This invention relates to electrical heating elements suitable for operation in open air and other atmosphere containing substances capable of attacking the resistor element. In particular the invention relates to electrical heating elements to be operated at high temperatures, such as 1400° to 1600° C. and more.

According to this invention the heating element consists of an electrical substantially metallic resistor which is capable of sustaining high temperatures such as 1400° to 1600° C. and more, without softening or melting. Suitable substances are in particular tungsten, tantalum, molybdenum and alloys thereof. For lower temperatures, such as 1400° C., a resistor element of chromium or an alloy thereof can be used.

It is well known in the art that such resistor elements when operated at high temperatures are subjected to attacks by the oxygen of the surrounding atmosphere or other gases in which the resistor is being operated. Furthermore, if the resistor is submerged into a substance which is to be heated it is liable to be attacked by some of the chemicals contained in those substances to be heated. Thereby the diameter of the resistor is continuously reduced and its resistance increased whereby its heating increases and its life is cut short.

It was suggested therefore to cover such resistor elements with suitable tubes or coatings which are resistant to the surrounding air or other substances and prevent the latter from reacting upon the resistor element at operation temperatures. Such covers or coatings were applied either closely upon the resistor or spaced therefrom. In the latter case an inert protective gas, or a vacuum, was applied between the cover and the resistor element.

It has been suggested to use for such cover or coating oxides having a high melting point, such as zirconia, alumina, magnesia, silica, sillimanite and mixtures thereof compounded by heat treatment. It was particularly suggested to use, partly or entirely, vitreous or vitrified substances for such covers or coatings.

Such coatings or covers, although suited for temperatures of about 1400° to 1600° C. do not remain gas-tight for an extended period of operation, nor do they withstand repeated electrical connecting and disconnecting.

It is an object of the invention to improve electrical heating elements of the type referred to so as to prolong their life when operated at high temperatures.

It is another object of the invention to make electrical heating elements capable of operation at higher temperatures than could be done up to this time.

It is still another object of the invention to render covered electrical heating elements capable of operation for a long period of time and notwithstanding repeated switching-in and out within temperature ranges between about 1400° and 1600° C. and higher, without impairing the gas-tight and other qualities of the cover.

This and other objects of the invention will be more clearly understood when this specification proceeds with reference to the drawing in which Figs. 1 and 2 show a cross-section through different types of resistors to which this invention pertains, without, however, being limited to them since they are cited as exemplification only.

According to this invention the cover consists of highly refractory substances, in particular oxides of metals selected from elements of the second, third, fourth and sixth group of the periodical system, and these refractory materials are used in amorphous but substantially other than nitreous form. Thereby a gas-tight cover is obtained which efficiently protects the resistor against the attacks of the surrounding atmosphere and substances, this quality being maintained during operation and heating to high temperatures, such as 1400° to 1600° C. and above.

Referring to the drawing, such a cover may either be made as a tube 3, Fig. 1, of any desired cross-section and the resistor 4 arranged within that tube, spaced from its inside walls. That space may be filled with inert gas either under atmospheric or super-atmospheric pressure or under lower than atmospheric pressure. There may also be applied a vacuum of any desired degree. The coating 5, Fig. 2, may also be applied directly upon the resistor 6, in particular in close touch therewith. The coatings 5 may also be prepared separately and in particular be fritted or finely sintered and then applied to the resistor 6. They may also first be fritted or presintered by heating the latter to adequately high temperatures. The highly heated resistor may also be submerged into a more or less plastic mass containing the selected constituents, with a resulting coating adhering to it, being fritted and sintered by that highly heated resistor which, after having been submerged into the mass and after having derived from it an adequate layer, is suitably removed from the mass and heated in open air or another, particularly neutral, atmosphere or vacuum, long enough to permit finely sintering the mass upon the resistor while at high temperatures.
temperature. Thereby the resistor obtains its largest volume, and the mass sintered upon it shrinks to the smallest volume, and upon cooling the resistor material will either shrink in the same proportion or to a higher degree than the coating material to it. In the former case the coating will remain adherent to the resistor; in the latter case the covering will slightly segregate from the resistor, creating a vacuum between it and the resistor. In any case, cracking of the coating during manufacture and operation is successfully prevented because the resistor will never be heated to temperatures higher than those at which the coating was finally sintered upon it.

