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[54] **PROCESS FOR ELECTRODEPOSITING TITANIUM DIBORIDE FROM FUSED SALTS**

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[58] **Field of Search** 204/39

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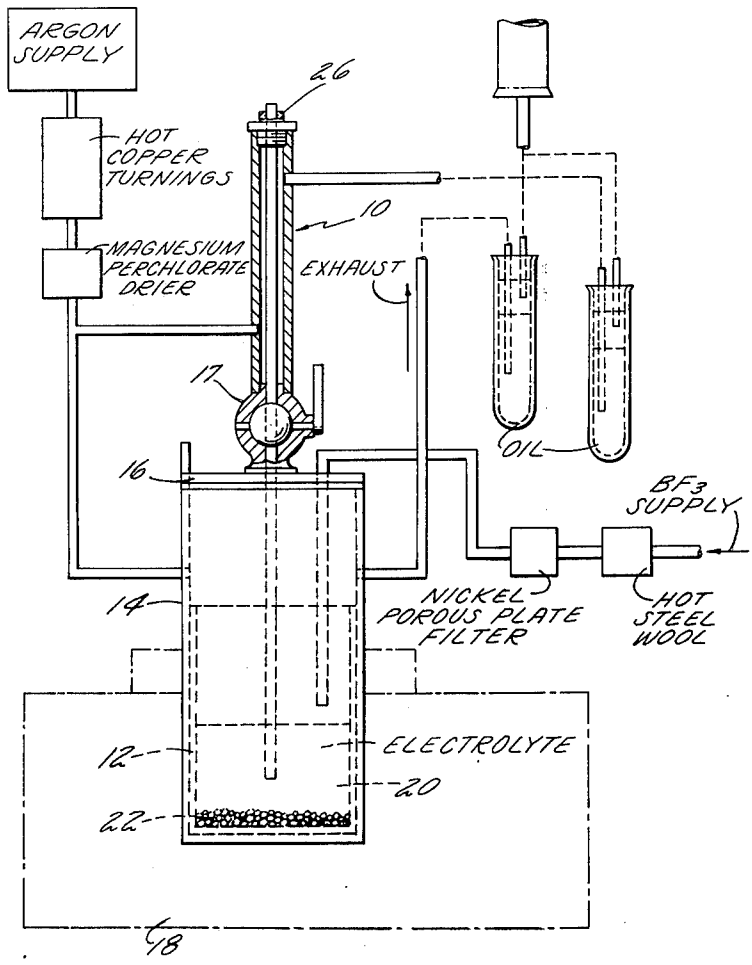
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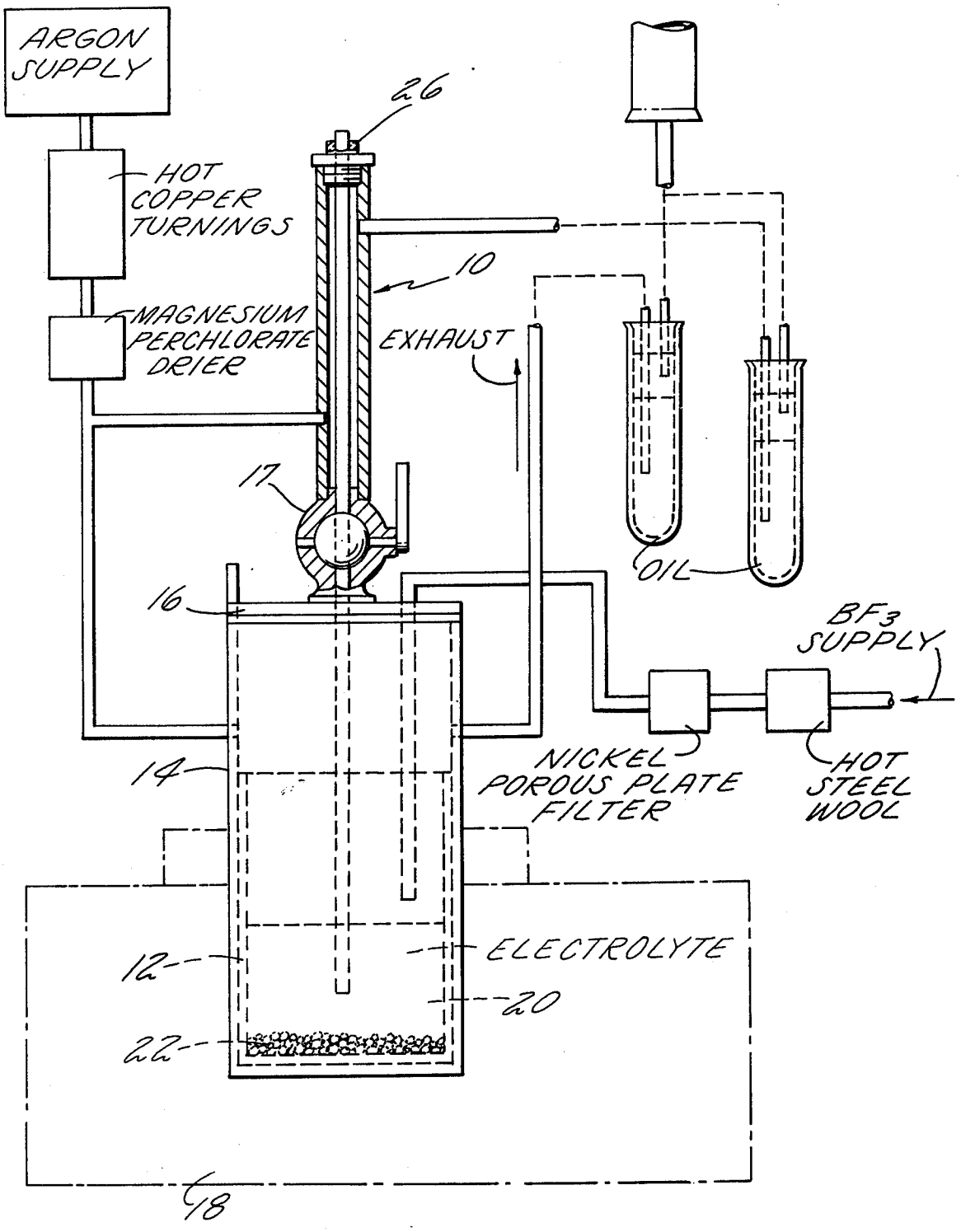
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[57] **ABSTRACT**

