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[54] **MANUFACTURE AND USE OF ZrB₂/Cu OR TIB₂/Cu COMPOSITE ELECTRODES**

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[73] Assignee: **Texas A & M University System**, College Station, Tex.

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[*] Notice: This patent is subject to a terminal disclaimer.

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[21] Appl. No.: **09/008,753**

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[22] Filed: **Jan. 19, 1998**

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Related U.S. Application Data

Y.M. Cheng and A.M. Gadalla, "Synthesis and Analysis of ZrB₂-Based Composites." *Materials and Manufacturing Processes*, 1996.

[63] Continuation-in-part of application No. 08/886,826, Jun. 18, 1997, which is a continuation-in-part of application No. 08/691,410, Aug. 2, 1996, Pat. No. 5,870,663.

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[51] **Int. Cl.**⁶ **B22F 3/26**

[52] **U.S. Cl.** **419/12**; 419/47; 419/36;
419/56; 75/244

Primary Examiner—Daniel J. Jenkins

[58] **Field of Search** 419/12, 47, 36,
419/56; 264/63, 65, 66, 61, 428, 434; 75/244

Attorney, Agent, or Firm—Baker & Botts, L.L.P.

[57] ABSTRACT

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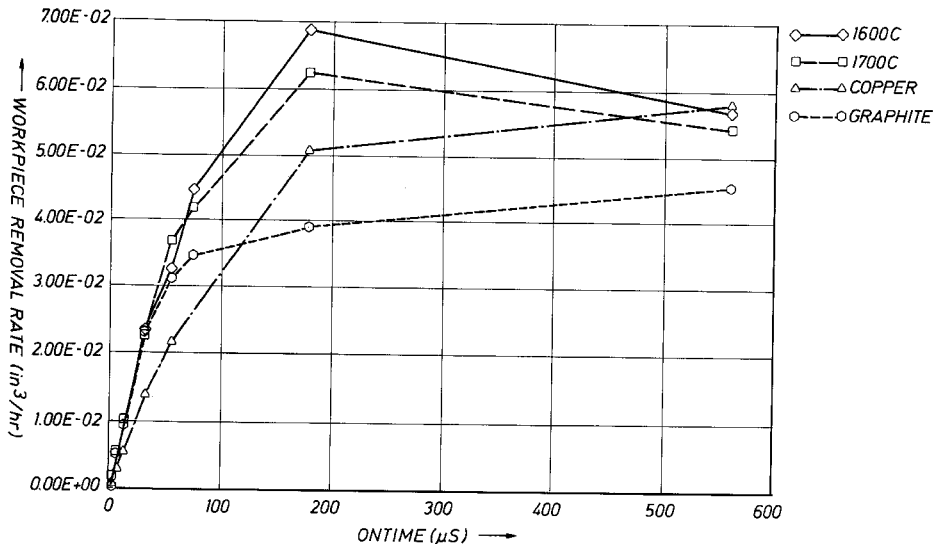
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The invention relates to ZrB₂/Cu composites, and more specifically to methods of making ZrB₂/Cu composite electrodes and methods of using ZrB₂/Cu composite electrodes. ZrB₂ powder is contacted with a polymer and shaped to a desired form. The polymer is vaporized and the ZrB₂ powder is sintered. The sintered ZrB₂ is contacted with Cu and heated above the melting point of Cu which causes the Cu to infiltrate the ZrB₂, forming the ZrB₂/Cu composite electrode.

