May 16, 1961 A. BLUM 2,984,807

CORROSION-RESISTANT HIGH-TEMPERATURE BODIES FOR METAL VAPORIZING HEATERS AND OTHER APPLICATIONS

Filed March 23, 1960 5 Sheets-Sheet 1

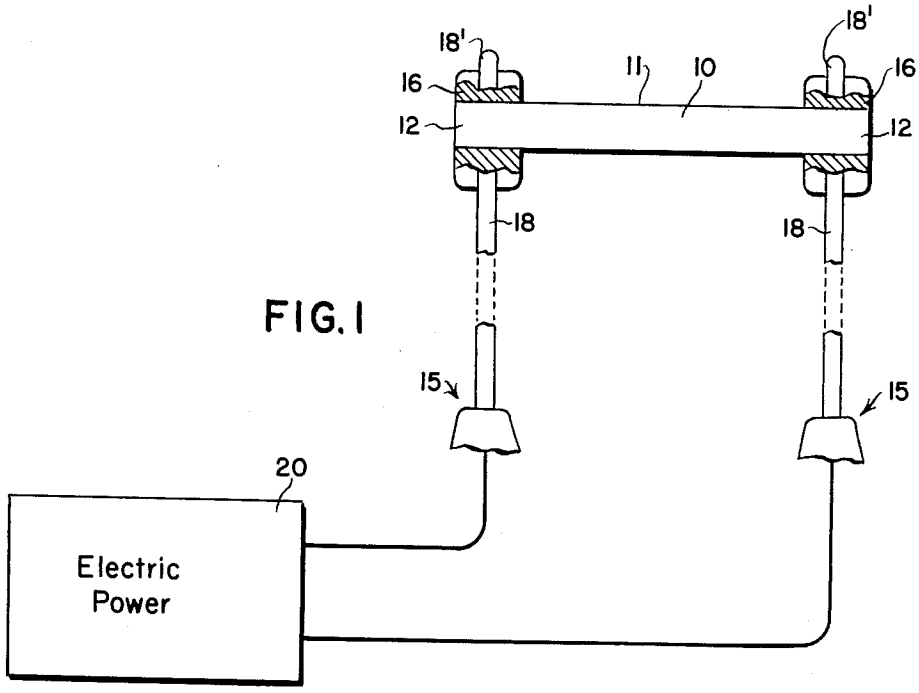


FIG. 1

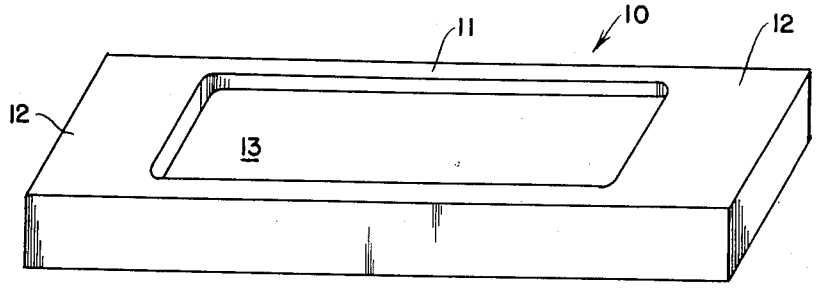


FIG. 2

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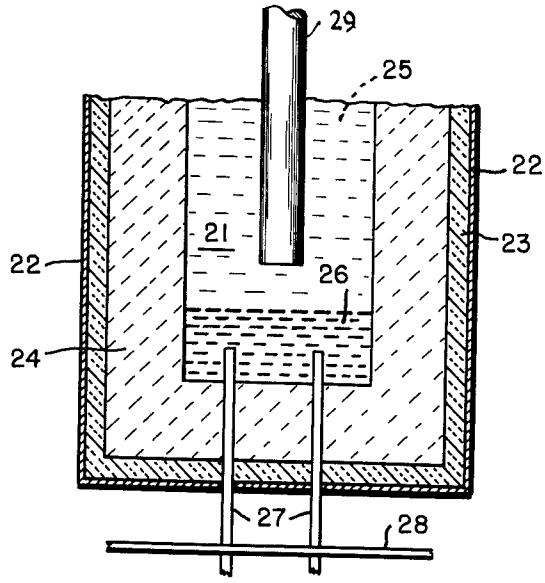


Fig. 3

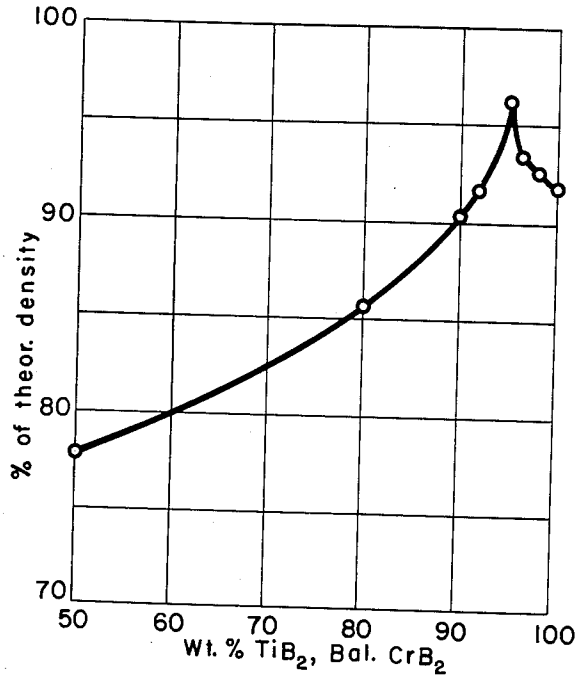


Fig. 4

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CORROSION-RESISTANT HIGH-TEMPERATURE BODIES FOR METAL VAPORIZING HEATERS AND OTHER APPLICATIONS

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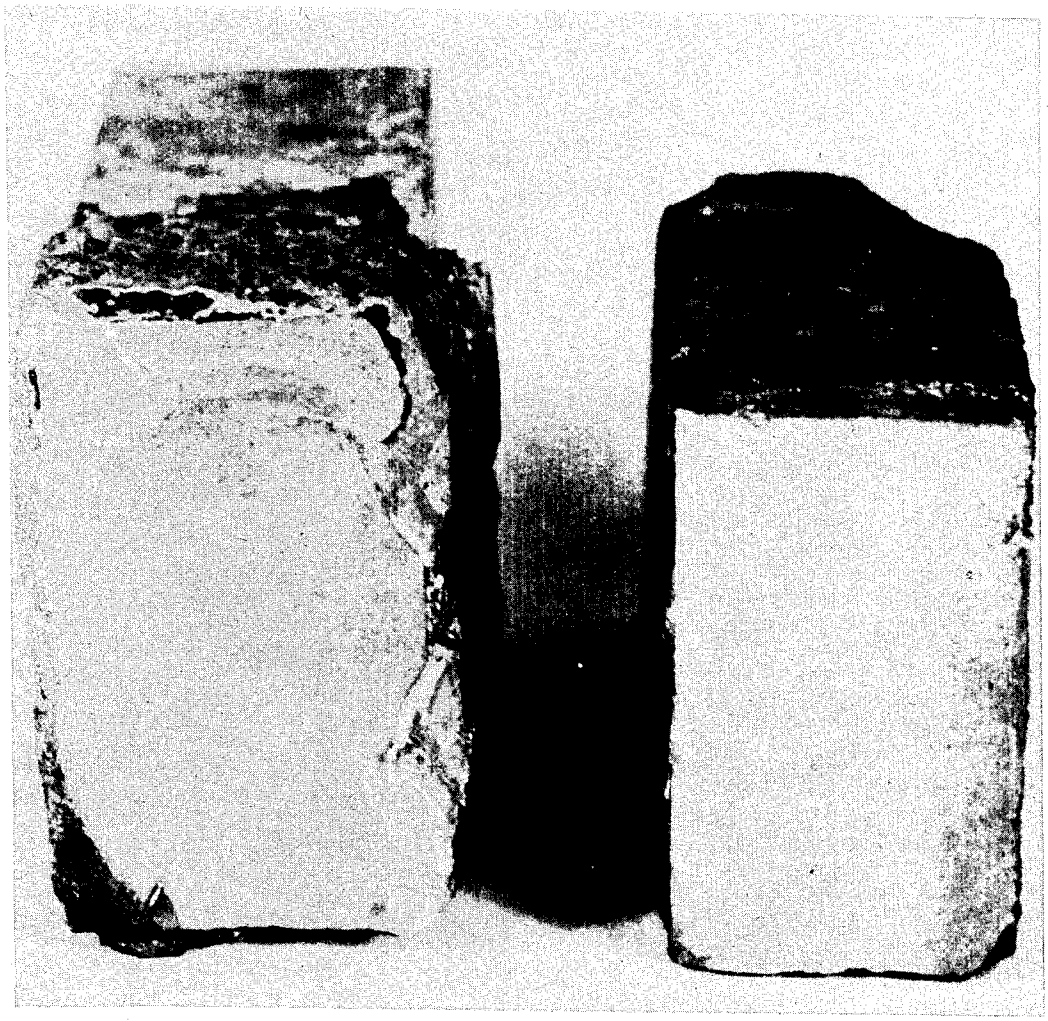


