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RESISTOR AND METHOD OF MAKING SAME

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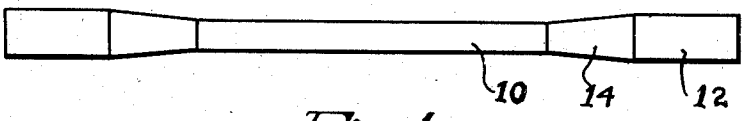


Fig. 1.

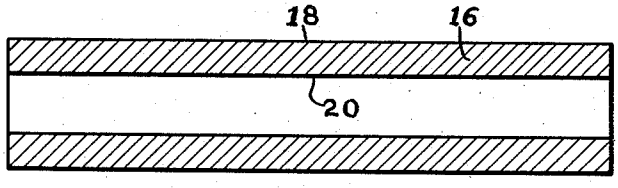


Fig. 2.

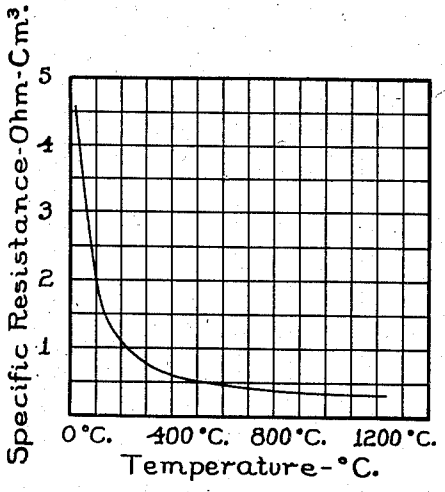


Fig. 3.

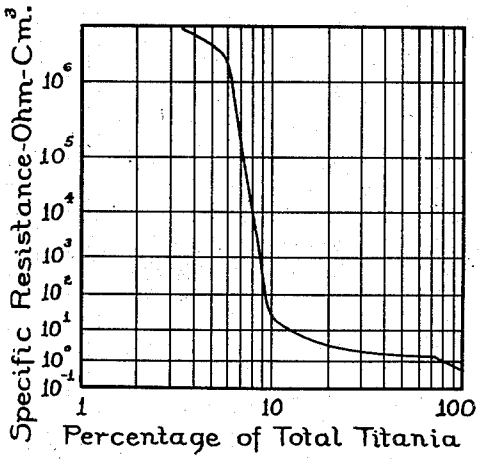


Fig. 4.

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RESISTOR AND METHOD OF MAKING SAME

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Application May 24, 1939, Serial No. 275,366

8 Claims. (Cl. 201—76)

The invention relates to resistor bars, compositions of matter for the manufacture of resistor bars and like products and methods of manufacture thereof.

One object of the invention is to provide a material for the manufacture of resistor rods for electric furnaces. Another object of the invention is to provide resistor rods of long life and good electrical properties. Another object of the invention is to provide a composition for resistor rods for high power furnaces of desired resistivity and great mechanical strength. Another object of the invention is to provide a composition for the manufacture of resistor bars which will make bars of long life.

Another object of the invention is to modify aluminum oxide so that in the fused condition it can be readily poured and on solidification will be conductive enough for use as a resistor for electric furnaces and will still have great strength. Another object of the invention is to provide a refractory conductor which will hold its electric conductive properties without deterioration. Another object of the invention is to provide a resistor capable of resisting a substantial amount of thermal shock. Another object of the invention is to provide a dense homogeneous oxide resistor free from pores and blebs with a surface free from welds and discontinuities. Another object of the invention is to provide a resistor having one or more of the characteristics indicated which will resist fusion up to a temperature of 1600° C. Another object of the invention is to provide a bar which even at high temperatures may be supported only at its ends. Another object of the invention is to provide a resistor bar with a self-formed glaze which seals the interior thereof against further oxidation. Another object of the invention is to provide a tube which has a refractory non-conductive coating integral therewith on the inside thereof so that it can act as a refractory container while the body of the tube acts as a resistor and radiates heat.