For the coating mixtures of oxides of at least two oxides of the type referred to above are used, sintered into a dense and gas-tight body without, however, developing glass or vitreous substances to any substantial extent, i. e. if any vitreous component will develop during manufacture they will amount to substantially less than 3% to 10% of the entire mass. Vitreous substances, if present, have the disadvantage that they devitrify after a short period of service, rendering the cover brittle and permeable to gases. This holds true for all vitreous amorphous substances if present in the cover in substantial amounts and may be termed an aging phenomenon. Sintered alumina as suggested for covers of electrical heating elements contains usually small amounts only of vitreous amorphous constituents. Nevertheless it is permeable to gases, though to a smaller extent, and the aging phenomenon occurs quickly if such a cover is continually used at high temperatures.

The present invention established by numerous and extended experiments that sintered mixtures of oxides melting about 1600°C selected from oxides of the second, third, fourth and sixth group of the periodical system provide gas-tight, incombusible products if treated in a manner to be described later on. As oxides suitable for the purposes of the invention the following may be mentioned by way of example: SiO₂, Al₂O₃, Cr₂O₃, Co₂O₃, TiO₂, ThO₂, BeO, MgO, ZrO₂, BeO, Al₂O₃, Al₂O₃, ZrO₂, Al₂O₃, SiO₂, 3Al₂O₃·2SiO₂, MgO·Cr₂O₃, Al₂O₃·TiO₂, MgO·(Al₂O₃)·(Cr₂O₃) or combinations of these substances. Two or more of these substances are chosen in suitable proportions and thereupon shaped in powdered state and subjected to compoundng under heat treatment. However, this heat treatment is taking place at temperatures where no melting occurs, i.e. sintering. In particular, by sintering a powdered shape mixture according to the present invention it is densified by heat treatment so that the powdered mass substantially shrinks and crystallization, or recrystallization, just starts. This may also be termed a reaction of the crystals of the powdery substance upon each other while still in solid state, in contrary distinction to melting or a partial melting process in which at least part of the substances present is melted and starts—if vitreous in character— to vitrify. In that latter case the higher melting oxides will remain more or less solid and coalesce to a kind of skeleton the interstices or pores of which are filled with the lower melting substances which are caused to melt by the heat treatment. These lower melting and actually melted vitreous amorphous products fill the pores of the skeleton, and upon cooling they may entirely or partially devitrify. According to the present invention, pure sintering is applied which causes an at least beginning crystallization or recrystallization without melting substantial amounts of substances present and, consequently, within the former case the coating will remain adherent to the resistor; in the latter case the covering will slightly segregate from the resistor, creating a vacuum between it and the resistor. In any case, cracking of the coating during manufacture and operation is successfully prevented because the resistor will never be heated to temperatures higher than those at which the coating was finally sintered upon it.

Other conditions deserving particular consideration are the temperatures and duration of heating. According to the invention these two conditions are determined so that at least two different types of crystals will result in the final product which, therefore, is hereinafter and in the appended claims called a heterogeneous product. By this heterogeneity the new product according to this invention is principally differentiated from products which consist of a single type of crystal only such as sintered alumina which is also called sintered corundum.

Comparative microscopic investigations of sintered alumina and the product according to this invention both in their new state and after having been used for an extended period of time and under high operating temperatures, explain the different behavior of sintered alumina and of the product according to the invention, although I do not wish to confine myself to any scientific explanation of my invention.

Uniformly crystallized substances, such as sintered alumina, show before being put to use and while in the state as obtained by sintering phenomena, a mosaic-like structure. After prolonged continuous heating, however, gliding-planes will form between the individual crystals which in time will develop more and more and ultimately will reach from one surface to the other of the body. Along these gliding surfaces between the crystals gas may flow from one side to the other of the body, and its original quality of gas-tightness will gradually disappear.