Fig. 5-B Fig. 5-A

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CORROSION-RESISTANT HIGH-TEMPERATURE BODIES FOR METAL VAPORIZING HEATERS AND OTHER APPLICATIONS

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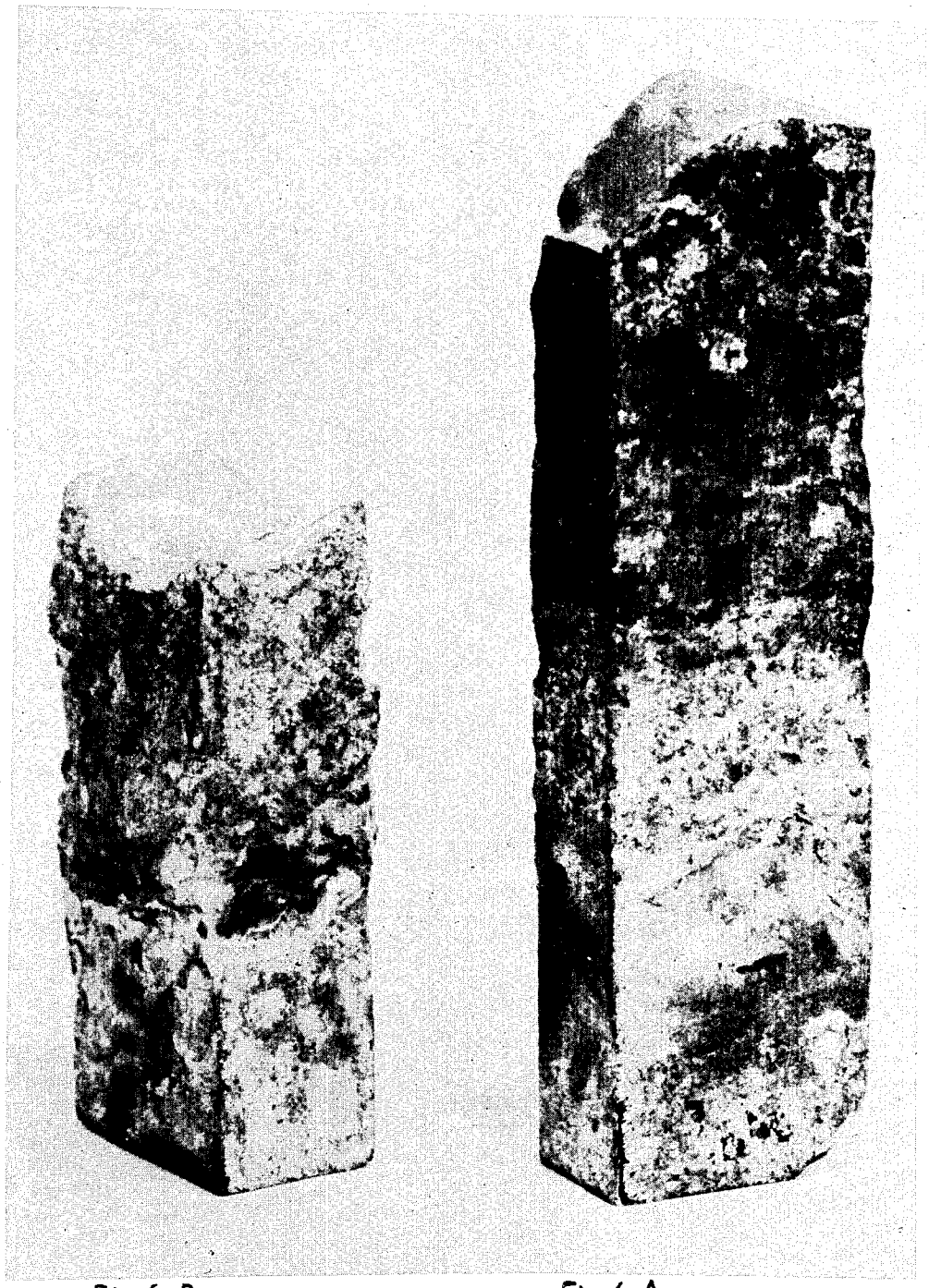


Fig. 6-B

Fig. 6-A

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CORROSION-RESISTANT HIGH-TEMPERATURE BODIES FOR METAL VAPORIZING HEATERS AND OTHER APPLICATIONS

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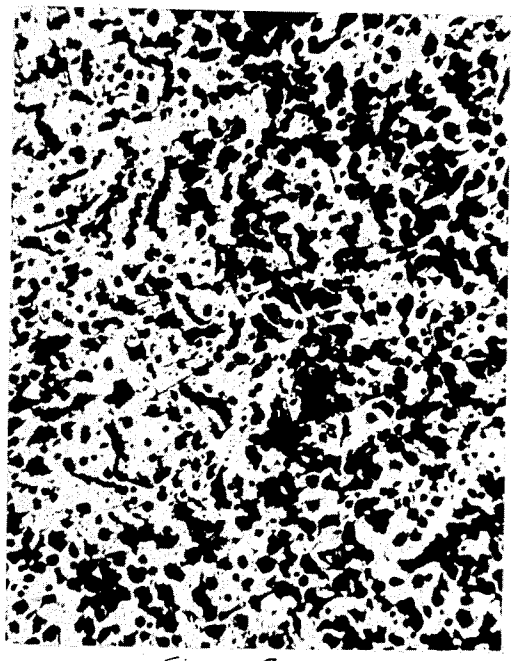


Figure 8

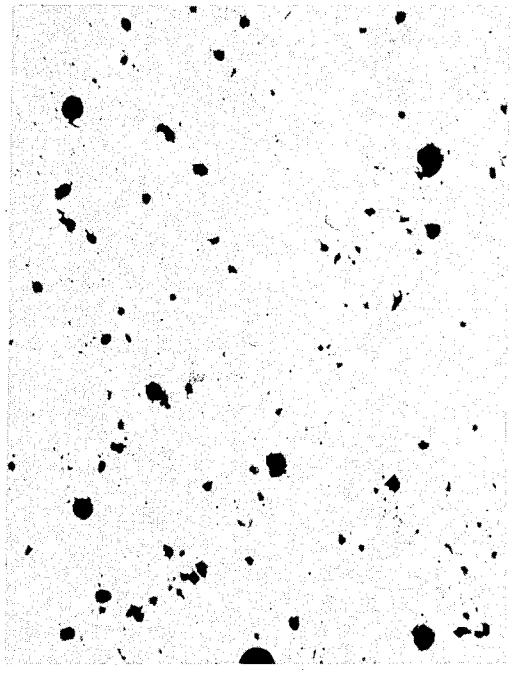


Figure 7

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United States Patent Office 2,984,807 Patented May 16, 1961

2,984,807

CORROSION-RESISTANT HIGH-TEMPERATURE BODIES FOR METAL VAPORIZING HEATERS AND OTHER APPLICATIONS

Arnold Blum, Pitcairn, Pa., assignor to Borolite Corporation, Pittsburgh, Pa., a corporation of Delaware

Filed Mar. 23, 1960, Ser. No. 17,008

14 Claims. (Cl. 338—330)

This application is a continuation-in-part of my application Serial No. 775,258, filed November 20, 1958, as a continuation-in-part of my earlier-filed application Serial No. 691,948, filed Octoer 23, 1957, now abandoned.

One primary phase of the invention relates to electric heating, and more particularly to solid material or bodies suitable for use as heater bodies which are able to maintain a heating temperature of a least 1300° C., or in excess of 1300° C., such as 1350° C. or 1400° C. to 1500° C. for a prolonged period of time when heating substances which form corrosive vapors and liquids.

Such heater bodies are required in applications such as metal vapor coating systems in which a sheet of steel or like material held in an evacuated enclosure has deposited thereon, vapor of aluminum or similar metal which is evaporated by a heater body held within such vacuum enclosure. The best electric heater bodies heretofore available for such applications, failed after short use, and could not be used for operating such vapor-coating systems on a continuous basis in which a vapor-deposited coating is continuously formed within an evacuated enclosure on a continuously moving sheet or wire of steel or like material which has to be protected against corrosion.

A broader phase of the invention—which grew out of or is based on the primary phase of the invention—is a unique cemented body composition consisting of a critically narrow range of proportions of a solid solution of titanium diboride and chromium diboride having a high density close to that of a 100% dense body of such composition, which high body density suppresses infiltration and corrosion of such body when exposed to molten corrosive metal, such as aluminum, during a long operating life.

Among the objects of the invention is an electric heater body which will not fail and will continue to operate in vaporizing reactive metals under vacuum in such metal vapor coating systems for a prolonged period of time and which makes it possible to operate such vacuum vapor coating system on a continuous, automatic basis for automatically coating a coil of sheet metal such as steel with vapors of aluminum or like reactive metal as the metal coil is unrolled within the vacuum enclosure.

Among the broader objects of the invention is a critically proportioned cemented composition body of the diborides of titanium and chromium, having high density, which suppresses infiltration and corrosion of such body when exposed for a long operating life to molten corrosive metals, such as aluminum.

