Nov. 3, 1964 L. H. MARSHALL 3,155,759

HIGH TEMPERATURE FURNACE

Filed July 3, 1962 2 Sheets-Sheet 1

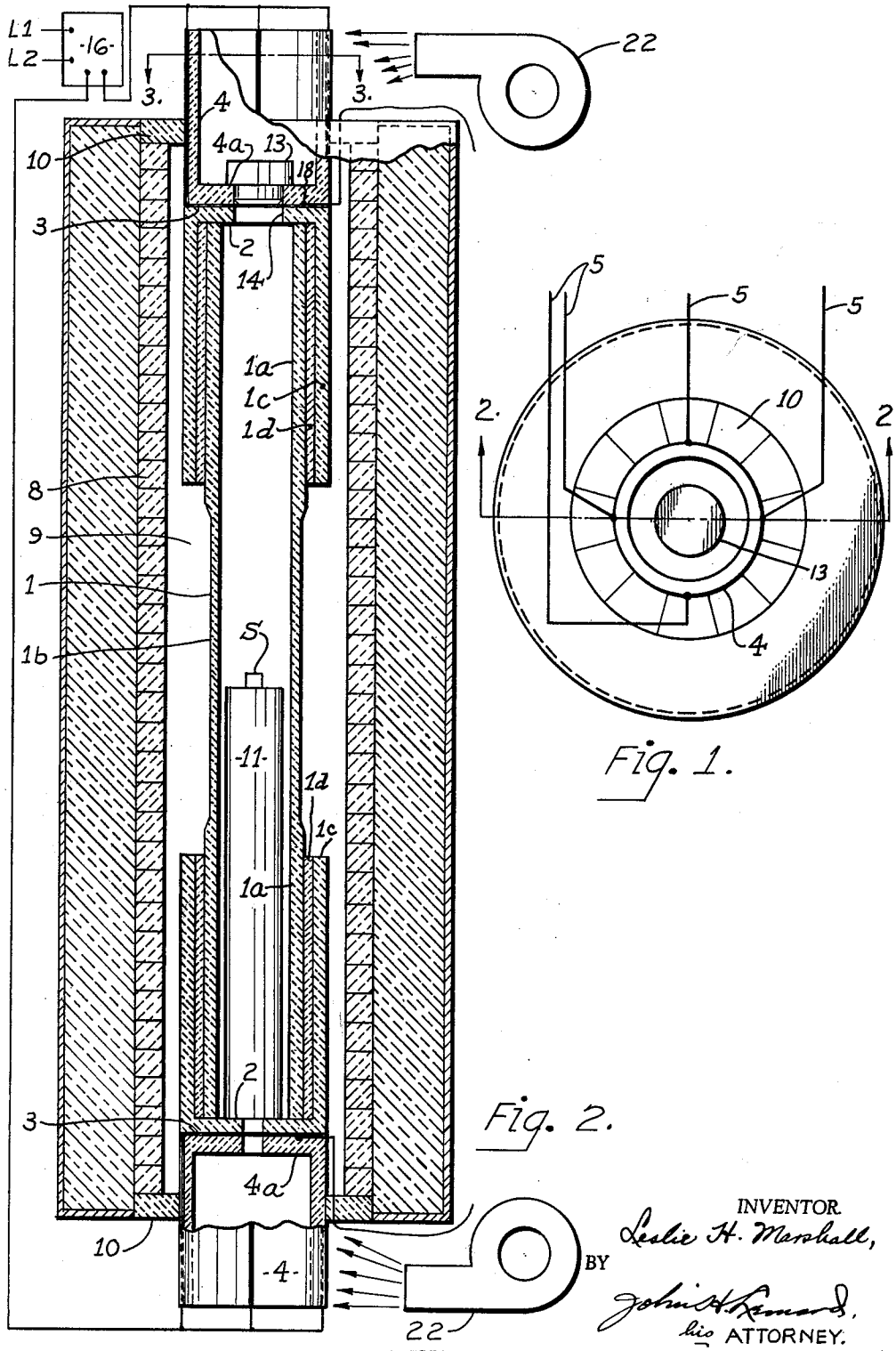


Fig. 1.

