METHOD OF COATING METALS WITH A BORIDE

Frederick Tepper, Butler, and John Wilson Manstaller and John C. Gerken, Forward Township, Butler County, Pa., assignors to M.S.A. Research Corp., Pittsburgh, Pa., a corporation of Pennsylvania

-No Drawing. Filed June 19, 1962, Ser. No. 203,462
23 Claims. (Cl. 148—6.11)

This invention relates to a method of treating metals and more particularly to coating base metals with a boride of the base metal.

Metal borides are known for their superior wear resistance, corrosion resistance and hardness, and they are particularly useful as coatings for base metals that do not possess these desirable properties. Conventionally, borides have been separated and then applied to a base metal with suitable heat treatment to form a coating thereon.

It is an object of this invention to provide a method of forming continuous boride coatings on base metals. Another object is to provide such a method which is simple, direct and easily performed. These and other objects will be apparent from the following description.

Broadly, this invention accomplishes the formation of a boride coating on base metals by contacting the base metal at an elevated temperature with a molten alkali metal bath which contains boron or a boron compound, such as a boron oxide or a boron halide.

It has been found that the reaction for the production of continuous boride coatings in accordance with the present invention preferably is conducted at a temperature of about 1600°F. to 1800°F. or higher, but can be conducted at temperatures as low as about 1300°F. It is generally desired to maintain the physical properties of the base metals and, in that case, the temperature used should be below that at which the base metal will be substantially altered.

The base metals suitable for use in this invention are the Group IVA metals, namely, titanium, zirconium and hafnium; the Group VA metals, namely vanadium, columbium and tantalum; the Group IIA metals, including the rare earths and actinides, that melt above the temperature required for coating, such as scandium, yttrium, lanthanum, cerium, neodymium, uranium, manganese, iron, nickel and tungsten; and also alloys having a major proportion of these suitable metals, such as, for example, stainless steels, Inconel and Hastalloy. Most of these base metals having melting points well above the temperature required for coating and therefore may be easily coated without adversely affecting the physical properties of the base metal. In order to form continuous, adherent and uniform coatings, the base metal surface should be clean and preferably free of oxide films, according to conventional platting and coating practice.

As a source of boron, elemental boron, suitably in a finely divided powdered or crystalline form, is preferred as the coatings generally are brighter and form at a faster rate than when using boron compounds. Boron oxides, such as boron oxide (B₂O₃) and dehydrated borax (Na₂B₂O₆) are especially attractive because of their low cost. When using a boron oxide source for coating actinides, Group IVA, and Group VA metals, which form stable oxides not reducible by an alkali metal, the boride coating formed may contain some base metal oxide. The various boron halides, e.g. boron trifluoride, boron trichloride, boron tribromide, etc., and boron hydrides, such as diborane, pentaborane, etc., also are suitable. In many cases, the by-product alkali metal salt, formed when using a boron source other than elemental boron, such as sodium halide, hydroxide or sulfide, remains at least partially dissolved in the alkali metal bath. We have found that the use of the boron compounds and/or the presence of the by product salts in the bath does not generally adversely affect the functional utility of the coating, but that a longer reaction time or higher temperature is frequently required to obtain a coating thickness comparable to that obtained when using elemental boron.

All of the alkali metals and mixtures thereof are suitable for use, although it is preferred to use sodium, potassium or their alloys since they are the least expensive. When using a boron oxide boron source it is preferred to use an alkali metal bath containing lithium, sodium or potassium because the rate of coating formation is very slow if only rubidium or cesium is used. The alkali metal bath is pyrophoric and must, therefore, be protected from the atmosphere, most conveniently by maintaining an atmosphere of argon or other inert gas over the bath. Commercial alkali metals generally contain some oxide, e.g., commercial sodium may contain 0.15% sodium oxide, much of which can be removed by filtration of the melted metal at comparatively low temperature. When using elemental boron as a boron source it is generally preferred to use filtered, or otherwise deoxidized, alkali metal to realize the full advantage of an oxide-free bath.

The method is simple to conduct since it comprises merely placing the base metal in the alkali metal bath which contains a boron source material at the aforementioned elevated temperature. The proportions of boron source material and alkali metal in the bath are not critical, so long as there is sufficient alkali metal to provide a fluid media for good contact with the base metal; generally it is preferred to use a major proportion of alkali metal.

Conveniently, a solid boron source material and the base metal to be coated are placed in a suitable container, such as stainless steel or carbon steel, having a closure with inlet and outlet connections for inert gas and alkali metal. The container is then closed and flushed with inert gas to remove the enclosed air; sufficient molten alkali metal is then introduced to the container to cover the base metal and the bath is heated to and maintained at the desired temperature for the desired length of time. The bath can then be drained from the container and the coated metal piece removed. Fluid boron sources, such as boron halides and boron hydrides, are conveniently bubbled or injected into a molten alkali metal bath. If desired, the bath of alkali metal and boron source material may be preformed and the base metal introduced and withdrawn from the bath through inert gas locks which prevent atmosphere contamination. The boron source material can be added to the bath periodically or continuously to replenish that consumed in forming the coating.

The coatings formed by this invention are borides of the base metal, and are believed to result from reaction of the base metal surface with the alkali metal containing a boron source material. Coatings of appreciable thickness are apparently formed by diffusion of boron or borides into the base metal. The coatings vary in thickness depending on the conditions of operation, particularly including the type of base metal employed, the time and temperature of operation and, to a lesser extent, the amount of boron source material in the alkali metal bath. Continuous coatings from about 0.0005 inch to 0.005 inch in thickness have been obtained.

