

1

3,201,286

METHOD OF BORONIZING

Vernon L. Hill and Thomas F. Stapleton, both of Indianapolis, Ind., assignors to General Motors Corporation, Detroit, Mich., a corporation of Delaware
No Drawing. Filed Mar. 15, 1962, Ser. No. 180,044
7 Claims. (Cl. 148—6.11)

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 method of preparing an immersion boronizing bath.

Other objects, features and advantages of the invention will become more apparent from the following description of preferred embodiments thereof. These objects of our invention are attained by introducing into a molten borate bath a metal which will react with the borate compound to liberate boron in the bath. A metal having a free energy of oxide formation greater than that of boron is introduced into a fused borate bath to liberate boron therein. The bath is placed in contact with the surface of a metal part at a suitable temperature for a sufficient duration for the liberated boron to impregnate the metal surface. When the desired degree of boron impregnation has been obtained, the contact is discontinued, the part cooled and, if desired, rinsed to prepare it for any further treatments. Among the 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 the cooling or after the rinsing.

As encompassed by the invention, a metal workpiece is impregnated in our bath solution with liberated boron. The boron is available from reaction of a metal having a free energy of oxide formation greater than the free energy of oxide formation of boron with the borate forming the base material of the bath. Among boron liberating metals are calcium, beryllium, cerium, lithium, magnesium, aluminum and titanium.

The particular physical state of the boron liberating metal used is not material to the operability of the bath, itself. Consequently, the boron liberating metal can be introduced in powder form, granular form, flake form, ingot form or the like.

On the other hand, the physical form of the boron liberating metal used can be relevant insofar as preparation of the bath is concerned. Our invention involves reaction of the borate base material with a free boron liberating metal. When introducing magnesium, for example, into a fused borate bath under an oxygen-containing atmosphere, the temperature of the fused bath may be sufficient to cause combustion of the magnesium before it is completely reacted with the borate. The magnesium in magnesium oxide is not a "free metal." Therefore, it is not effective in liberating boron in the bath. If the magnesium burns, it is not totally effective in liberating boron. Where such a competing reaction occurs, more magnesium must be added to attain the desired amount of liberated boron. Obviously powder, granular or flake form, would oxidize more quickly than ingot and, in addition to being poorly efficient in liberating boron, creates severe fire hazards. Similar problems are associated with other useful metals, such as lithium.

Accordingly, we prefer to prepare our bath in such a

2

manner as to avoid this problem. The boron liberating metal can be introduced into the bath in ingot form under an inert atmosphere. Atmospheres of helium, argon or the like can be used. Of course, the use of the protective atmosphere, itself, is sufficient to obviate any problem, but as an additional precaution the ingot form is also preferred. It should be appreciated that the use of the ingot form, alone, can obviate the need for a protective atmosphere. If the ingot floats in the bath, it can be mechanically maintained below the surface of the bath liquid until it is completely dissolved, as is a frequent practice in adding magnesium to a melt when making a zinc base alloy. In such instance little, if any, oxidation of the magnesium occurs before total ingot dissolution.

The molten borates considered for use in the base material which reacts with the boron liberating metal include boric oxide, metaborate salts, tetraborate salts, pentaborate salts and fluoborate salts. Of the various borate salts contemplated, the alkali metal salts are generally preferred. However, the salts of other metals, such as the alkaline earth metals, can also be used. More specifically, we have found that sodium tetraborate, by itself, is a highly satisfactory base material. It is to be understood that while baths containing a fluoborate are effective boronizing baths, such baths are not generally preferred. After approximately 48 hours at a comparatively high operating temperature, the fluoborate baths tend to decompose.

It is further understood that, although in many instances we prefer to use a single compound, for example, sodium tetraborate, as the base material of the bath, our invention is not restricted thereto. Combinations of borates can be used to form the base material. For example, a mixture of sodium, potassium and lithium tetraborates can be used. An appropriate mixture of these salts can be effectively used at temperatures from as low as 1250° F. to as high as about 2150° F. While this salt mixture is liquid as low as 1200° F., the mixture is not very fluid at this temperature and it is, therefore, not generally preferred to use the mixture below a temperature of approximately 1250° F. The appropriate mixture of these salts is 20 to 60 mole percent sodium tetraborate, 20 to 60 mole percent potassium tetraborate and 20 to 60 mole percent lithium tetraborate. Equal molar ratios have been found to be quite satisfactory. Thus, while sodium tetraborate mixtures become rather viscous below temperatures of approximately 1500° F., boronizing can be accomplished at a lower temperature using this salt combination.

Our boronizing baths can be used for boronizing such metals as ferrous base alloys, nickel base alloys, cobalt base alloys, molybdenum 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.

A boronizing bath can be formed in accordance with the invention in various ways. The base material can be fused, the boron liberating metal added and then the workpiece immersed in the bath. On the other hand, the workpiece and the boron liberating metal can be introduced into the molten base material concurrently, or the workpiece before the boron liberating metal. While not generally practical, the base material can be fused after the boron liberating metal is added to it.

