

June 8, 1954

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2,680,771

HIGH-TEMPERATURE RESISTOR FOR ELECTRIC FURNACES

Filed Sept. 15, 1950

2 Sheets-Sheet 1

Fig. 1

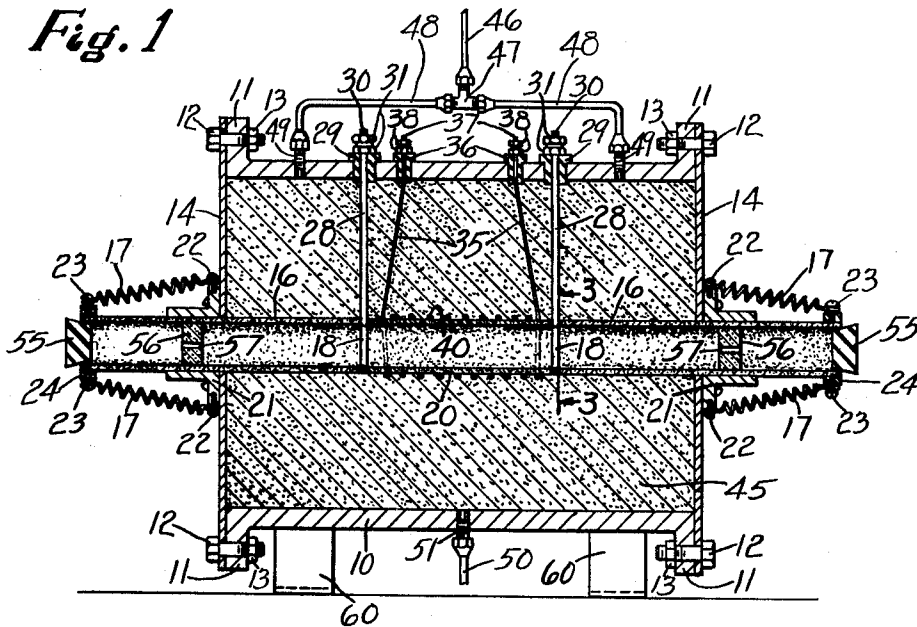


Fig. 3

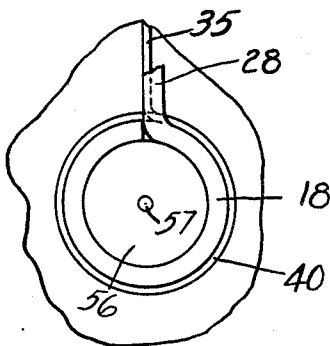
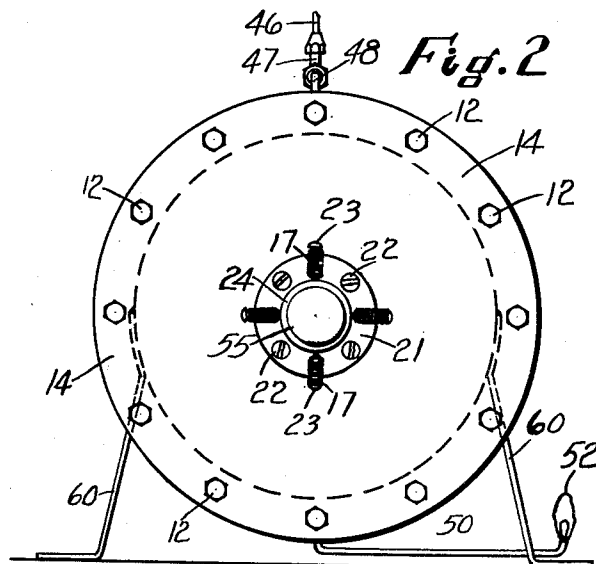


Fig. 2



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2 Sheets-Sheet 2

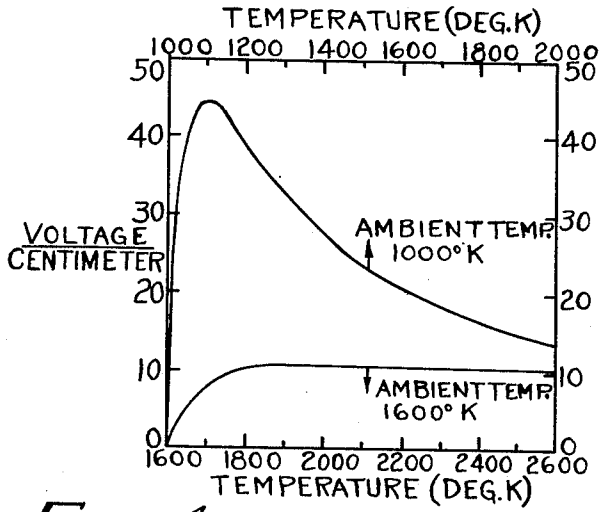
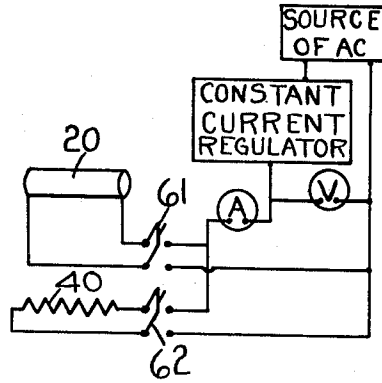


Fig. 4

Fig. 7



CRITICAL
TEMPERATURE
(DEG.K)