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73 Claims, 3 Drawing Sheets



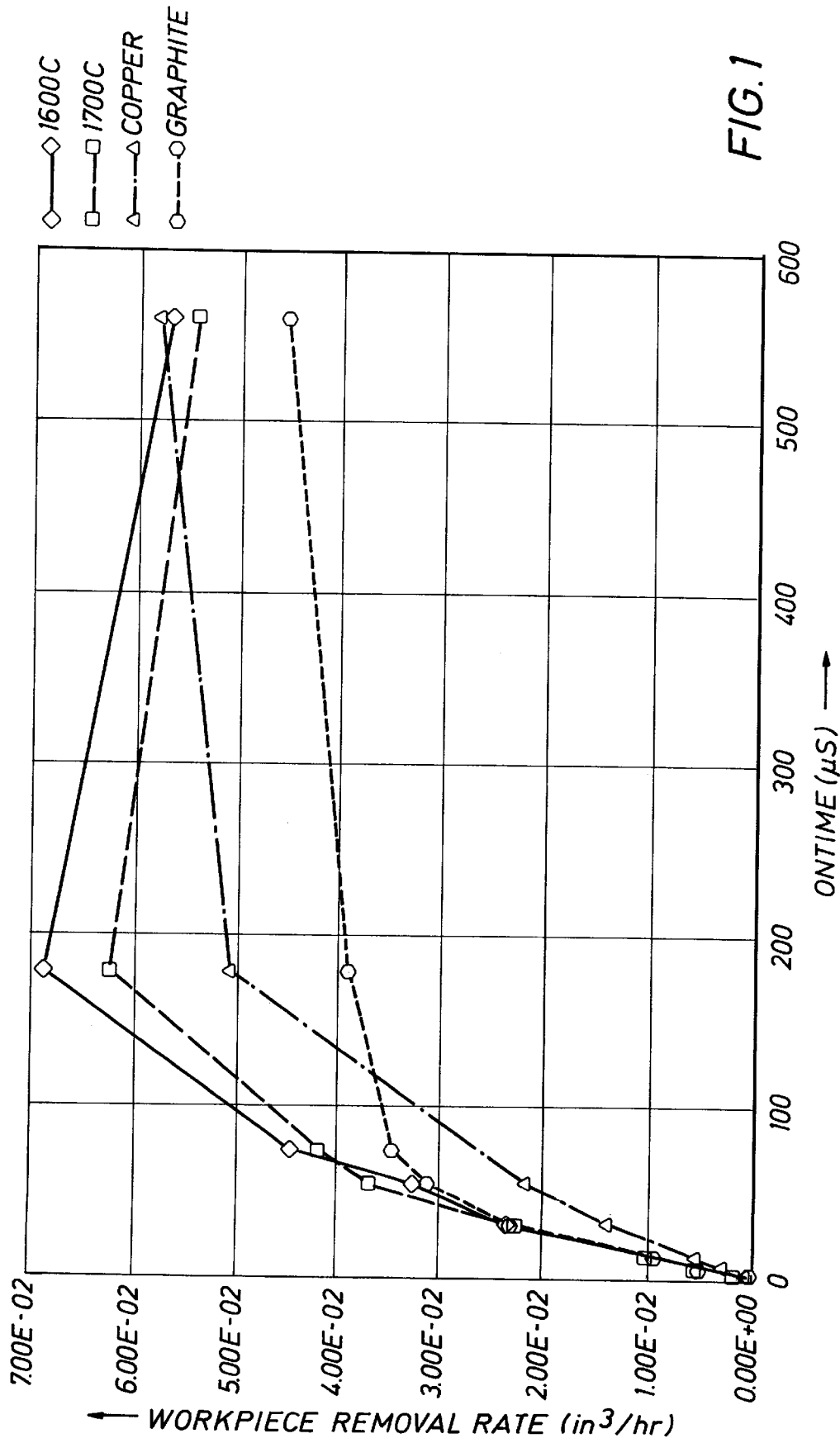


FIG. 1

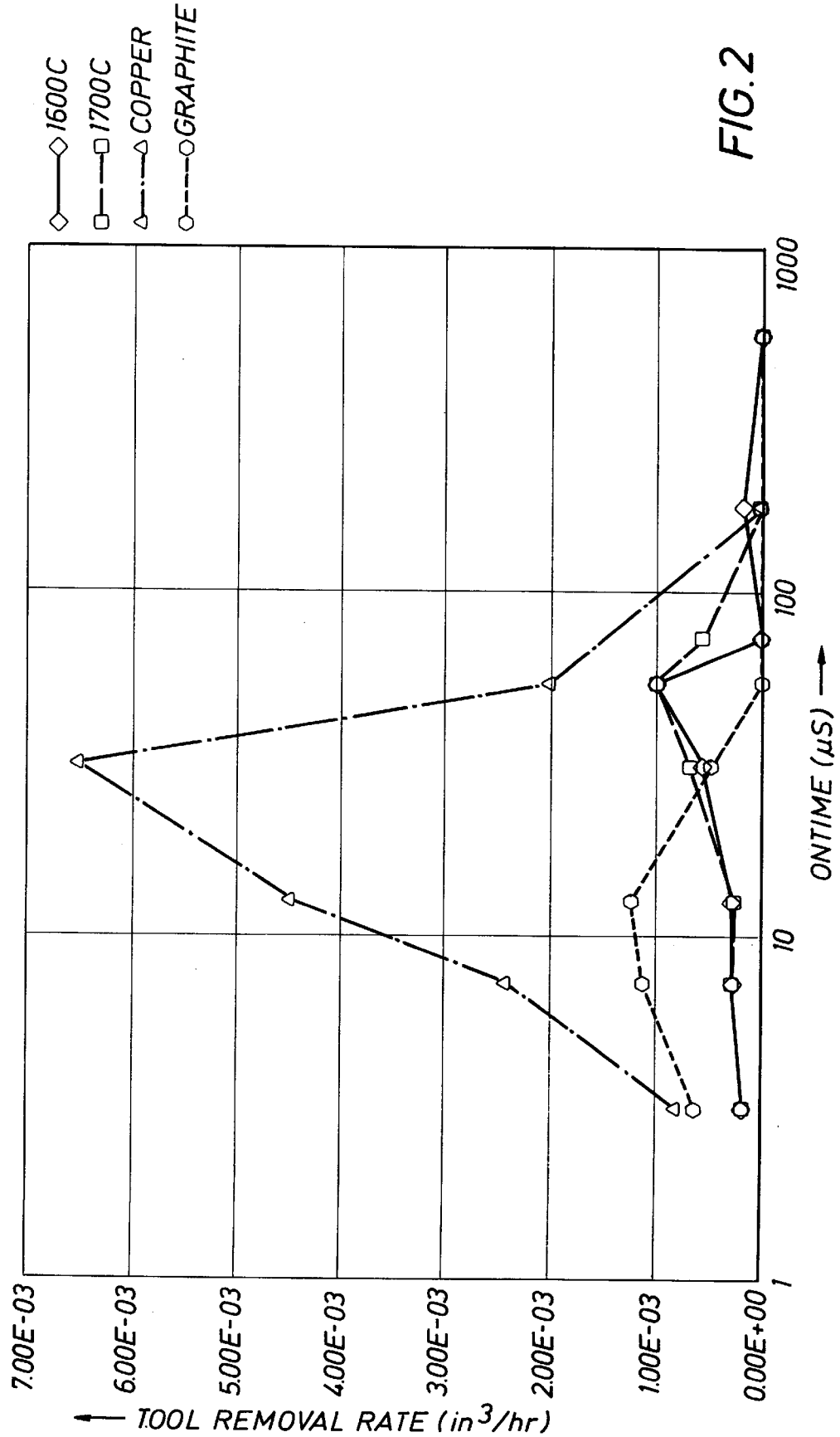


FIG. 2

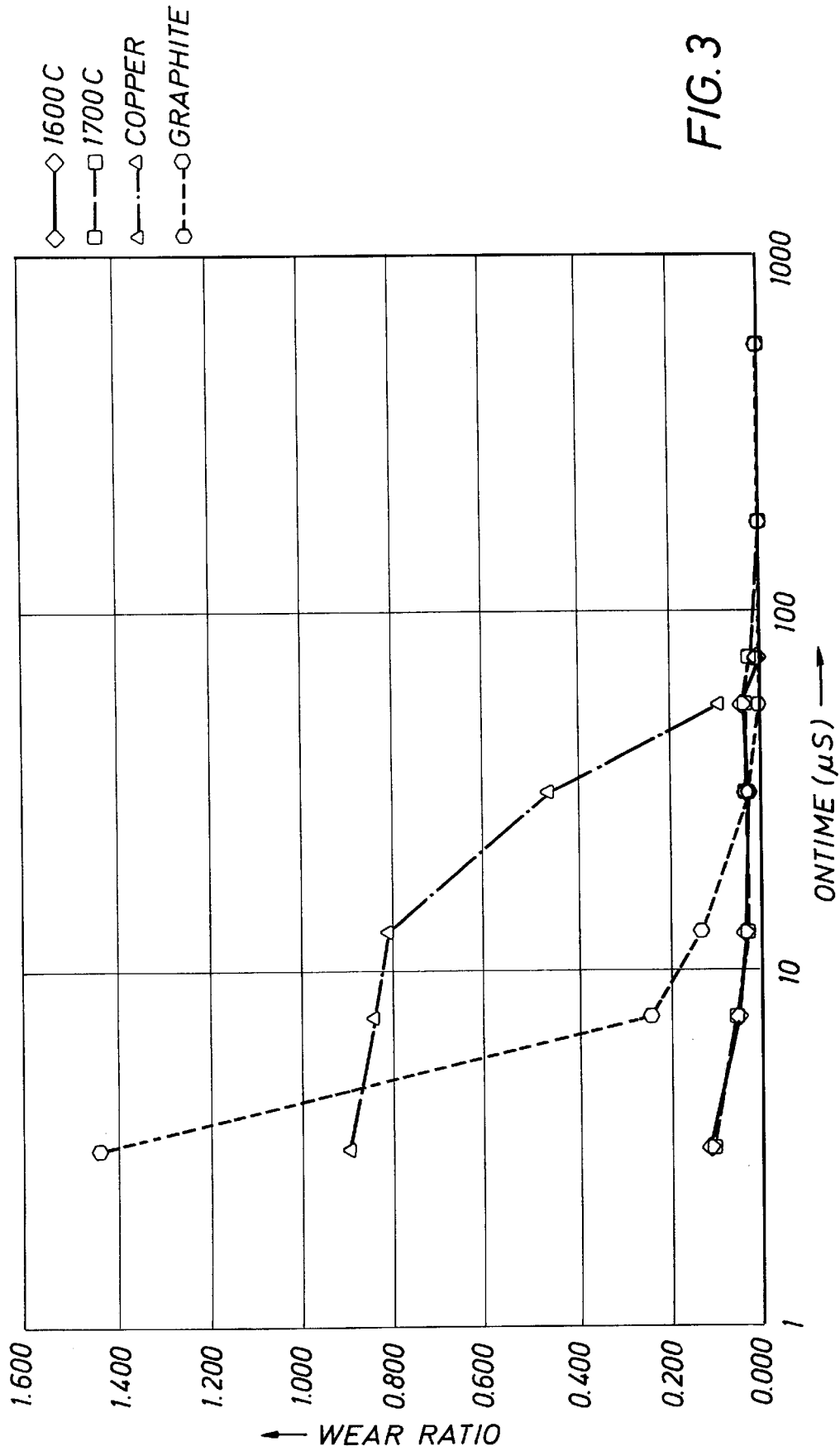


FIG. 3

MANUFACTURE AND USE OF ZrB₂/Cu OR TiB₂/Cu COMPOSITE ELECTRODES

This application is a continuation-in-part of application Ser. No. 08/886,826, filed on Jun. 18, 1997 pending, which is a continuation-in-part of application Ser. No. 08/691,410 filed Aug. 2, 1996, now U.S. Pat. No. 5,870,663.

