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METHOD AND MEANS FOR CONTROLLING THE RESISTANCE
OF OXIDIC SEMICONDUCTORS
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FIG. 1

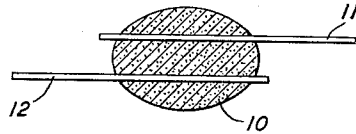


FIG. 2

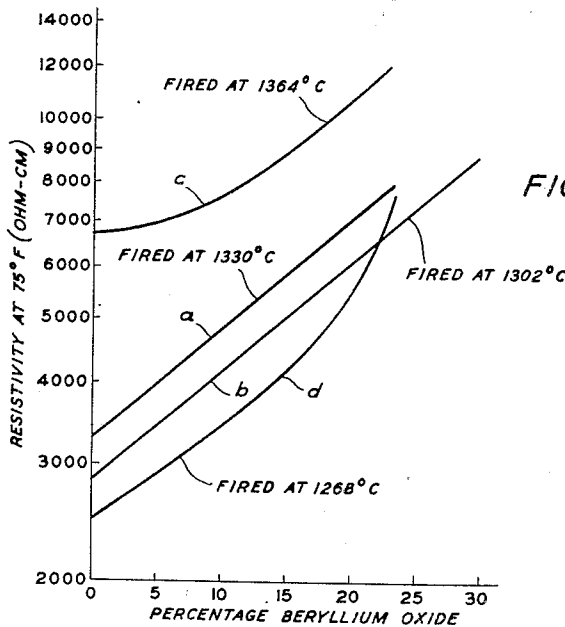
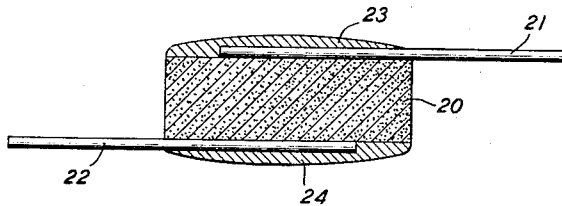


FIG. 3

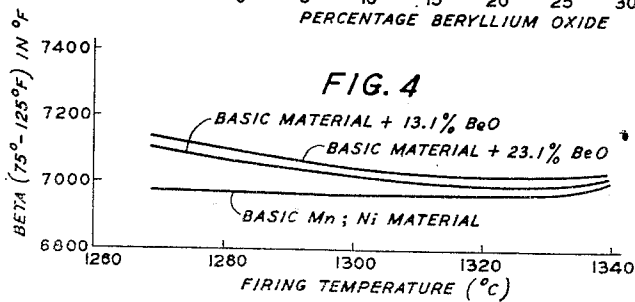


FIG. 4

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METHOD AND MEANS FOR CONTROLLING
THE RESISTANCE OF OXIDIC SEMICON-
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5 Claims. (Cl. 252-490)

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This invention relates to resistors and resistance materials having high negative temperature coefficients of electrical resistance and to a method of making such resistors and resistance materials. More particularly, the invention relates to resistance materials containing combinations of metal oxides.

Methods have been previously disclosed whereby resistance materials having particularly desirable characteristics are produced from combinations of metal oxides in proper relative proportions. For example, to mention only one specific type, the finished material may comprise combined oxides of manganese and nickel in the ratio of 4 atoms of manganese to 1 atom of nickel. The use of these resistors, sometimes referred to as "thermally responsive semiconductors" is now well understood in the art.

In connection with certain applications of semiconductors of the general type referred to, it is highly desirable to bring about a substantial increase in the specific resistance of the device over that prevailing in the instance of the devices heretofore disclosed without, at the same time, causing any appreciable change in the temperature coefficient over that previously prevailing.

An object of the invention is to improve resistors and resistance materials made from metal oxides.

A more specific object of the invention is to increase the specific resistance of resistors and resistance materials made from metal oxides.

A still more specific object of the invention is to materially increase the specific resistance of such resistors and resistance materials without materially changing the temperature coefficient thereof.

A feature of the invention resides in the addition of beryllium oxide in proper proportions to the metal oxides of the resistance material.