Fig. 6

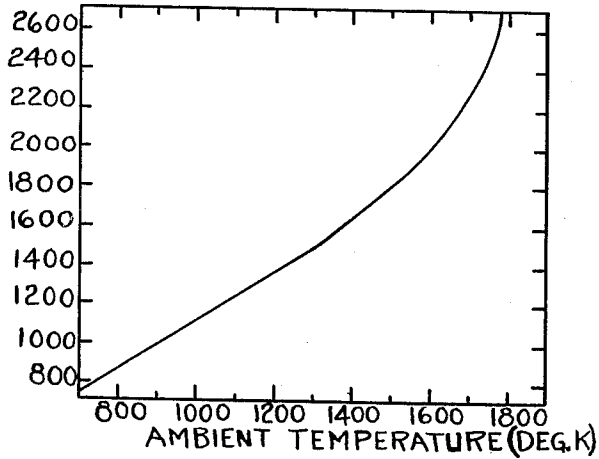
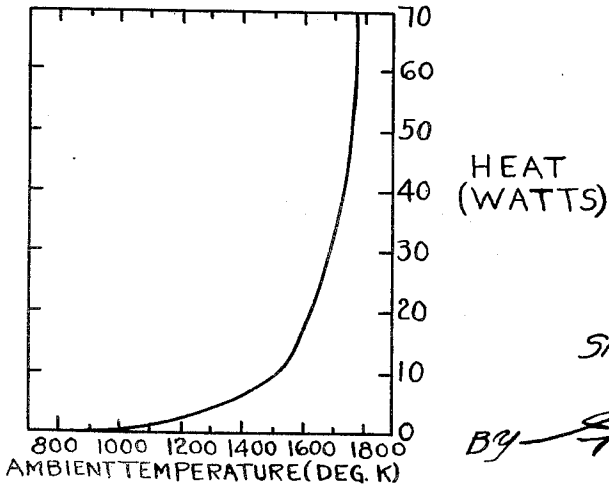


Fig. 5



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UNITED STATES PATENT OFFICE

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HIGH-TEMPERATURE RESISTOR FOR
ELECTRIC FURNACESSamuel S. Kistler, West Boylston, Mass., assignor
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ration of Massachusetts

Application September 15, 1950, Serial No. 184,927

14 Claims. (Cl. 13—22)

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The invention relates to high temperature electrical heating resistors.

One object of the invention is to provide an electric furnace capable of reaching high temperatures and of operating at high temperatures over a long period of time. Another object of the invention is to provide an electric furnace with an oxide resistor which will not channel. Another object of the invention is to provide a resistance element of such material, shape and characteristics that it can be operated at high temperatures without channeling and without burning out.

Another object is to overcome starting difficulties in connection with oxide heating resistors. Another object of the invention is to provide heating resistors and furnaces utilizing them of particular utility in research laboratories for the attainment of high temperatures. Another object is to provide high temperature resistors that can be used in many different atmospheres. Another object of the invention is to provide a high temperature electric furnace with a hydrogen atmosphere for operation between 2000° C. and 2400° C.

Other objects will be in part obvious or in part pointed out hereinafter. The invention accordingly consists in the features of construction, combinations of elements and arrangements of parts, as will be exemplified in the structure to be hereinafter described and the scope of the application of which will be indicated in the following claims.

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

Figure 1 is a vertical axial sectional view of a furnace having a resistor constructed in accordance with the invention,

Figure 2 is an end elevation of the furnace,

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

Figure 4 is a graph illustrating stable and unstable conditions in such a furnace under different loads and at different temperatures,

Figure 5 is a graph of critical temperatures for a zirconia resistor in different ambient temperatures,

Figure 6 is a graph of the heat radiated per square centimeter of a zirconia resistor at the critical temperature for different ambient temperatures,

Figure 7 is an electrical diagram.

As conducive to a clearer understanding of certain features of the present invention it is

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pointed out that while it has long been known that many oxides are electrical conductors at elevated temperatures, these oxides in general have negative temperature coefficients of resistance, especially those which seem from all standpoints to indicate usefulness as heating resistors. Since zirconium oxide, also referred to as zirconia, doesn't melt until the extremely high temperature of about 2700° C. is reached, it would at first blush appear to be an excellent material for a heating resistor; but besides having a negative temperature coefficient of resistance, it undergoes a sharp volume change upon heating and cooling. Also it is such a poor conductor at low temperatures that it must be heated by another source of heat before it will operate. Hence when used as a heating resistor, the furnace has to be heated by another means in order to make the zirconia resistor or resistors conducting. Furthermore the negative temperature coefficient results in a decreasing resistance as the temperature rises and on a constant potential source the resistor either becomes progressively hotter and hotter until it burns out, or it cools off and ceases to conduct. Moreover the negative temperature coefficient of zirconia has caused rods made thereof to become molten along the axis because the current always tends to flow wherever the material is hottest. This phenomenon is known as channeling and has been pronounced in cases where furnaces have been provided with large oxide heating resistors. Channeling can also occur in tubular resistors, the material heating more along one side or axial strip, with consequent failure. Other difficulties have heretofore been encountered. One of the objects of this invention is to overcome such disadvantages and difficulties.

Referring now to Figure 1, this furnace may have a steel shell 10 which most conveniently is a cylinder with flanges 11. By means of bolts 12 and nuts 13, end plates 14 also desirably made of steel can be fastened to the shell 10 forming a substantially gas tight chamber. The end plates 14 have centrally located holes slidably receiving zirconia tubes 15 which are urged by springs 17 against molybdenum rings 18 between which is the zirconia resistor tube 20 which is at once the heating element and also the container for articles to be heat treated.

The zirconia tubes 15 are slidable axially under the influence of the springs 17 and to that end they pass through and are supported by hubs 21 welded to the plates 14 and the hubs 21 support screws 22 each holding one end of one of

the springs 17; the other end of each of the springs 17 is anchored to a screw 23 secured to a metal ring 24 which by means of the screws 23 is fastened to the outer end of a tube 16.