This invention relates to a process for producing substantially pure coherent titanium diboride on a cathode by electrodeposition from a fused salt bath consisting essentially of at least one alkali metal fluoride selected from the group consisting of the fluorides of lithium, sodium, potassium, rubidium and cesium. The process comprises heating the bath to a temperature of about 1,000°–1,500°F in a noncontaminating atmosphere, establishing in the bath a fluoborate ion concentration of approximately 1–20 percent, by weight, and a titanium ion concentration of approximately 0.5–4 percent, by weight, and establishing a current density at the cathode of approximately 9–500 ma/cm^2.

12 Claims, 1 Drawing Figure




ARGON SUPPLY
HOT COPPER TURNINGS
MAGNESIUM PERCHLORATE DRIER
26
10
EXHAUST
17
16
OIL
BF3 SUPPLY
NICKEL POROUS PLATE FILTER
HOT STEEL WOOL
14
ELECTROLYTE
12
20
22
18

PROCESS FOR ELECTRODEPOSITING TITANIUM DIBORIDE FROM FUSED SALTS

BACKGROUND OF THE INVENTION

This invention relates to electrochemical processes and more particularly relates to an electrolytic process for depositing substantially pure coherent coatings of titanium diboride from a fused haloborate bath.

Recent research efforts have centered on the development of electrolytic processes for depositing coatings of various refractory metals and compounds. See, for example, copending application Ser. No. 234,306 by Russell et al filed Mar. 13, 1972 of common assignee as the present case and U.S. Pat. No. 3,444,058 to Mellors et al. issued on May 13, 1969 and assigned to Union Carbide. One of the most promising coatings, in view of its extreme hardness, oxidation resistance and stability at high temperatures is titanium diboride. Although it is known to electrolytically deposit a continuous phase of titanium diboride on a nickel alloy substrate from a molten salt electrolyte such as $NaBO_2$ and $LiBO_2$ as disclosed by Schlain et al., "Electrodeposition of Titanium Diboride Coatings," *Journal of the Electrochemical Society*, Vol. 116, No. 9, pp. 1227–1228 (Sept. 1969), the process is of relatively high temperature (900°C or 1,652°F). Because of the economics involved as well as the fact that titanium, as a substrate, degrades at temperatures of 1,400°F and higher, it will be appreciated that a process which can deposit homogeneous, coherent, high strength, adherent and hard titanium diboride at relatively low temperatures, i.e., below 1,400°F, would be novel and advantageous.

SUMMARY OF THE INVENTION

In accordance with this invention, means have been formulated to provide a relatively low temperature electrolytic deposition process for providing a hard protective coating of substantially pure coherent titanium diboride of essentially unlimited thickness upon a variety of substrates. More particularly, the present invention contemplates the precise control of critical processing variables such as temperature, current density and electrolyte composition in a fused salt electrolyte comprised of an alkali or alkaline earth metal fluoride mixture containing predetermined amounts of titanium and fluoborate ions.

