

PATENT SPECIFICATION (11)

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 (72) Inventor ERWIN G. PREUSCHEN



(54) PROCESS FOR BORIDING

(71) We, VAC-HYD PROCESSING G.m.b.H., a company organized and existing under the laws of Germany, of Kisdorfer Weg, 2358 Kaltenkirchen, West Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the boriding of the surface of metal workpieces, wherein the surface of a workpiece is first cleaned and then brought into contact with a boron-containing compound at a temperature above 700°C.

Processes of this kind are known as case hardening processes. They are employed to effect special hardening of the surface of certain parts when only the surface must have this hardness and lower hardness is sufficient for the core of the parts treated in this manner. In addition, it is known that even at high temperatures boron is soluble in steel only in extremely small percentages, but that hardenability is appreciably increased even with these small amounts. Thus, through the boriding of the surface of e.g. a steel workpiece it becomes unnecessary to use expensive alloying elements for the material of the entire workpiece.

Similarly, low-carbon case-hardening steels are carburised in media giving up carbon in known processes, which may then be followed by hardening as with normal carbon steels. Carburising pastes which effect cementing only on the parts to which they are applied have also been developed for this purpose.

In addition, it is known to increase the nitrogen content of the surface of a nitriding steel by a nitriding process, in order to form a very hard but thin nitrided layer. For this purpose the steel is treated in a current of ammonia at 500°C, and is then slowly cooled. Nitriding provides the advantage that the material is not distorted, since quenching is not necessary. The disadvantages of the nitriding process are that the treatment takes a fairly long time—about 50 to 100 hours, and that heavy expenditure for energy is

consequently incurred. Another disadvantage is the slight thickness of the hardened layer obtained. Although this layer is harder than one produced by case-hardening with carbon, it is more brittle and thinner, so that under heavy pressure the layer may be perforated. Another disadvantage of this process which can be applied to steel is that substances forming nitrides, for example chromium, molybdenum, and in particular aluminium, must be contained in the steel from the outset.

In boriding processes such lengthy heat treatments are not necessary. The attainable hardness is also usually greater than that achieved in carburising processes. In the so-called diffusion annealing, in which a workpiece is introduced into a composition from which boron migrates into the surface of the workpiece at the treatment temperature, it is difficult to achieve an adequately uniform surface layer. The surface of a workpiece treated in this manner usually has a very uneven crystalline structure. For workpieces for which certain tolerances must be observed machining may therefore be necessary. Machining of this kind is particularly difficult and expensive because of the boriding.

The invention therefore seeks to provide a method of boriding which makes it possible to achieve a surface layer having a very uniform structure and uniform thickness, so that machining to the extent hitherto customary is not necessary.

The present invention provides a process for the boriding of the surface of a substantially completely machined metal workpiece, which comprises the steps of cleaning the workpiece, thereafter applying to the surface of the workpiece a layer of a composition which contains a boron-containing compound, and then heating the workpiece to a temperature in the range from 700°C to 1100°C in a medium which comprises a deoxidising and/or reducing gas. By repeated application and heating of the workpiece, particularly accurate proportioning is possible by the method of the invention. The walls of bores whose diameter is of the order

of magnitude of the desired layer thickness can, for example, also be adequately borided in this manner.

5 The invention also provides for the application to the workpiece which is to be treated of a composition which contains a boron-containing compound or boron-containing compounds and a binder which is decomposed in the temperature range between 100°
10 500°C. It is preferably to work with a binder which decomposes in a temperature range above 250°C.

In order to prevent the undesirable action of decomposition products on the surface of
15 the workpiece, it is preferable to work with the medium providing an annealing medium which can be adjusted accordingly. When binders based on synthetic resins are used the annealing medium preferably consists of
20 or contains hydrogen.

Further advantages and features of the invention will be seen from the claims and the following description and also from the accompanying drawings, wherein the inven-
25 tion is explained and illustrated in greater detail.

In these drawings,

Figure 1 is an enlarged photograph of a section through the surface of a workpiece
30 borided in known manner, and

Figure 2 is a photograph, produced in the same manner as Figure 1, of a section through the surface of a workpiece borided in accordance with the invention.

35 The process of the invention permits above all the production of an extremely uniformly borided surface layer. The uniformity relates both to the structure of the layer and to its thickness. The invention makes it possible for the thickness of the
40 layer, that is to say the depth of penetration of the diffusion to be accurately determined within practical limits. Through the application to the surface of the workpiece
45 of a composition suitable for diffusion annealing, it is finally also possible for only parts of the surface of a workpiece to be subjected to the boriding process.