The inner end of each zirconia tube 16 is hollow ground and each end of the zirconia resistor tube 20 is hollow ground and therefore the molybdenum rings 18 seat in the ends of the tubes and misalignment of the three tubes is precluded. The molybdenum rings 18 are simply part of and a loop on the end of molybdenum rods 28 extending upwardly through insulators 29 inserted in the wall of the shell 10 and terminating in screw threaded portions 30 holding nuts 31 by means of which to secure electric cables to convey the current to the rings 18. Molybdenum rods 35 similarly extend through insulators 36 in the wall of the shell 10 and have screw threaded portions 37 on which are nuts 38 by means of which electric cables can be connected to the rods 35. The rods 35 are a continuation of a molybdenum coil 40 and thus this furnace is a wire wound furnace since the rods 35 together with the coil 40 constitute one piece of molybdenum wire which is a winding around the zirconia tube 20. This is the starting coil which can be used to start the furnace but one of the great advantages of this furnace is that the rods 28 and 35 can be cross connected inside or outside of the shell 10. That is to say one conductor can be connected to the left hand screw threaded portions 30 and 37 and another conductor can be connected to the right hand screw threaded portions 30 and 37, these two conductors constituting the two lines leading power to the furnace. The furnace therefore starts up because the molybdenum winding 40 carries the current at low temperatures but when the furnace gets hot the zirconia resistor tube 20 carries the current or most of it.

The entire space between the outside of the tubes 16 and 20 and inside of the shell 10 and between the end plates 14 is packed with zirconia grain 45. A pipe 46 is connected to a T-union 47 which is connected to pipes 48 each of which is secured to a nipple 49 in the wall of the shell 10 and thereby hydrogen is introduced to the inside of the shell 10 and can be exhausted by a pipe 50 secured to a nipple 51 in the bottom of the wall of the shell 10, thus to exhaust the hydrogen which is conveniently burned in a flame 52. The hydrogen of course passes through the packing of zirconia grain 45 which preferably should include as small a percentage of fines as possible in order that it shall not sinter together. Furthermore the tubes 16 and the tube 20 are porous and therefore the hydrogen atmosphere penetrates these tubes and exists inside of the tube 20 where the articles are being treated. Rubber plugs 55 can be used to plug the outside ends of the tubes 16 and zirconia blocks 56 with holes 57 therethrough are preferably located inside of the tubes 16 to form baffles to retain the heat. These blocks 56 cut off the radiation and practically all of the convection and thus effectively hold the heat in the furnace.

The furnace can be mounted in any convenient or desired way and I have merely shown four legs 58 made out of bent strip metal welded to the outside of the shell 10 to support the furnace.

The zirconia resistor tube 20 and preferably also the zirconia tubes 16 are made out of stabilized zirconia ZrO_2 preferably stabilized with from 3% to 6% lime, CaO , and the material may be made in the following manner. An electric arc furnace of the type disclosed in U. S. Letters

Patent No. 775,654 patented November 22, 1904 to Aldus C. Higgins is provided. Furnaces of this type comprising iron shells cooled all over with a cascade of water have been in use practically ever since the date of the above patent and are well known to electro-chemists and therefore need not be further described herein. A furnace mixture of zirconia ore, coke, iron, carbon, and lime (CaO) is prepared. Various zirconia ores or partially purified zirconia powder can be used. In generally these are zircon and baddeleyite ores. However chemically purified zirconia can equally well be used but is of course more expensive.

The quantity of carbon provided in the furnace mixture should be two-thirds of the theoretical quantity of carbon required completely to reduce the silica plus 100% of the theoretical quantity required to reduce all of the other oxides (except the zirconia) to metal plus about 20% excess over all of these quantities. This quantity can be varied from the above with no excess to the above or with 40% excess. The reason why only two-thirds of the theoretical quantity of carbon required completely to reduce the silica is provided is that about one-third of the silica is volatilized during the furnacing operation. On the other hand the excess mentioned is provided because some of the coke is used up by combining with oxygen other than that provided by the oxides to be reduced.

The quantity of iron should be enough to form with the silicon that is reduced from silica a ferro-silicon having an iron content of from 75% to 85%. The purpose of the iron is to combine with the silicon to form a ferro-silicon alloy which has a much higher specific gravity than elementary silicon and therefore will go to the bottom of the furnace and, after solidification, form a ferro-silicon button containing also other reduction products that can readily be separated from the rest of the ingot. The amount of iron to add is enough to make with two-thirds of the silicon present in the ore a ferro-silicon having an iron content of from 75% to 85% minus the amount of iron obtained by the reduction of the iron oxide in the ore to iron and this of course must take into account that a small percentage of iron oxide remains in the final product.

The quantity of lime as a stabilizing agent to be added should be from 3% to 6% of the amount of ZrO_2 in the ore. The reason for providing the stabilizing agent in the above percentages is that less will not satisfactorily stabilize the zirconia, and more will form a eutectic thus making the product less refractory. The stabilizing agent in the range given causes the zirconia to crystallize predominantly in the cubic system, but when less of the stabilizing agent is used the crystals are predominantly monoclinic. Ordinary or natural baddeleyite is monoclinic whereas the product of this invention is predominantly cubic. The monoclinic form of zirconia will not withstand many cycles of heating to over 2000° C. and cooling to 100° C. and even lesser temperature changes may cause cracking or fracturing of the heating element if it is made of monoclinic zirconia. A zirconia of predominantly cubic crystal form will, however, withstand heat shock for many cycles. When the lime is as much as 6% the crystals are nearly all cubic, when the lime is as low as 2.7% about 35% of the crystals are cubic. Zirconia having 3% to 6% of lime on the ZrO_2 is referred to as stabilized zirconia; the expression "stabilized" means that the zirconia does not have a detrimental volume change at the

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critical temperature of inversion of baddeleyite, normally about 1000° C. However I do not want to be limited to lime stabilized zirconia nor to the precise furnace operation described herein since magnesium oxide (3% to 6%) is likewise a stabilizing agent and other processes of combining the stabilizing agent with the zirconia can be effectively used. However the best material now known to me for the manufacture of the resistor heating elements 12 is that above described.