In the preferred embodiment, the inventive process contemplates a pretreatment of the electrolyte prior to electrolysis to reduce the concentration of contaminating agents to a level below that which will interfere with the deposition process. In brief, the present invention provides for the production of homogeneous, coherent, strong, adherent and hard titanium diboride coatings of substantial purity by the establishment of a titanium ion concentration of ½–4 percent, by weight, of the bath, a fluoborate ion concentration of 1–20 percent, by weight, of the bath, a current density of approximately 9–500 ma/cm² and a temperature of 1,000–1,500°F. By substantial purity is meant a purity of approximately **90** percent or better. The invention also includes a means for insuring that the titanium diboride produced is of a purity which exceeds 99 percent which means comprises purifying the fused salt bath, prior to electrolysis, until the residual oxianion contamination level therein is no greater than that amount which will produce a current maximum of 10 ma/cm² when an anodic potential of 1.5 volts is impressed on a carbon reference electrode therein. In a more preferred process, the temperature is 1,000°–1,400°F, the fluoborate concentration is 2–5 percent, the titanium ion concentration is 1–2 percent and the current density is 50–300 ma/cm².

BRIEF DESCRIPTION OF THE DRAWING

An understanding of the invention will become more apparent to those skilled in the art by reference to the following detailed description when viewed in light of the accompanying drawing wherein there is shown an electrolytic cell, taken in elevation and partially in cross section, which is suitable for use in the practice of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring to the drawing, the electrolytic cell is designated generally by the numeral **10** and includes a graphite or carbon crucible **12** placed inside a heat resistant, metal shell or pot **14** made of nickel, stainless steel or other suitable metal. The outer pot **14** is fitted with a covering lid **16** having an airlock **17** so that the melt can be kept under an inert atmosphere during electrolysis as well as during a change of cathodes. The cell is externally heatable by an electric resistance furnace **18** surrounding the lower portion of the cell. The crucible **12** is filled or partially filled with an electrolyte **20** in which are disposed an anode **22** and a cathode **24**, the cathode being electrically insulated from the pot and crucible by a teflon Swaglok bushing **26.**

The fused salt electrolyte **20,** sometimes referred to hereinafter as a fused salt bath, comprises preferably at least one alkali metal fluoride selected from the group consisting of lithium, sodium, potassium, rubidium and cesium, with or without at least one alkaline earth metal fluoride selected from the group consisting of magnesium, barium, calcium and strontium. It may also include other fluorides whose cations have a reduction potential more negative than that required for titanium diboride deposition, e.g., scandium, yttrium, etc. It will be appreciated that when a mixture of fluorides is chosen, the proportions of the various components are preferably matched so as to make a eutectic or "near eutectic" mixture thereof in order to keep the electrolyte melting point as low as possible. For the purposes of the present invention the term "near eutectic" is defined to mean a mixture which has a melting point higher than that of the eutectic mixture but at least 100°F lower than the electrolyzing temperature and in no case higher than 1,400°F. In any event, the present process requires the bath to be treated so as to contain a concentration of approximately ½–4 percent, by weight, preferably 1–2 percent, titanium ions and 1–20 percent, by weight, preferably 2–5 percent fluoborate ions, with the current density being 9–500 ma/cm², preferably 50–300 ma/cm². In general, the temperature of the fused salt bath is maintained within the range of approimately 1,000°– 1,500°F, preferably 1,000°–1,400°F, the exact temperature required being dependent upon the concentration of fluoborate and titanium ions in the electrolyte, the current density at which the boride is being plated, and the physical configuration of the cell. In this regard, it should be noted that fluoborate is quite volatile and although it is possible to electroplate at above 1,500°F, the fluoborate is lost from solution at a rate which is too fast to economi-

cally replenish. As a practical matter therefore, the upper limit of 1,500°C is set. The lower limit of 1,000°F is critical since it was found during experimentation that coatings could be achieved at that temperature but not at 990°F.

With respect to current density, it will be appreciated that below 9 ma/cm², electrodeposition is too slow to be practical. Above 500 ma/cm², an impure coating results due to salt entrainment and the inclusion of two much boron therein.

Overall, the most preferred conditions consist of a fluoborate ion concentration of 2–5 percent, by weight, a titanium ion concentration of 1–2 percent, by weight and at a temperature of 1,000°–1,100°F a current density of 9–35 ma/cm², at a temperature of 1,100°–1,250°F a current density of 25–100 ma/cm² and at a temperature of 1,250°–1,350°F a current density of 40–300 ma/cm². If the ion concentrations are increased, then the current density at the particular temperature would be increased to compensate.

