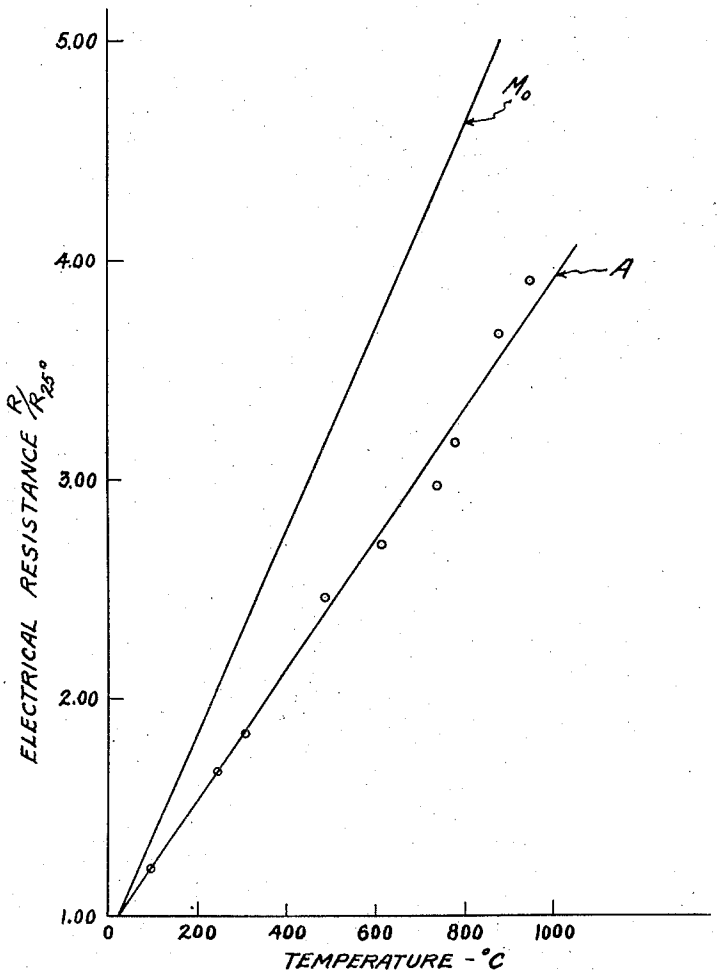
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METAL-CERAMIC ELECTRICAL RESISTORS

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METAL-CERAMIC ELECTRICAL RESISTORS

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This invention relates to a ceramic composition containing finely divided dispersed metallic particles, the composite material having a positive temperature coefficient of resistance. It is particularly concerned with electrical resistor elements comprising a matrix of kaolin or alumina ceramic or the like containing a dispersion of a metal such as tungsten or molybdenum or mixtures thereof and the method for producing such a resistor.

Electrical resistance elements and particularly such elements which are used as heating elements in evacuated apparatus or apparatus having an inert or reducing atmosphere, have in the past customarily been constructed from metallic wire elements. Resistance elements of this type have usually been constructed by winding a resistance wire composed of molybdenum or tungsten or the like upon a ceramic support. These wound wire resistors and heaters are relatively expensive to manufacture and further are not particularly durable, repeated heating and cooling cycles having an embrittling effect upon the wire. Previous attempts to lower the resistance of ceramic materials, of which I am aware, have either involved coating a ceramic body with a conductive material, such as carbon, for example, or introducing a conductive substance such as metal powder into the powered ceramic material before forming and firing it. In the case of the latter procedure, great difficulty is experienced in consistently obtaining intermediate resistivities. For example, very high resistivities of the order of 10,000 ohm-centimeters or greater and very low resistivities of the order of 0.01 ohm-centimeters or lower, are relatively easily prepared by such a procedure but great difficulty has been encountered in consistently preparing metal-ceramic resistors having a resistivity of the order of 0.04 to 10.0 ohm-centimeters. The above-cited resistivities are room temperature values. For many applications it is desirable that resistors and resistance heating elements have a positive temperature coefficient of resistance, i. e., as the temperature of the resistor element is raised, the resistance of the element increases. Additionally, it is frequently desirable that this positive change in resistance with a corresponding change in temperature be linear, particularly in instrument or control circuits and the like. It is to the solution of the previously stated problems that this invention is directed.

A principal object of my invention is to provide a metal-ceramic electrical resistance composition having a positive temperature coefficient of resistance. A further object of my invention is the provision of a metal-ceramic heating element for use in a vacuum or a reducing or neutral atmosphere. A still further object of by invention is the provision of a method whereby metal-ceramic resistors having a positive temperature coefficient of resistance may be made.

Briefly stated, in accordance with one aspect of my invention, I provide an electrical resistor comprising a formed ceramic body having dispersed therethrough finely divided metal which permits the conduction of an electrical current. Addiitonally, I provide a method for producing such a formed ceramic body which includes the step of reducing finely divided oxides of the conductive metal in place during firing of the ceramic body.