For the manufacture of tubes of zirconia I may take zirconia grain and slip cast it, ram it, or extrude it to form the "green" shapes, then dry the shapes and fire them at cone 35. However a very convenient way is to press the material to produce the tube shapes. The grit size of the zirconia has some relation to the size of the tube, for example it is not desirable to try to make very small tubes with coarse grit. However this matter is not critical and the ceramist will readily know how to select proper grit sizes especially in view of the following example:

For the manufacture of a stabilized zirconia tube 6 inches long with a 1½ inch diameter bore and a 1¾ inch outside diameter, I selected stabilized zirconia of grit sizes 24-mesh and finer down to 2 microns. This was simply the material produced by grinding the zirconia until it would pass a 24-mesh screen. This grain was wet with a solution of 2% water and 1% dextrine, the percentages being on the weight of the zirconia. This wet mixture was then charged into a rubber mold having a steel arbor and was pressed at 5000 pounds to the square inch. The molded "green" tube was then stripped from the mold, was dried, and was fired at cone 35. This tube containing about 5% of lime on the total ZrO₂ made a highly satisfactory heating resistor, illustratively tube 20 in Figure 1. Tubes 16, 16 were similarly made and dimensioned, but were each 10 inches long.

Illustrative dimensions of the zirconia heater tube 20 of Figure 1 are given above, namely, a length of 6 inches, a bore of 1½ inch in diameter, and an outside diameter of 1¾ inches. These dimensional relations between diameter and wall thickness are preferably predetermined according to certain features of my invention so that the wall thickness of the zirconia tube is not too thick relative to the diameter of the tube and meets the criterion that—

$$\frac{ID}{Wa} \text{ is not less than } 2$$

where ID is the inside diameter of the tube and Wa is the wall thickness. This preferred aspect of my invention will presently be further amplified. It is a factor that contributes toward overcoming limitations and difficulties heretofore encountered and toward achieving a number of practical advantages and results heretofore impossible so far as I am aware.

As above indicated, the end faces or surfaces of the tubular element 20 are preferably shaped or faced, as by grinding, to give even and uniform surface contact with the respectively adjacent rings 18, 18, thus to aid in achieving uniform contact resistance throughout the engaged surfaces whereby substantial uniformity of current flow per unit area of the cross section of the resistor tube is more nearly achieved. Resistor tube 20, being a hollow cylinder, may be regarded for analytical purposes as comprising a number of individual longitudinal resistor elements arranged in a circle and in intimate side

wall contact with each other and each carrying the same amount of heating current there-through, and if the resistor tubes are dimensionally within the above criterion, it is possible to achieve operation of the resistor and of the furnace without materially disturbing the just described uniformity of current flow through these imaginary longitudinal subdivisions or elements of the hollow cylinder, as will be later described.

Uniformity of the surface contacts just mentioned above is further enhanced by the continuity of the yielding pressures with which these serially successive surfaces are held in engagement with each other. As better shown in Figure 1, the springs 17, 17 supply and maintain this contact pressure continuously pressing the rings 18, 18 against the end faces of tube 20 and acting through the long tubes 16, 16; the latter are externally cold where they project beyond the casing and engage the springs. Moreover this feature of yieldability also permits the various pressed-together parts to partake of dimensional changes in response to temperature changes, all without subjecting any of the parts to detrimental stress and without disturbing uniformity and continuity of application of the contact pressure.

The oxide resistor element or elements of the furnace may be energized from any suitable source of current, preferably an alternating current source, as is diagrammatically indicated in Figure 7, and to the output thereof the furnace of Figure 1 is connected through suitable switching arrangements. The electrical system preferably comprises any suitable means for automatically maintaining constancy of current supply thereto and for purposes of illustration I have diagrammatically indicated in Figure 7 any suitable form of constant current regulator, preferably one in which the standard or magnitude of the current value to be kept constant may be manually set. Thus, also, during the operation of the furnace, the manual setting may be changed at will.

As above described and as shown in Figure 1, the heater coil 40 is provided with external binding posts 33, 33, and the oxide resistor element 20 also has external binding posts 31, 31, and, as earlier noted, the conductive rods 35, 35 and 28, 28, which respectively lead to these pairs of binding posts, can be cross-connected, if desired, thus to place the two elements 40 and 20 in parallelism; for illustrative purposes, on such a parallel arrangement, as well as to illustrate certain flexibilities of control or operation which it may be desirable to employ, I have shown in Figure 7 the oxide resistor element 20 and the heater coil 40 connected to the power supply line through switches 61 and 62 respectively, both of which, if closed, of course, place the elements 20 and 40 in parallel.

Accordingly, by the heat energy developed in the heater coil 40, the oxide resistor element is raised in temperature and becomes progressively more and more conductive, and where it is made of zirconia as above described, the heating-up process may be considered as substantially completed when the temperature of the oxide tube 20 has reached about 1500° C., a temperature at which the zirconia tube begins to conduct significantly.

According to certain features of my invention, I am enabled to achieve such substantial freedom from hazards and deficiencies heretofore met with and to make possible the reliable

operation of oxide heating elements of large surface area. In operating the furnace I preferably effect the initial heating of the tube element in a manner to avoid giving rise to ruinous conditions of instability and, once it is heated to carry sufficient current, I again effect controls and conditions that avoid instability, and in these connections the dimensional criterion of the tubular heater element plays a part.