In one embodiment of the process for plating pure titanium diboride coatings, a mixture of lithium fluoride and potassium fluoride is used as an electrolyte base. A mixture comprising 40–60 mol percent lithium fluoride, preferably 50 mol percent, and 60–40 mol percent potassium fluoride, preferably 50 mol percent, is suitable. In another embodiment of the process, a eutectic mixture of the fluorides of lithium, potassium and sodium is used.

In any event, it is to be noted that electrolyte contaminants such as heavy metal ions must be kept out of the electrolyte. By utilizing a cell configuration as shown in FIG. 1, the electrolyte contacts carbon structural materials only and this objective is achieved.

In order to reduce the starting concentration of dissolved gases, the base halide salts are preferably subjected, before the addition of boron or titanium in any form, to a vacuum at a teemperature just below their melting point for a period sufficient to achieve an equilibrium pressure of 10^{-4} mm Hg. After the foregoing pretreatment, a fluoborate forming compound such as BF_3 gas, itself purified of oxygen-containing gases, is added to the base halide salts in appropriate amounts to produce the desired concentration of fluoborate ions. A concentration of 1–20 percent, by weight, of fluoborate ion content in the electrolyte is considered satisfactory, although a content between 2–5 percent, by weight, is preferred.

It will be appreciated by those skilled in the art that the heat-vacuum conditioning treatment of the base halide salts must be carried out prior to the introduction of the BF_3 and consequent formation of fluoborate in the melt since, with fluoborate present, the decontamination of the electrolyte by vacuum treatment cannot be effectively accomplished due to the fact that the outgassing of BF_3 from the electrolyte restricts the level of pressure to which the system can be evacuated.

In an alternative pretreatment technique, the electrolyte can be purified subsequent to the formation of fluoborate. In this procedure, the base halide salts are melted and a fluoborate-forming compound such as BF_3 gas or KBF_4 powder is added. The electrolyte is then conditioned by the addition of a reducing element such as elemental boron. The boron reacts with dissolved gases and vapors such as water, oxygen and carbon dioxide and also with oxianionic contaminants, such as carbonate and hydroxide to reduce their concentration to below interfering levels. It is to be noted that heavy metals in solution are also reduced out of solution by the elemental boron.

In the practice of the invention, reagent grade anhydrous salts were weighed, mechanically mixed in a dry box and placed in the cell. The salts were dried under a stream of argon at just under their melting temperature for 2 days prior to a vacuum treatment wherein the fluorides were subjected to a temperature from 100°–420°C at a pressure from 10^{-2} to 10^{-6} mm Hg for up to **200** hours. Argon gas, which was either passed through a magnesium perchlorate dryer and a bed of hot copper turnings or simply passed through a bed of hot titanium turnings was then introduced over the salts and the temperature was raised to melt the salts. Tests showed that after the aforesaid hard vacuum-high temperature treatment, the residual dissolved moisture and gases, as determined by direct measurements of water, carbon dioxide and carbon monoxide in the argon purge gas, was extremely small. Carbon dioxide and carbon monoxide have proved to be particularly effective indicators of contamination level since water and oxygen, which are the most important contaminants, react with the carbon crucible to produce these gases. It has been determined that a satisfactorily purified melt exhibits less than 10 ppm/V each of carbon monoxide and carbon dioxide in the purge gas at a flow rate of 30 cm³/min.

The residual contamination level is also determined by voltammetry. The degree of residual oxianion contamination may be determined from the observed current when an anodic potential sweep (20 mV/min) is made on a carbon electrode dipping into the conditioned melt. A current maximum is consistently observed when the potential reaches about 1.5 volts more positive than a second carbon "quasi reference" electrode. The height of the current maximum may be related to the contamination level. Assignment of the current to oxianion discharge is possible from the observed elution of carbon dioxide and carbon monoxide from the working carbon electrode as measured in the argon purge gas. In a properly conditioned melt, a maximum current of about 0.5 ma/cm² is observed, again with less than 10 ppm/V each of carbon dioxide and carbon monoxide in the effluent purge gas at a flow rate of 30 cm³min. Although a current maximum of 0.5 ma/cm² or lower is preferred, depositions of over 99 percent purity may be made with current maximums up to approximately 10 ma/cm².