Also among the broader objects of the heater-body phase of the invention is a solid body consisting of sintered refractory particles, which is adapted to be exposed to corrosive fluids at high temperatures, and which during prolonged operation is heated to a high temperature of at least 1300° C. at which metals of lower melting temperature will be vaporized when fed to said body, and which sintered-particle body has a high density of at least

4.15 grams per cubic centimeter, at which it will suppress infiltration of its interior with metal vaporized or sublimated along its exterior surfaces.

Among the objects of the invention is a hard material of sintered refractory particles having a density of at least 4.15 grams per cubic centimeter, and which will retain high density and will not corrode and will not be infiltrated when exposed at temperatures in excess of 1300° C., such as from 1300° C. to 1500° C. to molten or vaporized aluminum or other molten or vaporized reactive metals.

The foregoing and other objects of the invention will be best understood from the following description of exemplifications thereof, reference being had to the accompanying drawing, wherein:

Fig. 1 is an elevational view of a heater body of an electric heater system forming part of a metal vapor coating system (not shown);

Fig. 2 is an enlarged perspective view of one form of a heater body of the invention for such electric heater system;

Fig. 3 is a diagrammatic cross-sectional view of a portion of an electrolytic reduction cell for producing a nonferrous metal such as aluminum, and operating with cathode electrodes formed of body compositions of the invention;

Fig. 4 is a graph illustrating the critical range of constituent-proportions of the bodies of the invention;

Fig. 5–A is a macrograph of a cross-section 2½ x 1½ inches large, of a cathode body of the invention after thirty days' exposure to the fused salt body of an aluminum reduction cell;

Fig. 5–B is a similar macrograph of a similar cathode body consisting only of titanium diboride, after exposure to the same medium for the same time;

Figs. 6–A and 6–B are macrographs of the same two cathode bodies as in Figs. 5–A and 5–B, respectively, standing on the ends which projected into the reduction cell, with the body of Fig. 6–B having been fractured while operating as a cell electrode;

Fig. 7 is a 200-diameter micrograph of a transverse cross-section of a body of the invention; and

Fig. 8 is a similar micrograph of a similar body consisting only of titanium diboride.

For many years past, continuous, concentrated efforts have been made to provide a heater body which will be able to operate over a long period under vacuum in vaporizing aluminum and make it possible to deposit the aluminum vapors on a great length of wire or sheet or steel which is kept moving in the vacuum enclosure on a continuous basis.

The best heaters heretofore devised for such aluminum vaporizing systems consisted of an elongated carbon heater body having a protective coating of titanium carbide, tungsten carbide, molybdenum carbide, zirconium carbide, or the like, as described, for instance, in Clough et al. Patent 2,703,334 and Patton Patent 2,730,986, both assigned to National Research Corporation. The aluminizing-vaporizing electric heater bodies of these and other patents of this assignee, consisted of a carbon rod about 2" to 6" long, ¼" to ½" thick, having on the top a shallow elongated groove ⅛" wide and ⅛" to 5/32" deep, which is filled with molten aluminum from an aluminum rod fed to the groove for vaporizing it within the vapor-coating enclosure maintained under vacuum on the order of a micron of mercury, the heater rod having a protective refractory carbide coating. With such heaters it was possible to evaporate at most about 8.4 grams of aluminum per cm.^{2} of the evaporator surface before the heater body had to be discarded. It has also been proposed to make such heater bodies of pure titanium diboride or pure zirconium diboride. However, when evaporizing

aluminum with heater bodies of pure titanium diboride or pure zirconium diboride, the aluminum penetrates and infiltrates the interior of such heater bodies from the very beginning of the aluminum vaporizing operation, and they have to be discarded after an evaporation of only 8.1 grams of aluminum per cm.^{2} of the vaporizing surface.

One phase of the present invention is based on the discovery that a hard body which will remain free of corrosion for a long period of time at temperatures in excess of 1300° C. and as high as 1500° C., in the presence of vapors of aluminum or molten aluminum in contact therewith, may be produced on a commercial basis by compacting and suitably sintering a critical range of proportions of a mixture of particles of titanium diboride TiB_2 and chromium diboride CrB_2, namely in the critical range of proportions of 97% to 93% by weight of TiB_2 and 3% to 7% by weight of CrB_2, until all sintered particles in these critical proportions of the two diborides go into solid solution with each other and form a body of the invention having a density of at least 4.15 grams per cubic centimeter (gr./cc.).

The present invention is based also on the discovery that the desired electric heater bodies suitable for continuously vaporizing aluminum or like reactive metals within an evacuated enclosure of a metal vapor coating system, which enable continuous, automatic operation of such systems, may be produced on a commercial basis by compacting and suitably sintering a critical range of proportions of a mixture of particles of titanium diboride TiB_2 and chromium diboride CrB_2, namely in the critical range of proportions of 93% to 97% by weight of TiB_2 and 7% to 3% of CrB_2 by weight, until all sintered particles in these critical proportions of the two diborides go into solid solution with each other and form a heater body having a density of at least 4.15 grams per cubic centimeter (gr./cc.).

Throughout the specification and claims, all proportions are given in weight, unless otherwise specifically indicated.

Very good results are obtained with an electric heater body consisting of such solid solution of titanium diboride and chromium diboride, which has a density of about 4.42 gr./cc., this density being obtained by sintering under vacuum 95% TiB_2 and 5% CrB_2, until they are full in solid solution and have reached such high density. Satisfactory aluminum vaporizing heater bodies of the invention may also be formed with a higher titanium diboride content, within the critical range, up to a solid solution of 97% TiB_2 and 3% CrB_2, which has been sintered to give the heater body a density of 4.15 to 4.25 gr./cc. Satisfactory aluminum vaporizing heater bodies of the invention may also be formed with a lower titanium diboride content within the critical range down to a solid solution of 93% TiB_2 and 7% CrB_2, which has been sintered to give the heater body a density of 4.15 gr./cc. to 4.25 gr./cc.

Such heater bodies of the invention consisting of a solid solution of 93% to 97% TiB_2 and 7% to 3% CrB_2, and sintered to maximum density approaching theoretical 100% density, operate for a long period of time at temperatures of 1400° C. to 1500° C. when exposed to reactive metals such as aluminum in molten or vaporized state. As a result, such electrically energized heater bodies of the invention make it possible to use them in vacuum enclosures of automatic aluminizing vapor coating systems for continuously vaporizing aluminum or like reactive metals brought in contact with the heater body for continuously depositing the vaporized aluminum on a continuously moving sheet, ribbon or wire of steel or like material that is to be protected by a coating of the deposited vaporized aluminum.

On the other hand, when the proportions of TiB_2 in the sintered bodies consisting of solid solutions of TiB_2 and CrB_2, is increased above 97% TiB_2 or decreased below 93% TiB_2, the density of such body decreases relatively sharply and such bodies undergo rapid corrosion when subjected at the aluminum vaporizing temperatures, such as 1400° C. to 1500° C., to liquid aluminum or aluminum vapor, or to other liquid or vaporized reactive metals.

The invention is based on the discovery that a mixture of particles of titanium diboride and chromium diboride in the critical range of proportions from 97% TiB_2 with 3% CrB_2 to 93% TiB_2 with 7% CrB_2, which has been sintered to form a solid solution of these ingredients will yield a heater body of higher density when the proportions of these two ingredients is chosen so that it is close to 95% TiB_2 with 5% CrB_2, and remains within the range of 97% to 93% TiB_2 and 3% to 7% of CrB_2. The density of such sintered heater body of the invention decreases from the maximum density of about 4.42 gr./cc. to the lower density of 4.15 to 4.25 gr./cc. as the proportion of TiB_2 is increased from 95% to 97%. The density of such sintered heater body of the invention decreases from the maximum density of about 4.42 gr./cc. to the lower density of 4.15 to 4.25 gr./cc. as the proportion of TiB_2 is decreased from 95% down to 93%. Throughout the range of the foregoing critical proportions of TiB_2 and CrB_2, they form solid solutions when a mixture of their particles is sintered at a temperature at which the particle mixture developes a liquid phase. Within the specified critical range of ingredients, a heater body consisting of a solid solution of 95% TiB_2 and 5% CrB_2, may be sintered to a maximum density of about 4.42 gr./cc. A heater body having such maximum density has the longest useful life when exposed to vapors of aluminum or like reactive metals when such metal is brought into contact with the heater body for vaporizing it. For longest useful life, it is desirable to make the heater bodies of the invention out of a solid solution of TiB_2 and CrB_2 consisting of 94% TiB_2 to 96% TiB_2, with the balance of CrB_2, with the solid solution of the two diborides sintered to a density of 4.2 to 4.3 gr./cc. or higher.

As an example, heater bodies of the invention consisting of 95.5% TiB_2 and 4.5% CrB_2, and having a density of 4.3 to 4.35 gr./cc. will, when heated to 1400° C. to 1500° C. in the vacuum enclosure of an aluminum-vapor sheet coating system, evaporate aluminum at the rate of 83 gr./cm.^{2}.

In contrast with heater bodies of the invention which decrease in density from the maximum value obtained with bodies consisting of 95% TiB_2 in solid solution with 5% CrB_2, as the proportion of TiB_2 is decreased to 93% or increased to 97%—the theoretical density of a body formed of the same ingredients increases in one direction only as the proportion of TiB_2 is decreased from 100% to lower values. As used herein, "theoretical density" means the density or specific weight in grams per cubic centimeter of a 100% solid body containing the same proportions of the same ingredients. The data given in Table 1 hereinafter and the curve of Fig. 4 show that in contrast with the humplike changes in the actual density of the critically proportioned body compositions of the invention, the theoretical density increases in the same direction as the TiB_2 constituent thereof is increased from 50% to 100%.

