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3,827,954

## ELECTRODEPOSITION OF METALLIC BORIDE COATINGS

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No Drawing. Continuation-in-part of application Ser. No. 816,020, Apr. 14, 1969, now Patent No. 3,697,390.

This application Aug. 17, 1972, Ser. No. 281,353

The portion of the term of the patent subsequent to Oct. 10, 1989, has been disclaimed

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9 Claims

### ABSTRACT OF THE DISCLOSURE

Titanium diboride is electroplated on conductive substrates from a fused, borate-type bath. Use of a titanium diboride anode allows increased plating rates, enhances bath stability and decreases bath conditioning time compared to use of a titanium metal anode.

This application is a continuation-in-part of copending, commonly assigned application, Ser. No. 816,020, filed Apr. 14, 1969, now U.S. Pat. 3,697,390.

### 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), pages 60-66, Mellors et al. disclose the electrodeposition 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 found that titanium diboride may be deposited as a coherent, adherent electroplate of controllable thick-

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ness on conductive substrate materials. Smooth, consolidated coatings are obtained by electrodeposition from a fused, borate-type bath having dissolved therein at least one titanium compound. Use of a titanium diboride anode, rather than a titanium metal anode, allows increased plating rates, enhances bath stability and decreases bath conditioning time compared to use of a titanium metal anode.

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.

### 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 titanium compounds. Preferably these compounds comprise either titanium oxide or alkali and alkaline earth salts of titanium oxy acids such as sodium and lithium titanates. Initial concentration of titanium compounds in the electrolyte may be in the range of about 0.1 to 3%, reported as the metal, and preferably is in the range of 0.5 to 1.5%. As electrolysis and deposition proceeds, titanium content of the electrolyte is constantly replenished by dissolution of the anode.

Titanium diboride powder is commercially available and may be manufactured by techniques such as those disclosed by Sindeband. Our titanium diboride anodes may be fabricated from such powders by hot pressing techniques. Shape of the anode is not particularly important but conveniently is in the form of a cylinder, bar or plate. Cathodes used in our process must be electrically conductive and must have a higher melting point than the operating temperature of the bath. Metals such as nickel, molybdenum, stainless steel, steel and copper have been used successfully as cathodes. Other metals such as tungsten cannot be plated directly from the fused bath but can be given a precoat of another metal, such as nickel or copper, and thereafter plated with titanium diboride. While the cathode must be conductive, it is not necessary that the cathode substrate be conductive. Cathodes may also comprise non-conducting materials, such as ceramics, which have been precoated with a conducting material. Bath agitation is necessary during deposition to achieve a high quality plate. We have found it convenient to agitate the bath by rotation of the cathode during the plating process.

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° to 950° C.

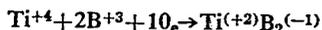
Cathode current density for the production of a satisfactory metal boride coating can range from about 0.05 to as much as 15 or more amps per square inch. We prefer, however, to operate our process at cathode current densities within the range of 0.25 to 2.5 a.s.i. Current densities within this range produce an electroplate of generally excellent quality at a plating rate of about 1 to about 10 mils per hour. 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.

Titanium diboride anodes have proven to have significant advantages over titanium metal anodes in our plating process. Such advantages are (1) a TiB<sub>2</sub> anode reduces the period of electrolyte "conditioning" required; (2) the electrolyte remains more stable over a longer period of time; and (3) plating rate may be increased without sacrifice of plate quality.

The step of electrolyte "conditioning" consists of electroplating from a fresh batch of electrolyte for a period of time sufficient to stabilize the bath and achieve high quality plates. A fresh batch of electrolyte will first produce on the cathode a loosely attached, generally fine, dark powder having the nominal composition of TiB<sub>2</sub>. After a period of time, the character of the cathode deposit changes to a bright, adherent plate consisting of crystalline titanium diboride. Conditioning time required is variable and may be influenced by the purity of the electrolyte components. Generally the time required to condition an electrolyte bath using a titanium diboride anode is about one third to one half that time required using a titanium metal anode. A bath may achieve a conditioned state in 4-5 hours using a titanium diboride anode but may take as long as 12-15 hours when a titanium metal anode is used.