When it is ascertained that the melt is sufficiently purified, commercially available BF_3 gas is dissolved in the melt through a hollow carbon tube until the selected concentration of fluoborate ions is produced. The gas is processed before entering the cell by passing it over steel wool heated to 450°F to remove air, sulfur dioxide and other oxygen-containing gases which are generally present in the commercial supplies, and then passed through a particulate filter to take out the boric oxide "smoke" formed in that process. Almost all of the BF_3 added is absorbed in the melt, and therefore the fluoborate produced may be closely determined by the volume of gas introduced. However, confirmation of the precise fluoborate concentration is accomplished electrochemically by chronopotentiometry and by chemical analysis.

In an alternative technique, a less rigorous melt purification procedure may be used and the BF_3 make-up

gas and the argon sweep gas need not be purified as described above. The concentration of dissolved contaminants may instead be substantially controlled by treating the electrolyte containing the fluoborate with elemental boron. The boron additive reacts with interfering contaminants in the melt to reduce their concentration, although the exact action of the elemental boron is incompletely understood. When boron is first added, evolution of a gas, suspected to be hydrogen, is generally observed. This ceases after a short period of time. The boron addition is then characterized by a decrease in the concentration of fluoborate in the electrolyte with an increase in the concentration of boron present as soluble ionic species other than floborate. Boron chips subsequently retrieved from the electrolyte, at times, show that heavy metals such as iron also are being reduced on their surfaces. When the electrolyte becomes passive to the further addition of elemental boron, the treatment is considered complete. It is presently believed that the elemental boron combines with both the fluoborate and dissolved contaminants to produce less interfering ionic boron oxifluoride species. It is desirable to use fine boron chips in the treatment, of a size, for example, of 2–5 mm since the reaction with the electrolyte produces a coating on the boron surface which deactivates it, leading to long reaction time and material waste. The appropriate action of elemental boron is not accomplished under electrolysis if the boron is being used as an anode.

In the practice of titanium diboride plating, various anodes may be used. The working anode preferred is one of boron and titanium such as, for example, a boron and titanium filled carbon tube or most preferably, a loose anode **22** of boron and titanium on the bottom of the graphite crucible **12** with the crucible acting as part of the anode. In practice the boron and titanium are added and then allowed to settle to the bottom of the cell to serve as the anode. Periodic additions of titanium and boron are necessary to maintain the titanium ion concentration (probably TiF_6) as titanium diboride is removed from the cell. The size of the boron and titanium which is added is not critical.

While a boron and titanium anode is preferred, it is possible to practice the present process by utilizing an inert anode such as graphite or any metal having an oxidation potential greater than the potential existing between the anode and cathode so long as there is a source of titanium and fluoborate ions in the melt. Such procedure is useful, for example, in coating only the interior of a hollow article.

Various substrates may be employed as cathodes and include graphite, copper, steel, molybdenum, tungsten and niobium. Titanium may also be plated particularly if first coated with a layer such as nickel or iron in an aqueous plating bath in order to protect it from reaction from the molten fluoride bath. In general, any metal and alloy inert to the fused bath salts and suitable for use as a cathode may be plated with titanium diboride. The cathodes may be in the form of strips which are suspended from above the cell using copper rods after being cleaned in, for example, an acid such as dilute HCl or dilute HNO_3 and dried with acetone.

During the plating operation, a constant slow sweep of purified inert gas, such as argon, is maintained over the electrolyte at a pressure slightly above atmospheric. The argon sweep is advantageous in that in prevents the inflow of atmospheric air and also facilitates periodic analyses of the effluent gas mixture from the cell. Over a period of time, however, there is a cumulative loss of BF_3 gas from the system wherein the BF_3 gas must be replenished. In addition, as indicated hereinbefore, periodic additions of titanium and boron are also necessary to keep up the titanium ion concentration.

The following specific examples are illustrative of the present invention.

EXAMPLE 1

In the practice of the invention, apparatus similar to that shown in the drawing was utilized. A carbon crucible 4 inches in diameter and 13 inches in depth was used. Reagent grade anhydrous salts, KF (1,385 grams) and LiF (615 grams) were weighed in a dry box (a lucite airtight box continuously supplied with dried argon and equipped with a lock for introducing and removivng material, and rubber airtight gloves for working inside) and then placed in a vacuum oven at 180°C for 24 hours. The hot, partially dried salts were then transferred to a similarly baked out carbon crucible and installed quickly within the electrolyte cell, which was then evacuated to 10^{-4} mm Hg for 168 hours at 400°C. Argon gas was passed through the magnesium perchlorate dryer and a bed of hot copper turnings to remove oxygen and then introduced over the salts. The temperature was raised to 1,306°F to melt the salts. At that temperature, 100,000 cm^3 of BF_3 gas was passed through a graphite tube over steel wool heated to 450°F and a porous nickel filter at a flow rate of approximately 100 cm^3/min and dissolved in the melt until a fluoborate ion concentration of approximately 15 percent, by weight, was achieved. One hundred grams of 2–8 mesh boron of 99.7 percent purity from United Mineral and 100 grams of 99.6 percent pure 40 mil titanium wire were added and allowed to settle on the bottom of the cell to serve as the anode and to achieve a maximum titanium ion concentration of approximately 5 percent. A stainless steel sheet 5 × 2.8 × 0.1 cm served as the cathode. A current density of 99 ma/cm^2 was maintained for approximately 25 minutes and a smooth, hard, gray coating 0.8 mils thick was achieved.