Desirable heater bodies of the invention consisting of a solid solution of 93% to 97% TiB_2 with 7% to 3% CrB_2, may be given a higher density by forming such bodies out of powder particles of these proportions of TiB_2 and CrB_2, having admixed thereto .1% to 2% of tungsten carbide, WC. As an example, a heater body of the invention, formed of powder particles consisting of 94% TiB_2 and 6% CrB_2 to which was added 1.70% tungsten carbide (based on total content), and sintered to maximum density of 4.74 gr./cc., when similarly heated to evaporate aluminum at the same rate, makes it possible to evaporate 1209 grams aluminum in a coat-

ing period 11½ hours long, before replacement with another heater body. Heater bodies of the invention containing small tungsten carbide additions may be formed by mixing the critical proportions of powder particles of titanium diboride and chromium diboride with .1% to 2% of powder particles of tungsten carbide, and thereafter sintering the heater body compact formed of such powder mixture to highest density. Heater bodies consisting of a solid solution of the above-specified critical proportions of TiB_2 and CrB_2 with an addition of .1% to 2% WC, will be sintered to the desired highest density at a lower sintering temperature than required for forming similar heater bodies without the tungsten carbide addition. As an example, whereas a heater body consisting of a solid solution of 94% TiB_2 and 6% CrB_2 is sintered to highest density of about 4.3 gr./cc. at 2130° C., a heater body wherein 1.72% WC has been added to the same content of TiB_2 and CrB_2, is sintered to the highest density of about 4.74 gr./cc. at the lower sintering temperature of about 1950° C. The .1% to 2% powder addition of tungsten carbide may be added to the above-specified critical proportions of powders of TiB_2 and CrB_2 before the powder mixture is subjected to ball-milling as specified below. Alternatively, the powder mixture of the specified critical proportions of TiB_2 and CrB_2 may be ball-milled with balls of tungsten carbide, and the ball-milling process is effective in adding to the specified powder content of TiB_2 and CrB_2 the desired addition of .1% to 2% tungsten carbide powder. Such tungsten carbide balls are usually formed by cementing tungsten carbide powder with a cementing addition of 6% to 10% of cobalt or nickel. As a result, the heater body of the invention formed with .1% to 2% of a powder addition of tungsten carbide from the tungsten carbide balls, may also contain an impurity of about .1% of the cementing cobalt or nickel metal. It is not known as yet whether the small amount of .1% to 2% of tungsten carbide is or is not in solid solution with the TiB_2 and CrB_2 content of the finally sintered high-density heater body. In such heater bodies of the invention, the .1% to 2% of tungsten carbide addition may be replaced with a .1% to 2% molybdenum carbide addition.

Expressed in another way, such heater bodies of the invention consist of a solid solution of about 93% to 97% TiB_2 and 7% to 3% CrB_2, having present therein about $\frac{1}{10}$ percent of a carbide of either tungsten, molybdenum or their mixture, with such carbide content increasing up to about 2% of the total body content, with such heater body consisting of a solid solution of about 93% to 97% TiB_2 and 7% to 3% CrB_2, and having present therein up to about 2% of such carbide addition.

There are commercially available powders of titanium diboride and chromium diboride of high purity, such as a purity of 99% or better, which are suitable for forming heater bodies of the invention. Such high-purity diboride powders may be produced by any known practically used methods. Thus, as an example, high-purity TiB_2 may be produced by the reduction of titanium dioxide TiO_2 with boron oxide and carbon under a hydrogen atmosphere as described, for instance, by H. Blumenthal et al. in "Powder Metallurgy Bulletin," of April 1956. High-purity CrB_2 may be prepared by the direct synthesis of a stoichiometrically proportioned mixture of powder particles of metallic chromium and amorphous boron heated under a hydrogen atmosphere. Commercially available powder particles of TiB_2 and CrB_2 have in general a particle size of about —100 mesh. Quantities of the two constituent diboride powders are weighed in the proper stoichiometric proportions and mixed or blended together by ball-milling until they are thoroughly mixed and reduced to an average particle size of 1 to 3 microns. Available sizing apparatus, such as supplied by Fisher Scientific Company of Pittsburgh, Pennsylvania, are suitable for measuring the particle size

of the final powder mixture of the two diboride ingredients. Good results are obtained by milling the mixture of the two constituent powders with stainless steel balls within a stainless steel ball-mill. To facilitate compacting of the final powder mixture, there is also admixed to the milled diboride powder constituents a small amount of a binder or lubricant such as 2% of a camphor or paraffine.

Good results are also obtained by ball-milling the mixture of the constituent TiB_2 and CrB_2 powders with balls of tungsten carbide consisting, for instance, of cemented tungsten carbide powder particles sintered with a cementing addition of 6% to 10% cobalt or nickel.

The critical superiority and contrast between bodies made of compositions of the invention compared to sintered bodies consisting solely of titanium diboride are illustrated by the contrast between Figs. 5–A and 6–A and Figs. 5–B and 6–B of two electrode bars, respectively, that of Figs. 5–A and 6–A being formed of the critical composition of the invention, and that of Figs. 5–B and 6–B being formed solely of titanium diboride—after the two electrode bars have operated in the same manner for a period of about thirty days while immersed in the cell bath of an electrolytic reduction cell such as shown in Fig. 3. The electrode bar of the invention, which was formed of 95% titanium diboride and 5% chromium diboride and sintered to a density of 4.50 gr./cc., remained fully intact throughout this period, carrying full operating current throughout the time. This electrode bar had a transverse rupture strength of about 61,200 pounds per square inch. The comparative macrographs, Fig. 5–A with Fig. 5–B, and Fig. 6–A with Fig. 6–B, illustrate the relative effects of bath constituents upon a composition body of my invention as compared to a body of titanium diboride only. The macrographs show that the electrode formed solely of titanium diboride is permeated with cracks through which the bath constituents infiltrate into its interior, whereas the electrode of the composition of my material is free of cracks and shows negligible or no infiltration of bath constituents. In the micrographs of Figs. 7 and 8, the black areas show the relative degrees of porosity of the two different electrode bodies. The relative strength levels of the two bodies further explain, at least in part, why the electrode formed solely of titanium diboride cracked in service, whereas the electrode body of my invention survived the operation in an operative, unbroken condition.

I have found that a material composition having a composition range of about 93% to 97% TiB_2 and 3% to 7% CrB_2 (see the critical hump portion of the curve of the chart of Fig. 4) has a density after cold-pressing and sintering in the order of a minimum of about 4.15 grams per cubic centimeter density, with a transverse rupture strength of about 61,200 pounds per square inch, and an electrical resistivity at room temperature in the order of about 31.5 microhm centimeters.

Fig. 3 illustrates diagrammatically and in a general way, an aluminum reduction cell operating with an electrode body formed of a critical composition of my invention. The cell has a steel outer shell **22**, an insulating layer **23** of alumina brick, for instance, and an inner protective carbonaceous liner **24**. Molten electrolyte **25** is positioned above the molten aluminum **26** that is being formed in the bottom adjacent to the cathodes **27**. An anode **29** projects downwardly into the molten bath. The cathode electrodes **27** are shown projecting vertically upwardly through the bottom of the cell **21**, with the upper ends of the cathode electrodes **27** projecting into and being submerged within the molten metal **26**. The cathode electrodes **27** may be connected electrically to a conventional bus bar **28**.

Table 1 sets forth the values used in plotting the graph of Fig. 4. It will be noted that the percent of theoretical

density has a sharp rise and reaches a peak with the 95% TiB_2 and 5% CrB_2 composition.

The data for the following table was obtained with samples of the different body compositions which were sintered at about 1930° C. for about 40 minutes under vacuum. Such composition bodies may be given a higher density by pre-sintering of the compacts at 1900° C. for a short time, such as 1 to 5 minutes, in an evacuated space of high vacuum corresponding to a pressure of less than a mercury column of 100 microns. As an example, a body consisting of 95% TiB_2 and 5% CrB_2 may be given a higher density of 4.50 grams/cc. with pre-sintering at such high vacuum.

TABLE 1

Weight Percent of TiB_2 to CrB_2 Composition	Actual Density	Approximate Theoretical Density	Actual Density as percentage of Theoretical Density
50/50	3.93	5.06	77.8
80/20	4.05	4.73	85.8
90/10	4.17	4.62	90.3
92/8	4.18	4.57	91.5
95/5	4.37	4.55	96.0 (Max.)
96/4	4.23	4.54	93.2
98/2	4.18	4.52	92.4
100/0	4.15	4.52	91.8

The composition of the invention, irrespective of the particular use to which a body of it is to be applied, may be prepared as explained above. Also, small additions of refractory metal carbides, such as of tungsten carbide and molybdenum carbide, in amounts up to a maximum of about 2% by weight may be employed without adversely affecting the novel and improved characteristics of the inventive composition. Its relatively high hardness with high strength makes it superior to a TiB_2 composition from the standpoint of its resistance to wear and erosion. It has a hardness in the order of 92 to 93.5 Rockwell A.

