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METHOD OF MANUFACTURING ELECTRICALLY CONDUCTING MATERIAL HAVING A POSITIVE TEMPERATURE COEFFICIENT OF THE RESISTANCE, AND CONDUCTOR MANUFACTURED OF THIS MATERIAL

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ABSTRACT OF THE DISCLOSURE

A method of manufacturing electrically conducting material having a positive temperature coefficient of the resistance by sintering and reducing a mixture mainly comprising MgO and containing 0.25–1.5 mol percent of TiO_2, 0.35–2.5 mol percent of SiO_2 and 0.35–2.5 mol percent of CaO.

Conductors manufactured of a material obtained by using the method.

The invention relates to a method of manufacturing an electrically conducting material having a positive temperature coefficient of the resistance, and to a conductor manufactured of this material.

An electrically conducting material is known from the Netherlands Patent Application No. 298,534 published on 25th November 1965. This material can be obtained by reducing sintering of a mixture mainly comprising magnesium oxide and containing 0.5 to 3.0% by weight of titanium dioxide and 1.0 to 3.0% by weight of silicon dioxide. This material is very suitable for the manufacture of resistors which are exposed for long periods to comparatively high temperatures during operation.

Such resistors are frequently used as auxiliary resistors for limiting the ignition voltage in high-pressure mercury vapour discharge lamps in which the resistors are provided within the outer envelopes of the lamps. During the lifetime of the lamps (for example, 10,000 hours) the resistors are brought to a temperature of, for example, 600° C. Under these circumstances the resistance of the resistor is to remain substantially constant. This requirement is satisfactorily fulfilled by the resistors manufactured of the known electrically conducting material. Furthermore it has been found that the known resistors also have satisfactory mechanical properties and maintain these properties for very long periods.

A drawback of the known electrically conducting material is that the spread in the resistance of the conductors manufactured of this material is very large. A result thereof is that large numbers of the conductors have to be rejected because it is found that they do not have the desired resistance.

An object of the invention is to provide a method of manufacturing an electrically conducting material in which the above-mentioned drawback does not occur or substantially does not occur.

According to the invention a method of manufacturing electrically conducting material having a positive temperature coefficient of the resistance by sintering and reducing a mixture mainly comprising magnesium oxide and containing 0.25 to 1.5 mol percent of titanium dioxide and 0.35 to 2.5 mol percent of silicon dioxide which mixture also contains 0.35 to 2.5 mol percent of calcium oxide or compounds which produce the said quantity of calcium oxide upon heating.

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It has been found that when using a method according to the invention it is possible to obtain conductors whose resistance is very reproducible, i.e. in the manufacture of large numbers of conductors by means of a method according to the invention in which a given composition of the mixture to be sintered is chosen to be within the above-mentioned limits there is only a slight spread in the resistance. The conductors according to the invention, likewise as the known conductors, have satisfactory mechanical properties and also a very satisfactory temperature resistance so that the resistance in case of long exposure to high temperatures does not vary or varies to a slight extent only.

In a method according to the invention a mixture is preferably used which contains 0.4 to 0.9 mol percent of titanium dioxide, 0.6 to 1.35 mole percent of silicon dioxide and furthermore 0.6 to 1.35 mol percent of calcium oxide. In fact, conducting materials are then obtained whose resistances are most suitable for practical uses.

In an advantageous embodiment of a method according to the invention calcium oxide, titanium dioxide and silicon dioxide are present in the mixture in the molar ratio $(3\pm0.5):(2\pm0.5):(3\pm0.5)$. In fact, in that case optimum results are achieved as regards the reproducibility of the resistance and it is also found that the average resistance of the conductors manufactured of the material can very well be adjusted at a given desired value. This is particularly the case when the said molar ratio is substantially 3:2:3 and this ratio is therefore preferably used. The value of the average resistance of the conductors in case of a constant molar ratio of the oxides is determined by the total quantity of calcium oxide, titanium dioxide and silicon dioxide in the mixture. A given desired value of the resistance can be adjusted by varying the total quantity of the said oxides at a constant molar ratio (preferably 3:2:3), on the understanding that the resistance is larger as the total quantity of the oxides is chosen to be smaller.