With a heterogeneous product according to the present invention no uniform crystalline structure can be observed under the microscope. Depending upon the raw materials selected and the fineness of grinding same, furthermore depending upon the range of temperature and duration of heating, a large number of different crystals are ascertained to develop one alongside of the other, as is the case with homogeneous materials dealt with above, but which grow one into the other or one permeates the other. Thereby a mechanically strong structure is obtained which coheres in itself and assures continued high gas-tightness because no gliding planes or surfaces can develop between crystallites of different types which grew into each other or permeated each other. The lack of uniformity and regularity of the various crystals adjacent to each other is a definite advantage of the present invention making it superior to all products known and used heretofore for similar purposes.

Another most distinct advantage of the product according to the present invention consists therein that it cannot age in the manner previously described with regard to homogeneous materials. No gliding surfaces develop during prolonged use and gas-tightness of the product endures incomparably longer than is the case for the known homogeneous products.

According to a particular feature of the invention, materials are added to the ingredients which accelerate and promote the formation of crystals, which further increase the number of crystal grains and, lastly, assist in the growth...
of the crystals, thereby causing immediate devitrification of components present in the mixture if they happen to vitrify during manufacture. It is to be understood that the last mentioned action results only in the manufacture of the product. It may be done as an effect which vitrification removes at the very moment when it starts to occur. By selection and admixture in proper and small amounts of one or more substances of the effect described above, the number of types of crystals created within the product can be increased almost at will. Such substances are known as mineralisers. Such mineralisers are of particular advantage if they form either fluxes or if they are of themselves highly refractory and capable of entering the crystal lattice of the main constituents used for the product. Ordinarily, small amounts of such mineralisers suffice for the purpose of the invention. Therefore, in combination with alumina, fluxes may be used which are of a very strong nature because it is entirely immaterial whether the melting point of the final product is reduced by their admixture from 2050° C. to 2000° C. whereas it is of utmost importance that the temperature of manufacturing, i.e. the sintering temperature, be reduced, for example, from 1800° C. to 1600° C.

Up to the present time one was under the impression that impurities are to be avoided and that alumina should be used in as pure a state as possible for the manufacture of the sintered alumina (corundum). If, however, the admixtures to alumina are carefully chosen, as it is the case according to the invention, then the above advantages during manufacture can be obtained, and the final product can be rendered highly heterogeneous, containing two or more different types of crystals which have grown into each other and form a type of dense network of extraordinarily high mechanical strength. This network contains no pores or channels reaching from one to the other surface of the body and, consequently, is prefectly gas-tight. Due to this particular feature this gas-tightness is retained during use, and the body is of exceptional mechanical strength. No aging phenomenon can appear.

The following are examples of mixtures and methods of manufacture of coverings or coatings according to the invention. Any shape of the body, and any method of producing and applying the same may be used as outlined in the opening paragraphs of the specification. In particular, tee-like covers may be first finished by sintering and then be applied upon the substantially metallic resistor element. It is to be understood that suitable terminals, or electrodes, are to be connected to the ends of the heating elements in a well known manner which does not form part of this invention.

Example 1

About 93% anhydrous alumina (Al₂O₃) ground or particles of a diameter smaller than one micron is admixed to about 5% bentonite and about 2% fluor spar which are all ground to particles of less than one micron diameter. The mixture is shaped, preferably under pressure, and then heated to about 1650° C. for about 12 hours. A heterogeneous gas-tight product is obtained which can be used for heating temperatures up to about 1600° C. Without aging and without becoming permeable to gases. The amount of bentonite may be varied between about 2% to 6%, and that of fluor spar between 1% to 5%. The particles may be ground together or individually, and diameters up to about 20 microns are still suitable.

It is to be understood that by reducing said diameter the period of firing the mixture can be shortened whereas by increasing the amount of bentonite and fluor spar, which form substantially fluxes, the firing temperature can be reduced to about 1500° C.