If a constant potential is applied to a resistor and it is heated by some suitable means until the resistor become conducting, the conditions are in general unstable and, without more, the temperature will increase until the element is destroyed. On the other hand, if the applied voltage is so controlled that the temperature does not run away, the likelihood is that one side of the tube will become warmer than the other parts, thus becoming a better conductor with increase in current therethrough, which in turn leads to still higher temperature until virtually all of the current is channeling down one side of the tube, which usually results in breakage. It is this sort of thing that has been one of a number of major factors heretofore limiting the uses of conductive oxides and preventing employment in heating elements of large surface area.

According to certain features of my invention, these obstacles are overcome. I have investigated the factors involved therein and as of aid in describing how I overcome the above obstacles, let it first be assumed that an element, sufficiently small in diameter to heat uniformly throughout the cross section (say, on the order of 2 millimeters) is enclosed in a furnace maintained at a constant temperature T_0 . If a small current is passed through the element, heating it to some temperature T above that of the furnace, it will lose heat to the furnace through convection and radiation. At least, as a first approximation, one can reasonably represent the heat loss by the equation.

$$H = k(T - T_0) + k'(T^4 - T_0^4) \quad (1)$$

in which H represents the heat lost per square centimeter in watts, k is the heat transfer coefficient through convection, and k' is the heat transfer coefficient through radiation. Temperatures are on the Kelvin scale. As a first approximation, I have taken the values of k and $k' \times 10^{-2}$ and 1.75×10^{-12} watts. For practical purposes, at temperatures of interest in this art, the first term in the equation can be neglected. In calculating k' it was assumed that the emissivity of zirconia is 30% of black body. This figure is based upon measurements made in a laboratory.

Accordingly the heat lost from the heating element at any temperature above the furnace temperature can now be calculated. Knowing the resistance of zirconia at any temperature, the E. M. F. required to supply the heat lost can be calculated. Such calculations have been made for a tube of large bore with a wall thickness of 2 millimeters (in effect representing a series of small-cross-sectioned elements arranged in a circle), and the results are plotted in Figure 4 for two furnace temperatures, 1000° K. (abscissae at the top) and 1600° K. (abscissae at the bottom). It is assumed, for the moment and for purposes of this analysis, that this very thin-walled tube remains at uniform temperature throughout its cross section.

The specific resistance of lime-stabilized zirconia has been measured over a wide temperature

range, and while there are variations due to impurities, porosity, and grain size distribution, it can be represented reasonably well by the equation

$$\log_{10} R = \frac{5960}{T} - 2.82 \quad (2)$$

Both curves of Figure 4 go through a definite maximum, although the one for $T_0 = 1000^\circ$ K. rises much more steeply and attains its maximum much sooner than the other. At any temperature and constant voltage to the left of the maximum point the element will be stable, any fluctuation causing a higher temperature resulting in more energy being radiated than is generated, and the temperature will fall back to the equilibrium position. On the other hand, any potential and temperature to the right of the maximum point will lead to eventual run-away conditions, since any accidental displacement of the temperature upwards will cause a greater generation of heat than can be radiated and the temperature will rise at a progressively faster rate until fusion occurs.

Furthermore, the element is permanently unstable at any voltage above the maximum point. In this connection it should be pointed out that the voltage at the maximum point decreases as T_0 is increased, so that a potential that is safe at a low furnace temperature may become excessive as the furnace heats up.

The relation between the critical temperature (i. e., the temperature at maximum voltage) and the furnace temperature is given in Figure 5 and the following equation

$$T^4 - \frac{4}{B} T^5 = T_0^5 \quad (3)$$

In this equation, B comes from the variant of Equation 2,

$$R = A e^{B/T} \quad (4)$$

in which, for stabilized zirconia, $A = 0.00152$, and $B = 13,700$. Note that A , which contains such factors as porosity, grain size, shape of cross section of the element, and magnitude of the specific resistance, does not appear in Equation 3. It is inconsequential, therefore, from a stability standpoint, how the heating element is formed as long as the activation energy of the conduction process is not affected.

Figure 5 shows that at low temperature the critical temperature is very little above the ambient temperature, thus providing only a narrow region of stability, while at high furnace temperatures the stability limits are very wide. At furnace temperatures above 1800° K., instability is no longer possible with a voltage below that necessary to melt the zirconia element.

In Figure 6 is plotted the heat radiated from a square centimeter of zirconia at the critical temperature as a function of ambient temperature. It shows more strikingly than does Figure 5 that at low furnace temperatures the safe radiation from a heater is very low, while with high temperatures the performance per square centimeter can be large. This indicates that a large radiating surface per unit of heat output is very desirable.

Thus critical temperature and safe radiation desiderata are determinable for the oxide resistor whose wall thickness should not be great enough to permit detrimental or excessive radial temperature gradients, and specific criteria are above illustratively set forth for a stabilized-zirconia

element. No such radial gradients are present when, as has been assumed above for purposes of analysis, the assumed heating element is a solid cylindrical element so small in diameter and hence so small in cross section that its temperature is uniform throughout its cross section. Nor are they present in the large-bore thin-walled tube used in some of the above calculations. The latter, a large-bore thin-walled tubular heating element, is in effect an assembly of small-cross-sectioned parallel elements equally and uniformly energized electrically, and the conditions for stability within that assembly so energized are the same as those described above. Moreover, the thin-walled tube used in these calculations also meets the criterion for wall thickness earlier above set forth; the wall thickness is not great enough to permit excessive radial temperature gradients. The conditions for stability apply equally well to the stability of a multiplicity of identical heating elements connected in parallel in a furnace. It has been amply confirmed in experimental furnaces.

While the above mathematical derivations of the conditions for stability apply to a resistor radiating to furnace walls, the same conclusions can be reached where the outside of the tubular resistor is insulated and radiation is across the space in the interior.

