 16% borax, 10% potassium fluoride and 20% carbon in the form of finely ground charcoal.

The metallographically ascertained thickness of the boride layer imparted to a sample of steel Ck 15 by boriding at 900° C. for 5 hours was between 190 and 220 millimicrons. This layer also was pore free.

## EXAMPLE 4

A further experiment was carried out with a mixture of 34% boron carbide, 16% borax, 10% potassium fluoride and 40% carbon black.

A sample of steel Ck 15 was borided for 5 hours at 900° C. in this composition. The thickness of the boride layer as determined metallographically was then 150 to 170 millimicrons. The boride layer was free of pores.

## EXAMPLE 5

Another experiment was carried out with a mixture of 15% amorphous boron, 10% sodium fluoride, 8% carbon in the form of finely ground charcoal and 67% silicon carbide.

Samples of different kinds of cast iron were borided for 5 hours at 1000° C. in this composition. The sample of grey cast iron and nodular cast iron had a thickness of the boride layer of 180 to 220 millimicrons. The boride layer was not completely free of pores caused by the graphite inclusions, but of good quality.

## EXAMPLE 6

In this experiment a mixture of 20% boron carbide, 10% sodium fluoride, 5% carbon in the form of finely ground charcoal and 65% graphite was used.

Samples of nickel and molybdenum were borided for 5 hours at 900° C. in this composition. The boride layer on the nickel piece had a thickness of 120 millimicrons and consisted of the two compounds Ni<sub>2</sub>B and Ni<sub>3</sub>B.

The layer on the molybdenum sample was only 15 to 25 millimicrons thick and consisted of the compound MoB<sub>2</sub>.

The layers were in all cases completely free of pores. What is claimed is:

- 5 1. A process for the production of a pore free boride layer on a metal selected from the group consisting of iron, steel, nickel and aluminum, consisting essentially of placing an article made of said metal in a boriding powder composition containing a boron imparting agent selected from the group consisting of amorphous boron, crystalline boron, ferroboron, boron carbide and borax, an activator and finely powdered activated carbon in an amount of 2 to 40% of said composition and heating to 15 800 to 1100° C.
- 10 2. A process according to claim 1 wherein the metal is steel.
- 15 3. A process according to claim 2 wherein the activator is selected from the group consisting of ammonium halides, alkali metal halides and alkaline earth metal halides.
- 20 4. A process according to claim 3 wherein the activator is used in an amount of 2 to 10% and is selected from the group consisting of potassium chloride, sodium chloride, ammonium chloride, calcium chloride, barium fluoride, magnesium fluoride, potassium fluoride and sodium fluoride.
- 25 5. A process according to claim 4 wherein the amount of activator is 4%.
- 30 6. A process according to claim 2 wherein the amount of free carbon is 5 to 15%.
- 35 7. A process according to claim 2 wherein the composition consists essentially of boron imparting agent, 2 to 40% of free carbon and 2 to 10% of activator.
- 40 8. A process according to claim 7 wherein the boron imparting agent is selected from the group consisting of amorphous boron, crystalline boron, ferroboron, boron carbide and borax and the activator is selected from the group consisting of ammonium, alkali and alkaline earth chlorides and fluorides.
- 45 9. A process according to claim 8 wherein the boron imparting agent is a mixture of boron carbide and borax.
- 50 10. A process according to claim 1, wherein the heating is at 900° C.
- 55 11. A process according to claim 1, wherein the activated carbon is ground charcoal.
- 60 12. A process according to claim 1, wherein the activated carbon is carbon black.

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