Electrolyte stability is important in that it governs the amount of plating that may be done before an electrolyte change is required. Use of a titanium diboride anode increases the stability of an electrolyte bath and hence extends its useful life. In our process, we postulate an electrolytic reaction for the cathode as follows:



We believe that the reverse reaction occurs at the titanium diboride anode. We have observed that the amount of TiB<sub>2</sub> deposited on the cathode is usually a few percent less than the amount lost from the anode. Calculating current efficiencies based upon the above reaction formula, we obtain about 100 percent current efficiency at the cathode, and about 105 percent apparent current efficiency at the anode. It appears that some of the excess titanium and boron electrolytically dissolved at the anode goes into solution within the bath. However, we believe that much of the excess anode efficiency is due to mechanical loss of TiB<sub>2</sub> particles from the pressed powder anode. During the conditioning period, titanium content of the electrolyte remains essentially static. After a long period of use, we observe a small increase in titanium and boron content in the bath. For example, after 50 hours of electrolysis, a bath originally analyzing 1.0% titanium as the metal and 19.0% boron showed a titanium increase of about 0.2 to 0.3 percentage points and a boron increase of about

0.1 to 0.2 percentage points. Considerably larger changes in bath composition occur when a titanium metal anode is used thus indicating that use of a titanium diboride anode contributes substantially to the stability of the electrolyte.

From a practical point of view, plating rate is limited by the quality, smoothness and uniformity required in the plated article. We have found that use of titanium diboride anodes allows an increase in plating rate by a factor of about 3 for the same quality plate as compared to the use of titanium metal anodes.

Titanium diboride plates produced by our process are crystalline, adherent, coherent and extremely hard. Hardness values as measured using a Tukon microhardness tester and a Knoop diamond point indicator range from about 3000 KHN<sub>100</sub> to 5000 KHN<sub>100</sub>. In comparison, hardness tests performed on a tungsten carbide drill indicated a value of 1850 KHN<sub>100</sub> 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.

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 mixture was prepared using the following initial composition by weight: 625.26 gms. NaBO<sub>2</sub> (39.08%); 937.88 gms. LiBO<sub>2</sub> (58.62%); 15.7 gms.



(0.98%); 12.15 gms. Li<sub>2</sub>TiO<sub>3</sub> (0.76%) and 9.01 gms. TiO<sub>2</sub> (0.56%). The initial titanium metal content of the bath was one weight percent. The salt mixture was melted in an Inconel crucible under argon with an RF induction furnace. An anode of pressed titanium diboride powder and a molybdenum cathode were introduced into the electrolyte and the bath was conditioned at 900° C. at a cathode current density of 0.8 a.s.i. After 2 hours of electrolysis (conditioning), the cathode was removed and washed. The deposit consisted of a thin, dark coating covered with fine, dark, nonadherent powder (24% and 76% respectively). X-ray analysis of the powder indicated TiB<sub>2</sub> with minor amounts of TiO and amorphous material (probably very fine powder).

#### Example 2

Using the same electrolyte as in example 1, two additional hours of conditioning electrolysis were made. Following the conditioning period, an electrolysis was made at 900° C. using a pressed TiB<sub>2</sub> anode and molybdenum cathode at a current density of 0.65 a.s.i. The cathode was rotated. After 2 hours, the cathode was removed and washed. The cathode deposit was bright, smooth and had no loose material. The deposit was 4.5 mils thick and had a plating rate of 2.26 mils per hour. Based on the valence change of 10 electrons, the cathode current efficiency was 100 percent.