In one embodiment of the invention a
50 workpiece is first completely machined, that is to say the surfaces are given the shape and dimensions required for the finished workpiece. The workpiece machined in this manner is thoroughly cleaned. For this purpose
55 it is placed in a bath consisting of an aqueous solution of an ordinary metal cleaning medium, which is additionally energized ultrasonically. Thereupon the workpiece is rinsed and, for example, degreased in a bath
60 of trichloroethylene. Instead, other customary degreasing baths may be used. The workpiece coming from the degreasing bath is in addition washed with acetone in order to obtain a chemically clean surface. The
65 acetone bath removes in particular any resi-

dues from the degreasing process and also fingermarks. In order to avoid further soiling of the surface, the workpiece is taken out of the acetone bath and handled either mechanically with gripping devices or by hand with the aid of fabric gloves.

The composition to be applied to the workpiece for the purpose of boriding consists of a fine-grained powder containing a boron compound. The diameter of the grains of this powder are preferably between 1μ and 10μ. The grain size should preferably not exceed the upper limit given here. Boriding powders which can be used for this purpose are available under the names SO95 and EKabor from Elektroschemelwerk Kemmten. It is also possible to use powders marketed by Advanced Metals Inc., Boston, U.S.A., under the names Borkote (Trade Mark) and Implife (Trade Mark). Acrylic ester resins can for example be used as binders, e.g. the grade marketed by Röhm and Haas, U.S.A., under the name "Acryloid A-30". Acetone may be used as diluent. The quantitative composition and consistency of the composition applied will depend on the one hand on the thickness of the layer to be obtained and on the other hand on the method of application. It is preferable to select a method of application which also ensures a very uniform applied layer, for example spraying. For larger flat surfaces it is also possible to apply the composition with a spatula. Dipping is another possible method of application. For the treatment of the walls of bores, particularly those of small diameters, the bores are filled with the composition. After the composition applied has dried it is possible for those surfaces which are to be treated and those which are to be left untreated to be accurately demarcated by removing, mechanically and/or by means of solvents, any applied coating extending beyond edges or boundaries.

After the composition containing the boron-compound containing powder has been applied and dried, the workpiece is placed in the annealing apparatus. The surfaces which are to be borided should not be in contact with one another. The workpieces must be so arranged that they are bathed by the annealing medium particularly on the uncoated surfaces. Spot supporting of the workpieces to be treated should therefore
110 be adopted.

In the following diffusion annealing process a diffusion temperature is selected which amounts to between 700 and 1100°C depending on the material of the workpiece.
115 The annealing medium used should be a gas or gas mixture which has a deoxidising and/or reducing action and which ensures that oxides which may be formed on the surface of the workpiece through the heat
120 130

and the decomposition of the binder are immediately removed, so that no oxide remains even on the surface of the workpiece which is not covered by the treatment composition. When binders based on acrylic ester resin are used and acetone is used as solvent, a gas or gas mixture having a dew point of minus 58°C or lower is selected. Hydrogen, for example, complies with these conditions. Given suitable adaptation, it is also possible to use a forming gas mixture composed of nitrogen and hydrogen.

The treatment time in the diffusion annealing process depends on the temperature selected, the material of the workpiece, and the desired diffusion layer. It amounts to at least a few minutes and may extend to several hours. Workpieces for which particular precision is desired are preferably treated in the range of the lower temperature limit for a longer time up to 10 hours.

If subsequent heat treatment is required, hardening is preferably effected in vacuo. Quenching is then effected in oil in vacuo or by the undercooled gas bathing process. The workpieces are then tempered in a deoxidising atmosphere.

In order to remove any residues of the boriding coating applied, after-cleaning is effected. For this purpose the workpieces are first soaked in an aqueous solution of a cleaning agent at a controlled temperature, for example in a detergent solution at about 80°C. The workpieces are then introduced into a bath consisting of the same solution, but which has not yet been soiled with residues of the coating material and which is energised ultrasonically. The workpieces are then rinsed with clear water and dried in air. The dried workpieces are after-treated with a customary preserving of oil in order to protect the surface against atmospheric influences.

The process of the invention is employed mainly for steel workpieces. It may however also be used for workpieces of other metal alloys, provided that the surfaces permit the diffusion of boron. By repeated application of the process of the invention a greater depth of diffusion, that is to say a thicker borided layer, is achieved. In the treatment of steel workpieces in which parts of the surface remain untreated, the annealing medium then has the particular purpose of also preventing decarburisation of the surface layer. The gas is preferably passed through the treatment chamber under an elevated pressure such that the material is adequately bathed and permanent modification of the surface by oxidation and/or decarburisation is prevented.