Fig. 2.

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Filed July 3, 1962 2 Sheets-Sheet 2

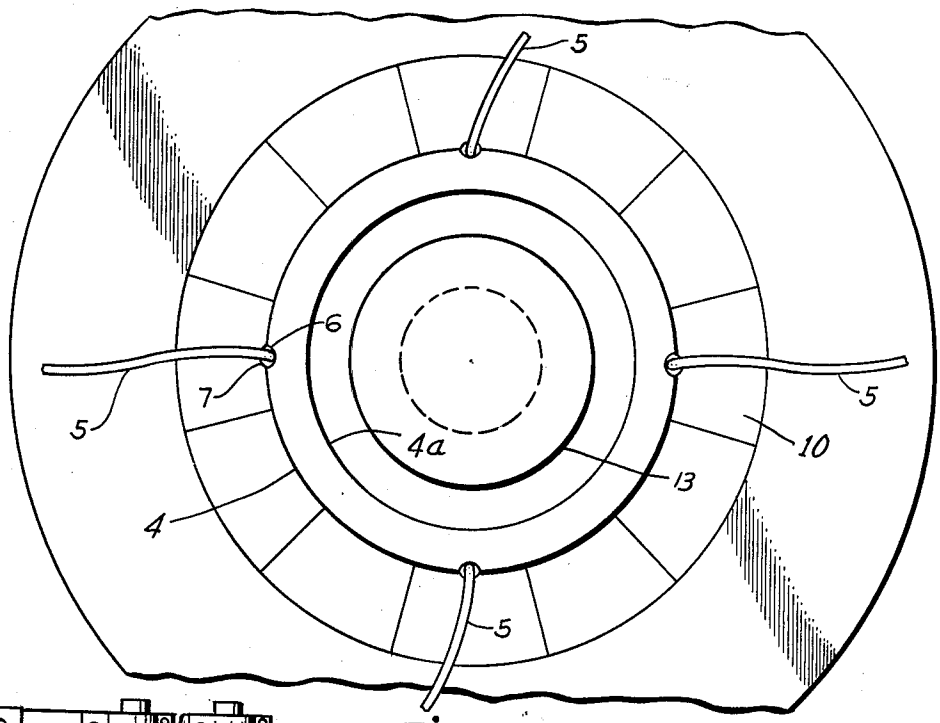


Fig. 3.

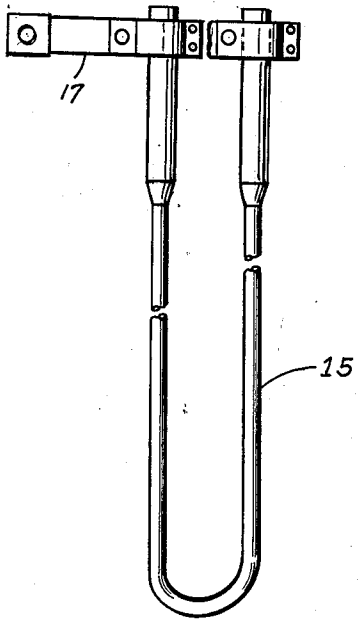


Fig. 4.

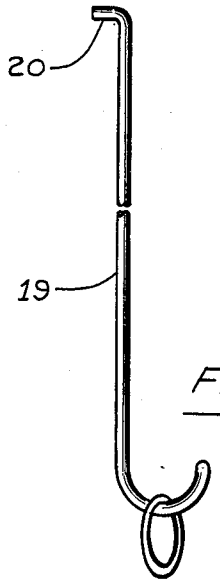


Fig. 5.

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HIGH TEMPERATURE FURNACE

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15 Claims. (Cl. 13—25)

This invention relates to high temperature electric furnaces of the type employing a heating element of a refractory oxide having a negative temperature coefficent of resistance, and particularly to heating elements for such furnaces.