EXAMPLE 2

The process of Example 1 was repeated except 0.002 inch molybdenum foil having a total surface area of 5.4 cm^2 was used as the substrate cathode. At a temperature of 1,321°F and current density of 89 ma/cm^2, a smooth, hard, gray coating 2 mils thick was deposited in 70 minutes.

EXAMPLE 3

The process of Example 1 was repeated at 1,320°F with a current density of 160 ma/cm^2. A smooth, hard, gray coating 15 mils thick was deposited in 276 minutes.

EXAMPLE 4

The process of Example 3 was repeated with a current density of 138 ma/cm^2 for 16 hours and 15 minutes. A bumpy, hard, gray coating 25 mils thick was achieved.

EXAMPLE 5

The process of Example 1 was repeated except that 150,000 cm^3 of BF_3 was dissolved in the electrolyte to achieve a fluoborate ion concentration of 8.5 percent.

Fifty grams of boron and 138 grams of titanium was used as the loose anode and to achieve a maximum titanium ion concentration of 6.8 percent. A 2.9 × 2.9 × .05 cm commercially pure nickel sheet was used as the substrate cathode. At a temperature of 1,280°F and current density of 101 ma/cm², a smooth, hard, gray coating 1.2 mils thick was deposited in 39 minutes.

EXAMPLE 6

The process of Example 5 was repeated except that a 2.4 × 2.4 × 0.1 cm Greek Ascaloy (AMS 5502) was used as the substrate cathode. At a temperature of 1,300°F and current density of 304 ma/cm² a rough, hard, gray coating 2 mils thick was deposited in **19** minutes.

EXAMPLE 7

The process of Example 5 was repeated except that a 5 × 2.5 × 0.15 cm nickel plated 0.001 inch thick titanium sheet was used as the substrate cathode. At a temperature of 1,250°F and current density of 120 ma/cm², a smooth, gray, hard titanium diboride coating 0.8 mils thick was deposited in 22 minutes.

EXAMPLE 8

In this example, the procedures of Example 1 were followed except that the bath consisted of 4,720 grams KF, **2,280** grams LiF and 1,016 grams NaF. One hundred thousand cm³ BF_3 was dissolved in the melt to achieve a fluoborate ion concentration of 4.2 percent. One hundred grams B and 100 grams Ti served as the loose anode and achieved a maximum titanium ion concentration of 1.25 percent. A steel compressor blade two inches long having a surface area of 9 cm² was used as the substrate cathode. At a temperature of 1,197°F and current density of 177 ma/cm², a 0.7 mil thick coating of titanium diboride was deposited in 17 minutes.

EXAMPLE 9

The process of Example 1 was repeated except that a 2.5 × 5 cm tantalum foil sheet 0.005 inch thick was used as the substrate cathode. At a temperature of 1,320°F and current density of 45 ma/cm², a 0.25 mil thick coating of gray, very smooth and hard titanium diboride was deposited in 17 minutes.

EXAMPLE 10

Using the conditions of Example 1, a 2.5 × 2.5 × 0.05 cm sheet of niobium was used as the substrate cathode. At a temperature of 1,250°F and current density of 90 ma/cm², a 1 mil thick coating of dark gray, very smooth and hard titanium diboride was deposited in 37 minutes. There was no embrittlement of the niobium.

EXAMPLE 11

The process of Example 8 was repeated except that a 1 inch O.D. steel tube 2 inches long was utilized as the substrate anode and a molybdenum rod, 0.25 inch O.D., was positioned therewithin and used as the anode. At a temperature of 1,250°F and a current density of 77.5 ma/cm², a 1 mil thick coating of titanium diboride was deposited on the inside of the steel tube. There was no coating on the outside thereof.

EXAMPLE 12

Using the conditions of Example 8, a 3 × 1.5 cm steel foil 0.005 inch thick was used as the cathode. At a temperature of 1,400°F and a current density of 190 ma/cm², a 2 mil thick coating of bumpy, gray and hard titanium diboride was deposited in 39 minutes.

