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3,697,390

ELECTRODEPOSITION OF METALLIC BORIDE COATINGS

Frank X. McCawley, Cheverly, Md., Charlie Wyche, Washington, D.C., and David Schlain, Greenbelt, Md., assignors to the United States of America as represented by the Secretary of the Interior

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9 Claims 10

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plate of controllable thickness on conductive substrate materials. Smooth, consolidated coatings are obtained by electrodeposition from a fused borate-type bath having dissolved therein at least one compound of the metal of the desired boride.

Hence, it is an object of this invention to deposit hard, adherent coatings on substrate materials.

It is a further object of this invention to produce adherent, coherent, metal boride coatings.

A specific object of this invention is to produce electroplates of titanium diboride on conductive substrates.

ABSTRACT OF THE DISCLOSURE

Platings of titanium, zirconium and hafnium borides are produced on substrate materials by electrodeposition from a fused, borate-type bath.

BACKGROUND OF THE INVENTION

The interesting and attractive properties of metal borides, particularly the Group IV—A metal borides, have long been recognized. Borides of Group IV—A metals (titanium, zirconium and hafnium) generally display a very high melting point, excellent electrical conductivity, extreme hardness and a general chemical inertness characterized by high resistance to oxidation at elevated temperatures and high corrosion resistance to molten glasses, salts and metals.

Metal borides have been obtained in a variety of ways. Exemplary methods include the reaction of metals with boron-containing compounds at high temperatures; thermal reduction of mixed boron and metal oxides with carbon and by the electrolysis of fused halide-boron oxide baths. This last method, generally attributed to Andrieux, is described in Rev. Met. (Paris), 45, 49–59, (1948) and a variation of the same technique is described in the Sindeband patent, U.S. 2,741,587.

Production of metal borides by fused salt electrolysis, such as is disclosed by Sindeband, results in the formation of an agglomerated mass of boride particles in the area adjacent to the cathode. After comminution and purification, the resulting product consists of a finely divided powder suitable for forming by powder metallurgy techniques. Use of these compounds has been quite restricted due to the fabrication difficulties and inherent size and shape limitations imposed by powder metallurgy. Machining of a formed article is also difficult because of the extreme hardness of these compounds.

In work published in the Journal of the Electrochemical Society, vol. 113, No. 1 (1966), pp. 60–66, Mellors et al. disclose the electro-deposition of coherent, adherent electroplates of zirconium diboride from salt baths of specific composition. They found that such plates could be obtained only from alkali metal fluoride baths containing both zirconium tetrafluoride and potassium fluoborate. Substitution of sodium fluoborate for the potassium compound resulted in production of dendrites and powders as did the use of chloride or mixed chloride-fluoride melts. Use of a chloride-boron oxide system resulted in the production of contaminated zirconium diboride powders.

SUMMARY OF THE INVENTION

We have now found that borides of the Group IV—A metals may be deposited as a coherent, adherent electro-

DETAILED DESCRIPTION OF THE INVENTION

Our process may be carried out in a manner similar to that employed in our previous work with fused salt baths illustrated, for example, in our patent, U.S. 3,369,978. Electrolyte used in the process comprises a fused, borate-type bath. Borate salts found to be satisfactory include the alkali and alkaline earth metal borates. Particularly preferred are the sodium and lithium metaborates. However, other borates of the alkali and alkaline earth metals, such as the orthoborates, diborates, tetraborates and pentaborates may also be used. From a practical view, choice of the appropriate borate compounds is governed primarily by availability, cost and melting point.

Borate salts require a thorough drying prior to use as the electrolyte. Drying may be conveniently accomplished by heating in a vacuum oven followed by fusion. Drying conditions are not critical but are typically performed at temperatures of about 200° C. and pressures on the order of a few millimeters of mercury. Naturally, care must be taken to avoid contact of the dried salts with moist air. Handling of the dried salts may be conveniently carried out within a dry box of conventional construction.