Another object of the invention is to produce a dense casting free from voids and gaseous inclusions. Another object of the invention is to provide a method of manufacture of the products indicated which is practical. Another object of the invention is to provide a method of production which will take care of the high shrinkages involved in refractory oxide products of the nature dealt with herein. 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, molecular and crystalline structure, arrangements of parts, and in the several steps and arrangement and order of each of said steps to one or more of the others thereof, as will be exemplified in the product, method and apparatus to be hereinafter described, and the scope of the application of which will be indicated in the following claims.

In the accompanying drawing:

Fig. 1 is a plan view of a resistor bar;

Fig. 2 is a sectional view of a resistor tube;

Fig. 3 is a resistance-temperature curve for a resistor embodying this invention; and

Fig. 4 is a curve showing the relation of specific resistance to the titania content of the resistor.

In accordance with this invention, an electrical heating resistance element may be made of titania interfused and crystallized with alumina. The titanium oxide of the resistor may be a mixture of TiO_2 and Ti_2O_3 which may be in the form of the composition and produced according to the method described and claimed in my copending application Serial No. 275,365 filed of even date herewith. As described in said copending application, as the starting material for the production of the desired mixture of TiO_2 and Ti_2O_3 I may meet and reduce purified titanium dioxide, TiO_2 to form a crystalline mass of TiO_2 containing from 5 to 50% of Ti_2O_3 and not over 5% of other refractory oxides selected from the group of zirconia and silica. The purified TiO_2 is an article of commerce and is produced by the chemical processing of rutile or ilmenite involving the solution of the mineral in chemical reagents and the reprecipitation of the dissolved TiO_2 in purified form. I preferable select a grade of TiO_2 comprising approximately 99% TiO_2 and I prefer that it have as much as 1% SiO_2 as this constituent favorably affects the physical structure of my final products. Commercial ceramic grade TiO_2 ordinarily has this much SiO_2 and I analyze samples to ascertain that my starting products contains such amount of silica. Preferably also my starting material has no more than a trace of any iron oxide, and the aforesaid commercial ceramic grade TiO_2 fills this specification. My starting material comes in the form of a light, fluffy, amorphous powder having a low apparent density and is comparatively free from moisture, having been calcined. I prefer a well calcined product. For the manufacture of partially reduced titanium oxide referred to above as a mixture of TiO_2 and Ti_2O_3 I provide

any suitable open top electric arc furnace such, for example, as a Higgins type furnace as disclosed in United States Patent Reissue No. 13,027 to Aldus C. Higgins, but preferably I provide a tilting furnace in order to be able to pour the molten charge. This furnace preferably has graphite electrodes and any suitable type of regulating mechanism. Any known size of furnace is suitable for carrying out the present invention.

I charge this furnace with my starting material of TiO_2. In a typical run using a furnace of total capacity of fifty pounds, when the power was maintained at from 60 to 75 kilowatts and the furnace voltage was 50 volts between the electrodes, the furnace feed rate was six-tenths of a kilowatt hour per pound of feed and the total run was completed in thirty minutes.

After the entire batch is thus fused, the fusing temperature being around 1650° C., I pour the melt into molds of any description to form blocks or bricks. I then crush these blocks or bricks to a grain or powder. As the result of fusing the chemically precipitated TiO_2 in the open type electric arc furnace there is produced a mixture of titanium oxides probably consisting mainly of TiO_2 and the remainder empirically identified as Ti_2O_3. The fusion described reduces only part of the TiO_2 to the suboxide represented by Ti_2O_3 and when carried out in the manner indicated does not reduce any substantial part of the starting material to the metallic form. With the rate of power input indicated the product will correspond to an analysis of about 85% TiO_2 and 15% Ti_2O_3. By using an open top electric arc furnace with graphite electrodes there is produced an atmosphere of carbon monoxide on top of the melt formed by the burning of the electrodes, and yet this is not pure nor is the atmospheric air so completely excluded that the reduction will go to an extreme extent. This fusion of titanium oxides in the percentage as indicated when cooled is a fairly coarse crystalline material having a dense black appearance and a conchoidal fracture and it is a conductor of electricity, its conductivity being along the order of that of poorly bonded carbon, carbonaceous materials, and the like.