This research was performed under a government grant, National Science Foundation Grant No. DMR-94203896, and under a National Science Foundation Graduate Research Fellowship, and the government may have some rights in this patent.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to the manufacture and use of zirconium diboride/copper (ZrB₂/Cu) composite electrodes. More specifically, the invention relates to a method of manufacturing ZrB₂/Cu composites which includes coating ZrB₂ powder with a polymer, utilizing rapid prototyping or cold pressing to shape or process the polymer coated powder to a desired form, sintering the shaped form to vaporize the polymer and sinter the ZrB₂ powder, and then infiltrating the sintered ZrB₂ with copper. The manufacturing technique provides ZrB₂/Cu composite electrodes with minimum electrode wear rates to be used in electrode applications where minimum wear is advantageous, including electrical discharge machining electrodes.

2. Description of the Related Art

ZrB₂ is a known intermetallic ceramic or cermet. However, due to its low thermal shock resistance and room temperature brittleness, ZrB₂ is rarely used for industrial purposes.

ZrB₂/Cu composites are known but rarely, if ever, used in industry because of the difficulty involved in fabricating the composite. Generally, its use has been limited to research purposes. The ZrB₂/Cu composite was investigated for possible use as a high-strength refractory coating for space ships subject to laser bombardment as well as for protection upon re-entry into the earth's atmosphere.

The only known way to make parts out of ZrB₂/Cu, particularly of complex and varying topographies, would be to hot press a mixture of ZrB₂ and Cu in a die that is the negative of the desired shape or to hot press a mixture and then machine it to the desired shape. Both of these processes involve significant shortcomings, including that they are very time and energy intensive and that the machining of a ZrB₂/Cu composite is known to be very difficult. Also, it is known that these techniques produce nonhomogeneous ZrB₂/Cu parts, leading to reduced performance of the parts.

SUMMARY OF THE INVENTION

There exists a need for ZrB₂/Cu composite electrodes which have minimum electrode wear rates and which are manufactured in a time and cost efficient manner and provide the dimensional accuracy and surface quality to make electrodes suitable for use as EDM electrodes.

The invention relates to a method of manufacturing ZrB₂/Cu composites comprising coating a ZrB₂ powder with a polymer and utilizing rapid prototyping or cold pressing to shape or process the polymer coated ZrB₂ powder into a desired form. The polymer coated ZrB₂ powder shaped form is sintered to vaporize the polymer and sinter the ZrB₂. The sintered ZrB₂ is then infiltrated with copper.

It is an object of this invention to manufacture ZrB₂/Cu composite electrodes, which have minimum electrode wear rates, in a time and cost effective manner, and in a manner which provides sufficient dimensional accuracy and surface quality so that the ZrB₂/Cu electrode can advantageously be used as an EDM electrode.

BRIEF DESCRIPTION OF THE DRAWINGS

A more complete understanding of the present invention and the advantages associated therewith may be acquired by referring to the accompanying drawings wherein:

FIG. 1 is a graph showing workpiece removal rates for copper, graphite, and ZrB₂/Cu composite electrodes at different on-times.

FIG. 2 is a graph showing tool removal rates for copper, graphite, and ZrB₂/Cu composite electrodes at different on-times.

FIG. 3 is a graph showing wear ratios for copper, graphite, and ZrB₂/Cu composite electrodes at different on-times.

DETAILED DESCRIPTION OF THE EXEMPLARY EMBODIMENTS

I. Forming ZrB₂/Cu Composite Electrodes

The electrode production path is generally a four step process. First, raw ZrB₂ powders are coated with a polymer which is optimized for use in an selective laser sintering (SLS) machine or other shaping step. Second, these polymer coated powders are preferably processed using SLS to "tack" together the ZrB₂ powders by sintering their respective polymer coatings, creating (shaping) a ZrB₂ part in the desired form—the underlying ZrB₂ is not thermally affected during this step. Third, a high-temperature furnace is used to both vaporize the polymer coating and sinter the ZrB₂ powder. Finally, the 30–70% dense network of zirconium diboride is infiltrated with an appropriate copper alloy.

A. ZrB₂ Powder Coated With Polymer

First, the appropriate size ZrB₂ powder must be obtained. Generally, ZrB₂ powder having a particle size of about 1 μm to about 10 μm, with an average of about 3 μm, is available and is suitable for cold pressing to shape the polymer coated ZrB₂ powder to desired forms as discussed below. However, for the selective laser sintering method as discussed below, generally a particle size of about 10 μm to about 100 μm is preferred. Suitable ZrB₂ powders may be obtained from Advanced Refractory Technology (ART) (Buffalo, New York). Suitable polymer coated ZrB₂ powder, particularly for selectively laser sintering as discussed below, may be obtained from DTM Corp. (Austin, Tex.). Suitable polymer coated ZrB₂ powder for processing by methods other than selective laser sintering may be obtained from ART.

The coating of ZrB₂ powder with low T_g polymer should be done in a way such that each particle is individually coated, e.g., fluidized bed, spray drying, etc., as is known to those of skill in the art. In coating the powder, consideration should be given to the production of the thinnest polymer coating possible consistent with coverage and good "tacking" together of the powder particles. The coating thickness also has an effect on shrinkage during laser sintering of the polymer coating to "tack" together the ZrB₂ particles and during sintering of the desired form which vaporizes the polymer coating and sinters the ZrB₂. A suitable low T_g polymer, particularly for selective laser sintering, is the acrylic based binder available from DTM Corp. Suitable polymers for the other rapid prototyping techniques may be obtained from vendors of the rapid prototyping technique of interest.

For the "cold pressing" process of shaping the ZrB_2 , as discussed below, the uniformity and thickness of the polymer coating is less critical as compared with the SLS process. Consequently, when cold pressing is used, less advanced techniques for coating the ZrB_2 powder may be employed. For cold pressing, suitable polymers include known pressing polymers, e.g., CERAMER 1608 (see Example 1).

B. Shaping ZrB_2 /Polymer to Desired Form

Particularly where mass production of simple shaped electrodes is desired, "cold pressing" of ZrB_2 powder with a polymer binder is the preferred method of shaping ZrB_2 /polymer to a desired form.

EXAMPLE 1

ZrB_2 powder was sent to ART Co. to be coated with a thin layer of polymer binder. The polymer binder, CERAMER 1608, was obtained from Petrolyte Corp. (St. Louis, Mo.). At ART Co., CERAMER 1608 was mixed with acetone to achieve a 25% by weight of the CERAMER 1608 binder in acetone. Three percent by weight of the CERAMER 1608 binder from the solution was then added to the ZrB_2 powder. This mixture was mixed using a stir bar while adding a small amount of acetone. After the acetone evaporated from the ZrB_2 mixture, the material was placed in a tumbler to break up the dried powder. The dried powder was then sieved through a 60 micron sieve to break the agglomerates.

The ZrB_2 coated with the polymer binder particles was then cold pressed at 10,000 psi in a square 1"x1" die to form a square electrode with a finished height of approximately 1.4". Lecithin mold release was used on the die to facilitate the removal of the rectangular electrode.

The rectangular electrode was then placed in the Thermal Technology Inc.'s (Santa Rosa, Calif.) GROUP 1000 graphite furnace. The furnace was then raised to about 600° C. for ½ hour to vaporize the polymer binder, and then subsequently heated to 1600° C. for one electrode and 1700° C. for another electrode for two hours to sinter the ZrB_2 . Argon was used as an inert operating gas. This process resulted in an approximately 50% dense part. Next, a copper alloy powder (copper and about 3 wt. % boron) was added to the crucible and fired at 1200° C. for 2½ hours to infiltrate the copper via capillary action. This resulted in an approximately 100% dense part. Each composite was then cut and milled into four ⅜"x⅜" electrodes.

An AGIETRON 1U (Losone, Switzerland) die-sinking machine was used to compare the performance of the ZrB_2 /Cu composite electrodes relative to copper and graphite electrodes at different on-times.

