

Specification

This invention relates to a process for the high temperature firing of a resistor material based on ruthenium oxide and/or ruthenates with a perovskite or pyrochlore structure by heat treating an article prepared from a ceramic substrate coated with a resistor compound which contains the above-stated resistor material and a fusible mineral binder.

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The area of application of the invention is the electronics industry: single component parts, multicomponents, electrical resistors, thick film hybrid circuits.

15 The invention comes within the context of the production of multi-function electronic components and in particular relates to a process in which a resistor paste based on RuO_2 is applied to an unsintered dielectric article and the two are together fired at elevated temperatures.

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Resistor compounds based on noble metals (Ag, Pd, Rh, Ru, Au, Pt, Ir), which compounds contain a mineral binder which melts at between 550 and 900°C are adequately known.

25 Resistor pastes are produced by thorough dispersion of the conductive substances and fluxes in an organic medium. This organic phase is necessary in order to allow application of the mixture, it is vaporised during firing of the resistor paste.

30 In order to obtain resistor layers having good reproducibility and, especially, elevated temperature stability (-50°C to +150°C), metal oxides are used as the active constituent of the resistors. RuO_2 and the compounds thereof, for example CaRuO_3 , $\text{Bi}_2\text{Ru}_2\text{O}_7$ and other mixed oxides
35 based on RuO_2 are well suited for this purpose. RuO_2 -based resistor pastes are today sintered at 850°C.

DE-A 16 40 561, for example, teaches a resistor composition prepared from 10 to 80 wt.% of finely divided ruthenium

oxide and 90 to 20 wt.% of glass, wherein part of the ruthenium oxide may be replaced by oxides from groups I, II and V of the periodic system. This resistor composition is fired on a non-conductive substrate at 650°C.

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Another resistor composition containing ruthenium oxide, glass and at least one oxide of the elements La, Nd, Pr and Sm is known from DE-A 32 47 224. Firing is performed at 850°C.

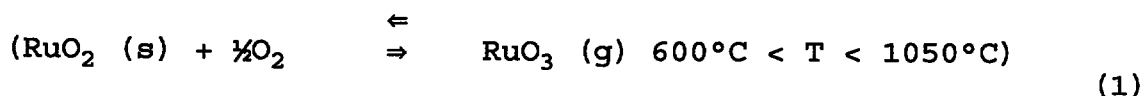
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JP-A 55086101 teaches a process for firing resistor elements, wherein during firing at last 50%, preferably the entirety of these elements lie in a powder bed of zinc oxide containing $\geq 0.2\%$ Bi_2O_3 .

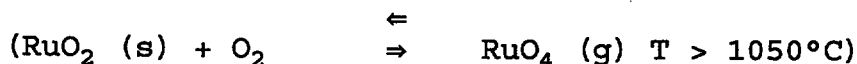
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The firing temperature of ruthenium oxide and RuO_2 -based mixed oxides cannot exceed 1000°C so that oxidation of the ruthenium IV is prevented. In fact, at temperatures of above 1000°C the ruthenium passes from oxidation number IV to oxidation number VI or VIII and forms RuO_3 or RuO_4 , oxides which are volatile at this temperature (*The thermodynamic properties and stability of ruthenium and osmium oxides*, A.B. Nikol'skii and A.N. Ryabov, *Russ. I. Inorg. Chem.*, vol. 10, n° 1 (1965)).

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Experience has shown that the ruthenium oxide based resistor layer is systematically volatilised at firing temperatures of above 1050°C in an atmosphere containing oxygen or a neutral atmosphere (N_2 , Ar).

In a neutral atmosphere, oxygen is introduced by the ceramic substrate or the mineral binder, a volatilisation reaction cannot be prevented.

Due to the volatilisation of ruthenium oxide, it has not been possible to fire resistor pastes based on RuO_2 or mixed oxides of RuO_2 as the active phase together with the ceramic substrate in the form of a central non-conducting component at elevated temperatures.

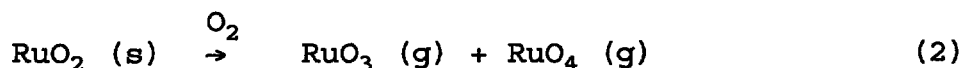
There was thus a need to develop a process in which the resistor material based on ruthenium oxide or compounds thereof is retained during firing of the ceramic substrate coated with the resistor compound at above 1000°C .