Comparison of Figures 1 and 2 clearly shows the improvement which can be achieved by the process of the invention. In Figure 1 the borided layer on the surface

of the workpiece has been produced by a conventional case-hardening process. The layer is relatively irregular both in structure and in depth of diffusion. Although adequate hardening may perhaps be achieved by this means, a layer of this kind is very sensitive. The coarse structure of the layer may even have the consequence that where close tolerances are prescribed after-machining will be necessary. By the known process it is also not possible to boride the walls of bores of small diameter.

On the other hand, Figure 2 clearly shows the improvement which can be achieved by the invention. The layer produced by diffusion has extremely uniform structure and thickness. Previously determined dimensions are not modified by treatment according to the invention. This applies particularly to parts of the surface which are to be left untreated.

Figure 1 shows a 4 mm chock wedge of 100 Cr 6 steel containing 1% C and 1.5—1.55% Cr which has been treated by the conventional case-hardening process for 2 hours at 1000°C. The thickness of the layer is irregular, amounting to 0.16 mm. The enlargement is 60×1.

Figure 2 shows a similar chock wedge, which however has been treated according to the invention for 1 hour at 870°C. The thickness of the layer is very uniform, amounting to about 30 μm. The enlargement is about 100×1.

WHAT WE CLAIM IS:—

1. A process for the boriding of the surface of a substantially completely machined, metal workpiece, which comprises the steps of cleaning the workpiece, thereafter applying to the surface of the workpiece a layer of a composition which contains a boron-containing compound, and then heating the workpiece to a temperature in the range from 700°C to 1100°C in a medium which comprises a deoxidising and/or reducing gas.

2. A process according to claim 1 wherein the steps of applying the composition to the workpiece and then heating the workpiece are repeated.

3. A process according to claims 1 and 2 wherein a composition which contains a binder decomposing in the temperature range between 100°C and 500°C is applied to the workpiece.

4. A process according to claim 3 wherein the binder decomposes in a temperature range above 250°C.

5. A process according to any one of claims 1 to 3 wherein the medium comprises hydrogen.

6. A process according to any one of claims 1 to 5 wherein the composition containing a boron compound is applied to part

and the decomposition of the binder are immediately removed, so that no oxide remains even on the surface of the workpiece which is not covered by the treatment composition. When binders based on acrylic ester resin are used and acetone is used as solvent, a gas or gas mixture having a dew point of minus 58°C or lower is selected. Hydrogen, for example, complies with these conditions. Given suitable adaptation, it is also possible to use a forming gas mixture composed of nitrogen and hydrogen.

The treatment time in the diffusion annealing process depends on the temperature selected, the material of the workpiece, and the desired diffusion layer. It amounts to at least a few minutes and may extend to several hours. Workpieces for which particular precision is desired are preferably treated in the range of the lower temperature limit for a longer time up to 10 hours.

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The process of the invention is employed mainly for steel workpieces. It may however also be used for workpieces of other metal alloys, provided that the surfaces permit the diffusion of boron. By repeated application of the process of the invention a greater depth of diffusion, that is to say a thicker borided layer, is achieved. In the treatment of steel workpieces in which parts of the surface remain untreated, the annealing medium then has the particular purpose of also preventing decarburisation of the surface layer. The gas is preferably passed through the treatment chamber under an elevated pressure such that the material is adequately bathed and permanent modification of the surface by oxidation and/or decarburisation is prevented.

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2. A process according to claim 1 wherein the steps of applying the composition to the workpiece and then heating the workpiece are repeated.
3. A process according to claims 1 and 2 wherein a composition which contains a binder decomposing in the temperature range between 100°C and 500°C is applied to the workpiece.
4. A process according to claim 3 wherein the binder decomposes in a temperature range above 250°C.
5. A process according to any one of claims 1 to 3 wherein the medium comprises hydrogen.
6. A process according to any one of claims 1 to 5 wherein the composition containing a boron compound is applied to part



of the workpiece and during heating the other parts of the surface are bathed by the annealing medium which is under elevated pressure.

- 5 7. A process according to any one of claims 1 to 6 wherein the composition containing a boron compound contains a binder based on acrylic resin.

- 10 8. A process according to any one of claims 1 to 7 wherein the consistency of the composition containing a boron compound which is to be applied to the workpiece is adjusted by acetone.

- 15 9. A process according to any one of claims 1 to 8 wherein residues of the composition applied to the workpiece are removed in a cleaning process after the heating.

10. A process according to any one of claims 1 to 9 wherein heat hardening in vacuo is effected after the annealing diffusion process and before the after-cleaning. 20

11. A process according to claim 1 and substantially as hereinbefore described with reference to Figure 2 of the accompanying drawings. 25

12. A workpiece having a surface treated by a process according to any one of the preceding claims.

ERIC POTTER & CLARKSON,
Chartered Patent Agents,
Kingsway,
London, WC2B 6QX.

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