#### Example 3

Using the same electrolyte as in examples 1 and 2, and after 24 hours of electrolysis with a TiB<sub>2</sub> anode, a deposit was made on a molybdenum cathode at a current density of 0.53 a.s.i. The temperature of the bath was 900° C. and the cathode was rotated. After 2 hours of electrolysis, the cathode was removed and washed. The deposit was a smooth, bright, adherent coating with no loose material. The deposit was 3.5 mils in thickness and had a plating rate of 1.76 mils/hour. X-ray diffraction analysis of the deposit indicated an orientated TiB<sub>2</sub> coating.

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## Example 4

Using the same electrolyte with a titanium diboride anode, a deposit was made on a molybdenum cathode at a current density of 1.03 a.s.i. After 2 hours of electrolysis at 900° C., the cathode was removed. The deposit was smooth and bright. The edges of the deposit were slightly thicker and rougher than the center. The coating was 7.13 mils thick and the plating rate was 3.56 mils per hour.

## Example 5

After 46 hours of electrolysis with a titanium diboride anode, a sample of the same electrolyte was removed while the bath was molten. Analyses of the bath by X-ray diffraction showed good patterns of NaBO<sub>2</sub> and LiBO<sub>2</sub>, small amounts of Li<sub>2</sub>TiBO<sub>3</sub> and TiB<sub>2</sub> and a fair amount of amorphous material, probably glassy fused electrolyte. Chemical analyses of the electrolyte indicated an increase of 0.18 and 0.4 percent of titanium and boron, respectively. Good deposits were still being made at this time.

## Example 6

In this experiment, we made 1600 grams of electrolyte which consisted of 8.9 grams of TiO<sub>2</sub>; 12.2 grams of Li<sub>2</sub>TiO<sub>3</sub>; 15.79 grams of Na<sub>2</sub>TiO<sub>3</sub>; 937.9 grams LiBO<sub>2</sub> and 625.2 grams NaBO<sub>2</sub>. The content by analysis was 1.1 and 19.0 percent titanium and boron, respectively. The bath mixture was melted in an Inconel crucible at 900° C. under argon with a resistance furnace. It was conditioned with a titanium metal anode and a cathode of Inconel for a total period of 12 hours at a cathode current density of 0.4 a.s.i. The deposit obtained from the first conditioning period of 4 hours was a thin dark coating covered with dark, nonadherent powder comprising about 78 percent by weight of the total deposit. At the completion of 8 additional hours of conditioning electrolysis, the deposit was smooth but dark and consisted of about 19 percent loose powder. Analyses of the electrolyte showed 1.89 percent titanium, an increase of about 0.8 percent, and no noticeable change in boron.

## Example 7

Using the electrolyte of example 6, an electrodeposit was made with a pressed titanium diboride anode and a molybdenum cathode at 900° C. and at a current density of 0.4 a.s.i. After 2 hours of electrolysis, the cathode was removed and washed. The deposit was smooth and dark gray with very little loose material (3 percent). The coating was 2.45 mils thick and had a plating rate of 1.22 mils/hour.

## Example 8

Utilizing the same bath as in examples 6 and 7, and after a total of 23 hours of electrolysis, a deposit was made with a titanium diboride anode and a molybdenum cathode. The cathode was rotated and had a current density of 1.98 a.s.i. After electrolysis of 15 minutes, the cathode was removed from the electrolyte and washed. The deposit was smooth and bright with very little loose material. The coating was 1.8 mils thick and had a plating rate of 7.3 mils per hour.

## Example 9

After about 32 hours of electrolysis, the above bath was used with a titanium diboride anode and a molybdenum rod as cathode. Electrodeposition was conducted for one hour at a cathode current density of 1.2 a.s.i. The cathode was removed and washed. The deposit was dark, rough and adherent. The deposit was 4 mils thick. The plating rate was 4 mils per hour.

## Example 10

The coated rod from example 9 was replated using identical conditions and the same electrolyte. The one-hour deposit was brighter and smoother. The plating rate for the second layer was 4.2 mils per hour. Four additional one-hour deposits were made using the same rod and a

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titanium diboride anode. Between deposits, nodular material was removed. At the completion of the electrolyses, the coating was smooth and gray and had a thickness of 18.9 mils. The average cathode current efficiency, based on valence change of 10 electrons, was 99 percent.