It has been found that the stated disadvantages of the known process may be avoided by a process for the high temperature firing of a resistor material based on ruthenium oxide and/or ruthenates with a perovskite or pyrochlore structure by heat treating an article prepared from a ceramic substrate coated with a resistor compound which contains the above-stated resistor material and a fusible mineral binder, wherein the heat treatment is performed at a temperature of above 1050°C in the presence of a powder bed of resistor material based on ruthenium oxide and/or ruthenates with a perovskite or pyrochlore structure of the same composition as in the resistor compound.

The powder bed saturates the environment of the resistor compound with gas, RuO_3 and/or RuO_4 . This environment blocks the volatilisation reaction of the ruthenium oxide (RuO_2) contained in the resistor compound.

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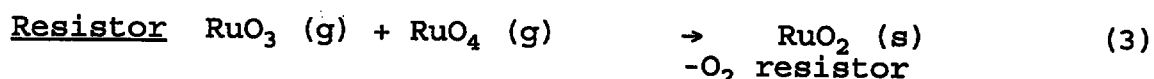
Powder



Reaction (2) is dependent upon:

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- $T^\circ\text{C}$
- powder volume
- O_2 partial pressure



Under these conditions, the resistor firing temperature may
5 exceed 1050°C.

The small quantity of material introduced by the resistors
does not alter the equilibrium (3). The active portion of
the resistor paste remains on the substrate.

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The resistor compound customarily consists of a resistor
material in the form of finely divided metal oxides, *inter*
alia ruthenium oxide and/or ruthenates with a perovskite or
pyrochlore structure and a powder of a mineral, fusible
15 binder, preferably a flux - the constituents are dispersed
in an organic medium. The electronic components are
produced by applying a layer of the resistor compound onto
a sintered or unfired ceramic substrate, this composite is
then thermally treated according to the claim in a covered
20 or open refractory crucible in a powder bed.

Thanks to the ruthenium oxide powder bed, the previously
applicable temperature limit of 1000°C may be exceeded and
the firing cycle specially adjusted to the conditions for
25 nonconductive ceramics for medium and high temperatures.
Firing is preferably performed at temperatures of between
1100 and 1300°C.

It is not necessary for the coated ceramic substrate to be
30 in direct contact with the RuO₂ powder. The powder may be
separated by a fine platinum grid in order to prevent a
flux or the ceramic support from possibly reacting the with
ruthenium oxide in the powder.

35 The following examples illustrate the practical realisation
of the invention in greater detail:

The starting material is an unfired ceramic substrate, for example barium titanate, magnesium titanate or titanium dioxide. This substrate has Ag/Pd contacts on its surface. The resistor paste is produced using customary methods. The
5 paste is applied in the desired structure by screen printing.

In order to ensure good reproducibility of the resistors, the thickness of the unfired layer is measured. The samples
10 are then dried and laid upon a platinum grid. The RuO_2 powder is located beneath this grid. The entire system (RuO_2 powder/grid/sample) is placed in a covered refractory crucible. The firing cycle is as follows:

15 Heating rate $5^\circ\text{C}/\text{min}$, holding time 1 hour 30 minutes at 1100°C , cooling rate $5^\circ\text{C}/\text{min}$ (guide values).

Resistor pastes based on RuO_2 with various contents and different fluxes were sintered using this process.

20 Substrate materials which may be used are electronics ceramics with low and high dielectric constants. The composite consisting of unfired ceramic, metal electrode and resistor is fired using the above-stated firing cycle. Some examples follow:

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Example 1

Resistor powder: Mineral binder 50%
Conductive phase 50%

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Mineral binder: Glass (Degussa product n° 90 564)
with the following properties:

Start of softening: 980°C

Hemisphere temperature: $> 1200^\circ\text{C}$

35 Coefficient of thermal expansion: $99 \times 10^{-7}/\text{K}^{-1}$

Conductive phase: ruthenium dioxide, obtained chemically from ruthenium chloride.