The materials were tested under a constant current of 24.8 A, off-time of 100, μ s and varying on-times ranging from 560–3.2 μ s. The dielectric fluid used was British Petroleum cutting oil, Dielectric 200 EDM Fluid (petroleum based hydrocarbon, available from an EDM supplier), and flushing was achieved from the vertical movement of the electrode. The material removal rate was calculated as the volumetric removal rate divided by the total time.

The workpiece removal rates are shown in FIG. 1 for the copper, graphite, and ZrB_2 /Cu electrodes at different on-times. FIG. 1 shows the superior workpiece removal rates of the ZrB_2 /Cu composite electrodes as compared to copper and graphite. At 180 μ s, the workpiece removal rates of the ZrB_2 /Cu electrode is 1.7 times better than graphite and 1.3 times better than copper. The data shows that ZrB_2 /Cu has a peak workpiece removal rate of about 5.71E-2 in³/hr.

The tool removal rates for copper, graphite, and ZrB_2 /Cu electrodes are shown in FIG. 2 for varying on-times. This

figure also shows the superior performance of the ZrB_2 /Cu composites. At an on-time of 3.2 μ s, the ZrB_2 /Cu is 4.7 times better than copper and 3.7 times better than graphite. At an on-time of 7.5 μ s, ZrB_2 /Cu is 10 times better than copper and 4.7 times better than graphite. At an on-time of 13 μ s, the ZrB_2 /Cu is 20 times better than copper and 6 times better than graphite. Thus, at low on-times where surface finishing is performed, ZrB_2 /Cu is a superior electrode to copper and graphite.

The wear ratios of copper, graphite, and ZrB_2 /Cu for different on-times is shown in FIG. 3. Again, this demonstrates the superior performance of the ZrB_2 /Cu composite electrode. According to the wear ratio at an on-time of 3.2 μ s, ZrB_2 /Cu is 7.8 times better than copper and 12.6 times better than graphite. At an on-time of 13 μ s, ZrB_2 /Cu is 37 times better than copper and 6 times better than graphite.

Modified versions of "rapid prototyping" are preferred where the electrode to be manufactured is of complex or varying topography or where limited numbers of electrodes are to be manufactured. "Rapid prototyping" is a known technology to facilitate rapid product development. Currently, commercial rapid prototyping techniques are generally capable of making only solids of polymer or paper. These polymer or paper solids are then used to evaluate the product or form molds for later casting. The modified versions of rapid prototyping as disclosed herein are suitable for processing or shaping ZrB_2 into a desired form. This is particularly advantageous for complex or varying topographies, since ZrB_2 is known to be difficult to machine into desired forms.

In rapid prototyping, a 3-D model produced on a computer-aided design (CAD) system is mathematically divided into a large number of thin layers, a few thousandths of an inch thick. The different processes for rapid prototyping generally work on the same basis principle, i.e., the desired part is built up in small layers, about 0.005" thick, one layer at a time, starting from the bottom and working up until the entire part is finished. Thus, the layers are built, and simultaneously consolidated to the preceding layer, using the description of that layer from the computer.

1. Selective Laser Sintering

The preferred rapid prototyping technique is "selective laser sintering" ("SLS"). SLS uses a CO₂ laser to sinter polymer coated powders by scanning in the horizontal plane only as dictated by a current layer description in a CAD model. The three dimensional solid is built up by the addition of material layers.

The SLS machine consists of hardware and software components. The hardware components include the process chamber and powder engine, the controls cabinet, and the atmospheric control unit. The process chamber incorporates the laser, pre-heater, and the powder handling equipment. The controls cabinet interprets the CAD drawing and controls and monitors the SLS process. The atmospheric control unit regulates the temperature and amount of N₂ flowing through the air in the chamber. It also filters the air that flows through the process chamber. The software components utilize the UNIX operating system and other DTM Corp. proprietary applications.

The CAD drawing is geometrically modified to horizontally divide the desired form into thin horizontal layers. These layers can be adjusted in thickness, but are typically about 0.005 in. The thin layers represent sintering planes to be traced by the CO₂ laser. In operation, a layer of polymer coated ZrB_2 is spread out. When the desired cross section of

the layer is traced out by the CO₂ laser, the temperature of the polymer coated particles is increased, and the polymer coatings fuse together. The part is then lowered in the SLS machine by about 0.005 in., and new layers are added in a similar fashion to form the solid mass. The SLS machine builds the part one layer at a time by creating the bottom layer first, and then adding layers until the part is finished.

The polymer coated ZrB₂ powder was laser sintered using the DTM SINTERSTATION 2000 machine which sinters only the polymer coating and not the underlying ZrB₂ powder. As described below, post processing is necessary to vaporize, sublime, or "burn off" the polymer coating and sinter the ZrB₂ powder. After this, the sintered ZrB₂ powder is infiltrated with copper. This post-SLS processing generally results in a small shrinkage due to the vaporization of the polymer coating and sintering of the ZrB₂ powder. By holding the processing variables constant, this shrinkage may be compensated for in the CAD design of the electrode, i.e., the CAD design provides for a slightly larger ZrB₂/polymer shaped form, such that upon shrinkage, the ZrB₂/Cu composite electrode will be the desired size.

Generally, for SLS shaping of the ZrB₂/polymer to the desired form, the polymer coated powder preferably has a particle size greater than 10 μm because the powder in the SLS machine is moved by a counter-rotating roller, and this method of powder transfer does not work well for finer powders.

The CO₂ laser used in the SLS machine is generally only capable of producing enough heat to fuse low-melting polymers such as nylon or polycarbonate; as such, it is these and similar low-melting point polymers which are used to coat the ZrB₂ powder when the SLS process is employed. Additionally, the polymer or copolymer used must suitably vaporize or sublime in the vaporization step prior to sintering the ZrB₂ powder. A suitable polymer coated ZrB₂ powder is available from DTM Corp. (Austin, Tex.).

2. Laminated Object Manufacturing

Laminated Object Manufacturing ("LOM") is a rapid prototyping technique wherein tapes of polymer coated ZrB₂ powder are cut and stacked to shape ZrB₂ into a desired form. Such an LOM technique is offered by Helisys Co. (Torrance, Calif.) and by ART (Buffalo, N.Y.).

3. 3-D Printing

There are two general methods which utilize 3-D printing to shape ZrB₂ into a desired form. In a first method of 3-D printing, a layer of ZrB₂ powder, without a polymer coating as discussed above, is sprayed with polymer from a spray jet similar to an ink jet printer spray jet. The spraying is computer controlled and based upon the CAD drawing, similar to that discussed above. The spraying of the polymer binds only the powder in that layer which comes in contact with the polymer. Then, another layer of ZrB₂ powder is laid out, the sprayer sprays polymer on the appropriate sections, and the desired form is built up in the layer by layer manufacturing technique.

In a second method of 3-D printing, a slurry of polymer and ZrB₂ powder is made up such that it has suitable flow characteristics such that it can be sprayed from a spray jet similar to an ink jet printer spray jet. The spraying of the slurry is computer controlled based upon the CAD drawing and the desired form is built up layer by layer.

These 3-D printing techniques are offered by MIT's Dept. of Mechanical Engineering and Dept. of Material Science and Engineering.

4. Fused Deposition Modeling ("FDM")

FDM employs a thermoplastic polymer and ZrB₂ combined in a formed wire. This polymer and ZrB₂ wire is fed through a nozzle which heats and extrudes the polymer and ZrB₂ into a thin layer. The thin layers are built up, layer by layer, to shape the polymer and ZrB₂ into a desired form. FDM is generally less preferred than the above noted manufacturing techniques. However, a suitable FDM technique is offered by Stratasys (Eden Prairie, Minn.).

Following each of the above rapid prototyping or cold pressing shaping methods, the ZrB₂/polymer may further be shaped, e.g., by machining or grinding. Generally, for this to be done, a high T_g polymer must be used or the machining or grinding step must be done in a cooled environment.