The following examples are illustrative of this invention and are not intended in any sense to limit the manner in which this invention can be practiced.

Example 1

Twenty-five grams of boric oxide and a titanium rod 1¼ inches in diameter and 1 inch long, supported on a stainless steel screen, were placed in a closed stainless
steel container with suitable inlet and outlet connections. The container was flushed with argon and 125 g. of liquid sodium was introduced, which completely immersed the titanium rod. The container was placed in a furnace and heated to 1800 °F. for six hours, cooled to just about the melting point of sodium, and the melt was drained from the container. The titanium rod, washed in alcohol to remove residual sodium, was coated with a continuous coating of titanium diboride, identified by X-ray diffraction analysis, which added 0.030 g. to the sample.

**Example II**

Example I was repeated except that 4.0 g. of boron and 13 g. of boric oxide were used in place of the boric oxide and substantially the same results were obtained.

**Example III**

Example I was repeated except that 9.0 g. of boron was used instead of the boric oxide and the temperature was 1600 °F. The titanium sample was coated with a continuous titanium boride coating 0.0024 inch thick after six hours, and 0.0044 inch thick after twenty-four hours.

**Example IV**

Example I was repeated except a nickel rod and a temperature of 1600 °F. were used and a continuous coating of nickel boride was formed on the metal piece as in the Example I.

**Example V**

The reactor used in Example I was equipped with stirrer. Example I was repeated using filtered sodium, a temperature of 1600 °F., 9.0 g. of boron instead of the boric oxide, and a section of nickel pipe in place of the titanium rod. After a six hour treatment the pipe was coated on all surfaces with a continuous nickel boride coating 0.0046 inch thick, and after a twenty-four hour treatment the coating thickness was 0.0083 inch.

**Example VI**

Example V was repeated using a section of type 304 stainless steel pipe in place of the nickel pipe. After six hours treatment the pipe was coated on all surfaces with a 0.0015 inch thick boride coating.

**Example VII**

Example V was repeated using Inconel pipe in place of the nickel pipe. After 6 hours treatment the boride coating formed on the pipe was 0.0016 inch thick, and after 12 hours treatment it was 0.0023 inch thick.

**Example VIII**

Example V was repeated using Hastalloy B tubing in place of the nickel pipe and a .0015-inch boride coating was formed on all surfaces of the tube.

**Example IX**

Example V is repeated a number of times using respectively in place of the nickel pipe, a piece of zirconium, hafnium, vanadium, columbium, tantalum, scandium, yttrium, praseodymium, thorium, uranium, iron, manganese and carbon steel, and in each case a boride coating is formed on the metal piece similarly as in Example V.

From the foregoing description and examples, it is seen that continuous boride coatings are formed on base metals by the direct and simple method of this invention. According to the provisions of the patent statutes, we have explained the principle of our invention and illustrated and described what we now consider to represent its best embodiment. However, we desire to have it understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically illustrated and described.

**We claim:**

1. A method of forming a boride coating on a base metal comprising contacting a base metal selected from the group consisting of the periodic groups IVA, VA, VIA including the rare earth and actinide elements, manganese, iron, nickel, tungsten and alloys thereof, with a bath consisting of a major portion of alkali metal and a minor proportion of a boron component selected from the group consisting of elemental boron and the halides, oxides, mixed metal oxide and hydrides of boron, under a non-oxidizing atmosphere at a temperature of at least about 1300 °F.

2. A method of claim 1 in which the temperature is between about 1600 °F. and 1800 °F.

3. A method of claim 2 in which the boron component is boron oxide and the alkali metal is selected from the group consisting of lithium, sodium, potassium and mixtures thereof.

4. A method of claim 3 in which the base metal is nickel.

5. A method of claim 3 in which the base metal is stainless steel.

6. A method of claim 3 in which the base metal is an alloy containing a major proportion of nickel.

7. A method of claim 2 in which the boron component is elemental boron.

8. A method of claim 7 in which the alkali metal is substantially free of oxide.

9. A method of claim 8 in which the base metal is titanium.

10. A method of claim 8 in which the base metal is hafnium.

11. A method of claim 8 in which the base metal is vanadium.

12. A method of claim 8 in which the base metal is columbium.

13. A method of claim 8 in which the base metal is tantalum.

14. A method of claim 8 in which the base metal is scandium.

15. A method of claim 8 in which the base metal is yttrium.

16. A method of claim 8 in which the base metal is thorium.

17. A method of claim 8 in which the base metal is uranium.

18. A method of claim 8 in which the base metal is manganese.

19. A method of claim 8 in which the base metal is iron.

20. A method of claim 8 in which the base metal is tungsten.

21. A method of claim 8 in which the base metal is nickel.

22. A method of claim 8 in which the base metal is stainless steel.

23. A method of claim 8 in which the base metal is an alloy containing a major proportion of nickel.

References Cited by the Examiner

**UNITED STATES PATENTS**

1,855,562 4/1932 Swine -------------- 148—6.35 X
2,823,151 2/1958 Yntema et al. --148—6.3 X
2,848,352 8/1958 Noland et al. --117—114 X
2,854,353 9/1958 Schwop. --
2,929,740 3/1960 Logan -------------- 117—114
3,085,028 4/1963 Logan -------------- 117—114

RICHARD D. NEVIUS, Primary Examiner.
R. S. KENDALL, Assistant Examiner.