It is to be understood that even small amounts of liberated boron in the bath are effective in producing boron impregnation, such as that produced by about 0.2 equivalent weight of liberating metal (e.g., 2.5 grams of magnesium) per 100 grams of base material. However, baths having larger amounts of liberating boron are preferred to

obtain the desired diffusion in a shorter period of time. In most instances, at least about 1 equivalent weight of the boron liberating metal (e.g., 12 grams of magnesium) per 100 grams of base material is needed to obtain appreciable results in a reasonable period of time, such as about two hours. However, by employing larger amounts of the boron liberating metal, about 3.2 equivalent weight (e.g., 26 grams of magnesium) per 100 grams of bath solution, a substantial increase in the rate of visible case depth formation can be realized. While little increase in the rate of visible case depth formation is obtained by using amounts of the boron liberating metal in excess of this amount, for commercial production applications a useful working margin is generally desirable and, for this reason, it is preferred to use about 3.2 equivalent weights (e.g., 40 grams of magnesium) per 100 grams of base material. All of these proportions, of course, are based on substantially 100% efficiency in introducing the free liberating metal into the solution. Where the liberating reaction is less than 100% effective, the amount of liberating metal should be appropriately increased. Care should be taken not to use the liberating metal much in excess of these amounts, since, in some cases, the liberating reaction may produce by-products which objectionably raise the melting point temperature of the bath. These reaction by-products should not exceed 50%, by weight, of the bath.

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 formed with 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 example, 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 proportion of boron liberating metal used (increasing liberated 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 base material 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 since sodium tetraborate rapidly evaporates 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 using larger amounts of boron liberating metal 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 reverses when 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 ferred 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 bath. For commercial production applications, we prefer to employ a silicon carbide 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 introducing into a fused borate bath a metal having a higher free energy of oxide formation than that of boron so as to liberate metallic boron therein, placing a surface of a metal having a melting point temperature higher than the bath temperature in contact with said bath without external electron connection to impregnate the metal with said liberated boron, and maintaining said contact at a boron-diffusing temperature for a sufficient duration to impregnate said surface with boron.

2. The process which comprises introducing into a fused borate bath a metal having a free energy of oxide formation higher than that of boron, immersing a metal part having a melting point temperature higher than the bath temperature in said bath to impregnate the part with said liberated boron, maintaining said part in said bath without external electron connection at a temperature at which boron will diffuse into the surface of said metal part and continuing said immersion for a sufficient duration to impregnate said part with boron.

3. The process which comprises introducing into a fused borate bath a metal having a free energy of oxide formation higher than that of boron, placing a surface of a metal part having a melting point temperature higher than the bath temperature in contact with said bath to impregnate the metal with said liberated boron, maintaining said contact at a boron-diffusing temperature for a sufficient duration without external electron connection to impregnate said surface with boron, discontinuing said contact and thereafter heating said part to obtain a deeper penetration of boron into the surface thereof.

4. The process which comprises introducing into a fused borate bath a metal from the group consisting of calcium, beryllium, cerium, lithium, magnesium, aluminum and titanium so as to liberate free boron therein,

applying said bath to the surface of a metal from the group consisting of ferrous base alloys, nickel base alloys, cobalt base alloys, molybdenum base alloys and tantalum base alloys to impregnate said metal with said liberated boron, said bath being maintained in a silicon carbide vessel at a temperature at which said liberated boron will diffuse into said surface without external electron connection, and continuing to apply said bath to said surface for approximately $\frac{1}{2}$ hour to 4 hours.

5. A process which comprises introducing into a fused borate bath at least about 0.2 equivalent weight of a metal having a free energy of oxidation formation greater than that of boron per 100 grams of bath so as to liberate boron therein, immersing a part of a metal having a melting point temperature higher than the bath temperature in said bath to impregnate said part with said liberated boron and continuing said immersion at a boron-diffusing temperature without external electron connection for a sufficient duration to impregnate said surface with boron.

6. The process which comprises introducing into a fused borate bath so as to liberate boron therein from about .2 to 3.2 equivalent weights of metal having a free energy of oxide formation greater than that of boron per 100 grams of bath, applying said bath to the surface of a metal consisting of ferrous base alloys, nickel base alloys, cobalt base alloys, molybdenum base alloys and tantalum base alloys to impregnate said metal surface with said liberated boron without external electron connection, maintaining said bath at a boron-diffusing temperature between approximately 1200° F. to 2150° F., continuing to apply said bath without external electron connection to said metal for approximately $\frac{1}{2}$ hour to 4 hours, discontinuing said bath application and thereafter heating said part at a temperature of approximately 1200° F. to 2150° F.

7. The process which comprises introducing a metal having a free energy of oxide formation greater than that of boron into a fused borate bath consisting essentially of 20 to 60 mole percent sodium tetraborate, 20 to 60 mole percent potassium tetraborate and 20 to 60 mole percent lithium tetraborate so as to liberate boron therein, placing a surface of a metal having a melting point temperature higher than the bath temperature in contact with said bath to impregnate said metal surface with said liberated boron, and maintaining said contact at a boron-diffusing temperature without external electron connection for a sufficient duration to impregnate said surface with said liberated boron.

References Cited by the Examiner

UNITED STATES PATENTS

2,465,989	4/49	Sowa	23—209
3,024,176	3/62	Cook	204—39

RICHARD D. NEVIUS, *Primary Examiner.*