Example 2

70% to 90% alumina, 6% to 26% magnesia, 2% to 6% bentonite are ground to particles the diameter of which is below 30 to 3 microns, and the mixture is fired to about 1600° C. for 24 hours. A particularly satisfactory result is obtained by using 70% alumina, 28% magnesia and 4% bentonite.

Example 3

1% to 5% chromium oxide, 1% to 6% bentonite, 1% to 4% magnesium phosphate, balance alumina, are ground to less than 30 micron diameter and heated at 1600° C. for 36 hours. Particularly satisfactory results are obtained with 2% chromium oxide, 92% alumina, 4% bentonite and 2% magnesium phosphate.

Example 4

1% to 10% magnesia, 1% to 20% chromium oxide, 2% to 8% beryl llite, balance alumina, are ground to less than 20 microns diameter of the particles are heated to 1620° C. for about 30 hours. Particularly good results are obtained with 4% magnesia, 10% chromium oxide, 80% alumina and 6% beryl liltte (c.f. Journ. of the American Ceramic Society, issue of August 1938, p. 276/7).

Example 5

20% to 60% sillimanite, 1% to 10% chromium oxide, 2% to 8% beryl liltte, 2 to 6% calcium borate, balance alumina, are ground to particles of less than 30 microns in diameter and fired at 1520° C. for about 48 hours. Particularly satisfactory results are obtained with 30% sillimanite, 56% alumina, 40% chromium oxide, 6% beryl liltte and 4% calcium borate.

Example 6

10% to 30% zirconia, 2% to 6% bentonite are ground to less than 6 microns in diameter of their particles and admixed to about 5% to 15% ground talc of 325 mesh. To this a balance of alumina is admixed, ground to less than about 55 microns diameter of its particles. Particularly satisfactory results are obtained with 65% alumina, 20% zirconia, 10% talc and 5% bentonite, fired to 1580° C., for 120 hours. After it is finished, this product is incapable of water absorption at any temperature.

Example 7

10% to 30% cerium oxide, 1% to 8% magnesium phosphate, 2% to 8% beryl liltte, balance alumina, are ground to particles of less than 20 microns diameter of the particles and fired. Particularly good results are obtained with 20% chromium oxide, 70% alumina, 5% magnesium phosphate and 5% beryl liltte, ground to less than about 670 microns diameter of the particles and fired for 72 hours at 1600° C.

Example 8

About 5% beryllium oxide, about 45% chromi-
um oxide, about 45% alumina, about 5% bentonite are ground to less than 20 microns diameter of the particles and fired for about 24 hours at about 1680° C.

**Example 9**

5 to 25% titanium dioxide, 5% to 15% talc, 2% to 8 bentonite, 5% to 25% zirconia, balance alumina, are ground to less than 20 microns diameter of their particles and fired for about 30 to 40 hours at about 1680° C. Particularly satisfactory results are obtained with 65% alumina, 10% zirconia, 10% titanium dioxide, 10% talc and 5% bentonite. The addition of talc results in a slight reduction in temperature, and bentonite serves as a flux.

**Example 10**

5% to 15% talc, 5% to 25% cerium oxide, 2% to 8% bentonite, balance chromium oxide, are ground to less than 20 microns in diameter of their particles (talc to about 25 mesh), mixed and fired for about 24 hours at about 1620° C. Particularly good results are obtained with about 65% chromium oxide, about 10% talc, about 20% cerium oxide and about 5% bentonite.

**Example 11**

70% to 90% MgO·Cr₂O₃, 3% to 8% zirconium silicate, 2% to 8% beidellite, balance alumina, are ground to less than about 20 microns in diameter of their particles and fired for about 48 hours at about 1620° C. Particularly good results are obtained with 80% MgO·Cr₂O₃, 10% alumina, 5% zirconium silicate and 5% beidellite. The latter acts as a mineralizer, as does bentonite, and causes the formation of different types of crystallites by the other components.