For the purposes of illustration, the invention is disclosed herein specifically as embodied in a furnace employing a zirconia tube heating element preferably having end portions with a heating portion of reduced cross section therebetween, its application to furnaces employing, as heating elements, tubes or rods of other such refractory oxides and of other shapes being apparent from the illustrative example.

High temperature furnaces employing rod and tubes of zirconia and other such negative coefficient refractory oxides as heating elements are well known in the art.

In general, the tube heating elements are connected across a source of preselected alternating current voltage by means of lead-in wires which are connected to the ends of the tubes. Generally, for zirconia tubes, the lead-in wires are platinum. In one prior practice, electrical contact between platinum lead-in wires and the zirconia tube is obtained by embedding the end portions of the wires in the ziroconia. However, the coefficients of expansion of platinum and zirconia differ considerably from each other and, as a result, such embedded wires tend to loosen and break away from the zirconia tube, causing inefficient electrical contact between the tube and lead-in wires. Differentials in contact efficiency cause electric currents to localize and concentrate at the areas of better contact, once the conductive temperature of the zirconia has been reached. Since zirconia has a negative temperature coefficient of resistance, once the tube is heated at on area of efficient contact to a conducting temperature substantially above that of adjacent portions, the localized current increases at an accelerated and proportionate rate. This, in turn, further increases the current flow at the localized portion, so that there is a further concentration of current and increase in heating. This self-augmenting chain of current and heating phenomena soon raises the temperature at the localized portion to destructive heights, so that localized channelling and burn-out of the tube result.

Later attempts have been made to introduce current into a tube by coiling platinum wires around the end portions of the tube. However, portions of the coiled wires expand out of contact with the zirconia tube, thereby causing localized areas of inefficient contact, with corresponding heat and current concentration at the areas of more efficient contact, and eventual melting and channelling of the zirconia tube.

Furthermore, platinum melts at a lower temperature than zirconia, and upon melting, due to surface tension, forms into drops of molten platinum which have poor surface contact with the zirconia. This leads to arcing. The arc temperatures are high enough to melt the zirconia in localized areas and thereby lead to further nonuniformity of current distribution.

The principal object of the present invention is to provide a more effective and durable connection between the refractory metal lead-in wires and a refractory oxide tube, having a negative temperature coefficient of resistivity, so as to assure durable, firm, uniform and efficient electrical contact for assuring uniform current conduction from the wires into the end portions of the tube and therefrom along the length of the tube.

Another object is to provide a large area of surface contact between the platinum sheet and the zirconia tube and thus reduce the amperes per square inch of surface to a low flow and avoid a concentration of current flow from the metal to the zirconia.

More specifically, the present invention is directed to connecting the lead-in wires for each end of the tube to a thin contact sheet of refractory conducting types of metal firmly bonded over its entire surface to the outer face of the associated end portion of the tube.

Another object is to mount the sheets on the tube by suitable moldable settable refractory material so that they are held fixedly in place in firm juxtaposition over their entire contacting faces and protected from the atmosphere.

Another object is to remove heat from the ends of the tube, sheet, and wires more readily, and otherwise protect them from excessive heating, thereby increasing their life and maintaining an effective electrical connection for longer periods than heretofore possible.

Another object is to provide a refractory oxide heating unit which can readily be brought up to preselected temperatures and readily controlled for maintained accuracy at the selected temperature, and into which specimens to be tested can readily be introduced and removed.

Another object is to control the heating of such a unit by controlling the amperage of the current in the tube.

Various other objects and advantages will become apparent from the following description wherein reference is made to the drawings, in which:

FIG. 1 is a top plan view of the furnace and heating element embodying the principles of the present invention;

FIG. 2 is a vertical axial sectional view of the furnace and heating element, and is taken on the line 2—2 in FIG 1;

FIG. 3 is a horizontal cross sectional view taken on the line 3—3 in FIG. 2, showing the lead-in wires for connecting the heating element to an external source of power;

FIG. 4 is a perspective view of a pre-heating unit for initially heating the element to conducting temperature; and

FIG 5 is a temperature checking device used in connection with the present furnace for determining the temperature therein.