The zirconia heater tube 20 meets the criterion of wall thickness above set forth, and the provisions for electrical end connections thereto above described insure that the current flows into and out of the end of the tubular element at uniform current density throughout the above described contact faces or surfaces at the respective ends thereof, and this action is assured though the parts partake of temperature-responsive dimensional changes. The preliminary heating has made the heater tube sufficiently conductive for the flow of current from one end to the other and the current flows therethrough at substantially uniform density throughout any cross section taken between the ends of the heater tube. It functions in effect like a set of small-cross-sectioned individual elements arranged integrally in a circle, and because the above relationship of wall thickness to inside diameter is not departed from, if any one of these imaginary elements or subdivisions of the zirconia tube heats up beyond the others, it can and does lose more heat by radiation than it gains, and thus the conditions that are otherwise conducive to channeling are counteracted. Thus continued heating up of the heater tube is facilitated, as is also subsequent operation of the furnace at the desired ultimate furnace temperature.

This action of continued heating up after the tube becomes conducting will thus also be seen to contribute toward maintaining uniform current density, and thus uniform heating up is reliably and more quickly attained. The action just above described might be said to achieve substantially automatic maintenance of temperature equilibrium throughout the mass of the heater, and a similar substantially automatic action takes place during the run of the furnace at its ultimate furnace temperature at which treatment of article or materials is desired to take place.

It is preferred to supply energy to the hollow cylindrical element of the furnace under conditions of constant current control, effected by setting the current regulator of the supply system of Figure 7 to the desired current value, the

regulator being manually set to function at the selected standard or value of current to be kept constant. It is possible, once the heater has been heated to become sufficiently conductive, to set the regulator at a current value that will ultimately give the desired operating furnace temperature upon completion of the heating up by the current itself, for the above-described dimensional criterion or characteristic of the zirconia tubular heater and the limitation of current or amperage effected by the current regulator coact to achieve prevention of conditions of instability such as those described above in connection with Figure 4. Because of such coactions and by setting the current regulator to successively different standards of operation, it is also possible to supply current to the heater tube at a different value during the heating-up period than is supplied during the continued operation of the furnace at its desired temperature, so long as the change in value is effected with due regard to the otherwise inherent conditions of stability and of instability that exist, respectively, to the left and to the right of the maximum points of the graphs, such as those of Figure 4, for the heater element. Because of the wide range of stability that exists to the left of the knee in the graphs, preciseness and closeness of control can be departed from and energization, throughout that range of stability, could even be effected at higher current values or at varying (e. g., increasing) current values, and in this latter connection the energy could be applied in successive stages at successively higher values, if desired, provided of course, as will now be clear, that substantial precision and closeness of constancy of current be instituted just before or when the critical temperature is reached, for thereafter, as above explained and demonstrated, conditions of instability can be brought about at potentials and temperatures to the right of the maximum point in the corresponding graph like that of Figure 4.

The winding 40, which in the illustrative embodiment is wound directly upon the zirconia heater tube 20 and is thus in intimate thermal relation to it, can be made to coact in carrying out the mode of operation just described and to coact in achieving continuity of stability throughout. The material of which the coil 40 is made, preferably and illustratively molybdenum, has a positive temperature coefficient so that its resistance increases with increase in temperature, whereas the oxide heater element has a negative temperature coefficient, its resistance decreasing with increase in temperature. The two are connected in parallel, by closing both switches 61 and 62, and at the start of the furnace operation the oxide element 20 is substantially non-conductive, so that all of the current flows through the heater coil 40 and substantially none flows through the oxide element 20. The turns of the heater coil 40, only diagrammatically indicated in Figure 1, are substantially uniformly distributed along the length of the resistor tube 20 and are of appropriate number and spacing to achieve substantial uniform heat transmission to the oxide element 20 throughout its length, so that the oxide element is substantially uniformly heated up throughout its mass. In being in good thermal contact peripherally with the oxide element, the turns of the heater coil virtually insure that no one side or longitudinal section of the tube 20 is heated more than any other.

When the heater tube 20 becomes conductive, current begins to flow through it from one end

to the other, as above explained, and it does so at substantially uniform current density throughout in transverse cross section, and as its resistance decreases, the current flow through the oxide tube increases; but at the same time as the temperature of the heater coil 40 increases, its resistance increases and the current flow in the circuit of the winding 40 decreases.

If, therefore, the current regulator of Figure 7 is set to deliver a fixed value of current at the start of the heating-up period, the delivered current value is divided between the heater coil 40 and the resistor element 20 in the manner just described, and in that manner a desirable sufficiently slow or gradual heating up occurs, well within the limits of stability above explained. If desired, and depending upon the initial setting of the regulator, the heating up can be effected in successive steps by successively, and at appropriate time intervals, raising the setting of the regulator. For each such setting, whether one or more are effected, the constant current regulator, in coaction with other features above explained, guards against producing conditions of instability in the oxide heater element, and heating up may be accomplished at the desired low rate.

During the heating-up period, under constant current control, the voltage increases rather steadily due to the increase in resistance of the molybdenum wire of the heater winding 40 as the temperature goes up, and voltage rise occurs up to about 1500° C., at which temperature the zirconia tube 20 has begun to conduct significantly and to carry most of the current that is divided between the two.

From that point on, higher temperatures are produced in the furnace by raising the setting of the current regulator in successive steps at suitable intervals, and though the amperage flowing through the zirconia tube 20 is in that manner and under such control increased, the accompanying voltage drops, for now, as between the resistance of the zirconia tube 20 and the resistance of the molybdenum winding 40, the former is of major significance in its effect on the parallel circuit, its resistance becoming less and less.