In the accompanying drawing, the change in electrical resistance with an increase in temperature is illustrated for a typical metal-ceramic of my invention compared to molybdenum, a typical resistance element metal, and will be discussed more in detail in the following specification.

Metal-ceramic resistors and heating elements of the present invention are prepared in general by mixing a finely divided oxide of a metal which is easily reducible in hydrogen with an insulating substance which may be formed and fired into a ceramic body. These materials are ground together wet, preferably in a ball mill or like type of apparatus into a finely divided, homogeneous mixture and formed into any desired shape, for example, a tube or rod. The formed elements are then fired in a hydrogen atmosphere or other reducing atmosphere capable of reducing a metallic oxide to the metallic state in place in the formed element. The time and temperature of firing may be varied in accordance with the shape and dimensions of the body and the particular ceramic employed. Selected areas of the fired ceramic element are then metallized to provide electrical contacts.

In order to disclose more fully certain aspects of my invention, the preparation of certain specific compositions will be discussed and the resulting electrical properties shown as examples of my invention.

In the following specific examples, molybdic oxide was used as the metallic oxide since it is an easily reducible oxide and metallic molybdenum possesses desirable resistance qualities. The ceramic material selected was kaolin. Since molybdic oxide is somewhat soluble in water, it is desirable to mill it in organic liquids. I have found methyl alcohol to be satisfactory for this purpose. In composition A the extrusion was made with polyvinyl alcohol in water, a practice not followed with other compositions. The other compositions which appear in the tables were extruded with Lucite (a polymerized methyl methacrylate resin) in ethylene dichloride. Since the function of these materials, i. e., Lucite in ethylene dichloride and polyvinyl alcohol in water, is merely to act as a lubricant in the die and as a binder of a temporary nature prior to firing, it will be appreciated that any material having these characteristics and qualities which is not incompatible with the organic milling liquid used, could be substituted for the particular materials herein disclosed by way of example. In these particular examples, the milled mixtures were extruded as rods although it should be appreciated that my invention is not limited to elements formed as extruded rods nor, in fact, to any particular shape. For example, tubes could equally well be extruded. It should also be pointed out that I do not wish to be limited to extrusion as a means of shaping or forming the material prior to firing. Any satisfactory method of forming the material may be used. The formed composite material is then fired in a reducing atmosphere. In all these examples hydrogen was used. Molybdic oxide melts at 795° C. and dissociates at a lower temperature if given time. Therefore, I have found that a firing cycle in which a temperature of be-

tween 500° C. and 700° C., preferably about 600° C., is held for a short time, for example, about an hour, before proceeding to a final temperature of the order of 1500° C. to be satisfactory. This cycle permits the finely divided particles of molybdic oxide to be reduced without the danger of the oxide particles first melting and coalescing and thereby forming larger reduced molybdenum particles. In this manner, a finely divided substantially even dispersion of metal in the ceramic matrix is assured. After firing, the several rods were metallized at their ends using molybdenum obtained by firing on molybdic oxide. Electrical resistance measurements were then made upon these rods between room temperature and about 1000° C. and the results summarized in the following tables.

Table I

	A	B
MoO_3 {MoO_3 content 83.6%, Mo content 55.7%}	60%	50%
#27 Georgia Kaolin	40	50
	100	100
Milled in	Methyl alcohol	Methyl alcohol.
Extruded with	Polyvinyl alcohol in water.	Lucite in ethylene dichloride.
Die diameter	.225"	.225".
Fired in H_2 at	1,500° C	1,500° C.
Fired diameter	.180"	.174"
Percent Mo by analysis	55.0	
Resistance for 1⅝" length Between terminals:		
25° C	12.8 ohms	Infinite.
975° C	50.0 ohms	
Room Temperature Resistivity.	0.512 ohm-cm	
Change per 1° C. per ohm	+0.0041	

Table II

	C	D
MoO_3 {MoO_3 content 99.5%, Mo content 66.2%}	64.8%	73.7%
#27 Georgia Kaolin	35.2	26.3
	100.0	100.0
Milled in	Methyl alcohol	Methyl alcohol.
Extruded with	Lucite in ethylene dichloride.	Lucite in ethylene dichloride.
Die diameter	.225"	.225".
Fired in H_2 at	{600° C, 1,500° C}	600° C, 1,500° C.
Percent Mo by analysis	58.3	67.6.
Fired diameter	.150"	.150".
Resistance for 1¼" length Between terminals:		
25° C	15.5 ohms	Less than 1 ohm.
1,000° C	68 ohms	
Room Temperature Resistivity.	0.561 ohm-cm	
Change per 1° C. per ohm	+0.0045	

In order to illustrate more clearly the temperature-resistance characteristics of materials made in accordance with my invention, the accompanying drawing graphically compares the change in resistance with corresponding change in temperature of one of my compositions with metallic molybdenum wire. The two respective lines are plotted as shown with the abscissa representing temperature in degrees centigrade and the ordinate the ratio of electrical resistance at elevated temperature to electrical resistance at 25° C., substantially room temperature. The relationship of resistance to temperature is shown only for composition A in order to most clearly illustrate this property. As can be seen from a comparison of the data contained in Tables I and II, the behavior of composition C is very similar to that of the illustrated composition and a plot of both would result in substantially overlying points which would not contribute to the clarity of the illustration.

