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BORONIZING BATH AND METHOD

Vernon L. Hill and Thomas F. Stapleton, Indianapolis, Ind., assignors to General Motors Corporation, Detroit, Mich., a corporation of Delaware
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This invention relates to the heat treatment of metals and more particularly to the case hardening of metals by impregnation of metal surfaces with boron.

It is an object of this invention to provide an economical and simple immersion, or nonelectrolytic, boronizing process. It is also an object of the invention to provide a bath composition for the boronizing of metals. It is a further object of the invention to provide a method of making a bath useful in boronizing of metals.

Other objects, features and advantages of the invention will become more apparent from the following description of preferred embodiments thereof. The objects of our invention are attained by dissolving metallic boron in a molten bath to provide dissolved free boron in the bath. A metal workpiece is immersed in the bath and maintained therein at a suitable boronizing temperature for a sufficient duration to obtain the desired degree of boron impregnation. When this impregnation has been obtained, the workpiece is withdrawn from the bath and cooled. If desired, it can then be rinsed to prepare it for any further treatments. Among further treatments which are contemplated for the invention is a subsequent heat treatment which is used to diffuse the boron further into the surface of the part and, concurrently, reduce the concentration of boron in those areas of the part closely adjacent its surface. This diffusion treatment can be accomplished immediately after boron impregnation, after cooling or after rinsing.

The physical state of the elemental boron used is not material to the invention and any available form can be employed.

The preferred solvent for our boronizing bath is one which will dissolve boron and which will form a molten solution with the boron at a temperature suitable for diffusion of boron into the metal surface which is being treated. The term "dissolved" is also to include "dispersed," as it appears that, particularly in the more highly concentrated baths, boron may also be dispersed in the bath. Molten alkalis, such as fused sodium hydroxide and potassium hydroxide, can be used as solvents in our bath when dissolving boron. Of course, the baths thus formed are extremely corrosive to most metals and are, therefore, of only limited use for boronizing. On the other hand, fused borates, including fused boric acid, are of considerably more importance as base materials for our bath. Baths formed with borate salts in which elemental boron has been dissolved are generally satisfactory for boronizing ferrous base alloys, nickel base alloys, cobalt base alloys, molybdenum base alloys, tungsten base alloys and tantalum base alloys. In referring to an alloy of a given base metal, e.g., ferrous base alloys, we mean to include all metals which contain at least 50%, by weight, of the stated base metal. Thus, the pure base metal, e.g., pure iron is also included within the scope of the term.

Boronizing baths can be formed by dissolving metallic boron in a base material formed with one or more of the following borates: boric acid, a metaborate salt, a tetraborate salt, a pentaborate salt and a fluoborate salt. Of the various salts, the alkali metal salts are generally preferred, but the salts of other metals, such as the alkaline earth metals, can also be used. More specifically, highly satisfactory results, particularly with respect to the alloys previously referred to can be obtained with

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sodium tetraborate. It is to be understood that while fused fluoborate baths containing dissolved metallic boron are effective boronizing baths, such baths are not generally preferred for commercial applications. After approximately 48 hours at a comparatively high operating temperature, the fluoborate baths tend to exhibit an undesirable degree of solvent decomposition. It is further understood that, although in many instances we prefer to use a single compound as, for example, sodium tetraborate as the base material, or solvent of the bath, our invention is not restricted thereto. Combinations of substances can be used to form the base material in which the boron is dissolved and maintained at an appropriate temperature for diffusing it into the surface of the metal being treated.

We have found that a mixture of sodium, potassium and lithium tetraborates can not only be used up to a temperature of 2150° F. but can be effectively used at temperatures as low as 1250° F. While a liquid mixture can be obtained as low as 1200° F., the mixture is not very fluid and it is, therefore, not generally preferred to use this mix below 1250° F. The salt mixture we employ as a base material contains 20 to 60 mole percent sodium tetraborate, 20 to 60 mole percent potassium tetraborate and 20 to 60 mole percent lithium tetraborate. Equimolar ratios have been found to be highly satisfactory mixtures of these salts. This salt mixture not only is capable of dissolving substantial amounts of boron but, as indicated, has a high fluidity below a temperature of approximately 1500° F., where sodium tetraborate is rather viscous. The melting point of sodium tetraborate, of course, is 1378° F. It is to be recognized that our sodium, potassium and lithium tetraborate salt mixture is suitable for use in any process of boronizing, electrolytic or nonelectrolytic, where sodium tetraborate, alone, can be used. However, in addition our salt mix can be used at even a lower operating temperature.