Referring to the preferred embodiment of the invention shown in the drawings, the heating element comprises an elongated tube or shell 1 which, in operating position, is preferably arranged upright. The tube 1 is refractory oxide having a negative temperature coefficient of resistance, preferably zirconium oxide, thorium oxide, and yttrium oxide. Other types of such refractory oxides may be used, such as those disclosed in United States Letters Patent No. 2,679,545, issued to Samuel S. Kistler, as inventor, on March 23, 1954.

Zirconium oxide is preferred, as mentioned, and will be referred to hereinafter for purposes of illustration. It has a melting point of 4600° F. and becomes electrically conductive at 2200° F. Further, its electrical conductivity increases with temperature, but has no sharp or well defined temperature at which it suddenly passes from non-conductivity to conductivity.

The outer peripheral wall of the tube is preferably circular at all cross sections of the tube, as also is the inner peripheral wall. The walls are coaxial. The tube has end portions extending from the ends part way toward the longitudinal midportion, these portions each having relatively thick peripheral walls. Intermediate the inner ends of the thick walled end portions, the tube has a thinner walled central heating portion. The tube may be formed originally with the thick walled end portions and a thinner walled central portion, as described, or

it may be formed originally of constant internal and external diameter with walls of uniform thickness and the greater wall thickness at the end portions then provided by cementing zirconia crucibles in telescopic coaxial relation on the end portions, respectively.

In the form shown for purposes of illustration, a combination of these approaches is used. The tube 1 is formed originally with end portions 1*a* and a central portion 1*b* having a wall thickness less than that of the portions 1*a* but not as much less as is desired. Crucibles 1*c* are secured in telescopic relation on the end portions 1*a*, respectively, by plain zirconia cement 1*d* tamped firmly into place between the peripheral walls of the portions 1*a* and 1*b* and allowed to set firmly. The specific manner of forming the tube 1 is not critical.

In order to supply electric current to the opposite ends of the tube, refractory metal conductors are used. In order to obtain an effective connection between the tube and the conductors, the tube is provided at its ends with end walls 2 which preferably are annular so as to afford access to the interior of the tube through their central openings for introducing and removing specimens to be heated. This provides a wide area of surface contact for the flow of electric current from the platinum sheet to the zirconia tube.

The tube illustrated is zirconia. It is about 24 inches long, with an internal diameter of 2 inches throughout. It has an external diameter of 2½ inches at the portion 1*b*, and 4⅛ inches at its ends. The central opening of each annular end wall is 1¼ inches in diameter. These proportions vary, of course, depending upon the particular uses to which the furnace is to be put and the oxide used.

In order to provide good electrical conections between the end walls of the tube and the lead-in conductors, the outer faces of the end walls 2 are made smooth, and thin sheets 3 of refractory metal about 0.005 of an inch in thickness are bonded to the outer faces in firm and smooth face to face juxtaposition over their entire area by means of electrically conductive material such as zirconia cement.

Thus, a very large area of contact between the platinum sheet and the zirconia surface is provided. In the above example, the area of contact between the platinum sheet and the annular end wall of the zirconia tube on which it is juxtaposed is about 12 square inches. It is apparent that a large contact area is desirable to reduce the amperes per square inch to a low value and thus avoid concentration of amperage at anyone point.

The lead-in conductors are welded directly to the metallic sheets for efficient electrical contact therewith.

It is desirable that the outer face of the metal sheets also be protected. For this purpose, each end of the tube is provided with a heat exchange element. Each heat exchange element preferably is one composed of refractory material having good heat conducting properties, such, for example, as aluminia or beryllia.

For purposes of illustration, an alumina crucible 4 is shown, this crucible being open at one end and having an annular end wall 4*a* at the other end. The upper crucible 4 is disposed with its open end uppermost and with its end wall 4*a* juxtaposed against and bonded to the outer face of its associated sheet 3. The end wall 4*a* is preferably coextensive with the outer face of the sheet.

Usuaully, the platinum sheet 3 is first cemented to the end wall 2 of the tube so that the sheet is planar and normal to the axis of the tube. For this purpose, a soft paste, which, when set, becomes electrically conductive and forms a good bond, is employed. Zirconia paste is satisfactory. The paste comprises finely powdered zirconia of a particle size of from 300 to 200 mesh and finer and a cereal binder. The cereal binder is one which will substantially completely burn out when heated above red heat, an example thereof being a binder commercially available known as "Mogul" binder No. 186. The binder is mixed with water. A suitable mix is 150 grams of zirconia powder, 0.3 gram of binder, and 30 cc. of water. This gives a consistency of fairly stiff mud when mixed.

The paste is applied by first spreading it on the platinum sheet and then juxtaposing the end of the tube onto the paste and pressing the end firmly thereagainst under a total pressure of about 70 to 100 pounds. Care is taken to maintain the tube and sheet with the tube axis normal to the plane of the sheet 3 during the bonding operation. This pressure is continued until the paste sets so that the sheet is firmly bonded to the tube over the entire end area of the tube. Next, alumina or other cement is placed on the outer face of the sheet 3 and the crucible 4 is disposed with its bottom wall 4*a* on the cement and normal to the axis of the tube and coaxial with the tube. Again pressure of about 70 to 100 pounds total is applied on the assemblage axially of the tube and maintained until the paste sets. The lower crucible is installed in like manner.

With this arrangement, very large uniform areas of contact between the tube and the sheet are obtained. The sheets are so shaped that the area or areas of contact of each sheet with its end of the tube are symmetrically distributed about the tube axis.

The bonding is such that danger of damaging the tube and sheets, and of loosening of the connections due to differentials in expansion and contraction of the sheets and conductors are eliminated. Further, an efficient heat conducting contact is maintained between the sheet and the crucibles 4. This is very desirable because the alumina of the crucibles is a very good heat conductor and the oxide of the tube is a poor conductor. By using the thickened peripheral walls at the ends of the tubes and the thin wall portion 1*b*, heating at the ends of the tube where the sheets are connected is greatly reduced, but remains at least at that required for conduction. By virtue of the highly conducting crucibles 4, the reduced heat that does reach the end walls of the tube is very rapidly dissipated.

The lead-in conductors for applying voltage to the sheets 3 are wires 5. The wires for each sheet are welded to the sheet at its periphery at points spaced equidistantly about the periphery of the sheet, so that the connections are disposed symmerically about the axis of the tube. The wires are laid in suitable channels 6 in the peripheral walls of their associated crucibles and extend longitudinally of the crucibles.

The wires are embedded in alumina cement, as indicated at 7, in the channels 6 so as to be retained in place and protected from the atmosphere and oxidizing gases and so as to increase the rate of heat loss from the wires.

The heating element thus described can be placed in upright position in a furnace or housing, preferably a cylindrical housing 8 of zirconia brick. The housing 8 has an inner diameter such that it accommodates the tube 1 with the outer peripheral wall of the tube in radially spaced relation to the inner peripheral wall of the housing 8, thereby providing a radial clearance space indicated at 9. This space also accommodates the preheating units 15. The housing 8 extends from between the upper and lower ends of the upper crucible 4 down to the point between the upper and lower ends of the lower crucible 4. The illustrative example is one wherein cooling at the ends of the furnace is desirable to protect the sheets 3 from excessive heat. This heat loss is offset by the heat produced in the tube. However, for lower temperatures, this heat loss might be too great, and if so, additional thickness of insulation may be applied on the ends of the furnace to reduce the heat loss therefrom. At the upper and lower ends of the housing, removable alumina brick 10 are provided for reducing the chimney effect during heating.

Within the tube 1 is a specimen supporting pedestal 11, preferably of zirconia or like high refractory material, which may be used, if desired. If so used it is positioned in the tube 1 so that it closes the central opening in the annular end wall of the tube. A suitable refractory cap

13 is placed in the upper crucible 4 in overlying relation to the passage 14 in the upper annular wall of the tube 1. The cap has a rim which preferably is of a diameter only slightly greater than that of the passage 14 so as to expose as much as possible of the wall 4a of the crucible to the air, to enhance heat dissipation.

Since the oxide of the tube must be heated to a predetermined temperature to render it conducting, suitable electrical resistance heating rods are provided for preheating the tube to raise it to its conducting temperature. Suitable heating rods 15 are shown in FIG. 4. They may be of any suitable high refractory material, such as molybdenum disilicide, or may be so-called commercial "glo-bars" of silicon carbide. They are connected by suitable lead wires 17 to the proper source of voltage for causing them to heat up. They are generally U-shaped in form. For heating, they are inserted into the clearance space 9 and are energized from their source and heat until the temperature of the tube 1 slightly exceeds 2400° F. and the tube becomes adequately conductive. Thereafter they are deenergized and removed so that they cannot cause any short circuits by reducing the clerance space at 9 between the tube and the housing.

Proper voltage is then applied to the lead wires 5 of the sheets 3 at the ends of the tube so that one end of the tube is connected to one side of the line and the other end to the other side of the line of a suitable A.C. source.

Since the resistivity of the zirconia changes with the temperature, it is best to control the input voltage in response to amperage. This provides a very simple and effective means of control, and may be done readily by a conventional variable transformer and ampere-responsive controller, indicated at 16. For example, in the zirconia tube illustrated, to start the heating of the zirconia by the voltage applied to its ends after the tube has become conductive initially, a voltage of about 270 volts of alternating current is employed. As the tube heats, the amperage tends to increase. As the amperage increases due to reduced resistivity, the voltage is gradually dropped until relatively constant amperage through the tube 1 is reached.

As mentioned, the alumina of which the crucibles 4 are made is a good heat conductor, whereas zirconia is a poor conductor. Heat reaches the sheets 3 rather slowly through the thick walls of the tube which themselves do not become heated rapidly and therefore maintain a higher electrical resistance than the thin wall at the central portion 1b. The crucibles, therefore, are adequate to carry away the heat and protect the sheets, assuring temperatures thereof of less than 2750° F. If temperatures thereabove begin to appear on the platinum sheets, ordinary air blowers are used so as to blow cooling air onto the crucibles for reducing the temperatures. Conventional thermocouple probes 18 are embedded in the various walls against the sheets 3, and are connected by conventional circuitry to the usual temperature indicating devices for monitoring the temperature of the platinum sheets, which temperatures should not exceed 2750° F.

With this arrangement, the proper current input, free from localized excessive current flow and consequent localized overheating, is provided.

The amperage applied to the tube should be increased very slowly initially; for example, at about 2 amperes every 15 minutes until the temperature of the interior of the tube reaches about 2800° F. This is desirable in order to reduce localization of current and localized overheating and resultant channelling. After the tube has reached 2800° F., the rate may be increased about 50%; that is, 3 amperes every 15 minutes.

As mentioned, in the form illustrated the heating element is a tube. However, the same electrical connections are applicable to rods and other shapes. The tube is preferred to the rod because the most intense heat

obtained in a rod or tube is at the axis, and with a tube the specimen can be placed at the axis.

To check the temperature at the place where the specimen S is to be heated, rods 19 of rhodium are provided. These rods can be suspended in the tube 1 from the upper end by removal of the cap 13. At its lower end, the rod 19 has a hook portion which is adapted to receive a small annulus or loop of temperature testing material. Platinum, rhodium, and alloys thereof, are very effective. Platinum has a melting temperature of 3223° F. when unalloyed. This may be varied a few degrees with each percent addition of rhodium. A rather exact and close temperature determination is obtainable because pure platinum melts at 3223° F. If alloyed with 10%, by weight, of rhodium, it melts at 3326° F., with 13% rhodium at 3345° F., with 20% rhodium at 3380° F. Since zirconia melts at about 4600° F., accurate determinations of temperature are obtainable at small increments throughout a greater portion of the possible range obtainable with zirconia tubes. The temperature increments desired are readily measurable by varying the percentage of rhodium within the range, as the ratio of temperature increase to percentage of rhodium added rises somewhat lineally.

Blowers 22 are provided for cooling. They can be controlled so as to keep the temperature at the base of each crucible 4 below 2750° F. and above 2200° F.

If desired, compressed air can be forced into the interiors of crucibles 4 for increasing the cooling effect.

In the form illustrated, the zirconia tube is one in which the thickened peripheral walls of the end portions are built up by laminations of an outer shell and an inner shell with rammed zirconia powder therebetween and bonded thereto. However, they may be cast integral with each other and the remainder of the tube.

With the illustrative heating element, each alumina crucible preferably is about seven and one half inches long, of four and one eighth inch outside diameter, and of three and one eighth inch inside diameter.

The alumina bricks for closing the ends may be of intumesced alumina brick.

The glow bars or heating rods may be molybdenum disilicide which can withstand 3000° F., or silicon carbide, which can withstand 2800° F.

The sheets 3 may be platinum, rhodium, or iridium, or alloys thereof. Alloys of platinum and rhodium are preferred, ranging from a trace of either to substantially 100% of the other. Of these, however, an alloy consisting essentially of platinum 90% and rhodium 10% is preferred.

It is desirable to make the end portions of the zirconia heating element as large as possible, thus reducing the temperature to which the sheets are subjected. The sheets need be no larger than the cross section of the thickened end portion of the tube.

The thickened end portions of the zirconia crucibles preferably are made as long as practical, thereby helping to reduce power consumption close to the ends of the tube. The cross sectional area of the reduced portion 1b of the tube is as small as possible consistent with strength and the use to which it is to be subjected.

As mentioned, the tube can be one which, when originally formed, is of uniform diameter, and the zirconia crucibles attached at the end portions to provide the greater wall thickness. However, the formation of the tube originally with a reduced wall thickness at the central portion is preferred for maximum temperatures.

In operation of the furnace, the glow bars or molybdenum disilicide preheating rods 15 are inserted in the clearance space 9 out of contact with the walls of the tube 1 and housing 8. Voltage for heating the rods 15 is applied and maintained until the rods 15 heat the zirconia tubes to about 2400° F. to 2500° F., whereupon the zirconia tube begins to conduct. Thereupon, the rods 15 are removed so that they do not reduce the air gap

between the zirconia tube, which is now conducting, and the zirconia bricks of the housing 8. About 270 volts of alternating current are initially applied across the zirconia tube through the sheets 3 to continue the heating. Heating of the zirconia tube continues causing a decrease in its resistivity. As the resistivity decreases, the voltage across the tube is dropped gradually to that required for maintaining the desired temperature. Thereafter, the amperage responsive control variable transformer is set to hold the amperage constant at about the proper amperage by changing the voltage the amount necessary, thus offsetting changes in resistivity of the tube.

The alumina crucibles conduct heat from the sheets 3 rapidly enough so that the tube ends are maintained at proper temperatures for many purposes. If the tube temperature should start to increase to more than desired, then blowers 22 are operated to blow cooling air on the alumina crucibles. If higher temperatures are to be maintained at the ends, insulation may be placed around the alumina crucibles.

Throughout the specification and claims reference is made to "refractory" metal. This term is used in the broader sense to include not only the metals as elements but alloys of such metals.