The several points from which the line representing the electrical characteristics of my composition A is shown were obtained by direct measurement of the resistance of a specimen at the various temperatures indicated, these resistance values then being divided by the resistance of the specimen at room temperature. These values are shown in Table III, following.

Table III

Temp., ° C.	Resistance (Ohms)	R/R25°
26.0	12.8	1.00
52.5	13.8	1.08
76.0	14.5	1.13
96.5	15.3	1.20
250.0	21.1	1.65
314.0	23.4	1.83
505.0	31.5	2.46
632.0	34.5	2.70
760.0	38.0	2.97
803.0	40.5	3.17
915.0	47.0	3.67
975.0	50.0	3.91

It was found that the resistance of this particular material exhibited an approximately linear four-fold increase with an increase in temperature from 25° C. to 975° C. and returned to its initial value on cooling. It is also apparent that these materials exhibit a positive temperature coefficient of resistance.

From the foregoing, it will be seen by a person skilled in the art that I have provided an inexpensive metal-ceramic material from which electrical resistor and heating elements may be conveniently fabricated and which may be advantageously substituted for conventional wire wound resistors and heating elements for use in a vacuum or in an inert or reducing atmosphere. I contemplate that such substitution could be made for example, in heaters for vacuum tubes, heaters in protective atmosphere or vacuum furnaces, and resistors requiring a positive temperature coefficient of resistance, among many other applications which would readily occur to a person skilled in the art. I further contemplate that such resistors or heating elements could be made according to my invention by substituting other reducible oxides of molybdenum, including molybdates for the molybdic oxide disclosed in the foregoing examples. I also contemplate the substitution of reducible oxides of tungsten, such as WO_3 and tungstates in whole or in part for the reducible molybdenum compounds. I further contemplate that many other known inorganic substances could be substituted for kaolin or alumina ceramic disclosed previously.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. An electrical resistance element consisting essentially of a fired body of a ceramic selected from the group consisting of kaolin and alumina providing a matrix which contains from about 35 weight percent to about 70 weight percent of a finely divided, substantially even dispersion of a metal selected from the group consisting of tungsten and molybdenum and mixtures thereof.

2. An electrical resistance element having a positive temperature coefficient of resistance consisting essentially of a fired body of a ceramic selected from the group consisting of kaolin and alumina providing a matrix which contains from about 35 weight percent to about 70 weight percent of a finely divided, substantially even dispersion of a metal selected from the group consisting of tungsten and molybdenum and mixtures thereof.

3. An electrical resistance element having a resistivity of between about 0.04 and 10.0 ohm-centimeters at about 25° C. and a positive temperature coefficient of resistance consisting essentially of a fired body of a ceramic selected from the group consisting of kaolin and alumina providing a matrix which contains from about 35 weight percent to about 70 weight percent of a finely divided, substantially even dispersion of a metal selected from the group consisting of tungsten and molybdenum and mixtures thereof.

4. An electrical resistance element as recited in claim

3 in which the ceramic body consists essentially of fired kaolin.

5. An electrical resistance element as recited in claim 4 in which the metal is molybdenum.

6. An electrical resistance element as recited in claim 5 in which the resistivity at 25° C. is between about 0.4 and about 0.6 ohm-centimeter and the molybdenum content is between about 50 and 60 weight percent.

7. The method of making a metal-ceramic electrical resistor comprising the steps of milling powdered raw ceramic material selected from the group consisting of kaolin and alumina and a reducible oxide of a metal selected from the group consisting of tungsten and molybdenum and mixtures thereof into a finely divided homogeneous mass, forming a finite body by compacting and shaping the homogeneous mass, firing the body in a reducing atmosphere at an elevated temperature below the melting point of the reducible metal oxide for a time sufficient to reduce substantially all the metal oxide to metal and raising the temperature after the metal oxide is reduced to a temperature and for a time sufficient to produce a hard stable ceramic matrix which contains from about 35 to about 70 weight percent of the so-reduced metal in a finely divided substantially even dispersion.

8. The method recited in claim 7 which includes the additional step of providing the fired body with metallic,

electrically conductive contacts at selected surface portions of the body.

9. The method recited in claim 8 in which the powdered raw ceramic material comprises kaolin.

10. The method recited in claim 9 in which the reducible oxide is an oxide of molybdenum.

11. The method recited in claim 10 in which the reducible oxide is molybdic oxide.

12. The method recited in claim 11 in which the reducing atmosphere is hydrogen gas.

13. The method recited in claim 12 in which the body is fired first at a temperature of about 500° C. to 700° C. for a time sufficient to reduce substantially all the metal oxide without melting and then the temperature is raised to about 1400° C. to 1600° C. for a time sufficient to produce a hard, stable, ceramic matrix.

14. An electrical resistance element as recited in claim 4 in which the metal is tungsten.

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