Even when small amounts of metallic boron, about 1%, by weight, and even lower, are used in the bath, they can be effective in producing boron impregnation. However, we prefer to dissolve larger amounts of boron in the bath in order to obtain the desired diffusion in a shorter period of time. We generally prefer to use at least about 4%, by weight, boron in the bath so that appreciable results can be obtained within a reasonable time, that is, about two hours. By dissolving larger amounts of metallic boron in the bath, up to about 8% by weight, a substantial increase in the rate of visible case depth formation can be obtained. While little increase in the rate of visible case depth formation is obtained by using more than about 8%, by weight, boron we prefer to use, particularly for commercial applications, approximately 12% boron to increase time between boron replenishment and insure consistent results. However, while it is not economically feasible, in most instances, to use bath solutions which are saturated with metallic boron, such solutions provide satisfactory results and can be used.

Treatment of metal in accordance with our invention preferably involves a precleaning of the surface which is to be treated. On the other hand, our preferred boronizing bath (one containing about 12%, by weight, metallic boron dissolved in sodium tetraborate) possesses excellent oxide dissolving characteristics. Thus, when using our preferred bath, if desired, the cleaning of the part prior to boronizing can be omitted. However, to reduce contamination of the boronizing bath and, therefore, to increase its active life, it is desirable to clean the part before it is boronized. Cleaning the metal surface in any normal and accepted cleaning manner is suitable as a preparation for boronizing. For ex-

ample, a ferrous base alloy can be cleaned by immersing it in a suitable oil film remover, as trichloroethylene or the like. If severely oxidized it can also be treated in an aqueous solution containing 1%, by weight, hydrochloric acid to remove surface rust and scale.

After the part is cleaned, it is immersed in the boronizing bath, with or without a preliminary preheating step. The specific physical disposition of the part in the bath is no more critical to the invention than is the disposition of a part in any liquid bath. Thus, of course, the part should be positioned to avoid forming air pockets which prohibit contact between the bath and any part of the surface which is to be treated. As indicated above, while, in some instances, preheating the part may be beneficial, it usually has little effect on the character of the product obtained.

The preferred time of immersion in the boronizing bath is variable and depends upon a plurality of factors, including the thickness of the case desired and the rate of visible case depth formation. The rate of visible case depth formation for many metals in our bath diminishes rapidly after about one hour of immersion. Two hours' immersion produces generally satisfactory results for most metals, and there is usually little added benefit in using case depths greater than those formed by four hours' immersion. However, in certain instances, exceptionally deep cases and, consequently, extraordinarily long immersion times may be preferred.

The rate of visible case depth formation is primarily dependent upon the nature of the basis metal, the bath composition and the operating temperature of the bath. As previously indicated, the rate of visible case depth formation is not only increased by increasing the concentration of boron in the bath but also by increasing the bath operating temperature.

The preferred operating temperature of the bath is not determined independently. In general, a bath formed in accordance with this invention is useful for boronizing at any temperature between its melting point temperature and its boiling point temperature, provided that the metal treated is not adversely affected by the temperature involved. On the other hand, the melting point of the metal, or the case formed, and the presence of characteristics derived from prior heat treatments can influence the preferred boronizing temperature. Boronizing baths in which sodium tetraborate is the predominant constituent are preferably operated at a temperature of at least 1500° F., the temperature at which these baths are highly fluid. Temperatures in excess of about 2150° F. are to be avoided when using the sodium tetraborate baths due to an undesirably high degree of solvent evaporation which occurs at these temperatures.

It is, therefore, to be appreciated that the boronizing treatment can be accomplished at a plurality of temperatures, durations and bath concentrations. By dissolving larger amounts of boron in the bath, a greater visible case depth in a lesser treatment time can be obtained. Elevating the treatment temperature increases the rate of visible case depth formation to reduce treatment duration.

The invention is applicable to a wide variety of different alloys: low carbon steels, such as SAE 1010 or SAE 1018, high alloy steels, including stainless steel, alloys such as SAE 310 and SAE 440, nickel base alloys, cobalt base alloys, molybdenum base alloys, tantalum base alloys and the like. Obviously, the rate of boron diffusion is not the same for every alloy. Hence, the treatment conditions necessary to attain a given visible case thickness and hardness may vary for one alloy from those preferred for another alloy. It appears that the greater the proportion of alloying ingredients in a ferrous alloy, the lesser the boron penetration rate. However, in general, the rate of boron penetration in ferrous base alloys is larger than in cobalt base alloys. While the rate of visible case depth formation is greater in low alloy steels than in nickel base alloys, this relationship can reverse when the alloy content in the steel increases.

In most instances it has been found that the rate of cooling the part after it has been boronized has little effect upon the character of the boronized case. Thus, air cooling, water quenching or slow cooling, such as furnace cooling, can be used, provided that the selected method of cooling does not adversely affect previously established characteristics of the basis metals involved.

After it is removed from the boronizing bath and cooled, the part can be rinsed in a suitable solvent, such as water, to remove residual salts that may be adhering to its surface. The rinsed part is then ready for any further treatments which are to be performed on it.