The powder mixture of the two diboride constituents with the 2% binder-lubricant content, is compacted into a compact within a die cavity corresponding to the desired shape of the elongated heater body. Good results are obtained by compacting the powder mixture within the die cavity with a pressure of 10 to 15 tons per square inch (t.p.s.i.). In practice, it has been found that increasing the compacting pressure above 10 t.p.s.i. does not yield a finally sintered heater body of greater density than attainable with a compacting pressure of 10 t.p.s.i. Compacts of the two constituent diboride powders which have been compacted with 10 to 15 t.p.s.i., undergo a linear shrinkage of approximately 13% to 14% when subjected to the subsequent sintering treatment. The dimensions of the compacting die cavity are proportioned to give an oversized powder compact which after undergoing shrinkage in the subsequent sintering treatment, will yield an elongated heater body of the desired dimensions and shape.

After removing the compact from the die, it is subjected to sintering in an oxygen-suppressing space, such as an evacuated space, at high temperatures at which at least some of the constituents of the compact form a liquid phase which fills the pores of the compact and densifies the same. Good results have been obtained with sintering temperatures of 2000° C. to 2150° C. and up to 2200° C. TiB_2 melts at higher temperatures, namely, between 2850° C. and 2950° C. under atmospheric pressure. By way of example, with a compact consisting of 95% TiB_2 and 5% CrB_2, a heater body of maximum density is obtained by sintering at temperatures from 2100° C. to 2130° C. With a powder compact containing 93% TiB_2 and 7% CrB_2, a heater body of maximum density is obtained by sintering at temperatures from 2000° C. to 2050° C. With a compact consisting of 97% TiB_2 and 3% CrB_2, a heater body of maximum density is obtained by sintering the compact at 2150° C. The iron picked up in the ball-milling treatment is vaporized in such sintering treatments. Heater bodies of the required high density are obtained by carrying on the sintering treatment in the manner described above, for about 40 minutes. Extending the sintering treatment for longer than about 40 minutes do not increase the density or otherwise improve the characteristics of the resulting heater body.

A distinct phase of the invention is the discovery that the critically proportioned diboride body compositions of the invention having the specified high density, may be produced by sintering a powder compact of its constituents at elevated temperatures in the range of only about 1925° C. to 1950° C. instead of the higher sintering temperatures of 2100° C. to 2130 C. heretofore believed to be essential for producing such bodies having the highest density. A further phase of the invention is the discovery that by sintering such critically-proportioned composition bodies of the invention at the lower elevated temperatures of 1925° C. to 1950° C., such sintered bodies of the invention have much finer grain structure and concomitant greater strength than a body of the invention which was sintered at 2100° C. to 2130° C. As an example, a powder compact composed of a mixture of powder particles consisting of 95% TiB_2 and 5% CrB_2, will be sintered into a body of highest density at temperatures in the range of about 1925° C. to 1950° C. in about 40 minutes, the resulting sintered body having a density of about 4.50 gr./cc. Bodies of compositions of the invention wherein the chromium diboride constituent is increased or decreased in the critical proportion range from 3% to 7% of CrB_2 may be similarly produced by sintering at temperatures of about 1925° C. to 1950° C. The lower sintering temperatures between 1925° C. and 1950° C. are also of great practical importance because they make it possible to use the required sintering furnaces for a much longer useful life. In contrast, sintered bodies consisting of TiB_2 only, have to be sintered at higher temperatures of 2100° C. to 2150° C., and the resulting sintered TiB_2 bodies have a lower order of relative density. This fact is shown graphically by a comparison of the photomicrographs of Figs. 7 and 8, wherein the black areas show pore spaces of the bodies.

Fig. 7 is a 200-diameter micrograph of a section of a body of the present invention. The pore spaces are indicated in black, and they have been measured as being equivalent to a porosity rating of about B–5, according to ASTM porosity standards in accordance with ASTM designation B–276–54. Fig. 8 is a 200-diameter micrograph of a section of a body of sintered titanium diboride. The large pore spaces indicated by the black areas have been measured as being greatly in excess of the high porosity rating of B–6 according to the same ASTM porosity standards.

A body formed of the composition of the invention is characterized by its excellent resistance to corrosion by the molten metal bath, has the ability of being sintered to a density approaching 100% of theoretical density at a sintering temperature that lies 150° C. to 200° C. lower than that of pure titanium diboride, and has a relatively low electrical resistance at room temperature in the neighborhood of 31.5 microhm centimeters and a substantially non-porous structure typified by ASTM porosity classification B–5. Bodies of the critical composition of the invention not only attain their best physical properties at a sintering temperature that is within a maximum of about 1950° C., but their unique high density makes it possible to use such bodies as electric heaters or as electrodes which are exposed to molten non-ferrous metal and/or their vapors at temperatures of up to about 1600° C. for a relatively long operating life.

Heater bodies of the invention made in the manner described above, have a sufficiently high density as to assure that molten aluminum held along their upper sur-

face when evaporizing aluminum, does not infiltrate into the pores of the interior of such heater bodies. Unless an aluminum vaporizing heater body has been sintered to the high density as given above, molten evaporized aluminum or other reactive metal which is evaporized, will infiltrate the interior pores of the lower-density heater body and be vaporized from all exterior surfaces of such body, thereby making it practically useless for vaporizing aluminum or similar reactive metal within a vacuum enclosure of a metal-vapor coating system.

When heater bodies of the invention are formed by combining the specified content of TiB_2 and CrB_2 with an addition of .1% to 2% of tungsten carbide or molybdenum carbide, the compacted mixture of the powder particle ingredients will form a liquid phase at a lower sintering temperature than in the case of heater bodies formed without such carbide addition. It is believed that the small tungsten carbide addition to the TiB_2 and CrB_2 content, causes the compact ingredients to form a liquid phase at a lower sintering temperature than in the absence of the small carbide addition.

Figs. 1 and 2 show by way of example one form of an electric heater arrangement for evaporation of aluminum within a vacuum enclosure of an aluminum vapor coating system operating with an electric heater body of the invention. Within a vacuum-tight housing or enclosure (not shown), which is maintained under vacuum, wherein a sheet of steel or like substrate is to be coated with aluminum vapor, there is held positioned an elongated electrically-heated heater body **10**, arranged so that its upper surface or face **11** underlies a moving portion of a substrate which is exposed to radiation from the heater body. The heater body **10** is shown held in proper position by two elongated supporting members **15** which may be of the same shape, and have upper supporting ends or holders **16** which engage and hold in position the opposite end portions **12** of the heater body **10**. The elongated upper face **11** of the heater body **10** which extends between its supported end portions **12**, has a relatively long and wide groove or depression **13** which holds a layer of liquid aluminum melted from an aluminum rod which is fed to the depression **13** for causing the molten aluminum along the upper heater face **11** to vaporize and become deposited on the irradiated, exposed, relatively large downwardly facing surface of the metal substrate moving past it.

The two supporting members **15** are of electrically conducting material, such as metal, and serve also as electric power supply connectors to the opposite ends **12** of the heater rod and supply it with electric from an electric power source **20** labeled "Electric Power," which heats the heater body **10** to a temperature of 1400° C. to 1500° C. at which it will evaporize the layer of liquid aluminum present on its upper heater face **11**. In the form shown, the support holders **16** have the shape of hollow collars with an opening in which the respective end portions **12** of the heater body are seated for making electric contact connection with the support holders **16**. To permit longitudinal expansion and contraction of the heater body **10** as it is heated from the normal low temperatures to its high operating temperature of 1400° C. to 1500° C., each support member **15** has a thin, flexible intermediate web **18** through which its heater holder **16** is connected to the wide mounting portion **17** of the supporting member **15**.

The web portions **18** are given such thickness, length, and width, as to cause them to flex when the heater body **10** expands from its shortest length at normal low temperatures to its maximum length when it is at a high aluminum-vaporizing temperature, and permitted to contract back to its normal low-temperature length, without imposing any substantial strains on the heater body **10**. Thus, in the arrangement shown, the mounting portions of the two heater supports **15** are insulatingly anchored on a proper insulating support while they are in a position in which their two heater-holders **16** are flexed inwardly on their flexible webs **18** to their nearest position corresponding to the shut-off, low-temperature shortest length of the heater body **10**. The flexible webs **18** of the two supports **15** permit the heater-holders **16** to move outwardly past the neutral position to their farthest separation position when the heater body **10** is heated from its low temperature to its operative high temperature and it expands to maximum length. When the heater is shut off, the flexible webs permit opposite movement of the heater-holders **16** without imposing any undue strains on the heater body **10**. The seat opening with the hollow heater-holder collars **16** may be given such size as to permit the contact end portions **12** of the heater body seated therein to slide therein as the heater body **10** expands when heated to the high temperature, and to contract when cooling, while maintaining sliding electric contact engagement along their relative sliding surfaces. With such arrangement, the web portions **18** of the two supports **15** need not be designed to permit their flexing under expansion and contraction of the heater **10**.

In order to assure long operative life for the heater body, it is desirable that when it is heated to its operative high temperature of 1400° C. to 1500° C., all portions of its body are maintained at substantially the same temperature. It is accordingly desirable that the end portions **12** at which the heater holders **16** make electrical contact therewith, shall likewise be maintained at the same high operating temperature as the other intermediate portions of the heater body **10**.

Below are given further examples of procedures for making heater bodies of the invention.

Example 1

Powder particles of 95.5% TiB_2 and 4.5% CrB_2 of +99% purity and −100 mesh average particle size, are ball-milled with stainless steel balls in a stainless steel ball-mill until there is obtained a blended mixture of the partices of the two diborides having 2 to 3 micron average particle size. To the so-blended and comminuted powders, is admixed a lubricant addition consisting of 2% paraffine dissolved in carbon tetrachloride, and the powder mixture containing the lubricant is stirred under a hood until the carbon tetrachloride content is evaporated and all powder particles are substantially homogeneously coated with the paraffine lubricant. The so-obtained fine blended powder is compacted with 10 t.p.s.i. in an oversize die cavity of a shape of the desired object, such as an elongated heater body for vaporizing aluminum, which yields after sintering, a compact of the desired size and shape, such as shown in Fig. 2. The so-obtained compact is then sintered for 40 minutes in a furnace under an atmosphere of pure dry hydrogen at a temperature of about 2130° C. The so-obtained sintered heater body consists of a solid solution of all its titanium diboride and chromium diboride content, and it has a density of about 4.35 gr./cc., and an electric resistivity of 48 microhm-cm. Such heater body, when electrically heated in an enclosure of a vapor-coating system with its stop face facing a substrate moving past it, is effective in continuously evaporizing aluminum from a layer of molten aluminum continuously formed in its top face groove and operates for a continuous prolonged time in causing vapor of aluminum to be deposited as an adhering, continuous, dense coating on a continuously moving substrate under vacuum on the order of a micron of mercury. The theoretical density of a similar 100% solid body is 4.54 gr./cc.

Example 2

Powder particles of 95% TiB_2 and 5% CrB_2 of +99% purity and −100 mesh average particle size, are ball milled with stainless steel balls in a stainless steel ball-mill until there is obtained a blended mixture of particles of the two diborides having 2 to 3 micron average parti-

cle size. To the so-blended and comminuted powder mixture, is admixed a lubricant addition consisting of 2% of camphor dissolved in ether, and the powder mixture containing the lubricant is stirred under a hood until the ether content is evaporated and the powder particles are substantially uniformly coated with the camphor lubricant. The so-obtained fine blended powder is compacted with 10 t.p.s.i. in an oversize die cavity which yields after sintering a compact of the desired size and shape. The so-obtained compact is then sintered for 40 minutes in a furnace under an atmosphere of pure dry hydrogen at a temperature of about 2100° C. to 2130° C. The resulting sintered heater body consists of a solid solution of all its titanium diboride and chromium diboride content, and it has a density of about 4.42 gr./cc., and the electric resistivity of 62 microhm-cm. Such heater body when electrically heated in an enclosure of a vapor-coating system with its top face facing a substrate moving past it, is effective in continuously evaporizing aluminum from a layer of molten aluminum continuously formed in its top face groove, and operates for a continuous prolonged time in causing vapor of aluminum to be deposited as an adhering, dense coating on a continuously moving substrate under vacuum on the order of one micron of mercury. The theoretical density of a similar 100% solid body is 4.55 gr./cc.

Example 3

Powder particles of 96% TiB_2 and 4% CrB_2, together with tungsten carbide powder particles forming 1.72% by weight of the total powder content, all of +99% purity and −100 mesh average particle size, are ball-milled with stainless steel balls in a stainless steel ball-mill until there is obtained a blended mixture of particles of the two diborides having 2 to 3 micron average particle size. To the so-blended and comminuted powder mixture, is admixed a lubricant addition consisting of 2% of camphor dissolved in ether, and the powder mixture containing the lubricant is stirred under a hood until the ether content is evaporated and the powder particles are substantially uniformly coated with the camphor lubricant. The so-obtained fine blended powder is compacted with 10 t.p.s.i. in an oversize die cavity which yields after sintering a compact of the desired size and shape. The so-obtained compact is then sintered for 40 minutes in a furnace under an atmosphere of pure dry hydrogen at a temperature of about 2130° C. The resulting sintered heater body consists of a solid solution of all its titanium diboride and chromium diboride content and containing in addition about 1.7% WC based on total content, and it has a density of 4.74 gr./cc. and electric resistivity of 37 microhm-cm. Such heater body when electrically heated in an enclosure of a vapor-coating system with its top face facing a substrate moving past it, is effective in continuously evaporizing aluminum from a layer of molten aluminum continuously formed in its top face groove, and operates for a continuous prolonged time in causing vapor of aluminum to be deposited as an adhering, dense coating on a continuously moving substrate under vacuum on the order of one micron of mercury. The theoretical density of a similar 100% solid body is 4.54 gr./cc.

Example 4

Powder particles of 93% TiB_2 and 7% CrB_2 of +99% purity and −100 mesh average particle size, are ball-milled as in Examples 1 and 2, until there is obtained a blended diboride particle mixture having 2 to 3 micron average particle size. To the so-blended and comminuted powders is admixed a lubricant addition consisting of 2% paraffine dissolved in carbon tetrachloride, and the powder mixture containing the lubricant is stirred under a hood until the carbon tetrachloride content is evaporated and all powder particles are substantially uniformly coated with the paraffine lubricant. The fine blended powder is compacted with 10 t.p.s.i., as in Examples 1 and 2, and the compact is then sintered for 40 minutes in a furnace under an atmosphere of pure dry hydrogen at a temperature of about 2000–2050° C. The so-obtained sintered heater body consists of a solid solution of all its titanium diboride and chromium diboride content, and it has a density of about 4.15 to 4.25 gr./cc. Such heater body when electrically heated in an enclosure of a vapor-coating system with its top face facing a substrate moving past it, is effective in continuously evaporizing aluminum from a layer of molten aluminum continuously formed in its top face groove, and operates for a continuous prolonged time for causing vapor of aluminum to be deposited as an adhering, continuous, dense coating on a continuously moving substrate under vacuum on the order of a micron of mercury. The theoretical density of a similar 100% solid body is 4.56 gr./cc.

Example 5

Powder particles of 97% TiB_2 and 3% CrB_2 of +99% purity and −100 mesh average particle size, are ball-milled as in Examples 1 and 2, until there is obtained a blended diboride particle mixture having 2 to 3 micron average particle size. To the so-blended and comminuted powders is admixed a lubricant addition consisting of 2% paraffine dissolved in carbon tetrachloride, and the powder mixture containing the lubricant is stirred under a hood until the carbon tetrachloride content is evaporated and all powder particles are substantially uniformly coated with the paraffine lubricant. The fine blended power is compacted with 10 t.p.s.i. as in Examples 1 and 2, and the compact is then sintered for 40 minutes in a furnace under an atmosphere of pure dry hydrogen at a temperature of about 2150° C. to 2160° C. The so-obtained sintered heater body consists of a solid solution of all its titanium diboride and chromium diboride content, and it has a density of about 4.15 to 4.25 gr./cc. Such heater body when electrically heated in an enclosure of a vapor-coating system with its top face facing a substrate moving past it, is effective in continuously evaporizing aluminum from a layer of molten aluminum continuously formed in its top face groove, and operates for a continuous long time for causing vapor of aluminum to be deposited as an adhering, continuous, dense coating on a continuously moving substrate under vacuum on the order of a micron of mercury. The theoretical density of a similar 100% solid body is 4.52 gr./cc.

Example 6

A heater body is made of a powder mixture of 96% TiB_2 and 4% CrB_2 and treated as in Example 3, except for ball-milling with balls of tungsten carbide cemented with 6% Co, and sintering at 1950° C. The resulting heater body consisted of a solid solution of 96% TiB_2 and 4% CrB_2 and contained 1.7% WC based on the total content. It had a density of about 4.74 gr./cc., and was otherwise similar to the heater body of Example 3.

Example 7

A heater body is made with a powder mixture of 95.5% TiB_2 and 4.5% CrB_2, together with 1.7% tungsten carbide (based on total content) and treated as in Example 6, with sintering at 1930° C. to 1950° C. The resulting heater body consisted of a solid solution of its diboride ingredients and contained about 1.7% WC. It had a density of 4.74 gr./cc. and was otherwise similar to the heater of Example 3.

Example 8

A heater body is made with a powder mixture of 95% TiB_2 and 5% CrB_2 together with 1.7% tungsten carbide (based on total content), and treated as in Example 6, with sintering at 1910° C. to 1950° C. The resulting heater body consisted of a solid solution of its diboride

ingredients and contained about 1.7% WC. It had a density of about 4.75 gr./cc., and was otherwise similar to the heater of Example 3.

Without thereby limiting the scope of the invention, there are given below further details of a practical long-life heater body of the type described above in connection with the foregoing examples. Such heater body had the following dimensions:

Length ---------- 3½" to 6"
Transverse width of top face **11** ---------- ½" to ¾"
Height ---------- 5/16" to ½"
Length of end portion engaged by the contact surfaces of the support holder **16** ---------- ½" to 1"
The top groove **13** extended over a major width of the top face **11**, and its side walls had a thickness of 5/32" to ¼".

There will now be described comparative results obtained with heater bodies of the invention consisting of 93% to 97% TiB_2 and 7% to 3% CrB_2 in comparison with bodies made with similar compositions containing smaller and larger amounts of TiB_2. In practical tests, it was found that when aluminum is continuously passed under vacuum through a heater body such as heater body **10** of the type described in connection with Figs. 1 and 2, the molten aluminum that is being passed through the heater body subjects the heater body to a strong corrosive action. When aluminum is fed to the depression **13** of a vaporizing heater such as heater **10** described above in connection with Figs. 1 and 2, it has been found that if such heater is made of a material other than the specified compositions of the invention, the molten aluminum will rapidly corrode the known prior heater bodies used in an aluminum-vaporizing and coating system. With such prior heaters, it has been found that even before the corrosion has progressed to a substantial degree, the molten and vaporized aluminum penetrates and infiltrates the interior of the heater body, and it evaporates not only from the top surface of the heater body but also from its bottom surface and from its side surfaces. In such aluminum-vapor coating system, a heater body which starts to evaporate the aluminum not only from its top surface but also from other exposed surfaces thereof, is considered inoperative and cannot be used in a practical aluminum vapor coating system, because most of the vaporized aluminum is lost and not deposited on the sub-strata of the material that is to be coated. The amount of aluminum in grams which has been evaporated from one square centimeter of the surface of a heater body of an aluminum vapor coating system before excessive penetration or infiltration of aluminum into the interior of the heater sets in, has been adopted in practice as a measure of the usefulness of such heater bodies.

The great effectiveness of heater bodies of the invention consisting of a solid solution of 97% to 93% TiB_2 and 3% to 7% CrB_2 in the specified critical range of proportions, in contrast with the low effectiveness of heater bodies containing the same ingredients in proportions outside the specified critical range of ingredients, is illustrated in the table below:

Composition of Heater Body	Ratio of TiB_2/CrB_2	Aluminum Evaporated, g./cm²
TiB_2/CrB_2	90/10	11.5
TiB_2/CrB_2	95/5	87.6
TiB_2/CrB_2	98/2	9.5

Tests with heater elements of pure TiB_2 and pure ZrB_2 show that the vaporized aluminum starts to infiltrate the interior of such heater bodies from the very beginning of the aluminum vaporizing operation, making them useless for practical use. With the best prior heater bodies tested in aluminum-vaporizing systems and consisting of carbon enclosed in a protective coating, such as described in the patents referred to above, the vaporized aluminum penetrates the interior of the heater body before vaporizing 8.4 grams of aluminum per centimeter square of the vaporizing surface, making such heaters likewise useless for practical use.

In the heater bodies of the invention described above, it was possible to give them the desired high density as described hereinabove for the specified critical range of proportions of their different ingredients, by using for their production on a commercial basis the process of compacting the powder mixtures of the ingredients followed by subsequent sintering under a protective atmosphere until the desired high density is obtained. However, such heater bodies could be given somewhat higher densities by subjecting them to an additional special hot-press treatment. Such hot-press treatment may consist of placing such heater body of the invention within a die cavity of heat-conducting material, such as graphite, which will withstand heating to high hot-pressing temperatures such as 2000° C., and subjecting the heater body to pressure while it is being so heated.

In the foregoing examples, the sintering of the compacts was effected under oxidation-suppressing conditions by carrying on the sintering operation under a hydrogen atmosphere. However, satisfactory sintering of bodies of the invention could also be effected under vacuum equivalent to a residual pressure corresponding to 20×10^{-3} millimeter of a mercury column.

Bodies of sintered refractory powder particles of the invention of the type described above, which consist essentially of 93% to 97% TiB_2 and 7% to 3% CrB_2, and which have a density of at least 4.15 grams per cubic centimeter, are of great value in various applications other than as metal-vaporizing heater bodies. Among applications in which bodies or body layers of such sintered refractory particles of the critically proportioned compositions of the invention are of great practical value, are crucibles, or the inner body layers of crucibles, used for melting aluminum, copper, magnesium and like reactive metals; pumps, valves, conduits and like confining structures for pumping, holding and controlling the flow of such reactive molten metals; protective tubes or enclosures for thermocouples used in measuring the temperature of molten reactive metals; atomizing nozzles for discharging corrosive fluids such as liquid or vaporized aluminum and other reactive metals; heater bodies for the sublimation of metals, for instance of chromium metal, into vapor under vacuum for depositing the vapor on objects to be coated; electrodes used in electrolytic cells for reduction of aluminum oxides to aluminum or for reduction of other metal oxides to pure metal; and other applications requiring a solid body or solid body layer which when exposed at elevated temperatures to corrosive fluids, will suppress corrosion and the infiltration of the interior of the body by such corrosive fluids, and retain its desired shape and surface for a desired prolonged operating period. Such other applications wherein bodies of the critically proportioned composition of the invention are of value, include, by way of example, bath level probes for molten metal baths having temperatures in the order of up to about 1600° C.; pouring orifices and control plugs, such as used in continuous casting operations for non-ferrous metals; mold components in continuous casting installations; transfer troughs to transfer molten non-ferrous metal, such as aluminum and its alloys, from melting or holding furnaces to a casting station in a casting installation; pulleys and sheaves as well as bearings and shafts that are submerged within a molten bath of a non-ferrous metal or alloy such as in a bath for coating steel wire, ribbon and sheet metal, as described, for example, in Brick U.S. Patent 2,926,103. It is also of great value to use bodies of the critically proportioned compositions of the invention in applications such as current conductors in electrolytic reduction cells, such as de-

scribed, for instance, in Lewis U.S. Patent 2,915,442 and Ransley's British Patent 784,695, published October 16, 1957.

In such heretofore known electrolytic reduction cells, for instance as used generally in pot lines of the primary aluminum industry, the reduction cell may consist of a steel shell the interior of which is lined with a heavy layer of carbonaceous material which serves as the cathode. Into a series of holes formed in the lower portions of the two major side walls of the cell are inserted ferrous collector bars that may be approximately three inches in diameter and several feet in length. The collector bars are connected in parallel to bus bars of the cathodic part of the cell, and carry current of about 1000 amperes flowing from the anode and the fused salt bath of the cell, the current passing through the carbonaceous liner and being carried away by the ferrous collector bars. As heretofore used, the ferrous collector bars extend horizontally into the cell, but do not penetrate into and are not exposed to the molten cell bath, but are imbedded within a carbonaceous cell liner. In other words, the interior parts of the ferrous collector bars lie several inches behind the interior surfaces of and are embedded in the carbonaceous cell liner that is exposed to the molten cell bath. Such carbonaceous liner protection for the ferrous collector bars was necessary because molten aluminum in the cell operating at a temperature of about 950° C. to 1050° C. or higher, subjects the steel and cast iron of the ferrous collector bars to highly corrosive action. To minimize this corrosive action, the working portions of the ferrous collector bars must be embedded in and protected by the carbonaceous material that is more resistant to the corrosive action of molten aluminum, cryolite, molten alumina, and the decomposition products of cryolite that are present in the fused salt bath of the reduction cell.

During the operation of such a reduction cell, the bath constituents tend to erode and infiltrate the interior of its carbonaceous liner. The infiltrating compositions of the bath, including molten aluminum, tend to react with the carbonaceous liner in situ, inside the pores of the carbonaceous material, to form aluminum carbide and other reaction products which have relatively high electrical resistivity. Because of the higher electrical resistivity of the aluminum-carbide formations, and other reaction products, the resistance of the cathodic part of the cell is increased, resulting in an increased voltage drop from the bath to the ferrous collector bars, and the concomitant electrical generation of heat. Since the cell circuit consumes a large amount of electric power, the increasing cathode losses present a large waste over the life of a cell, and has constituted a major problem in the operation of aluminum smelting pot lines or electrolytic reduction cells.

To meet this problem, Lewis U.S. Patent 2,915,442 proposed that diborides of titanium and zirconium should be used as the collector bars of an electrolytic reduction cell. Although when immersed in a bath of molten cryolite and alumina, an electrode bar consisting solely of titanium diboride or zirconium diboride exhibits a certain resistance to such bath constituents, it was found that the interior of such electrode bars becomes infiltrated with the molten constituents and that the so-immersed electrode bars break and fail within a relatively short time. This failure of electrode bars consisting only of titanium diboride or zirconium diboride, after a short period of immersion in the molten bath of an aluminum reduction cell, is believed to be caused by their high porosity (low density) and their concomitant mechanical weakness, and the fact that their interior pores are readily infiltrated by the corrosive constituents of the molten cell bath.