C. Sintering the Shaped ZrB₂/Polymer

After the polymer coated ZrB₂ powder is shaped to the desired form, the desired form is sintered to vaporize or sublime the polymer coating and to sinter the ZrB₂ powder. The vaporization step may be referred to by those skilled in the art as "burn-out"; however, this terminology is somewhat misleading in that it is preferred that substantially no oxygen be present during the sintering step. As discussed below, oxygen present in the sintering step may lead to reduced wetting in the copper infiltration step or oxidation of the ZrB₂. The vaporization step is accomplished by heating the desired form to a temperature of about 600° C. and holding that temperature for about 20 minutes. Then, the ZrB₂ sintering step is accomplished by heating the sintering furnace containing the desired form to about 1600° C. to about 1700° C. and holding that temperature for about two hours. Following the sintering step, the sintered ZrB₂ powder shaped form is allowed to cool.

In the sintering step, it is preferred that the polymer which coats the ZrB₂ powder vaporizes, and does not melt, as melting would lead to a degradation of the shape of the desired form.

The sintering step produces a sintered shaped form which is about 30 vol.% to about 70 vol.% occupied by sintered ZrB₂, i.e., about 30% to about 70% dense. The density may advantageously be varied depending upon the desired application, e.g., to minimize electrode wear rate in a particular application. The density or porosity may be altered by varying the size or size distribution of the ZrB₂ powder particles used, varying the polymer coating thickness, varying the manufacturing technique, etc. The density or porosity determines the ZrB₂-copper ratio and may be optimized to meet specific objectives.

It is preferred that the sintering step be substantially oxygen free, because, if oxygen is present, the ZrB₂ may oxidize to ZrO₂ and B₂O₃. B₂O₃ is gaseous and would be removed in the sintering process.

Following the sintering step, regardless of whether rapid prototyping or cold pressing was employed, the sintered ZrB₂ may be shaped to a second desired form, e.g., by machining or grinding. This may be done if certain dimensions need to be very accurate or even for general shaping of sintered ZrB₂ into a second desired form.

D. Infiltrating Sintered ZrB₂ with Copper

Tests indicated that ZrB₂ may not easily be wetted by pure copper or that perhaps there is an oxide coating on the ZrB₂ or carbon or ash contamination of the ZrB₂, perhaps formed during vaporization of the polymer coating or sintering of the ZrB₂, as discussed above. Thus, while pure copper is preferred due to its thermal and electrical conductivity if suitable wetting can be achieved, copper alloys have been

developed to make wetting more thermodynamically favorable. In particular, it has been found that copper which is alloyed with suitable amounts of boron or nickel, e.g., up to about 3 wt. % boron or up to about 10 wt. % nickel, provides for suitably wetting the ZrB_2 . Additionally, this wetting problem may be solved by providing a suitably inert atmosphere in the sintering furnace. It should be noted that this copper alloying reduces the thermal and electrical conductivity of the copper infiltrant, which may in turn reduce the electrode's resistance to erosion. Thus, attempts should be made to prevent significant reductions of the thermal and electrical conductivity of the copper infiltrant by, e.g., only using the minimum amount of boron or nickel which provides suitable wetting.

This wetting problem may be eliminated or alleviated by contacting the ZrB_2 with a mixture having a suitable amount of hydrogen and an inert gas, preferably argon, at an elevated temperature. The hydrogen serves to prevent the ZrB_2 and any Zr or B_2 present from oxidizing. The contacting with hydrogen in combination with the heating step may be conducted before, during, or after the sintering step, preferably during the sintering step, and involves contacting the ZrB_2 and hydrogen/inert gas mixture and heating to at least about $1000^\circ C.$, preferably, between about $1300^\circ C.$ – $1800^\circ C.$ The hydrogen is present in an amount of about 2 vol. % to about 20 vol. %, preferably, about 5 vol. % to about 15 vol. %, and most preferred, about 6 vol. % to about 8 vol. %.

This wetting problem may also be eliminated or alleviated by acid washing the ZrB_2 , preferably after the polymer coating has been vaporized or sublimed. Preferably, the acid washing is performed before or after the ZrB_2 sintering step. While the acid employed may be any suitable acid, the acid wash is preferably conducted with hydrofluoric acid, boric acid, or mixture thereof. With any acid employed, and particularly with boric acid, it is preferred to conduct the acid wash at an elevated temperature. Also, with any acid, and particularly with boric acid, it is preferred to acid wash the ZrB_2 just prior to the sintering step, retain a thin acid coating on all surfaces of the ZrB_2 , and then sinter as described above. The acid wash, and preferably the acid wash at elevated temperatures, removes oxides and other contaminants from the ZrB_2 , allowing the ZrB_2 to be wetted more easily by the copper, and may eliminate or reduce the need for the copper to be alloyed with boron or nickel as discussed above.

The infiltration is accomplished by placing powder or small chunks of pure copper or the copper alloy discussed above on one side of the shaped ZrB_2 form, placing this in a furnace and heating above the melting point of the copper ($1084^\circ C.$) or the copper alloy, such that by capillary action, the copper or copper alloy is infiltrated into the open area of the shaped ZrB_2 form to produce the ZrB_2 /copper composite in the desired form with an about 100% density. It has been found less preferable to place the copper or copper alloy around the shaped ZrB_2 form, as this causes lines of imperfection within the composite caused by capillary fronts from more than one direction.

The copper, prior to or during the infiltration step, may similarly be contacted with a mixture of hydrogen and an inert gas to remove oxides from the copper to improve wetting and the conductivity of the electrode. Preferably, the copper is contacted with a hydrogen/inert gas mixture at an elevated temperature of at least about $500^\circ C.$ If done during the infiltration step, the hydrogen also serves to prevent the ZrB_2 and any Zr or B_2 present from oxidizing. If done during the infiltration step, it is preferred that the infiltration step be conducted at about $1100^\circ C.$ to about $1300^\circ C.$

Another, but less preferred method of infiltrating the shaped ZrB_2 form is by vapor deposition of copper or a copper alloy. Generally, vapor deposition is less preferred as it does not completely fill the open areas as does the above noted capillary action. However, vapor deposition may alleviate the wetting problem discussed above, thus allowing pure copper or a purer copper alloy to wet the shaped ZrB_2 form.

II. Uses for ZrB_2 /Cu Electrodes

The preferred uses for the ZrB_2 /Cu composite electrode of the present invention are listed below. These uses currently utilize copper, graphite, or similar electrodes and have electrode erosion, such that the electrode must be replaced, preventing prolonged, continuous use.

A significant advantage of the present invention is that ZrB_2 /Cu composite electrodes have minimum electrode wear rates. The ZrB_2 /Cu composite electrodes of the present inventions are suitable for replacing currently used copper, graphite, or similar electrodes. This replacement will occur most frequently where the currently used electrode has electrode wear or erosion and must be replaced. The applications which have electrode erosion where ZrB_2 /Cu composite electrodes are preferred to be utilized include:

A. Electrical Discharge Machining

A particularly preferred use of the ZrB_2 /Cu composite electrodes of the present invention is for electrodes in electrical discharge machining (EDM). EDM allows the "machining" of materials, such as tool steels, which are otherwise too hard to machine using traditional machining methods. EDM is an electrical erosion process where the electrode and workpiece (typically the anode and cathode, respectively) are separated by a liquid dielectric. A voltage is applied to the gap of approximately $40 \mu m$ between the electrode and the workpiece. This energy transfer causes the electrode and the workpiece to be eroded. The time the current flows between the electrode and the workpiece is termed the on-time. This on-time is followed by an appropriate off-time, where the current drops to zero and the dielectric is allowed to "flush" out eroded material. These on-times and off-times for die-sinking EDM machines are generally on the order of $10 \mu s$ to $200 \mu s$.