In certain instances it may be desired to produce an unusually deep boronized case of lesser hardness. This can be accomplished by a diffusion treatment after boronizing. The time and temperature for this diffusion treatment, as in the boronizing treatment, are variable but, as a general rule, boronizing temperatures can be used. However, in some instances, it may be desired to use a lower temperature. The preferred duration of the diffusion treatment generally is less than the bath immersion time. Since the subsequent diffusion treatment concurrently also produces a softer and less wear-resistant outer surface, the subsequent diffusion treatment is not preferred when utmost hardness and wear resistance are desired.

It is also to be understood that in some instances it may be desirable to otherwise heat treat and boronize a metal part simultaneously. In such instance, the preferred boronizing temperature and duration would also be determined by reference to the most desirable other heat treating conditions.

In the event that it is preferred to boronize only a portion of the surface of a part which is to be treated in accordance with the invention, electrodeposited copper can be applied to stop off appropriate areas. The surface can be selectively plated with copper to leave exposed those areas which are to be boronized, or the entirety of the surface can be copper plated and subsequently selectively etched to expose the basis metal in those areas which are to be boronized.

While corrosion-resistant metals, such as stainless steels, and ceramics, such as aluminum oxide, can be used as a container for our bath solution, containers of these materials are not the best for our boronizing baths. For commercial production applications, we prefer to employ a container formed of substantially a pure silicon carbide which is low in silicon dioxide, as this is both thermally stable and resistant to attack by our preferred bath solution at the usual boronizing temperatures. Other silicon carbide substances, such as silicon carbide bonded with silicon nitride, are also useful.

Although this invention has been described in connection with certain specific examples thereof, it is to be understood that no limitation is intended thereby except as defined in the appended claims.

We claim:

1. The process which comprises dissolving metallic boron in a molten borate bath to provide a metallic boron concentration therein of at least about 1%, by weight, immersing a metal part in said bath without electron connection to said part, said part being of a metal into which boron will diffuse, and continuing said immersion in said bath at a boron-diffusing temperature for a sufficient duration to impregnate said surface with boron.

2. The process which comprises dissolving metallic boron in a molten borate bath to produce a metallic boron concentration therein of at least about 4%, by weight, to saturation, applying said bath to the surface of a metal without electron connection to the metal, said metal being selected from the group consisting of ferrous base alloys, nickel base alloys, cobalt base alloys, molybdenum base alloys, tungsten base alloys and tantalum base alloys, maintaining said bath at a boron-diffusing temperature within the range of approximately 1250° F. to 2150°

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F., continuing to apply said bath for approximately 1/2 hour to 4 hours, discontinuing said bath application and thereafter heating said part at a temperature of approximately 1200° F. to 2150° F.

3. The process which comprises dissolving metallic boron in a molten sodium tetraborate bath to produce a metallic boron concentration therein of at least about 4%, by weight, to saturation, applying said bath to the surface of a metal without electron connection to the metal, said metal being selected from the group consisting of ferrous base alloys, nickel base alloys, cobalt base alloys, molybdenum base alloys, tungsten base alloys and tantalum base alloys, maintaining said bath at a boron-diffusing temperature within the range of approximately 1500° F. to 2150° F., continuing to apply said bath for approximately 1/2 hour to 4 hours, discontinuing said bath application and thereafter heating said part at a temperature of approximately 1200° F. to 2150° F.

4. A method of boronizing which comprises fusing a mixture containing about 20 to 60 mole percent sodium tetraborate, 20 to 60 mole percent potassium tetraborate and 20 to 60 mole percent lithium tetraborate, dissolving metallic boron in said mixture to produce a metallic boron concentration of at least about 1%, by weight, placing a surface of a metal in contact with said bath without electron connection to said metal, said metal being selected from the group consisting of ferrous base

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alloys, nickel base alloys, cobalt base alloys, molybdenum base alloys, tungsten base alloys and tantalum base alloys, and maintaining said contact at a boron-diffusing temperature for a sufficient duration to impregnate said surface with said dissolved boron.

5. A boronizing bath containing sodium, potassium and lithium tetraborates in the relative proportions of about 20 to 60 mole percent sodium tetraborate, 20 to 60 mole percent potassium tetraborate and 20 to 60 mole percent lithium tetraborate, and at least about 1%, by weight, of dissolved metallic boron.

References Cited by the Examiner

UNITED STATES PATENTS

1,795,512	3/31	Schmidt et al.	204-39
2,984,605	5/61	Cooper	204-39
3,024,176	3/62	Cook	204-39

FOREIGN PATENTS

677,113	5/39	Germany.
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OTHER REFERENCES

Hoge: Metal Progress, vol. 52, November 1947, pp. 819-23.

RICHARD D. NEVIUS, *Primary Examiner.*