Applicant has discovered that if beryllium oxide be added to the metal oxides of the resistance material in proper proportions, as subsequently described in detail, the resistivity of the semiconductor will be increased to the higher value essential for certain applications of the device while the temperature coefficient thereof will not be materially changed; this last-mentioned effect is essential.

A complete understanding of the invention may be gained from the following detailed description and the attached drawings in which:

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Fig. 1 is a sectional view of one type of resistor illustrating one embodiment of the invention;

Fig. 2 is a sectional view of another type of resistor illustrating another embodiment of the invention;

Fig. 3 is a curve showing resistivity vs. per cent of beryllium oxide added at four different firing temperatures; and

Fig. 4 is a curve showing the beta values (temperature coefficient) for two materials containing beryllium oxide compared with the beta values of the material without the beryllium oxide.

The expressions "metallic elements present" or "metals present" are not intended to refer to metals as such but to the metallic elements in the oxide combination, the atomic viewpoint being intended. The term "temperature coefficient of resistance" is to be taken in its commonly used sense, i. e., as indicating variation of electrical resistance with changes in temperature. The term "beta" as used herein is a measure of the temperature coefficient, being related thereto by the formula $\beta = \alpha T^2$.

As previously disclosed, thermally responsive semiconductors having certain desirable characteristics may comprise 80 atomic per cent manganese and 20 atomic per cent nickel in the form of oxides. According to applicant's novel discovery, the specific resistance of such semiconductors (and those of other compositions) may be substantially increased, as desirable for certain applications, without materially changing the temperature coefficient thereof which is equally essential.

While in the following detailed description applicant's novel method will be disclosed in connection with semiconductors having the composition of 80 atomic per cent manganese-20 atomic per cent nickel in the form of oxides, it will be understood that it is not so limited but is applicable as well in connection with other compositions of metal oxides. Applicant has found that in the instance of the specific composition mentioned, the resistivity of the unit increases approximately 6 per cent for each 1 per cent of beryllium oxide added, this being in the firing temperature range of 1300° C.-1330° C.

In the preparation of resistance material of the type contemplated by the present invention, various established procedures may be followed. For example, in the preparation of one specific combination, an intimate mixture of manganese oxide and nickel oxide in the ratio of 4 atoms Mn to 1 Ni may first be formed by suitable steps

which may include calcining at a temperature of the order of 850° C. Beryllium oxide is then introduced in sufficient amount whereby it constitutes approximately 9.1 per cent of the total material present. The material is then thoroughly mixed by ball milling for approximately 62 hours in the presence of a suitable solvent. The intimately mixed oxides are then formed into a paste by combining with a suitable binder and formed into bodies of suitable size and shape for the particular purpose contemplated. These bodies are heat treated at temperature ranging from 1100 degrees to 1400 degrees.

A bead type unit such as that illustrated in Fig. 1 may be made by forming the paste into small beads 10 on parallel wires 11 and 12 of suitable refractory conductive material such as platinum. The beads are then dried and heat treated.

A unit of the disc or plate type, as illustrated in Fig. 2, may be made by intimately mixing finely divided oxides and pressing them into a body 20. Units of this type may be heat treated in a manner similar to that employed in the instance of the bead type units. Contact electrodes may be applied to opposite faces of the disc by suitable means. A suitable connection can be made by applying metallic paste to two surfaces and embedding conductive leads 21 and 22 therein. The units are then heat treated to solidify the paste into electrodes 23 and 24 firmly bonding the leads 21 and 22 to the resistance body 20.

While in the example given above, beryllium oxide in an amount comprising approximately 9.1 per cent of the total was mentioned, it will be understood that this is by way of illustration only. Other specific combinations contemplated are such as to result in the beryllium oxide comprising in approximate figures, 13.1 per cent; 16.7 per cent; and 23.1 per cent respectively of the total material.

The oxide mixture may be affected also by steps which include adding the beryllium oxide to carbonates of the manganese and nickel (the latter two elements in the ratio of 4 to 1); mixing in a colloid mill; reacting at 500° C.-600° C.; and calcining at 800° C.