This fusion of titanium oxides in the preferred form identified as having an analysis of about 85% TiO_2 and 15% Ti_2O_3 is, so far as the present invention is more specifically concerned, the starting material thereof. While substantially pure TiO_2 has a resistivity of about 11,730 ohms to the $cm.^3$, the partly reduced titanium oxide specified has a resistivity of about 340,000 microohms to the $cm.^3$. In other words the pure titanium dioxide TiO_2 has roughly thirty-five thousand times the resistance of the 85% TiO_2 15% Ti_2O_3 mixture.

I now charge the same Higgins furnace above referred to with the reduced titanium oxide powder which is the starting material more specifically for this present invention and some chemically pure prefused alumina preferably in the proportions of about 12 parts of the reduced titania to 88 parts of the alumina. Suitable alumina (aluminum oxide Al_2O_3) for use in carrying out this invention may be produced as described in my own prior Patent Reissue No. 20,457 reissued November 2, 1937. I may also use alumina produced as described in Patents No. 1,798,261 and No. 1,871,793 to Basil T. Horsfield. Furthermore any alumina such as produced by chemical precipitation and rather high temperature treatment to remove the soda will also do for the purpose. The foregoing are to be considered as examples and any relatively pure alumina will enable one to carry out the present invention.

It is preferred to crush the alumina to a powder as well as the reduced titania. I feed the reduced titania and the alumina preferably in powdered or grain form either separately or mixed to the Higgins furnace at the rate of about one pound of oxides per eight-tenths kilowatt hour input. I usually operate the furnace at about 65 to 75 volts with the electrodes adjusted to produce slightly reducing conditions but not enough to reduce the oxides to metallic alloys. When the charge is completed I hold the power on until the bath becomes a complete homogeneous thin liquid under the arcs. I have found in order to produce a denser casting with desired refractory fine grained structure that it is advisable to shut off the power and allow the melt to stand in the furnace crucible for a few moments before pouring. This allows the temperature to fall to a point where it is just above the crystallizing point of the liquid and when the melt is in this condition it is ready for pouring and will quickly crystallize to form the desired castings, which may be shaped as shown in Figs. 1 and 2 or otherwise as desired.

In a typical run 100 pounds of the oxides were fused using power at the rate of 35 kilowatts. The mixture was 11% titanium oxide and 89% aluminum oxide. The pouring temperature selected was 1700° C. and the liquid was poured into a mold heated to 1000° C.

The resistor bars are dense and have a fine granular blue-black structure which is mechanically strong and has a linear coefficient of expansion of approximately 80×10^{-7}. A microscopic study of the product shows that it consists of two phases, an intergrown phase of crystal alumina surrounded with a continuous network of $TiO_2.Ti_2O_3.Al_2O_3$ glass and slag which imparts the conductive properties to the mass. This reduced titania-rich phase seems to diffuse into the alumina crystals imparting a blue coloration to them.

For electric furnaces whose temperatures range up to 1100° C. oxidation resistant metal conductors have usually constituted the heating elements. Above this range, however, metal resistors have not in general been very useful because they deteriorate rapidly with use. Above the range of 1100° C. silicon carbide resistor rods have been chiefly used but such resistor rods while more suitable than metal products nevertheless deteriorate with use since they slowly oxidize resulting in the gradual rising of the resistance. Resistor bars made according to the present invention form in use a thin film of oxidized material, that is to say the Ti_2O_3 is probably re-oxidized to TiO_2. This film which may be of the order of one thirty-second of an inch thick protects the remainder of the resistor bar and over a long period of time no further oxidation takes place and the resistance value remains substantially constant.