EXAMPLE 13

The process of Example 8 was repeated except that a 1 × 2 × 0.05 inch steel sheet was used as the cathode. At a temperature of 1,250°F and a current density of 16 ma/cm², a 0.4 mil thick coating of very light gray, smooth, hard titanium diboride was deposited in 88 minutes.

EXAMPLE 14

In this example, the procedures of Example 8 were followed except that in addition to the 100 grams of B and 100 grams of titanium, there was also added 80 grams of powdered K_2TiF_6. The total titanium ion concentration was therefore 1.45 percent. A 0.005 inch thick steel foil having a total surface area of 44 cm² was used as the cathode. At a temperature of 1,000°F and current density of 9.1 ma/cm², a 0.5 mil thick coating of smooth, dark gray titanium diboride was deposited in 180 minutes.

EXAMPLE 15

Using the conditions of Example 8, a 1 × 2 × 0.05 inch titanium sheet plated with 0.5 mil thick coating of iron was used as the cathode. At a temperature of 1,200°F and current density of 30 ma/cm², a 0.1 mil thick coating of smooth, gray, hard titanium diboride was achieved in 17 minutes.

Under the varied combinations of operating parameters as indicated in the above examples, all of the coatings were homogeneous, coherent and adherent. Many samples were examined and when polished and etched, cross sections of the TiB_2 as, for example, on a steel substrate, showed a columnar structure of the crystal grains. Chemical analysis of the coatings has shown that they consist of, by weight, 69.7 ± .7 percent titanium which is consistent with a high degree of purity (99.5 percent). The x-ray pattern is typical of hot pressed TiB_2 when exposed to copper K radiation in a Debye camera. The hexagonal crystals are highly oriented (over 90 percent) with the C axis parallel to the plane of the substrate. Microhardness measurements in a Reichert tester at 84 grams load indicate a hardness of 4060 ± 200 VHN. The utility of such a relatively high hardness coating compound becomes clear when contrasted to the hardness of other compounds such as SiC (2,500 VHN), TiC (3,200 VHN), Al_2O_3 (3,000 VHN) and diamond (7,000 VHN).

Electroplated titanium diboride produced according to the inventive process has been evaluated for erosion resistance using a S.S. White Airbrasive unit that directs a stream of 30 μ Al_2O_3 particles at 1,000 ft/sec nozzle velocity at a small area of the sample. The results are listed below along with some other coatings for comparison.

TABLE I

EROSION RESISTANCE

Sample	Coating Thickness	20° Impingement Angle	90° Impingement Angle
TiB_2 on		5,600–6,060	955–1,130

TABLE I-Continued

EROSION RESISTANCE

Sample	Coating Thickness	20° Impingement Angle	90° Impingement Angle
steel	.2 mil	sec/mil	sec/mil
TiB_2 on titanium	.8 mill	6,960–10,720 sec/mil	1,430–2,440 sec/mil
TiC		1,190 sec/mil	
W		16.5 sec/mil	
NiB_2		40 sec/mil	
Steel		20 sec/mil	

The strength of the electroplated TiB_2 was measured by bending a cantilevered beam comprised of 1 mil TiB_2 on each side of a stainless steel foil 2 mils thick. The stress at which the stress strain curve became nonlinear was taken as the breaking stress of the coating, given by the formula

$$S = 6M_o/bh^2$$

where b is the width of the beam, h the thickness and M_o the moment. Utilizing the above procedures the value of S was 38,000 psi ± 2,000 for five different samples. A fatigue strength test on a 1 mil TiB_2 coating on steel compressor blades was also conducted and showed a 10–20 percent loss of strength at 10^7 cycles. This loss of strength is approximately equal to that experienced with a nickel-cadmium plating which is presently applied to the blades for corrosion resistance and represents the only hard facing for steel that has not reduced the fatigue strength below acceptable limits.

The density of electroplated TiB_2 was determined in a density gradient tube. The tube contained a water solution of thallium formate-thallium malonate (50–50 mol percent) with a density ranging from about 2 grams/cm^3 at the top to about 5 grams/cm^3 at the bottom. The entire tube was enclosed in a glass jacket through which water was circulated to maintain a constant temperature. Once established, the gradient persisted for several days. Floats of known density were dropped in the tube and were used as standards. Densities of TiB_2 samples ranged from 4.49 to 4.56 grams/cm^3 similar to the literature values for pure TiB_2 and no differences from varying plating parameters were noted.

Oxidation resistance of the coating was measured by determining the weight gain at various temperatures in air. It was found that below 950°C the oxidation rate was very small, less than 5 mg/cm^2/hr. Above that temperature, the protective boric oxide coating began to break down and the oxidation rate increased abruptly.