However, the use of an electrode as an EDM electrode requires that the electrode be suitably formed with dimensional accuracy and surface quality. Generally, any material with less than 1 ohm-m of electrical resistivity, regardless of hardness, can be machined using EDM. EDM also allows the convenient production of complex shapes in the tool cavity, as complex topographies can often be more easily formed on the electrode than inside a cavity. Even certain simple shapes such as rectangular or square cavities are often easier to produce using EDM than conventional machining.

The most common, currently used electrode materials for EDM are graphite and copper. These materials have a combination of electrical and thermal properties which makes them well suited for EDM electrodes. Additionally, these materials are relatively easy to machine to a desired form. Even with these advantages, however, EDM machining is precluded from many market niches by the relatively high cost of current electrode production. The cost of current electrode fabrication is generally greater than 50%, and sometimes as great as 80%, of the total cost of fabricating a die using EDM. In EDM, the high wear rate of graphite and copper electrodes requires the use of multiple electrodes in the production of each cavity because the electrode is worn away and loses its initial shape too quickly. Thus, the replacement of graphite and copper electrodes with the

inventive ZrB₂/Cu composite electrodes, which are more wear resistant, significantly improves the cost effectiveness of EDM tool production.

Furthermore, many molds or other tools having multiple cavities, manufactured with current EDM machining techniques, use a different electrode for each separate cavity because it is more cost effective and easier to machine several small, simply-shaped electrodes than it is to machine one large, complex electrode. This requires a greater total sink time in the EDM machine, since multiple electrodes are used sequentially rather than simultaneously.

For EDM electrodes, several variables are used to measure performance. The most important variables are (1) wear ratio [(wear rate of electrode)/(wear rate of 5 workpiece)]; (2) volumetric removal rate of the workpiece (sink rate); (3) dimensional accuracy of the cavity produced; and (4) surface finish of the cavity produced. The first two variables relate to the efficiency of the EDM process. Here, the wear ratio is an important variable as this determines how often the electrode must be removed and replaced. The volumetric removal rate is a measure of the speed of producing a cavity in the workpiece. The last two variables relate to the quality of the product produced by the EDM process. Tools and dies produced by EDM for metal stamping and forging are often required to have dimensional accuracy, while dies produced by EDM for injection molding usually need a higher quality surface finish on the cavity produced.

Generally, the surface finish of the workpiece is directly proportional to the on-time. At low on-times, a higher surface quality finishing is obtained. At higher on-times, a rougher workpiece surface finish is obtained.

EDM has the significant advantage of allowing a tool part to be heat treated to its full hardness before a cavity is produced therein, which eliminates the need for heat treating after milling. Thus, there will be no distortion in the final part due to the heat treatment. Also, the EDM process imparts minimal work hardening or mechanical stresses since there is no contact between the workpiece and the tool. Further, EDM offers higher dimensional accuracy and ease of production of complex shapes in the tool cavity compared to conventional machining.

A particular advantage of the present invention is the use of SLS to produce an EDM electrode. SLS provides the advantage of allowing the production of complex shaped EDM electrodes. Thus, with the low wear rate of ZrB₂/Cu composite electrodes and the ability to make complex shapes, one complex shaped ZrB₂/Cu composite electrode can replace several currently used EDM copper electrodes, leading to a quicker and less expensive tool and die manufacture.

EXAMPLE 2

Anodes of (1) copper, (2) graphite, and (3) ZrB₂/Cu were measured for spark erosion when machining steel in an AGIETRON 1 U EDM die-sinking machine. The machine operating conditions were the same for the three different electrodes: current of 63 amperes; pulse time at 18 μs; pause time at 320 μs. These conditions, i.e., high current and short pulse time, were chosen for this test, as, generally, these conditions provide unusually high electrode erosion rates. The results in Table 1 show that the graphite electrode wear ratio of 0.150 is 4.3 times more than the ZrB₂/Cu electrode wear ratio of 0.0346. Table 1 further shows that the copper electrode is worn down 16.6 times more than the ZrB₂/Cu electrode at these conditions.

TABLE 1

	ELECTRODE		
	Copper	Graphite	ZrB ₂ /Cu
Erosion Rate of Steel (mm ³ /min)	3.40	4.84	3.12
Erosion Rate of Electrode (mm ³ /min)	1.97	0.717	0.108
Wear Ratio (electrode/workpiece)	0.58	0.15	0.035

Thus, ZrB₂/Cu electrodes provide a rapid sink rate with electrode wear ratios significantly less than copper or graphite.

B. Aluminum Recycling

In aluminum recycling, an electric arc is struck from an electrode to molten aluminum in a ladle. Purified aluminum is then separated from slag which contains paint and other impurities from the recycled aluminum cans. Generally, electrodes are consumed in the process at a rate such that three parallel production units are commonly used, two operating with the third shutdown for electrode replacement.

C. Spot Welding

In spot welding, electrodes are consumed and must be replaced periodically. In some cases, contamination of the weld with the eroded electrode material is a problem. This would be eliminated or, at least, substantially reduced with the ZrB₂/Cu composite electrodes of the present invention.

D. Arc Jet Plasma Reactors

Arc jet plasma reactors are used for a variety of applications. Current reactors can presently be operated for only about 10–30 hours before the current copper anode (an orifice) is eroded through, causing disintegration of the anode with small parts of the copper violently ejected out the reactor exhaust. The ZrB₂/Cu composite electrode of the present invention would allow longer anode life while also reducing this safety hazard.

E. Nuclear and Municipal Waste or Trash Remediation

New waste remediation plants are operating in Norway and France which use plasma arc devices for waste remediation. Current operation is continuous except for a daily shutdown of 1–2 hours for electrode replacement. Use of the ZrB₂/Cu composite electrodes of the present invention would allow longer run time before shut down for electrode replacement.

F. Rail Guns

Used mostly for military applications, arc-driven rail guns are used to accelerate massive projectiles to high velocities.

G. High-Current Switches for Pulsed Powder

There are many applications involving electrical switches where erosion of the switch electrodes is a problem. High powered switches exhibit a temporary arc when opened or closed. Frequent opening and closing, as in pulsed power supplies, can lead to electrode erosion and failure.

H. High-Power Ion Thrusters

Ion beam sources have been developed for space propulsion as well as ion machining and sputter coating applications.

I. Microelectronics Processing

Plasmas are currently used in about 30% of all microelectronics processing operations. Here, electrode erosion is often a problem due to contamination of the wafers.

J. Plasma Spray Coating

Plasma spray coating is best known for the spraying of aircraft surfaces with titanium. Currently, the electrodes last about 30 hours and then must be replaced by disassembling the plasma gun.

The ZrB₂ formed by the process of the present invention has excellent material properties such as high wear and

abrasion resistance, extreme hardness, high melting point, and good thermal and electrical conductivity. The addition of copper to the ZrB_2 matrix to produce the ZrB_2/Cu composite has a synergistic effect, providing a material far superior to either ZrB_2 or copper. The ZrB_2/Cu composite has an electrical conductivity near copper with much higher wear and abrasion resistance than copper, making it an excellent material for electrodes, particularly for electrodes where minimum electrode wear rates are advantageous. If the ZrB_2 was used alone as an electrode, mechanical failure of the electrode would occur, without melting, but by the overcoming of the bond strength with thermal stresses alone. This is called "thermal spalling", and it occurs as the ZrB_2 expands and contracts during sudden temperature changes at the surface of the electrode during erosion. When copper is used by itself, it erodes by melting. When the ZrB_2 is combined with copper, the combination allows for the copper to melt and resolidify to the higher-melting point ZrB_2 material, and the excess heat is carried away from the surface quickly because of the high thermal conductivity of the copper. The copper also aids in reducing the effects of thermal spalling because it is not brittle and it helps reduce the internal stresses that cause spalling.

The ZrB_2/Cu composite electrodes of the present invention provide the following advantages: (1) improved wear resistance over known copper and graphite electrodes; (2) improved sink rate over known copper and graphite electrodes; (3) control of dimensional accuracy on an EDM workpiece; and (4) an improved surface finish on an EDM workpiece.