It will be appreciated that in any resistor bar there is a desired range of resistivity. For example, one would not want the resistance to be lowered so that it would be the same as copper under certain power conditions, nor would one want the resistivity to be as high as that of aluminum oxide. I have found that by adding

approximately 12% of the starting product for this invention, which itself constitutes only about 15% Ti_2O_3, a resistor bar is achieved which has the desired resistivity for a high power electric furnace so that it can be embodied in bars whose cross-section is large enough to give adequate strength and whose length is about right for all practical considerations and furthermore the large proportion of alumina insures a strong resistor rod which will resist mechanical stresses and strains. At the same time a bar made as herein described is adequately resistant to thermal shock. In the resistor bar the conductive material is the Ti_2O_3 which is well dispersed as aforesaid.

Alumina is more refractory than titania and the large percentage of alumina in the resistor bars makes them highly refractory and also chemically stable. A typical resistor bar as described will resist softening or fusion up to 1600° C. and will absorb two kilowatts of energy and radiate it to the interior of an electric furnace while supported only at its ends. The resistor rod or bar is a vitreous fused oxide mixture and it has a clear metallic ring when struck with a hammer. Although as aforesaid it is resistant to heat shock this is a relative matter and being a vitreous or ceramic object it should be heated and cooled slowly. Its modulus of rupture at room temperatures has been determined to be 20,000 pounds a square inch. It has a specific gravity of from 4 to 4.1. Its specific resistance is .3 ohm/in.^{3} at room temperatures.

The curve of Figure 3 shows the temperature coefficient of the resistance. The curve of Fig. 4 shows the changes in resistance of different compositions of alumina with varying percentages of titania, of which 21% is Ti_2O_3. For different specific uses the amount of the ingredients Al_2O_3, TiO_2 and Ti_2O_3 will be varied. In order to produce resistor bars which are strong, refractory, and have the desired electrical characteristics, the quantity of total titania may range between 5 and 20 per cent, the balance being mainly alumina. Products having more than 50% alumina are highly refractory and have a chemical stability which makes them useful for many industrial applications. The starting material for this present invention and therefore also the final resistor bar preferably contains a small quantity of silica which causes the mass to crystallize as a fine grained structure and results in a smoother and denser casting of improved conductivity. Zirconia acts also to improve the crystal structure.

With regard to the formation of the oxide film I have found that when the resistor bar is placed on power and raised to a temperature between 1200 and 1400° C. the oxidation of the partially reduced material forms a glaze which seals the interior of the structure against further oxidation. This glaze may be between one thirty-second and one sixteenth of an inch thick and in a life test of a particular bar heated for ten thousand hours at 1100° C. the film at the end of the test was no thicker than one sixteenth of an inch at the thickest section.

I may cast the material herein described into many different shapes of resistor bars or other articles. Certain advantages inhere in a rod or bar which is square in cross-section because it thereby has a greater surface area and consequently radiates heat at a faster rate. In casting the mold should be cooled slowly, that is to say it should be covered or placed in a heated refractory container to avoid quick chilling of the mold.

Using a graphite mold which has been preheated to 1000° C. or thereabouts I have formed dense, homogenous, well knit resistor bars. These may be shaped as shown in Fig. 1 to provide a central cylindrical portion 10 of a diameter of five-eighths of an inch, cylindrical end portions 12 of a diameter of fifteen-sixteenths of an inch connected by frusto-conical portions 14, the longitudinal dimensions being 13¾ inches overall length with the end portions 2 inches and the central portion 6½ inches long. Also, as shown in Fig. 2, the bar may be shaped as a hollow tube 16 having an outer cylindrical surface 18 and an inner cylindrical surface 20, or any other suitable shape may be made. I may form tubes of the type shown in Fig. 2, and I have found that the glaze forms on the insides 20 of the tubes and the resistor bar is hence a refractory container. For many heat treatment products it is a decided advantage to have a resistor rod which is also a refractory container since dissipation of heat and power can readily be reduced. For example I might pack the resistor tube within magnesia cement and thus prevent it from radiating very much heat outwardly. As the heat would then radiate inwardly I could heat treat small articles with a minimum amount of power consumption.