In addition to the borate salts, the electrolyte includes in dissolved form one or more compounds of the metal of the desired boride. Preferably, these compounds comprise either metal oxides or alkali and alkaline earth salts of metallic oxy acids such as alkali metal titanates, zirconates and the like. Initial concentration of these compounds in the electrolyte is not critical and may be in the range of about 0.1 to about 5% based on the metal. As electrolysis and deposition proceeds, the metal content of the electrolyte is constantly replenished by dissolution of the anode.

Choice of electrodes is dependent upon the boride being plated and upon the characteristics of the desired product. The anode must comprise a metal of the desired boride; if titanium boride is being deposited, then the anode must comprise titanium. The cathode must be electrically conductive, such as a metal, and must have a higher melting point than the operating temperature of the bath. It is preferred that the cathode be rotated during electrolysis so as to agitate the bath and produce a higher quality plate.

Plating temperatures used will vary according to the specific composition of the bath. While plating may be accomplished over a fairly wide temperature range, from slightly above the melting point of the salt to temperatures as high as about 1200° C., it is preferred to operate the process at relatively low temperatures. When a mixture of sodium and lithium metaborates is used as the electrolyte, for example, it is preferred to operate the process at a temperature within the range of about 850°

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to 950° C. A most preferred temperature range for that system is from about 875° to 925° C.

Cathode current density for the production of satisfactory metal boride coatings can range from about 0.05 to as much as 5 or more amps per square inch. Coatings of excellent quality were obtained when operating in the general range of 0.2 to 1.0 a.s.i. Voltage drop across the electrodes is highly dependent upon cell geometry but will generally range from about 0.1 to 1 volt.

Coating thickness may be conveniently and accurately controlled by varying plating time. There does not appear to be an upper limit of coating thickness which can be produced by the process. Consequently, the process is applicable to electroforming which is to be considered merely a specific type of electroplating. Electroforming comprises the plating of a relatively thick coating onto a substrate which is later removed by dissolution, melting or similar processes.

Articles plated by this process may be used in extreme abrasive, high temperature and corrosive environments such as exhaust ducts, turbine blades, rocket motors and the like. Other appropriate uses include nuclear reaction chambers, electronic emission guns and as refractory molds, dies and crucibles for glass, salts and metals.

The following examples serve to more particularly illustrate the invention.

EXAMPLE 1

A fused salt electrolyte mixture was prepared having the following composition by weight: Sodium metaborate—39.1%; lithium metaborate—58.6%; sodium titanate—1.0%; lithium titanate—0.76%; titanium dioxide—0.55%. This composition corresponds to a total titanium content, as the metal, of 1.0%.

The mixture was melted under an argon atmosphere to 850° C. after which a titanium anode and molybdenum cathode were inserted into the bath. The electrolyte bath was then conditioned for a period of two hours by impressing a D.C. current of 0.42 a.s.i. across the electrodes. During this time, the bath was continuously agitated by rotation of the cathode. The electrodes were then raised from the bath and the cell was brought to room temperature. A deposit of finely divided dark powder was loosely attached to the cathode. This powder was identified as TiB₂ by X-ray diffraction analysis.

EXAMPLE 2

The bath of Example 1 was heated to 900° C. under an argon atmosphere. A titanium anode and an Inconel cathode were then immersed in the bath. A D.C. current of 0.41 a.s.i. was then impressed across the electrodes for a period of 2 hours. Again, the bath was constantly agitated by rotating the cathode. Voltage across the electrode was 0.31 v.

The deposit was a bright, adherent plate about 1.5 mils in thickness. Partially covering the plate was a dark, loosely adherent powder such as that obtained in Example 1. Metallographic samples could be cut only with a diamond saw indicating an extremely hard coating. Microscopic examination showed the coating to have a crystalline structure.

