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ELECTRICAL RESISTOR

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1

For the manufacture of electric resistances there were described different combinations of Fe_3O_4 with other double-oxides of the spinel type according to the formula: $R^{II}O.R_2^{III}O_3$, in which R^{II} is a bivalent and R^{III} is a trivalent element.

Furthermore it is known that with high load particularly stable resistances may be obtained by converting combinations of

$$FeO—Fe_2O_3—MgO—Al_2O_3$$

into a sintered mass which consists of a homogeneous spinel phase and which is not oversaturated with a second phase at a temperature of about 500° C.

A drawback which occurs more particularly in the manufacture of products according to the last-mentioned proposal was the high sintering temperature of from 1500 to 1600° C., which was troublesome in practice. By the use of fusing agents this drawback could not be obviated very well without detrimentally affecting the resistance properties and more particularly the stability.

It is true that according to another proposal the sintering temperature may be reduced to about 1400° C. by substitution Cr_2O_3 for Al_2O_3 in the combination of $FeO—Fe_2O_3—MgO—Al_2O_3$ but this temperature, too, is still disturbingly high especially in view of the requirements which the furnaces have in this case to satisfy with manufacture on a large scale.

The present invention purports further to reduce the sintering temperature whilst obtaining a product equivalent to that according to the two last-mentioned proposals.

According to the invention, the conductive material of the resistances consists to this end of mixed crystals of Fe_3O_4 with a spinel of the type $2R^{II}O.R^{IV}O_2$, in which formula R^{II} represents a bivalent and R^{IV} a tetravalent element. As such may be mentioned all titanates and stannates with spinel structure, for example Mg_2TiO_4, Zn_2TiO_4, Ni_2TiO_4 and Zn_2SnO_4 or their mixed crystals.

The resistance value as well as the temperature coefficient of resistances thus composed may be adjusted by the choice of the content of Fe_3O_4 and the presence, if any, of a second phase in the sintered product.

As regards the temperature coefficient it may be mentioned that this is highly negative in products consisting of a homogeneous spinel phase of which less than approximately half is built up from Fe_3O_4 molecules and which is not oversaturated with a second phase at a temperature

2

of about 500° C. If this condition is fulfilled any separation of a second phase at temperatures over 500° C., which would produce undesirable variations in the resistance properties, cannot occur. At lower temperatures the speed of separation is so small that no difficulty is encountered in this respect.

Products of a lower temperature coefficient may be obtained if more than approximately half of the spinel phase consists of Fe_3O_4 molecules. As the conductivity owing to the high percentage of Fe_3O_4, greatly increases it may in this case be desirable to influence the specific resistance by the presence of a second phase. For this purpose use may be made, for example, of semiconductive or insulating compounds which do not dissolve or dissolve only with difficulty in the spinel phase, for example MgO and ZrO_2.

For the manufacture of resistances according to the invention the required material is finely divided and intimately mixed and subsequently given the desired shape in a manner customary in ceramic technics, whereafter sintering to compactness may be effected at a temperature of about 1300° C. The conditions in the sintering and cooling processes, that is to say the temperature and the partial pressure of the oxygen in the surrounding gas as well as the composition of the initial mixture are chosen to be such that the molecular ratio of the Fe_3O_4 to the other spinels in the mass is adjusted in connection with the resistance properties desired. In order that during the subsequent cooling process this ratio may be retained as well as possible, the cooling process may be effected rapidly whilst driving out the atmosphere containing oxygen by means of a relatively inert gas such as nitrogen. The material may also be sintered in an atmosphere in which the partial pressure of the oxygen decreases with temperature, i. e. an atmosphere of nitrogen containing superheated water vapor which is dissociable into oxygen and hydrogen, the rate of dissociation being dependent upon the temperature.

Since the content of Fe_3O_4 and hence the molecular ratio FeO. Fe_2O_3 may be adjusted by the choice of the sintering temperature and of the sintering atmosphere, the initial material used for the resistances according to the invention may be any forms of iron oxide and, if desired, iron powder, while the other constituents already referred to above may be used wholly or in part in the form of double-oxides.

Besides, it is of particular advantage that, owing to the circumstance already favourable

per se that the sintering temperature may be reduced to approximately 1300° C., the sintering process may be carried out in an atmosphere of pure nitrogen without the Fe_3O_4 formed from Fe_2O_3 being reduced further to the FeO. Thus the reproducibility of the resistance value is also very high.