The following table gives values, for an illustrative run of the furnace, of successive increases in the value of total amperage held constant by the regulated power supply system, the accompanying temperatures, and the accompanying voltages:

Time	Amps.	Volts	Temperature, °C.
10:03 a. m.	33	60	1,530
10:20 a. m.	41	60	1,770
10:30 a. m.	48	50	1,930
10:50 a. m.	54	51	2,020
11:13 a. m.	69	47	2,125
11:30 a. m.	80	44	2,170
11:45 a. m.	80	44	2,170
11:56 a. m.	90	40	2,200
12:22 p. m.	98	36	2,215

Of the above tabulated current values at the highest temperatures, by far the largest part of the current passes through the oxide elements, because of the high resistance at high temperature of the material of the heater coil 40. For example, at 2200° C. the molybdenum winding has a resistance of 3.5 ohms, while the zirconia tube 20, between the current supply rings 16, 18, has a resistance of 0.35 ohm; thus, only about 9% of the total current passes through the winding.

The voltage values given in the table above are within the above explained criteria, and under the control of the constant current supply system voltages and temperatures do not reach those values which give conditions of instability, as above explained with respect to potentials and temperatures to the right of the maximum point in the corresponding graph like that of Figure 4. Moreover, the furnace operates very smoothly and has been successfully operated over a long period of time and with great reliability of function.

Thus it will be seen that, by my invention, many thoroughly practical advantages are successfully achieved. The risks, damage, losses, and limitations imposed or caused by channeling can be successfully avoided and controlled stability achieved according to the principles of my invention. While I have described my invention in connection with the use of zirconia resistor elements, and more particularly stabilized zirconia heater elements, I have done so because of the over-all superiority and many novel advantages that I am enabled thereby to achieve, but I do not wish to be limited thereto except as such limitation may be expressed in one or more of the claims. Many of the advantages and various of the results of my invention may be achieved by utilizing other known refractory oxides that are conducting at high enough temperatures. Of course, elements of expense or cost of some of these will enter as a consideration in their practical application. Also, the particular characteristics of any such other refractory oxide might make it more suitable for some particular purpose; for example, for very high temperatures, thorium may be employed in preference to zirconia because, for example, it has a higher melting point. Whatever the selected refractory oxide, stability of operation may be achieved according to the principles fully explained and illustrated above in connection with the use of stabilized zirconia, as, for example, by shaping it in the form of a tube in which the relation between the inside diameter and wall thickness is such that detrimental or excessive radial temperature gradients are not produced, and supplying electrical energy thereto so controlled that ambient temperature and resistor temperature are maintained within those ratios that mean stability, as is illustratively explained above in connection with stabilized zirconia tubular resistors.

It will also be seen that some known disadvantages or limitations met with heretofore are overcome, according to my invention, by the use of zirconia tubes instead of solid rods, others by the use of stabilized zirconia, others by the use of electrical connectors like the metal rings 13, 18 and their coacting parts, still others by an inter-related heater coil like coil 40, and still others by constant-current supply or current-limiting regulation, all as illustratively above described.

It will thus be seen that there has been provided by this invention a high-temperature resistor in which the various objects hereinabove set forth, together with many thoroughly practical advantages, are successfully achieved. As many possible embodiments may be made of the invention and as many changes might be made in the embodiment 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. A high temperature electric furnace comprising a refractory heat-resistant enclosure having therein a tubular resistor element made of a refractory oxide having a negative temperature coefficient of resistance, means for making electrical connection to said tubular resistor element comprising circuit-connecting metal rings at and in engagement with the respective annular ends of said tubular resistor element, means for holding said rings in conductive engagement with said annular ends of said tubular resistor element comprising refractory members, one for each ring and each extending from its ring through an aperture in said enclosure to the exterior of the latter, and means exterior of said enclosure and operating upon the exterior portions of said refractory members for mechanically holding them against such relative separating movement as will detrimentally diminish the contact pressure between said rings and the respective ends of said tubular resistor element.

2. A high temperature electric furnace as claimed in claim 1 in which at least one of said refractory members that engage said metal rings is tubular and presents an annular end portion in engagement with its associated metal ring and forms a passage communicating from the exterior of said enclosure to the interior of said tubular resistor element.

3. A high temperature electric furnace as claimed in claim 1 in which both of said refractory members that engage said rings are tubular and present annular end portions for engagement with their respective metal rings and form communicating passages leading to the interior of said tubular resistor element whereby the space within the latter is accessible from the exterior of said enclosure and from opposite ends thereof.

4. An electric furnace as claimed in claim 1 in which said tubular resistor element is pervious for the passage of gases through the walls thereof and said enclosure comprises a shell substantially impervious to gases, pervious refractory material filling the space between said shell and the walls of said tubular resistor element, and means for conducting a gas into the interior of said shell for passage through the pervious walls of said tubular resistor element to the interior of the latter.

5. An electric furnace as claimed in claim 1 provided with means for preheating said tubular resistor element to a temperature where it becomes significantly conductive so that current flow between said rings and through the walls of said tubular resistor element may take place to heat the latter, said means comprising a resistor element of axial length not greater than that of said tubular resistor element in thermal relation to said tubular resistor element and made of a material that has a positive temperature coefficient of resistance whereby heating current supplied to it diminishes as its temperature is raised by the heat generated in said tubular resistor element by current supplied to the latter through said rings.

6. A high temperature electric furnace comprising a heat insulating enclosure having therein a refractory resistor means of annular cross-section with current-carrying ring members of low resistivity coaxially engaging at its annular ends, said annular ends and said ring members having annular reentrant and annular projecting portions which interfit and thereby prevent relative radial shift between each ring and the annular

end with which it engages, means forming leads extending from said current-carrying members to the exterior of said enclosure for making connection to a source of current, and means for holding said conductive ring members in current-carrying contact with the respective annular ends of said resistor means and for holding them against relative separating movement in axial direction, said means comprising two refractory members engaging said conductive ring members and each extending through an aperture in said enclosure to the exterior of the latter where each has a substantial heat radiating surface and pressure-exerting means exterior of said enclosure and operating upon said refractory members to urge them inwardly and thereby press said conductive members and yieldingly hold said conductive members in contact with said resistor while permitting temperature-responsive dimensional changes of the parts to take place.