EXAMPLE 3

A conditioned salt bath having an original composition similar to that of Example 1 was heated to 900° C. A coating was deposited on a rotating Inconel cathode, again using a titanium anode, by impressing a current of 0.4 a.s.i. across the electrodes for a period of 3 hours. The coating was smooth, bright, adherent and coherent and had a thickness of about 3 mils. Samples of the coating and substrate were cut by means of a diamond metallographic saw, then mounted and polished on a diamond abrasive wheel.

Microhardness values were taken on the polished surface and on the cross section areas using a Tukon micro-

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hardness tester and a Knoop diamond point indicator. The hardness values ranged from 3300 KHN₁₀₀ on the cross sections to 5000 KHN₁₀₀ on the surface areas. "Lazy probe" spectrographic and X-ray fluorescence analyses indicated the coating to be composed only of titanium and boron in a ratio corresponding to the compound TiB₂.

EXAMPLE 4

A coating was electrodeposited at 900° C. from a conditioned bath having an initial composition similar to that of Example 1. A current of 0.4 a.s.i. was impressed between a titanium anode and an Inconel cathode for a period of 7 hours. The resulting coating had a thickness of about 6 mils and was smooth, bright, adherent and coherent. Analysis X-ray diffraction and by "lazy probe" spectrographic techniques indicated the coating contained only the metals titanium and boron in the form of TiB₂.

EXAMPLE 5

Samples of the coatings and substrate material produced in the manner set out in the preceding examples were cut by means of a diamond saw, mounted in Lucite and polished with diamond polishing compound. Microhardness values taken on polished surface and cross section areas of the coatings were in the range of 3000 to 500 KHN₁₀₀. In order to provide a comparison, similar hardness tests were made on a tungsten carbide drill. The value obtained was 1850 KHN₁₀₀ which corresponds closely to the value of 1880 generally assigned to tungsten carbide in the literature. As a further comparison, diamond is generally assigned a value of 7000 on this same scale.

EXAMPLE 6

An extended series of plating runs were made in the manner set out in Examples 2-4. Plating was continued until more titanium had been removed from the bath than had been originally introduced in the form of titanium compounds. Titanium metal content of the bath was maintained by dissolution of the titanium anode.

What is claimed is:

1. A process for the deposition of an adherent, coherent coating of a metal boride, chosen from the group consisting of titanium, zirconium and hafnium diborides, on a conductive substrate which comprises:

(a) providing a conditioned molten salt bath, the bath ingredients chosen from the group consisting of alkali metal borates and mixtures thereof and having dissolved therein a compound of the metal of the desired boride, said metal compound having a concentration within the bath between 0.1 and 5% reported as the metal and being chosen from the group consisting of alkali and alkaline earth salts of metallic oxy acids, oxides and mixtures thereof;

(b) passing direct current between an anode consisting of the metal of the desired boride and an electrically conductive cathode, and

(c) depositing on the cathode a coating consisting essentially of a metal diboride in the form of a tightly adherent, coherent electroplate.

2. The process of claim 1 wherein the cathode is subjected to movement within the bath during deposition so as to agitate the bath.

3. The process of claim 2 wherein said borates are chosen from the group consisting of lithium and sodium metaborates and mixtures thereof.

4. The process of claim 3 wherein the deposition is performed at a temperature in the range of 850° to 950° C.

5. The process of claim 4 wherein the desired boride is titanium diboride and wherein the anode is titanium metal.

6. The process of claim 5 wherein the titanium compound dissolved within the bath is chosen from the group consisting of titanium oxides, alkali metal titanates and mixtures thereof.

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7. The process of claim 6 wherein the cathode current density is in the range of 0.2 to 1.0 a.s.i.

8. The process of claim 7 wherein the deposition is performed at a temperature in the range of 875° to 925° C.

9. A coherent, adherent crystalline, electroplated coating of titanium diboride on a conductive substrate.

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JOHN H. MACK, Primary Examiner

R. L. ANDREWS, Assistant Examiner