It will be appreciated that the inventive process disclosed herein offers an economical electroplating process for hardcoating surfaces and for corrosion protection of items such as probes and the like in molten metals. Plating speeds are high enough to deposit a protective layer 1 mil thick in 5 minutes and in addition, the process lends itself well to scaling up since onlly a larger salt bath and furnace are required.

What has been set forth above is intended primarily as exemplary to enable those skilled in the art in the practice of the invention and it should therefore be understood that, within the scope of the appended claims, the invention may be practiced in other ways than as specifically described.

What is claimed is:

1. A process for producing substantially pure coherent titanium diboride on a cathode by electrodeposition comprising: providing a fused salt bath consisting essentially of at least one alkali metal fluoride selected from the group consisting of the fluorides of lithium, sodium, potassium, rubidium and cesium;

heating said bath to a temperature of about 1,000° to 1,400°F in a noncontaminating atmosphere;

establishing in the bath a fluoborate ion concentration of approximately 1–20 percent, by weight, and a titanium ion concentration of approximately 0.5–4 percent, by weight; and

establishing a current density at the cathode of approximately 9–500 ma/cm^2, said current density being approximately 9–35 ma/cm^2 at a temperature of 1000°–1,100°F, 25–100 ma/cm^2 at a temperature of 1,100°–1,250°F and 40–500 ma/cm^2 at a temperature of 1,250°–1,400°F.

2. The process of claim **1** wherein said fluoborate concentration is 2–5 percent, said titanium ion concentration is 1–2 percent and said current density is 50–300 ma/cm^2.

3. The process of claim **2** wherein said fused salt bath comprises a mixture of 40 to 60 mol percent potassium fluoride and 60 to 40 mol percent lithium fluoride.

4. The process of claim **3** wherein said fluoborate ion concentration is established by dissolving boron trifluoride gas into the fluoride mixture.

5. The process of claim **2** wherein said fused salt bath comprises a eutectic mixture or near eutectic mixture of the fluorides of potassium, lithium and sodium.

6. The process of claim **5** wherein said fluoborate concentration is established by dissolving boron trifluoride gas into the fluoride mixture.

7. The process of claim **1** wherein said fused salt bath additionally contains at least one fluoride selected from the group consisting of the fluorides of magnesium, barium, calcium, strontium and other metals having a reduction potential more negative than that required for titanium diboride deposition.

8. The invention of claim **7** wherein said current density is established by imposing a potential between said cathode and an anode consisting essentially of titanium and boron.

9. The process of claim **7** including the step of, prior to establishing said current density, purifying the fused salt bath until the residual oxianion contamination level therein is no greater than that amount which will produce a current maximum of 10 ma/cm^2 at an anodic potential of 1.5 volts impressed on a carbon electrode therein.

10. The process of claim **1** including the step of, prior to establishing said current density, purifying the fused salt bath until the residual oxianion contamination level therein is no greater than that amount which will produce a current maximum of 10 ma/cm^2 at an anodic potential of 1.5 volts impressed on a carbon electrode therein.

11. A process for producing substantially pure coherent titanium diboride on a cathode by electrodeposition comprising:

providing a fused salt bath consisting essentially of a eutectic or near eutectic mixture of the fluorides of potassium, lithium and sodium;

heating the bath to a temperature of about 1,000° to 1,400°F in a noncontaminating atmosphere;

establishing in the bath a fluoborate ion concentration of approximately 2 to 5 percent, by weight and a titanium ion concentration of approximately 1–2 percent, by weight;

purifying the bath by nonanodically introducing therein fine chips of elemental boron to react with contaminants therein; and

establishing a current density at the cathode of 9–500 milliamperes per square centimeter, said current density being approximately 9–35 ma/cm² at a temperature of 1,000°–1,100°F, 25–100 ma/cm² at a temperature of 1,100°–1,250°F and 40–500 ma/cm² at a temperature of 1,250°–1,400°F.

12. The process of claim **11** wherein the bath is purified prior to the establishment of the fluoborate concentration by subjecting the fluorides to a heat and vacuum treatment.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,880,729

DATED : April 29, 1975

INVENTOR(S) : JORDAN D. KELLNER

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 59: "approimately" should read --approximately--

Column 3, line 38: "teemperature" should read --temperature--

Column 5, line 40: "(probably TiF_6)" should read

--(probably $TiF_6^{\equiv}$)--

Column 6, lines 17 & 18: "removivng" should read --removing--

Column 9, line 63: "onlly" should read --only--

Signed and Sealed this

twenty-ninth Day of *July 1975*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks