June 22, 1954 G. E. COMSTOCK, 3RD 2,681,944

ELECTRICAL RESISTANCE

Filed Jan. 15, 1952 2 Sheets-Sheet 1

Fig. 1

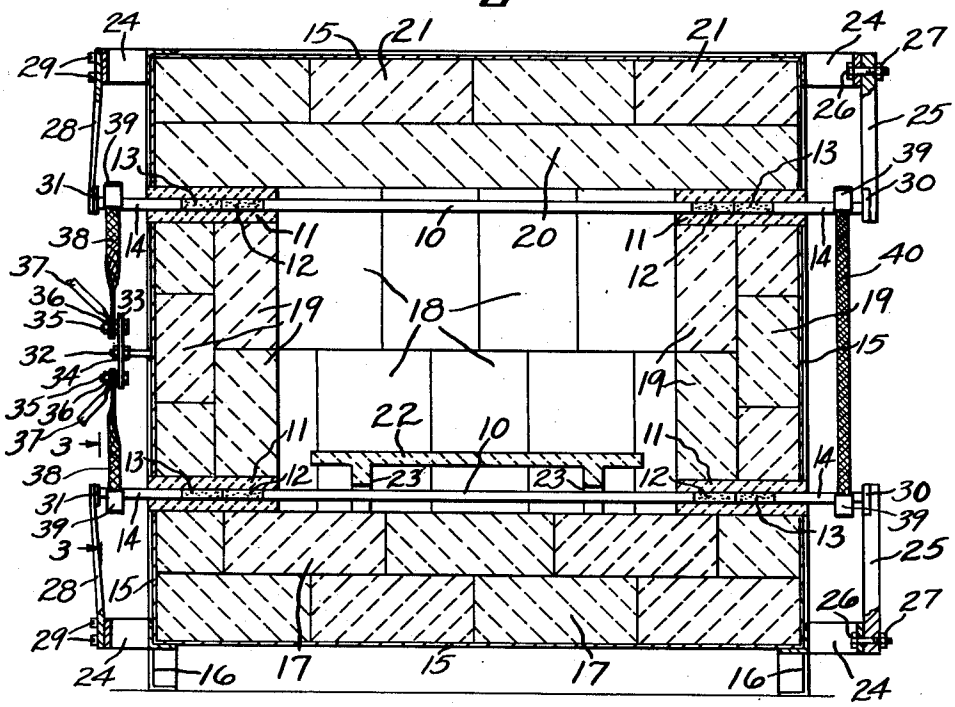


Fig. 2

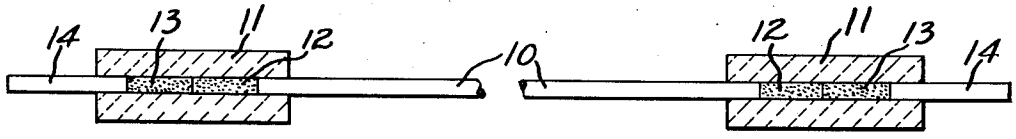
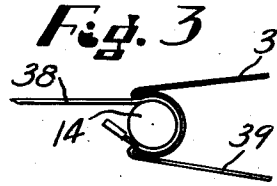


Fig. 3



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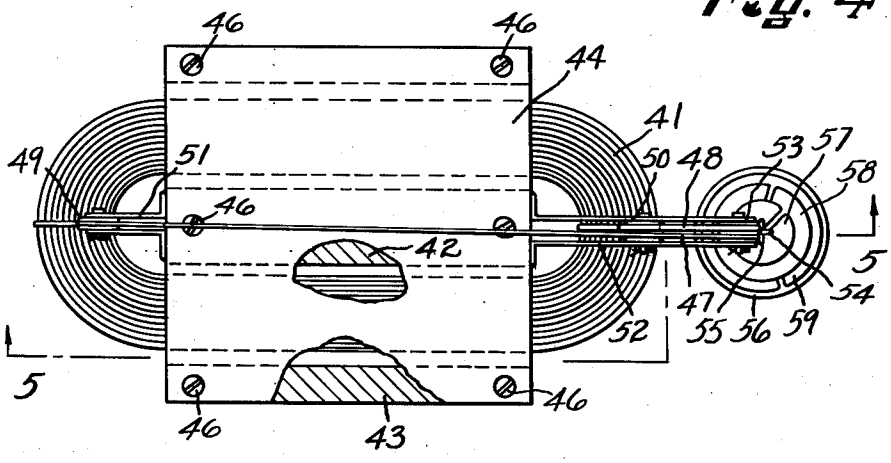
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June 22, 1954 G. E. COMSTOCK, 3RD 2,681,944

ELECTRICAL RESISTANCE

Filed Jan. 15, 1952 2 Sheets-Sheet 2

Fig. 4



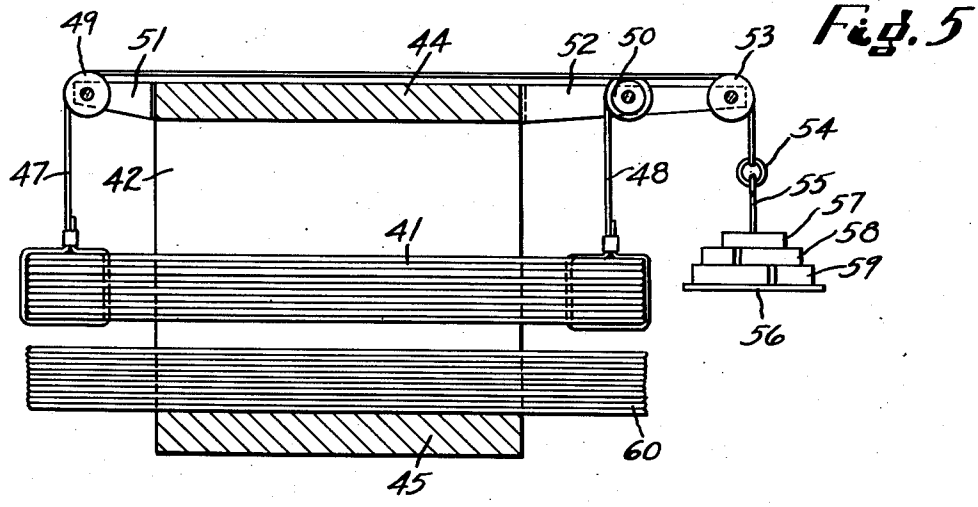


Fig. 5

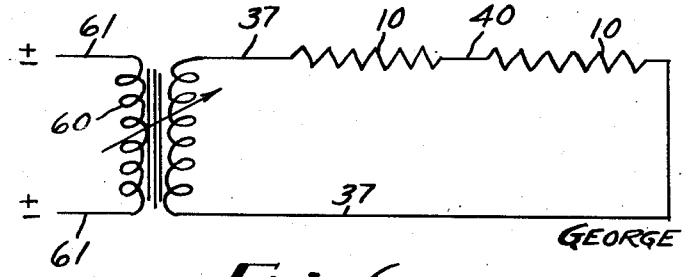


Fig. 6

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ELECTRICAL RESISTANCE

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9 Claims. (Cl. 13—25)

1

The invention relates to electrical resistances especially for heating furnaces.

One object of the invention is to provide a heating resistance capable of use at high temperatures in an oxidizing atmosphere. Another object is to provide a cold end construction for zirconia resistors greatly increasing their effectiveness. Another object is to provide a practical combination of electric transformer and zirconia resistor so that the refractoriness and resistance to oxidation of this material can be taken advantage of while avoiding detriment from the fact that it has a negative temperature coefficient of resistance.

Another object of the invention is to provide an electrical heating resistance that can be operated at very high temperatures and which has a life expectancy substantially not limited by chemical reactions between the atmosphere and the resistance.

Other objects will be in part obvious or in part pointed out hereinafter.

In the accompanying drawings illustrating one of many possible embodiments of the mechanical and electrical features of this invention:

Figure 1 is a vertical sectional view of a furnace having electrical resistances according to the invention,

Figure 2 is an elevation of an electrical resistance unit according to the invention, certain sleeves being shown in section,

Figure 3 is a fragmentary view on an enlarged scale taken on the line 3—3 of Figure 1,

Figure 4 is a plan view of a transformer,

Figure 5 is a sectional view of the transformer taken on the line 5—5 of Figure 4.

Figure 6 is a wiring diagram.

The resistance unit, which may also be called a resistor, has terminals of some refractory oxidation resistant metal such as nickel, stainless steel, or the well-known nickel-chromium alloy one variety of which is 60 Ni, 24 Fe, 16 Cr and 0.1 C. The outer ends of these terminals will be cold enough so that they can be in contact with copper or aluminum conductors or with spring metal clips or the like in order to connect the resistor in circuit. In order to protect the inner ends of these metal terminals from the intense heat liberated by the zirconia resistor rod in which most of the voltage drop occurs I provide cold ends connecting the zirconia resistor rod with the metal terminals which are refractory enough to withstand the heat liberated by the zirconia resistor rod and are conductive enough so that they will not overheat by reason of the heat liberated due

2

to the voltage drop therein, and preferably I utilize two oxide materials, one in contact with the zirconia resistor rod and the other in contact with the metal terminals. For the former or inner of these materials I use oxide selected from the group consisting of thorium dioxide, ThO_2, ceric oxide, CeO_2 and mixtures thereof and zinc oxide, ZnO, while for the latter or outer of these materials I use zinc oxide, ZnO; hence in one embodiment of the invention both materials are ZnO. In order to keep the oxide or oxides from fracturing I use it or them in powder form and hold it or them in place with refractory sleeves, preferably zirconia sleeves. Doubtless in the course of use the powder sinters somewhat but that is of no consequence as it works equally well as powder or sintered material and if, once having sintered, it later fractures, that is of no consequence either; I provide spring pressure to hold the rods against the oxide. In a preferred form of the invention I place discrete portions of thorium dioxide powder and zinc oxide powder in the sleeves, the former in contact with the zirconia resistors, the latter in contact with the metal rods. Thus I achieve a successive step down from the high temperature of the zirconia rods, to the very refractory thoria (thorium dioxide) to the less refractory zinc oxide to the metal terminal rods which, of course, are subject to oxidation but whose resistivity is so low they are heated practically only by conduction and their ends exposed to the atmosphere are at such low temperatures that they can be used for years without deterioration.

Another feature of the invention is the use of a constant current transformer of simple design so that the negative temperature coefficient of the zirconia resistors is no detriment at all. However a ballasting resistance or a servo-controlled motor driven variable transformer can be substituted for the simple constant current transformer in certain embodiments of the invention.

Referring now to Figures 1 and 2, I provide rods or bars 10 of sintered zirconia, that is to say made by pressing and sintering (either simultaneously or not) comminuted zirconia without any significant amount of binder except temporary binder. If desired a mass of zirconia particles mixed with a little temporary binder such as a solution of dextrine can be placed in a rubber mold having an elongated cylindrical molding space and the mass can be pressed by hydraulic pressure in a manner now well known in the art. Subsequently the pressed rods can be fired to sinter the zirconia particles together in a manner also well

known in the art. While I can use zirconia relatively free from impurities or addition agents I prefer to use the stabilized zirconia containing from 3% to 6% lime which is fully described in U. S. Letters Patent No. 2,535,526 granted on application of Ballard and Marshall December 26, 1950. This is because zirconia stabilized with lime as described in this patent does not have the abnormal and eccentric expansion behavior of unstabilized zirconia. Stabilized zirconia described in the aforesaid patent is predominantly cubic in crystalline structure whereas unstabilized zirconia having no lime or other stabilizing agent is predominantly of monoclinic crystal structure. I intend to include any content of hafnia under the designation zirconia because hafnia is so similar to zirconia in its chemical and physical properties as to be substantially indistinguishable therefrom except by X-ray analysis and because available zirconia ores contain a minor percentage of hafnia which, for most purposes including the manufacture of resistors, is not separated from the zirconia. Indeed it would be very expensive and highly impractical to try to remove the content of hafnia from the zirconia ore or from the purified zirconia obtained therefrom. Since hafnia is chemically so much like zirconia there is not a great deal of data on how much hafnia to expect in a given lot of zirconia or ore but it is known that the hafnia is always in minor proportion. So far as this invention is concerned the hafnia might as well be zirconia and it is not to be considered to be an impurity. Hafnia likewise has a monoclinic form and a cubic form and the monoclinic hafnia passes through the phase change or inversion and has the abnormal and eccentric expansion behavior of the monoclinic zirconia whereas hafnia stabilized with 3% to 6% of lime which crystallizes in the cubic system does not pass through the phase change or inversion and does not have the abnormal or eccentric expansion behavior of the monoclinic hafnia.

I provide a pair of zirconia sleeves 11 for each rod or bar 10, and these zirconia sleeves are advantageously made out of the same zirconia as is used for making the rods 10 and the sleeves can be manufactured in the same way as the rods 10, using a steel core in the rubber mold to form the bore. In the preferred form of my invention each sleeve 11 contains a quantity of thoria powder 12 and a quantity of zinc oxide powder 13, the former adjacent the rods or bar 10 which project into the sleeves 11 and the latter adjacent metal rods 14 which also project into the sleeves 11. The rods 14 constitute the terminals hereinbefore referred to.

The furnace can be of any desired shape or type and my invention is in no way limited thereto. Merely as an illustrative example of the use of mp resistances I disclose a steel box 15 of rectangular parallelepipedal shape supported on steel supports 16 and lined with bottom bricks 17, side wall bricks 18, end wall bricks 19, large top slabs 20 and top bricks 21, all of the bricks and slabs being made of refractory material. The furnace may have a ware support in the form of a flat slab 22 of refractory material with legs 23 so that one of the rods 10 can be located under the slab 22. For access to the inside of the furnace the box 15 has an open side and bricks 18 can be removed.

In order to provide the spring pressure against the powders in the sleeves 11 I can adopt any suitable expedient and the following mechanical arrangement is illustrative: steel brackets 24 are secured to the outside of the box 15 at the top and bottom thereof and at one end of the furnace steel bars 25 are bolted to the brackets 24 by means of bolts 26 and nuts 27 while at the other end of the furnace flat spring steel bars 28 are secured to the brackets 24 by means of screws 29. The steel bars 25 are rigid and have insulating pieces 30 at the free ends thereof against which the metal rods 14 bear; the insulating pieces 30 can be made of asbestos, alumina, mica or any other electrical insulating material which will not be affected by the moderate amount of heat delivered by the ends of the metal rods 14. The spring steel bars 28 have similar insulating pieces 31 at the free ends thereof which bear against the metal rods 14; thus compression is exerted by the rods 14 and the rods 10 upon the powder 12 and the powder 13 in all of the zirconia sleeves 11.

The electrical connections may be made in any desired way. As shown a stud 32 is welded to the outside of the box 15 and supports an insulating plate 33 (which can be made of hard rubber) secured in place by nuts 34 and through the far ends of the plate 33 extend binding posts 35 having nuts 36 connecting incoming conductors 37 to braided metal ribbon conductors 38. Referring now to Figure 3, the braided metal ribbon conductors 38 are electrically connected to the metal rods 14 by means of spring metal clips 39. At the other end of the furnace the other two rods 14 are connected together by a braided metal ribbon conductor 40 and spring metal clips 39.

Figures 4 and 5 illustrate a simple and inexpensive transformer the secondary 41 of which has a substantially constant current output rather than a substantially constant voltage output. The core of this transformer consists of a central rectangular parallelepiped 42 of iron and a pair of outside rectangular parallelepipeds 43 of iron, a top yoke 44 of iron and a bottom yoke 45 of iron, these parts being held together by screws such as the screws 46.

The secondary 41 is connected to cords 47 and 48 which pass over single pulleys 49 and 50 supported by brackets 51 and 52 connected to the top yoke 44; the cords then pass over a double pulley 53 and extend downwardly where they join under a ring 54; in other words a single cord can be used the two ends of which are designated 47 and 48. A hook 55 which can be suspended from the ring 54 has a scale pan 56 upon which slotted weights 57, 58 and 59 can be placed.

The transformer has a primary 60 which rests upon the bottom yoke 45 and which may be secured from accidental displacement in any manner, not shown. The wiring is extremely simple and is illustrated in Figure 6, wherein the primary connections 61 supply alternating current to the primary 60, and the secondary connections 37 are connected to the resistor rods or bars 10 in the manner already described, the connection between these rods 10 including the braided metal ribbon conductor 40.

Whenever the sum of the ohmic resistance of the rods 10 decreases which happens when the temperature thereof rises, more current flows through the secondary 41 which increases the repulsion between the primary 60 and the secondary 41 and the latter therefore moves upwardly. The weights 57, 58 and 59 counterbalance a considerable portion of the weight of the secondary 41 so that the net downward gravitational force on the system including the secondary 41 is only a fractional part of the weight of the secondary 41. For any particular ohmic

resistance of the two rods 10 taken together the secondary 41 will find a particular level and so sensitive can this transformer be made by selecting the weights 57, 58 and 59 properly, that is to say very nearly to counterbalance the secondary 41, that the residual variation in current is very small. Material the ohmic resistance of which decreases when the temperature thereof rises is said to have a negative temperature coefficient of resistance. This is characteristic of the rods 10, that is to say zirconia of all varieties described herein has a negative temperature coefficient of resistance.

In order to obtain data for calculating the parameters of circuits to be used in embodiments of my invention I performed a number of experiments. I formed a rod of sintered stabilized zirconia two inches long and one-quarter inch in diameter and provided sleeves 11 of the same material into which the rod projected and provided nickel terminal rods 14 also projecting into the zirconia sleeves the remaining space in which was filled with zinc oxide powder. Spring pressure held the zinc oxide powder under compression in the zirconia sleeves. This unit was run for many hours in the open air that is to say not in an enclosure and exhibited the characteristics indicated in Table I.

Table I

Voltage, Volts	Current, Amperes	Temperature Indicated by Optical Pyrometer, ° C.
155	1.30	1,235
148	1.70	1,295
140	2.17	1,370
128	2.62	1,420

In Table I the temperatures indicated may be as much as 100° C. or 200° C. lower than the actual surface temperatures of the zirconia rod because of the low emissivity of this material. Thoria powder as well as zinc oxide powder should be used when prolonged operation—that is, more than a few hours—at the higher junction temperatures is desired, since zinc oxide is not adequately stable for continuous operation when its temperature in any region is higher than approximately 1300° C. Table II shows the resistivities of zinc oxide and Table III shows the resistivities of thoria at the various temperatures listed.

Table II

Temperature, Degrees Centigrade	Resistivity of ZnO, ohm-cm.
559	1.67
810	0.261
1,062	0.016

Table III

Temperature, Degrees Centigrade	Resistivity of 90% Thoria, 10% Ceria, ohm-cm.
866	68.6
1,010	19.0
1,328	3.38
1,412	1.72

It will be seen that a heater constructed in accordance with this invention should be started with some outside source of heat, such as an auxiliary electric heater or with a flame. Silicon carbide resistors parallel to the rods 10 can be used and then withdrawn after the rods 10 are capable of carrying the load. It is very easy, however, to heat a furnace such as shown in Figure 1 with a gas flame which can be turned off whenever the rods 10 are able to carry the load.

As an indication of the varying resistivity of the stabilized zirconia referred to herein at various temperatures the following values were determined experimentally.

Table IV

True Temperature, Degrees Centigrade	Resistivity of Lime Stabilized Zirconia, ohm-cm.
450	1,500,000
832	1,430
1,158	61.2
1,340	12.0

Of the oxide materials mentioned thorium dioxide, ThO_2, is very refractory, having a melting point as given in handbooks of greater than 2800° C. and it has a lower resistivity than zirconia at working temperatures and hence the heat liberated therein will be less per unit length (same cross section assumed) at any given working temperature. Ceric oxide, CeO_2, is likewise refractory, having a melting point as given in handbooks of about 1950° C. and it likewise has a lower resistivity than zirconia at working temperatures. Mixtures of these oxides in all proportions are compatible in this invention and neither one of them nor any mixture thereof reacts with zirconia to any detrimental extent so far as I have observed or am aware. I do not want it to be understood that impurities cannot be present in fact I use readily available powders which certainly contain impurities which are probably beneficial as by increasing the conductivity. However it can be said that the powders are, commercially speaking, selected from the group aforesaid.

Zinc oxide, ZnO, which can be part or all of the cold end, is refractory and has a melting point as given in the handbooks of greater than 1800° C. and has a resistivity which is lower than that of thorium dioxide. It does not detrimentally react with zirconia nor with thoria nor with ceric oxide so far as I have observed or am aware at least when used as herein described but I do not use mixtures of zinc oxide with either or both of the other two oxides. The zinc oxide can also have impurities therein which are probably beneficial, and so long as commercially speaking the material is zinc oxide, ZnO, it is satisfactory in this invention.

The zirconia sleeves 11 have important functions besides that of holding the oxide powder or powders. They conduct more current and hence lower the resistivity per unit length of the sleeves as compared with the rods 10 by reason of the increased cross section and furthermore they deliver current to the rods 10 at the cylindrical surface thereof which appears to prevent channeling of the rods. Because of the negative temperature coefficient of resistance of zirconia there is a tendency for the current to flow chiefly in a narrow path around the axis of the rod or bar made thereof because this part is thermally insulated and therefore gets hotter and hotter since the

hotter it gets the more current flows therethrough until finally such central path melts or disintegrates. But by providing sleeves which deliver some current to the periphery of the rods 10 I appear to have prevented channeling at least in practical embodiments of this invention.

The zirconia of the rods 10 need not be pure either and can be defined as at least 97% pure zirconium oxide and hafnium oxide and lime if any; in other words it can have 3% of impurities and neither the hafnium oxide (hafnia) nor the lime are impurities except that the latter should not be over 6% of the total of zirconium oxide and hafnium oxide. By zirconium oxide and zirconia I mean ZrO_2 and by hafnium oxide I mean HfO_2 but the latter is calculated as ZrO_2. In commerce HfO_2 is reported as ZrO_2 when included therein and U. S. Patent No. 2,535,526 treats the hafnium oxide content as zirconia.

In the constant current transformer of Figures 4 and 5 the weight of the secondary coil 41 minus the balancing weights 57, 58 and 59 constitutes means urging the secondary coil towards the primary coil 60. For gravity spring pressure, pneumatic pressure or hydraulic pressure could be substituted. If a spring is used it should preferably be compensated; see U. S. Patent No. 1,393,758. Against this means urging the secondary coil is opposted the repulsion which coils carrying alternating current out of phase, as when one coil induces current in the other, exert on each other.

It will thus be seen that there has been provided by this invention electrical resistances or resistors in which the various objects hereinabove set forth together with many thoroughly practical advantages are successfully achieved. As various possible embodiments may be made of the above invention and as many changes might be made in the embodiments above set forth, it is to be understood that all matter hereinbefore set forth or shown in the accompanying drawings is to be interpreted as illustrative and not in a limiting sense.

I claim:

1. An electrical resistance comprising a rod of zirconia and a pair of ends therefor made of oxide selected from the group consisting of thorium dioxide, ceric oxide and mixtures thereof and zinc oxide.

2. An electrical resistance comprising a rod of zirconia, thorium dioxide in contact with the ends of said rod, and zinc oxide in contact with the thorium oxide.

3. An electrical resistance according to claim 1 having a pair of zinc oxide ends outside of and in contact with said ends made of oxide selected from the aforesaid group.

4. An electrical resistance according to claim 3 having a pair of zirconia sleeves fitting the ends of and surrounding said rod at the ends thereof, said pair of ends of oxide selected from the aforesaid group and said pair of zinc oxide ends being in said sleeves.

5. An electrical resistance according to claim 4 in which the oxide selected from the aforesaid group and the zinc oxide are powders thereof.

6. An electrical resistance according to claim 1 having a pair of zirconia sleeves fitting the ends of and surrounding said rod at the ends thereof, said pair of ends of oxide selected from the aforesaid group being in said sleeves.

7. An electrical resistance according to claim 6 in which the oxide selected from the aforesaid group is powder thereof.

8. An electrical resistance according to claim 1 in which the oxide selected from the aforesaid group is powder thereof.

9. An electrical resistance according to claim 8 having a pair of zinc oxide ends outside of and in contact with said ends made of oxide selected from the aforesaid group.

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