Having thus described my invention, I claim:

1. An electric heating unit comprising an elongated zirconia tube of which the inner and outer peripheral walls are coaxial and circular at each cross section, said tube having end portions and a heating portion of reduced cross sectional area intermediate the end portions, each end portion having an outer end wall of which the outer face is substantially planar and symmetrical with respect to the tube axis, thin sheets of platinum-rhodium alloy intimately bonded, by current conducting cementitious material, in face-to-face juxtaposition to the outer faces of each end portions, respectively, contact areas of each sheet and the outer face of its associated end wall being symmetrically arranged with respect to said axis, refractory heat conducting crucibles coaxial with the tube and bonded to the outer other faces of the sheets, respectively, sets of platinum-rhodium alloy lead-in wires connected to the sheets, respectively, and each set comprising a plurality of wires connected to the associated sheet at locations symmetrically arranged with respect to said axis.

2. The apparatus according to claim 1 wherein the element is disposed in a furnace, and said furnace comprises an elongated peripherally closed hollow housing of zirconia brick having its inner peripheral wall in laterally spaced relation to the outer peripheral wall of the unit, each crucible extending from a location inside the housing to and through the adjacent end of the housing, means on the ends of the housing closing the space between the housing and unit, and preheating elements removably receivable from one end of the housing into said space in spaced relation to said peripheral walls.

3. The apparatus according to claim 1 wherein passages are provided in the peripheral walls of the crucibles and extend endwise thereof, the lead-in wires are accommodated in the passages, and refractory protective material seals the wires in their associated passages.

4. An electric heating unit for high temperature furnaces, said unit comprising an elongated element of refractory oxide which has a negative coefficient of resistance, the outer periphery of each cross section of the element being circular, said element having end portions and having a heating portion therebetween of less cross sectional area than each of the end portions, each end portion having a smooth substantially planar outer end wall symmetrical with respect to the axis of the element, very thin sheets of highly refractory metal which is highly conductive electrically at elevated temperatures intimately bonded by electrically conducting cementitious material to the outer faces, respectively, of said end walls, in firm face to face juxtaposition, the area of contact between each sheet and its associated end wall outer face being circumferentially continuous and symmetrically arranged about said axis, and lead-in conductor means for the sheets, respectively, whereby electric current introduced into the ends of the element is introduced uniformly over said areas of contact of the end walls.

5. The apparatus according to claim 4 wherein an ampere responsive device is electrically connected to the element so that it can be disposed between the element and source for controlling the amperage through the element and therefore the heating thereof.

6. The apparatus according to claim 4 wherein refractory protective material of high thermal conductivity covers, and is permanently bonded by cementitious material to, the outer face of each sheet.

7. The apparatus according to claim 4 wherein each sheet has a thickness of from about 0.005 inch to 0.01 inch.

8. The apparatus according to claim 7 wherein the protective refractory material is in the form of an open end crucible having a bottom wall portion juxtaposed on, and firmly bonded to, the outer face of the sheet material.

9. The apparatus according to claim 8 wherein extraneous means are provided for cooling the crucible.

10. The apparatus according to claim 4 wherein the refractory sheet metal is from the class consisting essentially of platinum, rhodium, iridium, and alloys thereof.

11. The apparatus according to claim 10 wherein the conductor means are wires of refractory metal from the class consisting essentially of platinum, rhodium, iridium, and alloys thereof.

12. The apparatus according to claim 11 wherein the sheet metal and lead-in conductor means are of the same material.

13. The apparatus according to claim 4 wherein the refractory oxide is from the class consisting of zirconia, thoria, yttria, and mixtures thereof.

14. The apparatus according to claim 4 wherein the conductor means of each sheet comprises a plurality of refractory conductors connected to the sheet at locations which are spaced equidistantly from each other circumferentially of the associated end wall.

15. The apparatus according to claim 4 wherein the element is tubular, the inner of each cross section of the element is circular and coaxial with the outer periphery, the end walls are substantially planar, and each sheet of metal covers the entire associated end wall and is bonded thereto over substantially the entire outer face thereof.

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