Furthermore, the difficulties encountered in the manufacture of resistances according to the previous proposals are materially decreased. Thus, for example, the use of electric furnaces having a molybdenum winding in a protecting gas is possible since the latter at an operating temperature of approximately 1300° C. have a satisfactory period of life which is appreciably higher than at temperatures of approximately 1400° C. which had to be applied in sintering resistances on basis of Fe_3O_4 and magnesium chromite. Such advantages also occur with furnaces of any other type.

Owing to the circumstance that according to the invention, a product of high compactness is obtained, the resistances exhibit even with high load a particular stability which is equivalent to that of the above-mentioned resistances manufactured on basis of Fe_3O_4 and magnesium spinel or magnesium chromite.

The resistances according to the invention may be utilized, for example, for the suppression of current impulses, the stabilisation of the voltage or the compensation of the temperature coefficient of a circuit and, besides, for measuring temperatures.

Example I

0.375 gram-molecules of Fe_2O_3
1.5 gram-molecules of NiO
0.75 gram-molecules of TiO_2 are ground with alcohol in a ball-mill for 16 hours. The dried mass is worked with a solution of 20% methyl methacrylate in methyl-glycol acetate to form a kneadable mass and worked into rods of a diameter of 4 mms. with the aid of an extrusion press. The rods are subsequently sintered at 1300° C. for 1 hour in an atmosphere of pure nitrogen (oxygen content about 0.1%) and then cooled rapidly in a flow of nitrogen. The value of the specific resistance amounts to:

22000 ohms cm. at 22° C., 900 ohms cm. 138° C.
200 ohms cm. 227° C., 50 ohms cm. 332° C.

The resistances thus manufactured are suitable, for example, for measuring temperatures.

Example II

4.5 gram-molecules of Fe_2O_3
10.2 gram-molecules of ZnO
5.1 gram-molecules of TiO_2 are ground with ethyl acetate for 16 hours and with the use of a 10% nitrocellulose solution in ethyl glycol extruded into tubes of 6.3 mms. long having an external diameter of 8 mms. and an internal diameter of 4.5 mms. Subsequently, the tubes are heated at 1320° C. in a furnace of 30 cms. length at a travelling speed of 1 cm. per minute whilst using a flow of pure nitrogen (oxygen content about 0.1%) of 5 litres per minute.

The resistance value of the tube unloaded is 1600 ohms, whereas with a load of 100 milliamps. it decreases to 81 ohms. With this load the temperature at the hottest place is about 110° C. These resistances are suited, for example, to taking up current impulses.

What I claim is:

1. An electrical resistance having a negative temperature coefficient of resistance consisting of essentially mixed crystals constituted by 25 to 50 mol % of Fe_3O_4 and the balance a spinel having the formula $2R^{II}O \cdot R^{IV}O_2$, R^{II} being a bivalent metal selected from the group consisting of nickel and zinc and R^{IV} being a tetravalent metal selected from the group consisting of titanium and tin.

2. An electrical resistance having a negative temperature coefficient of resistance consisting of essentially mixed crystals constituted by about 25 mol % of Fe_3O_4 and the balance $2NiO \cdot TiO_2$.

3. An electrical resistance having a negative temperature coefficient of resistance consisting essentially of mixed crystals constituted by about 37½ mol % of Fe_3O_4 and the balance $2ZnO \cdot TiO_2$.

4. A method of manufacturing an electrical resistance having a negative temperature coefficient which comprises the steps of mixing about 25 to 50 mol % of Fe_3O_4 and 50 to 75 mol % of a spinel having the formula $2R^{II}O \cdot R^{IV}O_2$, R^{II} being a metal selected from the group consisting of nickel and zinc, and R^{IV} being a metal selected from the group consisting of titanium and tin, said spinel being formed by jointly heating the oxide of a metal of the first group with the oxide of the metal in the second group in the ratio of two mols of the former to one mol of the latter, and sintering the mixture in a nitrogen atmosphere at about 1300° C. for a sufficient time to produce mixed crystals constituted by about 25 to 50 mol % of Fe_3O_4 and the balance said spinel.

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