Although the self-forming glaze, which has the refractory properties of fused alumina for example as sold under the trade-mark Alundum, is substantially an insulating material, nevertheless the firm clamping of metallic electrodes to the ends 12 of the bar 10 or to the ends of the tube 16 stops the oxidation so that throughout a long life of the resistor rod or tube the current flows freely into and out of it. Although I have described the production of rods and tubes in detail it should be understood that I may also make other shapes for example plates which can be used in furnaces as electric heating agents. Also although the articles described are electrical resistors for power furnaces, nevertheless the composition may be put to other uses.

Although silica has been described as the other ingredient besides two kinds of titanium oxide and alumina, I might substitute zirconia. If silica is used the amount thereof, if the product is to be used as a resistor, will be limited to a few per cent since otherwise the resistance is too great.

I have found definite effects from prefusing, casting and crushing the titanium oxide as thereby a fine grained structure results. There is a distinct advantage, therefore, flowing from the method involving two fusing processes. However, so far as many features of the invention are concerned, I may, still using two fusings, mix precipitated titania with alumina, fuse and reduce to form an ingot, then crush this ingot and refuse to form the final melt which is poured into the mold. In this modification of the process there are still two fusing operations of the original ingredients.

It will thus be seen that there has been provided by this invention a method and an article 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 above 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 drawing, is to be interpreted as illustrative and not in a limiting sense.

I claim:

1. An electrical resistor formed as a shaped, self-bonded, coherent, dense, continuous, monolithic, prefused, crystalline structure having alumina crystals as the major phase intergrown with a phase of crystals containing essentially titanium dioxide and a lower oxide and forming an electrically conductive refractory body.

2. An electrical resistor formed of an intergrown crystalline structure comprising essentially a major phase of crystalline alumina interspersed with and surrounded by a lesser amount of an electrically conductive glassy phase containing TiO_2, Ti_2O_3 and Al_2O_3 crystallized from a prefused mixture of said oxides as a dense, self-bonded, monolithic structure.

3. An electrical resistor formed as a shaped self-bonded crystalline structure, 95% of which is composed of crystalline alumina forming 80 to 95% of the total mass and titania forming 5 to 20% of the mass, and wherein 50 to 95% of the titania is TiO_2 and the balance is a partially reduced titania empirically represented by the formula Ti_2O_3, said ingredients being associated as crystals intergrown from a fused mass thereof.

4. An electrical resistor formed as a shaped, self-bonded crystalline structure containing from 75 to 95% of alumina, from 5 to 20% of titania and from zero to 5% of ingredients selected from the group consisting of silica and zirconia, the titania consisting of 50 to 95% of TiO_2 and the balance being a lower titanium oxide, said ingredients being associated as crystals intergrown from a fused mass thereof.

5. An electrical resistor formed as a shaped, self-bonded, prefused crystalline body having alumina crystals as the major phase intergrown with an electrically conductive phase of crystals containing essentially titanium dioxide and a lower oxide, said body having a protective surface glaze of titanium dioxide thereon.

6. An electrical resistor formed of a crystalline mass, 95% of which is composed of alumina constituting 80 to 95% of the total and titania constituting 5 to 20% of the total, the titania consisting of from 50 to 95% of titanium dioxide and the balance being a partially reduced titania empirically represented by the formula Ti_2O_3, said resistor being a shaped dense body having a conchoidal fracture formed by crystallization in a mold of a fused mixture of said ingredients.

7. The method of making an electrical resistor comprising the steps of fusing titanium dioxide under reducing conditions and providing a material containing not over 50% of a lower titanium oxide and crystallizing an interfusion of said reduced material with a larger amount of alumina as a shaped body having an intergrown crystal structure formed of said oxides.

8. The method of making an electrical resistor comprising the steps of fusing purified titanium dioxide in an open top electric furnace under mildly reducing conditions and reducing a minor portion thereof to a lower oxide, fusing said product with a larger amount of alumina and crystallizing the interfusion as a shaped mass having an intergrown crystalline structure.

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