Preparation of paste for application by screen printing:

- 5 Mix mineral binder and conductive phase. Prepare a paste of the resistor powder with a screen printing medium (Degussa n° 2709)
- resistor powder 70%
 - medium 2709 30%
- 10 - screen printing
- drying
 - firing at 1100°C, 1 hour 30 minutes under the conditions according to the invention.
- 15 A RuO₂ based resistor layer with a resistance of $8 \cdot 10^{-3} \Omega \cdot \text{cm}$ is obtained (calculated from the measured value of $8 \Omega/\square$ and a layer thickness of $10 \mu\text{m}$).

Example 2

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Resistor powder: Mineral binder 75%
Conductive phase 25%

Mineral binder: as example 1

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Conductive phase: as example 1

Preparation of paste for application by screen printing:
as example 1

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A RuO₂ based resistor layer with a resistance of $12 \cdot 10^{-3} \Omega \cdot \text{cm}$ is obtained (calculated from the measured value of $12 \Omega/\square$ and a layer thickness of $10 \mu\text{m}$).

Example 3

Resistor powder: Mineral binder 50%
Conductive phase 50%

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Mineral binder: Flux (Degussa n° 90 255)
with the following properties:

Start of softening: 910°C

Hemisphere temperature: 1280°C

10 Coefficient of thermal expansion: $40 \times 10^{-7}/K^{-1}$

Conductive phase: as example 1

Preparation of paste for application by screen printing:
15 as example 1

A RuO_2 based resistor layer with a resistance of $5 \cdot 10^{-3} \Omega \cdot cm$
is obtained (calculated from the measured value of $5 \Omega/\square$
and a layer thickness of $10 \mu m$).

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Example 4

Resistor powder: Mineral binder 50%
Conductive phase 50%

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Mineral binder: Flux (Degussa n° E6.140.2)
with the following properties:

Start of softening: 810°C

Hemisphere temperature: 1250°C

30 Coefficient of thermal expansion: $56 \times 10^{-7}/K^{-1}$

Conductive phase: as example 1

Preparation of paste for application by screen printing:
35 as example 1

A RuO_2 based resistor layer with a resistance of $5 \cdot 10^{-3} \Omega \cdot \text{cm}$ is obtained (calculated from the measured value of $5 \Omega/\square$ and a layer thickness of $10 \mu\text{m}$).

5 **Example 5**

Resistor powder: Mineral binder 54%
Conductive phase 46%

10 Mineral binder: Vitreous ceramic (Degussa n° GPB01)
with the following properties:

Melting point: 1350°C

Coefficient of thermal expansion: $80 \times 10^{-7}/\text{K}^{-1}$

15 Conductive phase: as example 1

Preparation of paste for application by screen printing:
as example 1

20 A RuO_2 based resistor layer with a resistance of $1 \Omega \cdot \text{cm}$ is obtained (calculated from the measured value of $1 \text{ k}\Omega/\square$ and a layer thickness of $10 \mu\text{m}$).

Example 6

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Resistor powder: Mineral binder 60%
Conductive phase 40%

Mineral binder: as example 5

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Conductive phase: as example 1

Preparation of paste for application by screen printing:
as example 1

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A RuO_2 based resistor layer with a resistance of $100 \Omega \cdot \text{cm}$ is obtained (calculated from the measured value of $100 \text{ k}\Omega/\square$ and a layer thickness of $10 \mu\text{m}$).



Patent claims

1. Process for the high temperature firing of a resistor material based on ruthenium oxide and/or ruthenates with a perovskite or pyrochlore structure by heat treating an article prepared from a ceramic substrate coated with a resistor compound which contains the above-stated resistor material and a fusible mineral binder, wherein the heat treatment is performed at a temperature of above 1050°C in the presence of a powder bed of resistor material based on ruthenium oxide and/or ruthenates with a perovskite or pyrochlore structure of the same composition as in the resistor compound.
2. Process according to claim 1, characterised in that the firing proceeds at a temperature between 1100°C and 1300°C.
3. Process according to claim 1 or 2, characterised in that an unsintered electronics ceramic is used as the ceramic substrate.
4. Process according to one of claims 1 to 3, characterised in that the heat treatment proceeds in a covered or open refractory crucible in which the composite is placed on the powder bed or a grating above the powder bed.