In a method according to the invention it is possible to use, instead of magnesium oxide, a compound from which this oxide is produced upon heating, for example, magnesium carbonate. Titanium dioxide, silicon dioxide and calcium oxide may be present in the starting mixture as such or entirely or partly in a bound state, for example, as magnesium titanate or magnesium silicate. Calcium oxide may be used, for example, as calcium carbonate or as a coprecipitate of calcium carbonate and magnesium carbonate.

For performing the method according to the invention a starting mixture is preferably used which in addition to the same constituents contains an organic binder, for example, methyl cellulose or nitrocellulose. Before sintering the mixture in a reducing manner the binder can be removed by heating at a comparatively low temperature, for example, at 1300–1400° C. Already some sintering takes place at this heat treatment.

Sintering and reducing may be effected, for example, in a gas mixture consisting of approximately 85 vol percent of nitrogen and approximately 15 vol percent of hydrogen at temperatures of between 1700 and 2000° C. and preferably at approximately 1800° C., for example, for 5–30 minutes.

The invention will now be described in detail with reference to the following example.

A pulverulent mixture consisting of 97.1 mol percent of magnesium oxide, 1.1 mol percent of calcium carbonate, 0.7 mol percent of titanium dioxide and 1.1 mol percent of silicon dioxide is intimately mixed with a binder consisting of 4.8% by weight of methyl cellulose and 95.2% by weight of water and subsequently it is moulded into bars. The bars are dried in air and subsequently heated for 60 minutes at approximately 1350° C. Subsequently the bars are heated in an atmosphere of approximately 92% by volume of nitrogen and approximately 8% by volume of hydrogen for 15 minutes at approximately 1800° C. Electrodes are provided in a manner known *per se* on the conducting bars thus obtained for use as auxiliary resistors in high-pressure mercury vapour discharge lamps.

What is claimed is:

1. In the method of producing an electrically conducting material having a positive temperature coefficient of resistance in which a mixture of 0.25 to 1.5 mol percent of titanium oxide, 0.35 to 2.5 mol percent of silicon dioxide, and the balance principally magnesium oxide is heated in a reducing gas atmosphere at a temperature of about 1700° C. to 2000° C. for a time sufficient to sinter said mixture, the step of adding to said mixture 0.35 to 2.5 mol percent of calcium oxide to increase the reproducibility of the resistance of said material.

2. A method as claimed in Claim **1** in which the reducing gas is a mixture of nitrogen and hydrogen.

3. A method as claimed in Claim **2** in which the reducing gas is 85% by volume of nitrogen and 15% by volume of hydrogen.

4. A method as claimed in Claim **3** in which the heating time is about 5 to 30 minutes.

5. A method as claimed in Claim **1** in which the mixture comprises 0.4 to 0.9 mol percent of titanium dioxide and 0.6 to 1.35 mol percent of silicon dioxide, and 0.6 to 1.35 mol percent of calcium oxide.

6. A method as claimed in Claim **5**, in which the calcium oxide, titanium dioxide and silicon dioxide are present in a molar ratio of $(3\pm0.5):(2\pm0.5):(3\pm0.5)$.

7. A method as claimed in Claim **6**, in which the molar ratio of calcium oxide, titanium dioxide and silicon dioxide is substantially equal to 3:2:3.

8. An electrical conductor having a positive temperature coefficient of resistance and consisting essentially of the heat reaction product of 0.25 to 1.5 mol percent of titanium dioxide, 0.35 to 25 mol percent of silicon dioxide and 0.35 to 2.5 mol percent of calcium oxide, and the balance principally magnesium oxide, said electrical conductor being made in accordance with the process defined in Claim **1**.

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