## Example 11

In this experiment we used an electrolyte with the same initial composition as described in example 6 but which had been conditioned with a TiB<sub>2</sub> anode. After 24 hours of electrolysis with a TiB<sub>2</sub> anode, a 2-hour coating was made on a nickel sheet at a current density of 1 a.s.i. The deposit was fairly smooth and adherent, with some small nodules. The coating was 6.2 mils thick and had a plating rate of 3.1 mils per hour. Based on a valence change of 10 electrons, the cathode current efficiency was 97 percent and the anode current efficiency was 104 percent.

## Example 12

In this experiment we used 600 grams of electrolyte consisting of 39.08 percent NaBO<sub>2</sub>; 58.62 percent LiBO<sub>2</sub>; 0.99 percent Na<sub>2</sub>TiO<sub>3</sub>; 0.70 percent Li<sub>2</sub>TiO<sub>3</sub> and 0.55 percent TiO<sub>2</sub>. The electrolyte contained one percent titanium. The mixture was melted in a graphite crucible at 900° C. The bath was conditioned for 14 hours with a titanium anode and an Inconel cathode at a current density of 0.4 a.s.i. After 36 additional hours of electrolysis with a titanium anode or a titanium diboride anode, a 2-hour deposit was made on an Inconel substrate using a titanium diboride anode at a current density of 0.81 a.s.i. at 900° C. After electrolysis the cathode was removed and washed. The deposit was very smooth, bright and adherent. The deposit was 3.08 mils thick and had a plating rate of 1.54 mils per hour.

## Example 13

Using the same electrolyte after 17 additional hours of electrolysis, a deposit was made on an Inconel cathode at a current density of 2 a.s.i. using a TiB<sub>2</sub> anode. The one-hour deposit was removed and washed. The deposit was smooth and bright. Edges were heavy and nodular. The coating was 6.1 mils thick and the plating rate was 6.1 mils per hour.

## Example 14

A 20-minute deposit was made on Inconel at 2.0 a.s.i. in the same electrolyte using a TiB<sub>2</sub> anode. The coating was 1.35 mils thick. The plating rate was 4.0 mils per hour.

## We claim:

1. A process for the electrodeposition of an adherent, coherent coating of titanium diboride on a conductive substrate which comprises:

preparing an electrolyte bath by fusing a mixture of ingredients chosen from the group consisting of alkali metal borates and mixtures thereof and having dissolved therein a compound chosen from the group consisting of titanium oxides, alkali metal salts of titanium oxy acids and mixtures thereof, said compound being present within the bath in a concentration in the range of 0.1 to 3% reported as the metal; conditioning the fused and molten electrolyte bath by passing a direct current through the bath between an anode, fabricated of a material chosen from the group consisting of titanium metal and titanium diboride, and a cathode for a period of time sufficient to stabilize the bath, and

electroplating at a cathode current density in the range of 0.05 to 15 amps per square inch a titanium diboride coating on a cathode by passing a direct current between a titanium diboride anode and the cathode at temperatures above the melting point of the bath.

2. The process of claim 1 wherein the alkali metal borates are chosen from the group consisting of sodium and lithium metaborates and mixtures thereof.

3. The process of claim 2 wherein the conditioning and electroplating steps are performed at a temperature in the range of 850 to 950° C.

4. The process of claim 3 wherein the electrolyte bath comprises a mixture of sodium and lithium metaborates.

5. The process of claim 4 wherein the cathode current density is in the range of 0.25 to 2.5 amps per square inch.

6. The process of claim 5 wherein the electroplating step is performed at a temperature in the range of 875 to 925° C.

7. The process of claim 6 wherein the conditioning step is performed using a titanium diboride anode.

8. The process of claim 7 wherein the anode is fabricated from hot pressed titanium diboride powder.

9. The process of claim 8 wherein the cathode is rotated during electro-deposition.

References Cited

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