It has been found that titanium diboride/copper (TiB_2/Cu) composite electrodes have essentially the same advantages, performance characteristics, and uses as ZrB_2/Cu composite electrodes. TiB_2/Cu composite electrodes are made in essentially the same manner as described above for ZrB_2/Cu composite electrodes. TiB_2/Cu composite electrodes were manufactured and tested as EDM electrodes and it was determined that TiB_2/Cu composite electrodes have wear ratios, sink rates and surface roughness very comparable to ZrB_2/Cu composite electrodes used as EDM electrodes. Thus, TiB_2/Cu composite electrodes provide for the same advantages as ZrB_2/Cu composite electrodes, namely: (1) improved wear resistance over known copper and graphite electrodes; (2) improved sink rate over known copper and graphite electrodes; (3) control of dimensional accuracy on an EDM workpiece; and (4) an improved surface finish on an EDM workpiece.

The present invention solves the problems mentioned above by providing ZrB_2/Cu composite electrodes, and particularly EDM electrodes, which may be time and cost efficiently manufactured and which provide sufficient dimensional accuracy and surface quality such that the ZrB_2/Cu composite electrode may be used as an EDM electrode.

Although the present invention has been described in detail, it should be understood that various changes, alterations, and substitutions may be made to the teachings herein without departing from the spirit and scope of the present invention as defined by the appended claims.

We claim:

1. An electrode produced by a process comprising: shaping ZrB_2 or TiB_2 powder into a desired form; sintering the shaped ZrB_2 or TiB_2 powder; contacting the sintered ZrB_2 or TiB_2 with Cu and heating the sintered ZrB_2 or TiB_2 and Cu above the melting point of Cu to infiltrate the ZrB_2 or TiB_2 with Cu to form a ZrB_2/Cu or TiB_2/Cu composite electrode.

2. The electrode of claim 1, wherein shaping ZrB_2 or TiB_2 powder into a desired form comprises a method selected from the group comprising selective laser sintering, laminated object manufacturing, 3-D printing, fused deposition modeling, and cold pressing.

3. The electrode of claim 1,

wherein the shaping step further comprises contacting the ZrB_2 or TiB_2 powder with a polymer and utilizing the polymer to hold the ZrB_2 or TiB_2 powder in the desired form;

and further comprising the step of vaporizing the polymer prior to sintering the shaped ZrB_2 or TiB_2 powder.

4. The electrode of claim 3, wherein the polymer is vaporized at a temperature of about 350° C. to about 700° C.

5. The electrode of claim 1, wherein the sintering step is conducted in a substantially oxygen free environment.

6. The electrode of claim 1, wherein the sintering step produces a sintered shaped form which is about 30 vol. % to about 70 vol. % occupied by sintered ZrB_2 or TiB_2 .

7. The electrode of claim 1, wherein the sintering step comprises heating the desired form from about 1300° C. to about 1900° C.

8. The electrode of claim 1, wherein the contacting the sintered ZrB_2 or TiB_2 with Cu step comprises the Cu being alloyed with a suitable amount of boron for the Cu alloy to suitably wet the sintered ZrB_2 or TiB_2 .

9. The electrode of claim 8, wherein the amount of boron is up to about 3 wt. % boron.

10. The electrode of claim 1, wherein the contacting the sintered ZrB_2 or TiB_2 with Cu step comprises the Cu being alloyed with a suitable amount of nickel for the Cu alloy to suitably wet the sintered ZrB_2 or TiB_2 .

11. The electrode of claim 10, wherein the amount of nickel is up to about 10 wt. % nickel.

12. The electrode of claim 1, wherein the ZrB_2/Cu or TiB_2/Cu composite electrode has a wear ratio less than a copper electrode or a graphite electrode in a similar service.

13. The electrode of claim 1, wherein, after the step of sintering the shaped ZrB_2 or TiB_2 powder, the process further comprising the step of shaping the sintered ZrB_2 or TiB_2 to a second desired form.

14. The electrode of claim 1, the process further comprising the step of contacting the shaped ZrB_2 or TiB_2 powder with a mixture of hydrogen and at least one inert gas.

15. The electrode of claim 1, the process further comprising the step of acid washing the shaped ZrB_2 or TiB_2 powder.

16. The electrode of claim 15, wherein the step of acid washing the shaped ZrB_2 or TiB_2 powder comprises contacting the shaped ZrB_2 or TiB_2 powder with an acid selected from the group comprising hydrofluoric acid, boric acid, or mixtures thereof.

17. A method of producing an electrode, comprising the steps of:

shaping ZrB_2 or TiB_2 powder into a desired form;

sintering the shaped ZrB_2 or TiB_2 powder;

contacting the sintered ZrB_2 or TiB_2 with Cu and heating the sintered ZrB_2 or TiB_2 and Cu above the melting point of Cu to infiltrate the ZrB_2 or TiB_2 with Cu to form a ZrB_2/Cu or TiB_2/Cu composite electrode.

18. The method of claim 17, wherein shaping ZrB_2 or TiB_2 powder into a desired form comprises a method selected from the group comprising selective laser sintering, laminated object manufacturing, 3-D printing, fused deposition modeling, and cold pressing.

19. The method of claim 17,

wherein the shaping step further comprises contacting the ZrB₂ or TiB₂ powder with a polymer and utilizing the polymer to hold the ZrB₂ or TiB₂ powder in the desired form;

and further comprising the step of vaporizing the polymer prior to sintering the shaped ZrB₂ or TiB₂ powder.

20. The method of claim 19, wherein the polymer is vaporized at a temperature of about 350° C. to about 700° C.

21. The method of claim 17, wherein the sintering step is conducted in a substantially oxygen free environment.

22. The method of claim 17, wherein the sintering step produces a sintered shaped form which is about 30 vol. % to about 70 vol. % occupied by sintered ZrB₂ or TiB₂.

23. The method of claim 17, wherein the sintering step comprises heating the desired form from about 1300° C. to about 1900° C.

24. The method of claim 17, wherein the contacting the sintered ZrB₂ or TiB₂ with Cu step comprises the Cu being alloyed with a suitable amount of boron for the Cu alloy to suitably wet the sintered ZrB₂ or TiB₂.

25. The method of claim 24, wherein the amount of boron is up to about 3 wt. % boron.

26. The method of claim 17, wherein the contacting the sintered ZrB₂ or TiB₂ with Cu step comprises the Cu being alloyed with a suitable amount of nickel for the Cu alloy to suitably wet the sintered ZrB₂ or TiB₂.

27. The method of claim 26, wherein the amount of nickel is up to about 10 wt. % nickel.

28. The method of claim 17, wherein the ZrB₂/Cu or TiB₂/Cu composite electrode has a wear ratio less than a copper electrode or a graphite electrode in a similar service.

29. The method of claim 17, wherein, after the step of sintering the shaped ZrB₂ or TiB₂ powder, the process further comprising the step of shaping the sintered ZrB₂ or TiB₂ to a second desired form.

30. The method of claim 17, further comprising the step of contacting the shaped ZrB₂ or TiB₂ powder with a mixture of hydrogen and at least one inert gas.

31. The method of claim 17, further comprising the step of acid washing the shaped ZrB₂ or TiB₂ powder.

32. The method of claim 31, wherein the step of acid washing the shaped ZrB₂ or TiB₂ powder comprises contacting the shaped ZrB₂ or TiB₂ powder with an acid selected from the group comprising hydrofluoric acid, boric acid, or mixtures thereof.

33. In a process utilizing an electrode in an application in which the electrode has erosion, the improvement comprising utilizing a ZrB₂/Cu or TiB₂/Cu composite electrode.