7. A sub-assembly for a high temperature electric furnace comprising a tubular resistor made of a refractory oxide that has a negative temperature coefficient of resistance and having its annular ends recessed to provide annular re-entrant surface portions at its respective ends which form coaxial annular end seats, a preheater for said tubular resistor comprising a helix of resistance wire carried thereby and coaxial therewith and of an axial length less than the distance between said annular surface portions, and means for making electrical connections comprising metal rings one for each annular end of said tubular resistor and each cross-sectioned for entry into its associated recessed annular end and making substantially uniform engagement with the re-entrant annular surface portion of the end seat for substantially uniform current flow therebetween whereby each metal ring is held against detrimental shift in radial direction, and terminal leads at the respective ends of said wire helix.

8. A high temperature electric furnace comprising terminal connectors adapted to be insulatively supported, two end tubes and an intermediate tube, said tubes being of substantially the same inside and outside diameters and made of a refractory oxide that has a negative temperature coefficient of resistance and that has to be heated to become significantly conductive, said tubes each having a ratio of surface area to cross-sectional area greater than that at which, for a given uniform temperature at which it is conductive, heat is generated therein, in response to electric current flow, faster than heat can be lost through said surface area, and conductive rings which are respectively associated electrically with said terminal connectors and are interposed between the adjacent ends of one end tube and the intermediate tube and between the other end tube and the intermediate tube, said intermediate tube being hollow ground at both ends and said end tubes being hollow ground each at an end adjacent the intermediate tube to form companion ring-like seats for each of said conductive rings and coacting with the latter to align and substantially coaxially key together said tubes and rings for pressure engagement of the rings with the ends of the intermediate tube.

9. A high temperature electric furnace comprising terminal connectors adapted to be insulatively supported, a tubular resistor made of a refractory oxide that has a negative temperature coefficient of resistance and that has to be heated to become significantly conductive, said tubular resistor having a ratio of surface area

to cross-sectional area greater than that at which, for a given uniform temperature at which it is conductive, heat is generated therein, in response to electric current flow, faster than heat can be lost through said surface area, said tubular resistor presenting annular end faces each of substantially uniform radial dimension throughout its annular extent and each being hollow ground to increase its exposed area thereby to form an annular recessed seat at each end, a conductive ring for each of said annular seats and of a cross-section to present an external surface substantially matching with that of the hollow-ground annular seat, said conductive rings being respectively seated in said annular seats whereby each is coaxially keyed to its associated tube end and being in electrical connection respectively with said terminal connectors, and two tubular members made of a refractory oxide for respective engagement with said conductive rings to press them substantially uniformly against and into their respective seats.

10. A high temperature electric furnace comprising two end tubes and an intermediate tube, said tubes being of substantially the same inside and outside diameters and made of a refractory oxide that has a negative temperature coefficient of resistance and that has to be heated to become significantly conductive, said tubes each having a ratio of surface area to cross-sectional area greater than that at which, for a given uniform temperature at which it is conductive, heat is generated therein, in response to electric current flow, faster than heat can be lost through said surface area, and conductive rings interposed between the adjacent ends of one end tube and the intermediate tube and between the other end tube and the intermediate tube, said intermediate tube being hollow ground at both ends and said end tubes being hollow ground each at an end adjacent the intermediate tube to form companion ring-like seats for each of said conductive rings and coating with the latter to align said tubes and rings for pressure engagement of the rings with the ends of the intermediate tube, said intermediate tube being made of refractory oxide selected from the group consisting of zirconia and thoria, stabilized, containing from 3% to 6% of alkaline oxide selected from the group consisting of lime and magnesia.

11. A high temperature electric furnace comprising a tubular resistor made of a refractory oxide that has a negative temperature coefficient of resistance and that has to be heated to become significantly conductive, said tubular resistor having a ratio of surface area to cross-sectional area greater than that at which, for a given uniform temperature at which it is conductive, heat is generated therein, in response to electric current flow, faster than heat can be lost through said surface area, said tubular resistor being hollow ground at its ends to form an annular recessed seat at each end, a conductive ring seated in each of said seats, and two tubular members made of a refractory oxide for respective

engagement with said conductive rings to press them against their respective seats, said tubular resistor being made of refractory oxide selected from the group consisting of zirconia and thoria, stabilized, containing from 3% to 6% of alkaline oxide selected from the group consisting of lime and magnesia.

12. A tubular resistor made of refractory oxide that has a negative temperature coefficient of resistance and that has to be heated to become significantly conductive, said tubular resistor having a ratio of surface area to cross-sectional area greater than that at which, for a given uniform temperature at which it is conductive, heat is generated therein, in response to electric current flow, faster than heat can be lost through said surface area, said tubular resistor having its annular ends each of substantially uniform radial dimension, said annular ends being hollow ground throughout their annular extents to provide increased annular surface areas for contact and to form annular recessed seats for reception of a circuit-connecting conductive ring and to coact to hold the latter and the tube end against relative radial shift.

13. A tubular resistor made of refractory oxide selected from the group consisting of zirconia and thoria, stabilized, containing from 3% to 6% of alkaline oxide selected from the group consisting of lime and magnesia at least one annular end of said tubular resistor being recessed throughout its annular extent to provide an annular re-entrant contact surface and forming a coaxial annular hollow seat adapted to receive an annular connecting conductive member therein and coact to substantially key it against radial shift.

14. A high temperature electric furnace according to claim 1 in which said tubular resistor element is made of refractory oxide selected from the group consisting of zirconia and thoria, stabilized, containing from 3% to 6% of alkaline oxide selected from the group consisting of lime and magnesia.

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