**Example 12**

10% to 30% thoria, 10% to 30% chromium oxide, 2% to 8% bentonite, 1% to 6% talc, balance alumina, are ground to less than about 20 microns diameter of the particles and to 35 mesh, respectively, and fired for about 24 hours at about 1650° C. Particularly favorable results are obtained with 20% thoria, 20% chromium oxide, 55% alumina, 5% bentonite and 2% talc.

It is to be understood that the invention is not limited to any of the examples given above but is to be derived in its broadest scope from the appended claims.

What I claim is:

1. A refractory ceramic gas-tight cover for a substantially metallic electrical resistor element, comprising a layer consisting of uniformly distributed and finely divided oxide compound and refractory substance other than said oxide compound, said oxide compound forming the major portion of said layer and being selected from oxide compounds, including oxide, melting above about 1600° C. of elements of the second, third, fourth and sixth group of the periodical system, said refractory substance forming the minor portion of said layer and comprising substantial amounts of an agent selected from fluxing and mineralizing agents, said oxide compound and substance sintered into a heterogeneous essentially crystalline structure substantially free of a vitreous phase.

2. In a refractory cover as described in claim 1, said oxide compound present in a minimum amount of about 80%, said agents comprised by said refractory substance present in an amount of about 1% to 15%.

3. A refractory ceramic gas-tight cover for a substantially metallic electrical resistor element, comprising a layer consisting of uniformly distributed and finely divided oxide compound and refractory substance other than said oxide compound, said oxide compound selected from oxide compounds melting above about 1650° C. of elements of the second, third, fourth and sixth group of the periodical system, said refractory substance forming the balance being capable of decreasing the sintering temperature of said oxide compound and exemplified by talc, said substance and oxide compound sintered into a heterogeneous essentially crystalline structure substantially free of a vitreous phase.

4. A refractory ceramic gas-tight cover for a substantially metallic electrical resistor element, comprising a layer consisting of uniformly distributed and finely divided oxide compound and refractory substance other than said oxide compound, said oxide compound forming the major portion, as exemplified by a minimum of about 80%, of said layer and selected from oxide compounds melting above about 1600° C. of elements of the second, third, fourth and sixth group of the periodical system and being present as amorphous particles of less than 5 to 30 microns diameter, said refractory substance forming the minor portion of said layer and substantially non-vitreous, said substance comprising substantial amounts of an agent selected from fluxing and mineralizing agents, said oxide compound and substance sintered into a heterogeneous essentially crystalline structure substantially free of a vitreous phase.

5. A refractory ceramic gas-tight cover for a substantially metallic electrical resistor element, consisting of uniformly distributed and finely divided oxide compound and a refractory substance, said oxide compound present in a minimum amount of about 80% and crystalline substantially non-vitreous particles of less than 5 to 30 microns diameter and being selected from oxide compounds melting above about 1600° C. of elements of the second, third, fourth and sixth group of the periodical system, said refractory substance forming the balance and consisting of essentially non-vitreous material substantially selected from a group consisting of bentonite, beidellite, talc and fluoropar, said cover sintered into a heterogeneous essentially crystalline structure substantially free of a vitreous phase.

6. In a refractory cover as described in claim 5, said refractory substance derived from comminuted particles corresponding to at least 325 mesh.

7. A refractory ceramic gas-tight cover for a substantially metallic electrical resistor element, comprising a layer consisting of uniformly distributed and finely divided essentially crystalline non-vitreous oxide compound and highly refractory substance, said oxide compound forming a major portion exemplified by a minimum of about 80% and selected from oxide compounds, including oxide, melting above about 1600° C. of elements of the second, third, fourth and sixth group of the periodical system, said refractory substance forming the balance and consisting of appreciable amounts of agents selected from fluxing and mineralizing agents and less than 3% to 10% vitreous material, said oxide compound and said highly refractory substance forming a layer consisting of uniformly distributed and finely divided oxide compound and refractory substance other than said oxide compound.
sintered into a substantially heterogeneous crystalline structure.