34. The process of claim 33, wherein the process utilizing an electrode in an application in which the electrode has erosion is selected from the group comprising electrical discharge machining, aluminum recycling, spot welding, arc jet plasma reactors, waste remediation, rail guns, high-current switches for pulsed power supplies, high-power ion thrusters, microelectronics processing, and plasma spray coating.

35. The process of claim 33, wherein the ZrB₂/Cu or TiB₂/Cu composite electrode is formed by a process comprising:

shaping ZrB₂ or TiB₂ powder into a desired form;

sintering the shaped ZrB₂ or TiB₂ powder;

contacting the sintered ZrB₂ or TiB₂ with Cu and heating the sintered ZrB₂ or TiB₂ and Cu above the melting point of Cu to infiltrate the ZrB₂ or TiB₂ with Cu to form the ZrB₂/Cu or TiB₂/Cu composite electrode.

36. The process of claim 35, wherein shaping ZrB₂ or TiB₂ powder into a desired form comprises a method selected from the group comprising selective laser sintering, laminated object manufacturing, 3-D printing, fused deposition modeling, and cold pressing.

37. The process of claim 35,

wherein the shaping step further comprises contacting the ZrB₂ or TiB₂ powder with a polymer and utilizing the polymer to hold the ZrB₂ or TiB₂ powder in the desired form;

and further comprising the step of vaporizing the polymer prior to sintering the shaped ZrB₂ or TiB₂ powder.

38. The process of claim 37, wherein the polymer is vaporized at a temperature of about 350° C. to about 700° C.

39. The process of claim 35, wherein the sintering step is conducted in a substantially oxygen free environment.

40. The process of claim 35, wherein the sintering step produces a sintered shaped form which is about 30 vol. % to about 70 vol. % occupied by sintered ZrB₂ or TiB₂.

41. The process of claim 35, wherein the sintering step comprises heating the desired form from about 1300° C. to about 1900° C.

42. The process of claim 35, wherein the contacting the sintered ZrB₂ or TiB₂ with Cu step comprises the Cu being alloyed with a suitable amount of boron for the Cu alloy to suitably wet the sintered ZrB₂ or TiB₂.

43. The process of claim 42, wherein the amount of boron is up to about 3 wt. % boron.

44. The process of claim 35, wherein the contacting the sintered ZrB₂ or TiB₂ with Cu step comprises the Cu being alloyed with a suitable amount of nickel for the Cu alloy to suitably wet the sintered ZrB₂ or TiB₂.

45. The process of claim 44, wherein the amount of nickel is up to about 10 wt. % nickel.

46. The process of claim 35, wherein the ZrB₂/Cu or TiB₂/Cu composite electrode has a wear ratio less than a copper electrode or a graphite electrode in a similar service.

47. The process of claim 35, wherein after the step of sintering the shaped ZrB₂ or TiB₂ powder, the process further comprising the step of shaping the sintered ZrB₂ or TiB₂ to a second desired form.

48. The process of claim 35, further comprising the step of contacting the shaped ZrB₂ or TiB₂ powder with a mixture of hydrogen and at least one inert gas.

49. The process of claim 35, further comprising the step of acid washing the shaped ZrB₂ or TiB₂ powder.

50. The process of claim 49, wherein the step of acid washing the shaped ZrB₂ or TiB₂ powder comprises contacting the shaped ZrB₂ or TiB₂ powder with an acid selected from the group comprising hydrofluoric acid, boric acid, or mixtures thereof.

51. An electrode produced by a process comprising:

obtaining ZrB₂ or TiB₂ powder substantially coated with a polymer;

utilizing selective laser sintering to shape the polymer coated ZrB₂ or TiB₂ powder into a desired form;

vaporizing the polymer from the desired form;

after the vaporizing step, sintering the ZrB₂ or TiB₂ powder in the desired form;

contacting the sintered ZrB₂ or TiB₂ with Cu and heating the sintered ZrB₂ or TiB₂ and Cu above the melting point of Cu to infiltrate the ZrB₂ or TiB₂ with Cu to form a ZrB₂/Cu or TiB₂/Cu composite electrode.

52. The electrode of claim 51, wherein the polymer is vaporized at a temperature of about 350° C. to about 700° C.

53. The electrode of claim 51, wherein the sintering step is conducted in a substantially oxygen free environment.

15

54. The electrode of claim **51**, wherein the sintering step produces a sintered shaped form which is about 30 vol. % to about 70 vol. % occupied by sintered ZrB_2 or TiB_2 .

55. The electrode of claim **51**, wherein the sintering step comprises heating the desired form from about 1300° C. to about 1900° C.

56. The electrode of claim **51**, wherein the contacting the sintered ZrB_2 or TiB_2 with Cu step comprises the Cu being alloyed with a suitable amount of boron for the Cu alloy to suitably wet the sintered ZrB_2 or TiB_2 .

57. The electrode of claim **56**, wherein the amount of boron is up to about 3 wt. % boron.

58. The electrode of claim **51**, wherein the contacting the sintered ZrB_2 or TiB_2 with Cu step comprises the Cu being alloyed with a suitable amount of nickel for the Cu alloy to suitably wet the sintered ZrB_2 or TiB_2 .

59. The electrode of claim **58**, wherein the amount of nickel is up to about 10 wt. % nickel.

60. The electrode of claim **51**, wherein the ZrB_2/Cu or TiB_2/Cu composite electrode has a wear ratio less than a copper electrode or a graphite electrode in a similar service.

61. The electrode of claim **51**, wherein, after the step of sintering the ZrB_2 or TiB_2 powder, the process further comprising the step of shaping the sintered ZrB_2 or TiB_2 to a second desired form.

62. The electrode of claim **51**, the process further comprising, after the vaporizing step, the step of contacting the ZrB_2 or TiB_2 with a mixture of hydrogen and at least one inert gas.

63. The electrode of claim **51**, the process further comprising, after the vaporizing step, the step of acid washing the ZrB_2 or TiB_2 .

64. The electrode of claim **63**, wherein the step of acid washing the ZrB_2 or TiB_2 comprises contacting the ZrB_2 or TiB_2 with an acid selected from the group comprising hydrofluoric acid, boric acid, or mixtures thereof.

16

65. An electrode produced by a process comprising: shaping ZrB_2 or TiB_2 powder into a desired form; sintering the shaped ZrB_2 or TiB_2 powder;

utilizing copper vapor deposition to at least partially infiltrate the sintered ZrB_2 or TiB_2 with Cu to form a ZrB_2/Cu or TiB_2/Cu composite electrode.

66. The electrode of claim **65**, wherein shaping ZrB_2 or TiB_2 powder into a desired form comprises a method selected from the group comprising selective laser sintering, laminated object manufacturing, 3-D printing, fused deposition modeling, and cold pressing.

67. The electrode of claim **65**,

wherein the shaping step further comprises contacting the ZrB_2 or TiB_2 powder with a polymer and utilizing the polymer to hold the ZrB_2 or TiB_2 powder in the desired form;

and further comprising the step of vaporizing the polymer prior to sintering the shaped ZrB_2 or TiB_2 powder.

68. The electrode of claim **67**, wherein the polymer is vaporized at a temperature of about 350° C. to about 700° C.

69. The electrode of claim **65**, wherein the sintering step is conducted in a substantially oxygen free environment.

70. The electrode of claim **65**, wherein the sintering step produces a sintered shaped form which is about 30 vol. % to about 70 vol. % occupied by sintered ZrB_2 or TiB_2 .

71. The electrode of claim **65**, wherein the sintering step comprises heating the desired form from about 1300° C. to about 1900° C.

72. The electrode of claim **65**, wherein the ZrB_2/Cu or TiB_2/Cu composite electrode has a wear ratio less than a copper electrode or a graphite electrode in a similar service.

73. The electrode of claim **65**, wherein, after the step of sintering the shaped ZrB_2 or TiB_2 powder, the process further comprising the step of shaping the sintered ZrB_2 or TiB_2 to a second desired form.

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