Reference to Fig. 3 shows that for firing temperatures in the range of 1300° C.-1330° C. the resistivity of the material increases logarithmically for linear increases in the percentage of beryllium oxide added (curves *a* and *b*). Curves *c* and *d* show the effect of lower and higher firing temperatures on the shape of the curve.

Reference to Fig. 4 shows the beta values for two of the beryllium oxide containing materials (13.1 per cent beryllium oxide and 23.1 per cent beryllium oxide, respectively), compared to the beta values of the basic manganese-nickel composition. As indicated the beta values are not changed substantially by the addition of the beryllium oxide which, as previously brought out, is a particularly advantageous feature of the invention.

For compositions in which the beryllium oxide is not above 13 per cent of the total material present, firing temperatures in the range 1300° C.-1330° C. have been found desirable. In this range the 13 per cent beryllium oxide has the values:

Resistivity: 4300-5300 ohm-centimeters
Beta: 7000° F. (3900° C.)

For the 23 per cent beryllium oxide mixture a firing temperature of not less than 1330° C. is considered desirable.

While in the preceding detailed description applicant's novel method has been disclosed in connection with a resistance material including 80 atomic per cent manganese and 20 atomic per cent nickel in the form of oxides, it is applicable as well in connection with other resistance materials. For example, the contemplated method (i. e., basically the addition of beryllium oxide as described above) is applicable also in connection with resistance materials comprising the oxides of manganese, nickel and cobalt; the oxides of manganese, nickel and copper; the oxides of manganese and iron; and the oxides of iron and zinc. By way of example, the beryllium oxide may be added to a semiconductor having the composition of 52 atomic per cent manganese, 32 atomic per cent copper and 16 atomic per cent nickel in the form of oxides and the beryllium oxide may be added in sufficient amount whereby the beryllium oxide constitutes approximately 4.75 per cent of the total material present. In accordance with another specific mixture the beryllium oxide may constitute approximately 13 per cent of the total material present. It has been found that the resistivity of the unit increases by between 5 per cent and 10 per cent for each 1 per cent of beryllium oxide added while the beta value is not changed appreciably by the addition of the beryllium oxide.

While certain specific embodiments of the invention have been selected for detailed description the invention is not, of course, limited in its application to such embodiments. The selected embodiments should be looked upon as illustrative rather than as restrictive.

What is claimed is:

1. A thermally responsive semiconductor having a high negative temperature coefficient of resistance comprising a heat treated body of intimately mixed manganese, nickel and beryllium oxides, and electrodes attached to said body, the metallic elements of said body consisting of manganese and nickel in the ratio of 4 atoms to 1 respectively and an amount of beryllium oxide approximately 13.1 per cent of the total material present.

2. A thermally responsive semiconductor having a high negative resistance-temperature coefficient and relatively high specific resistance comprising a heat treated body of intimately mixed manganese, nickel and beryllium oxides, and electrodes attached to said body, the metallic elements of said body consisting of manganese and nickel in the approximate ratio of 4 atoms to 1 respectively and an amount of beryllium oxide which does not exceed 20 per cent of the total material present.

3. A thermally responsive semiconductor having a high negative resistance-temperature coefficient and relatively high specific resistance comprising a heat treated body of intimately mixed manganese, nickel and beryllium oxides, and electrodes attached to said body, the metallic elements of said body consisting of manganese and nickel in the approximate ratio of 4 atoms to 1 respectively and an amount of beryllium oxide which is approximately 9.1 per cent of the total material present.

4. A thermally responsive semiconductor having a high negative resistance-temperature coefficient and relatively high specific resistance comprising a heat treated body of intimately mixed manganese, nickel and beryllium oxides, and electrodes attached to said body, the metallic elements of said body consisting of manganese

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and nickel in the approximate ratio of 4 atoms to 1 respectively and an amount of beryllium oxide which is approximately 16.7 per cent of the total material present.

5. A thermally responsive semiconductor having a high negative resistance-temperature coefficient and relatively high specific resistance comprising a heat treated body of intimately mixed manganese, nickel and beryllium oxides, and electrodes attached to said body, the metallic elements of said body consisting of manganese and nickel in the approximate ratio of 4 atoms to 1 respectively and an amount of beryllium oxide which is approximately 23.1 per cent of the total material present.

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