In sharp contrast with electrode bars consisting solely of titanium diboride or zirconium diboride, electrode bars formed with the critically proportioned body compositions of the invention, have a high density approaching 100% of the theoretical density, and they have long useful operating life while immersed in the molten bath of an aluminum reduction cell. This contrast is illustrated by the macrographs of Figs. 5–A and 5–B, and Figs. 6–A and 6–B, of two electrode bars—one formed of the critically proportioned composition of the invention, the other formed solely of titanium diboride, respectively—after the two electrode bars have been subjected to identical operating conditions immersed in the bath of an aluminum reduction cell for about thirty days. Each of the two different bars of these figures was produced with the same care and controls. The electrode bar that was formed solely of titanium diboride, and shown in Figs. 5–B, 6–B, was prepared by cold-pressing, followed by sintering at about 2130° C. In its sintered condition it had a density of 4.15 gr./cc., and a transverse rupture strength of about 27,600 pounds per square inch. It had a porosity rating greatly in excess of ASTM classification B–6. The so-produced electrode bar is representative of the best quality of titanium diboride bodies produced by cold-pressing and sintering, without intentional or unintentional addition of binder substances, such as by pick-up of other constituents in processing. The production of bodies formed solely of titanium diboride requires a sintering temperature of approximately 150° C. to 200° higher than in the production of bodies formed of the critically proportioned compositions of the present invention. Since bodies formed solely of titanium diboride require a higher sintering temperature, the life of a sintering furnace that has to be operated at the higher temperatures in the order of 2100° C. to 2150° C. for a TiB_2 body, is materially shortened, as compared to furnaces operating with a sintering temperature in the order of 1925° C. for producing bodies of the invention.

Furthermore, the relatively high degree of residual porosity of such sintered titanium diboride body limits its mechanical strength, and makes it readily vulnerable to infiltration by constituents of the molten bath in which it is submerged.

Figs. 5–A, 6–A, and Figs. 5–B, 6–B, are macrographs of two electrode bars 27, of the two different compositions, respectively, which operated in upright position in an aluminum electrolytic reduction cell, as indicated in Fig. 3, wherein each respective electrode bar 27 projected about 3 inches into the molten aluminum 26 in the bottom of cell 21, and was thus operated for thirty days in reducing aluminum. Figs. 5–A and 5–B are macrographs of cross-sectional slices taken on each thus-used different electrode bar, respectively, at locations about 1 inch below the projecting top of the respective bar, to show corrosion and the general condition of each, the electrode bars of Figs. 5–A and 6–A being formed of the critical composition content of my invention, and the electrode bars of Figs. 5–B and 6–B being formed solely of TiB_2 and corresponding to the electrode bars of Ransley British Patent No. 802,905 of October 15, 1958, and Lewis U.S. Patent No. 2,915,442. Figs. 6–A and 6–B are macrographs of the same two different electrode bars, respectively, before being sliced, each electrode bar 27 standing on the end surface which projected into the reduction cell of Fig. 3. In contrast with Figs. 5–A and 6–A, which show the good operating condition of the electrode bar of the invention, Figs. 5–B and 6–B show that the electrode formed solely of titanium diboride has multiple cracks and severe corrosion. Since this electrode had relatively high porosity, it was infiltrated with the constituents of the molten cell bath not only through the cracks but also through its pores.

The high density of sintered, critically-proportioned compositions of the invention consisting essentially of 93% to 97% titanium diboride and 7% to 3% CrB_2, makes them of great value not only as metal vaporizing heaters and electrodes in high-temperature electrolytic cells, such as aluminum reduction cells, but also in the various other applications requiring a solid body or layer

which when exposed at elevated temperatures to corrosive fluids, will suppress infiltration and corrosion of the interior of the body, and which will retain its shape and operating characteristics for a desired long period. In addition, bodies of the compositions of the invention, being sintered at temperatures of about 1925° C. to 1950° C., have a much finer grain than similar bodies which have been sintered at higher temperatures of about 2100° C. to 2150° C.

For purposes of disclosure, the contents of my co-pending application Serial No. 775,258, filed November 20, 1958, are hereby made part hereof.

It will be apparent to those skilled in the art that the novel principles of the invention disclosed herein in connection with specific exemplifications thereof, will suggest various other modifications and applications of the same. It is accordingly desired that in construing the breadth of the appended claims they shall not be limited to the specific exemplifications of the invention described above.

I claim:

1. In an electrical heater for heating and vaporizing metal fed thereto, an elongated heater body having terminal end portions for passing electric heating current therethrough, and heating said body to at least 1300° C. and thereby vaporizing metal fed thereto, at least about 97% of said body consisting essentially of a solid solution of 93% to 97% of titanium diboride with 7% to 3% of chromium diboride, said body having a density of at least 4.15 grams per cubic centimeter, the density of said body decreasing from a maximum density to a lower density as the proportion of the chromium diboride constituent of said body is decreased and increased from a value intermediate the above-specified range of proportions of chromium diboride in said body.

2. In an electrical heater for heating and vaporizing metal fed thereto, an elongated heater body having terminal end portions for passing electric heating current therethrough, and heating said body to at least 1300° C. and thereby vaporizing metal fed thereto, at least about 97% of said body consisting essentially of a solid solution of 94% to 96% titanium diboride and 6% to 4% chromium diboride, said body having a density of at least 4.15 grams per cubic centimeter, the density of said body decreasing from a maximum density to a lower density as the proportion of the chromium diboride constituent of said body is decreased and increased from a value intermediate the above-specified range of proportions of chromium diboride in said body.

3. In an electrical heater for heating and vaporizing metal fed thereto, an elongated heater body having terminal end portions for passing electric heating current therethrough, and heating said body to at least 1300° C. and thereby vaporizing metal fed thereto, said body consisting essentially of a solid solution of 93% to 97% titanium diboride with 7% to 3% chromium diboride, and having a density of at least 4.15 grams per cubic centimeter, the density of said body decreasing from a maximum density to a lower density as the proportion of the chrominum diboride constituent of said body is decreased and increased from a value intermediate the above-specified range of proportions of chromium diboride in said body.

4. In an electrical heater for heating and vaporizing metal fed thereto, an elongated heater body having terminal end portions for passing electric heating current therethrough, and heating said body to at least 1300° C. and thereby vaporizing metal fed thereto, said body consisting essentially of a solid solution of 93% to 97% titanium diboride with 7% to 3% chromium diboride, and having present therein about 0.1% to 2% of at least one carbide selected from the group consisting of the carbides of tungsten and molybdenum based on the total weight of the body, said body having a density of at least 4.15 grams per cubic centimeter, the density of said body decreasing from a maximum density to a lower density as the proportion of the chromium diboride constituent of said body is decreased and increased from a value intermediate the above-specified range of proportions of chromium diboride in said body.

5. In an electrical heater for heating and vaporizing metal fed thereto, an elongated heater body having terminal end portions for passing electric heating current therethrough, and heating said body to at least 1300° C. and thereby vaporizing metal fed thereto, said body consisting essentially of a solid solution of 94% to 96% titanium diboride and 6% to 4% chromium diboride, and having present therein about 0.1% to 2% of at least one carbide selected from the group consisting of the carbides of tungsten and molybdenum based on the total weight of the body, said body having a density of at least 4.15 grams per cubic centimeter, the density of said body decreasing from a maximum density to a lower density as the proportion of the chromium diboride constituent of said body is decreased and increased from a value intermediate the above-specified range of proportions of chromium diboride in said body.

6. A solid body of sintered refractory particles having an exterior surface adapted to be exposed to corrosive fluids at high temperatures, said body consisting essentially of a solid solution of 93% to 97% titanium diboride and 7% to 3% of chromium diboride, said body having a density of at least 4.15 grams per cubic centimeter, which density is high enough to cause said body to suppress infiltration of its interior with metal vaporized along its exterior surfaces while said body is heated during prolonged operation to a temperature of at least 1300° C. and vaporizing metal is fed thereto, the density of said body decreasing from a maximum density to a lower density as the chromium diboride constituent of said body is decreased and increased from a value intermediate the above-specified range of proportions of chromium diboride in said body.

7. A solid body as claimed in claim 6, constituting a current-conducting element which is at least in part exposed to molten reactive metals selected from the group consisting of aluminum, magnesium, copper, and alloys of these metals.

8. A solid body as claimed in claim 6, constituting a current-conducting element which is at least in part exposed to molten reactive metals consisting principally of aluminum.

9. A solid body of sintered particles consisting essentially of a solid solution of 93% to 97% titanium diboride and 7% to 3% of chromium diboride, said body having been sintered to a density approaching the theoretical density of the composition, the density of said body decreasing from a maximum density to a lower density as the chromium diboride constituent of said body is decreased and increased from an intermediate value of the above-specified range of chromium diboride in said body.

10. A solid body as claimed in claim 9, containing in addition up to about 2% of at least one carbide selected from the group consisting of the carbides of tungsten and molybdenum based on the total weight of said body.

11. A solid body of sintered particles consisting essentially of a solid solution of 93% to 97% titanium diboride and 7% to 3% of chromium diboride, said body having been sintered to a density approaching the theoretical density of the composition, the density of said body decreasing from a maximum density to a lower density as the chromium diboride constituent of said body is decreased and increased from an intermediate value of the above-specified range of chromium diboride in said body, said body having been sintered at a sintering temperature of at most about 1950° C. and exhibiting a finer grain structure than a body of the same composition sintered at temperatures above 2000° C., said body having a transverse rupture strength of at least about

61,200 pounds per square inch and a density of at least about 4.15 grams per cubic centimeter.

12. A solid body as claimed in claim 9, having a density of at least about 4.15 grams per cubic centimeter and constituting an electric conductor which is at least in part exposed to an environment of molten nonferrous metal.

13. A solid body as claimed in claim 9, and constituting an electrically conductive cathode conductor having an end region projecting into molten aluminum of an electrolytic cell.

14. A solid body as claimed in claim 6, consisting essentially of a solid solution of 94% to 96% titanium diboride and 6% to 4% of chromium diboride.

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