6. A refractory ceramic gas-tight cover for a substantially metallic electrical resistor element, consisting substantially of a sintered heterogeneous essentially crystalline mass substantially free of a vitreous phase and containing about 27% to about 97% alumina, about 1% to about 11% material of fluxing and mineralizing qualities as exemplified by bentonite, beidellite, talc and fluor spar, balance substantially oxide compound, including oxide, other than alumina selected from oxide compounds melting above about 1600° C. of elements of the second, third, fourth and sixth group of the periodical system.

9. A refractory ceramic gas-tight cover for a substantially metallic electrical resistor element, consisting substantially of a sintered heterogeneous essentially crystalline mass substantially free of a vitreous phase and consisting of about 20% to 60% sillimanite, about 1% to 10% chromium oxide, about 3% to 8% beidellite, about 2% to 6% borate, balance alumina.

10. A sintered refractory ceramic gas-tight cover for a substantially metallic electrical resistor element, comprising a layer of uniformly divided and distributed oxide compound and highly refractory substance, said oxide compound forming the major portion as exemplified by a minimum of 80% of said layer and consisting of at least two oxide compounds selected from oxide compounds, including oxide, melting above about 1600° C. of elements of the second, third, fourth and sixth group of the periodical system; said oxide compounds present in heterogeneous essentially crystalline structure, said refractory substance forming the balance of said layer and containing substantial amounts of an agent selected from fluxing and mineralizing agents capable of entering the crystal lattice of said major portion, said oxide compounds and agent heat treated to substantially permeate each other.

11. A refractory ceramic gas-tight cover for a substantially metallic electrical resistor element, substantially consisting of about 1% to 5% chromium oxide, about 1% to about 6% bentonite, about 1% to about 4% magnesium phosphate, balance aluminum oxide, sintered into a heterogeneous essentially crystalline structure substantially free of a vitreous phase.

12. A refractory ceramic gas-tight cover for a substantially metallic electrical resistor element, substantially consisting of about 70% to 90% MgO·Cr₂O₃, about 3% to 8% zirconium silicate, about 2% to 8% beidellite, balance aluminum oxide, sintered into a heterogeneous essentially crystalline structure substantially free of a vitreous phase.

13. A method of manufacturing gas-tight ceramic covers and coatings suitable for electrical heating elements adapted for operation in open air and under other conditions detrimental to the resistor material at operating temperature, comprising the steps of commingling a major portion of oxide compounds selected from oxide compounds melting above about 1600° C. of elements of the second, third, fourth and sixth group of the periodical system and in which at least said oxide compounds substantially permeate each other is obtained.

14. A method of manufacturing gas-tight ceramic covers and coatings suitable for electrical heating elements adapted for operation in open air and under other conditions detrimental to the resistor material at operating temperature, comprising the steps of forming an intimate powdery mixture of amorphous particles of less than 5 to 30 microns diameter of at least two oxide compounds, including oxide, selected from oxide compounds, including oxide, melting above about 1600° C. of elements of the second, third, fourth and sixth group of the periodical system, as a major portion exemplified by a minimum of 80%, and of highly refractory material comminuted to at least 320 mesh as a minor portion, shaping and firing the mixture between about 1500° C. and 1750° C. until crystallization and permeation of said oxide compounds without melting them occurs and a sintered body of substantially heterogeneous crystalline structure and in which at least said oxide compounds substantially permeate each other is obtained.

FELIX SINGER.
CERTIFICATE OF CORRECTION.


FELIX SINGER.

It is hereby certified that error appears in the above numbered patent requiring correction as follows: In the grant, line 1, and in the heading to the printed specification, line 3, residence of inventor, for "New York N. Y." read --South Croydon, Surrey, England--; page 4, second column, line 9, claim 3, for "1699° C." read --1699° C.--; line 62, claim 7, for "uniformly" read --uniformly--; page 5, first column, line 32, claim 10, for "meting" read --melting--; same page, second column, line 25, claim 13, for "crystalline" read --crystalline--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 24th day of September, A. D. 1940.

Henry Van Arsdale,
(Seal)
Acting Commissioner of Patents.
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Henry Van Arsdale, (Seal) Acting Commissioner of Patents.