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A characterization of thick-film PTC resistors

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Abstract

Thick-film PTC resistors (5093, Du Pont, 1 kΩ/sq.) with a high, linear and positive TCR were fired at temperatures between 750 and 950 °C. The development of the resistors' conductive phase and microstructure was investigated by X-ray powder-diffraction analysis and by scanning electron microscopy, respectively. Temperature coefficients of resistivity, sheet resistivities and noise indices were measured as a function of firing temperature. The 5093 resistor material is based on ruthenate, which decomposes during firing at temperatures over 800 °C into RuO_2. As the needle-like RuO_2 crystals form, the sheet resistivities decrease from very high values to a nominal resistivity of around 1 kΩ/sq. At firing temperatures higher than 850 °C the volume of the single-crystal RuO_2 grains increases and therefore their number in a given volume of thick-film PTC layer decreases. The network of "needles " starts to break, leading to increased sheet resistivities and increased noise indices.

Keywords: PTC thick-film resistors; Firing; Electron microscopy; X-ray spectra

1. Introduction

The main requirements for thick-film resistors are long-term stability and relatively narrow tolerances of the sheet resistivities after firing. An important characteristic is a low temperature coefficient of resistivity (TCR). After screen printing and firing, thick-film resistors basically consist of conducting and glass phases. In most modern resistor compositions the conductive phase is either RuO_2 or ruthenates, mainly lead or bismuth rithenates. In addition, some other oxides are added either as modifiers of the TCR or modifiers of the temperature coefficient of expansion of the glass phase [1–4]. During firing, resistors reach the highest temperature (typically 850 °C) in 10 or 20 min, and are only a relatively short time (typically 10 min) at this temperature. During the firing cycle the constituents of the material react with each other. The reactions presumably do not reach equilibrium, so the characteristics of the fired materials are a consequence of this frozen non-equilibrium state [5,6].

For some temperature-sensing applications resistors with a large, positive and linear temperature dependence of resistivity are required. Thick-film platinum-based materials have a TCR of around $+3500 \times 10^{-6}\,K^{-1}$, but the sheet resistivity is low, between 50 and 100 mΩ/sq. Another way to prepare PTC (positive temperature coefficient) thick-film resistors is to "load" a high concentration of RuO_2 into a glass phase. RuO_2 has a relatively low specific resistivity, $40 \times 10^{-6}\,\Omega\,cm$, and a positive, linear, metallic-like resistivity versus temperature dependence, with a TCR of $7000 \times 10^{-6}\,K^{-1}$ for single crystals and a few $1000 \times l0^{-6}\,K^{-1}$ for sintered microcrystalline samples [7,8]. Due to the high concentration of RuCh, the sheet resistivities are again relatively low, of the order of 10 Ω/sq. However, it is interesting to note—though admittedly not very relevant to this paper—that thick-film materials prepared either from "pure" fine-grained RuO_2 without a glass phase [9] or from a simple mixture of fine-grained RuO_2 and glass [10] have a TCR between $+500 \times 10^{-6}$ and $+600 \times 10^{-6}\,K^{-1}$, which is an order of magnitude lower than the TCR of RuO_2 single crystals.

Some ruthenate-based thick-film resistors with high, positive TCRs are described in the patent literature. Materials

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based on $(Ca,Cu)_2Ru_20_6$ or $(La,Cu)_2Ru_20_{7-x}$ pyrochlores have TCRs up to $2000 \times 10^{-6}\,K^{-1}$ [11]. Even higher TCRs were obtained for materials, based on $Pb_2Ru_2O_{6.5}$ with an addition of Cu_2O [12,13]. However, when the copper oxide was added to the resistor compositions based on RuO_2 instead of ruthenate the TCR was only around $1000 \times 10^{-6}\,K^{-1}$. Jiang et al. [14] investigated 10 Ω/sq. PTC resistors (5091, Du Pont), based on lead ruthenate with a copper oxide addition, by X-ray diffraction analysis as well as transmission electron microscopy (TEM). They concluded that during firing, as a result of a specific crystallographic relationship between the CuO and the RuO_2, which is formed due to the decomposition of ruthenate, long needle-like RuO_2 crystals grow and form a conductive network throughout the resistor body. The PTC characteristics are therefore due to the formation of elongated RuO_2 needle-like crystals during firing and not as a result of the original composition, i.e., ruthenate, copper oxide and glass in the resistor paste.

In this paper the characterization of the Du Pont PTC resistor 5093 as a function of firing temperature will be described and discussed. The TCR of 5093 resistors is $2750 \pm 250 \times l0^{-6}\,K^{-1}$ and the nominal resistivity is 1 kΩ/sq., which is rather high for commercial thick-film PTC materials [15].

2. Experimental

Thick-film resistors were printed on 96% alumina substrates, dried for 15 min at 150 °C and fired for 10 min at temperatures from 750 to 950 °C, and for 1 and 3 h at 950 °C. The resistors were terminated with a Pd/Ag conductor that was prefired at 850 °C. The electrical characteristics (sheet resistivity and noise) were measured mainly on resistors with dimensions of $1 \times 1\,mm^2$. Resistivity vs. temperature was measured on resistors with dimensions $1 \times 1\,mm^2$, $2.5 \times 2.5\,mm^2$ and $8 \times 1\,mm^2$, to estimate the contribution of possible resistor/termination interactions on the TCR values. Cold TCRs (from −25 to 25 °C) and hot TCRs (from 25 to 125 °C) were calculated from resistivity measurements at −25, 25, and 125 °C. Current noise was measured in dB on 100-mW loaded resistors by the Quan Tech method (Quan Tech Model 315-C). Resistors were also evaluated by complex-impedance analysis (Hewlett Packard 4192-A, 5 Hz to 13 MHz).

The dimensions of the resistors for the microstructural analyses and the X-ray diffraction analyses, which were printed and fired without conductor terminations, were $8 \times 8\,mm^2$. The dried resistors and the resistors fired at different temperatures were examined by X-ray powder-diffraction (XRD) analysis with a Philips PW 1710 X-ray diffractometer using Cu Kα radiation. The X-ray diffraction spectra were measured from $2\Theta = 20°$ to $2\Theta = 70°$ in steps of 0.02°. For the microstructural investigation the resistors, which were printed and fired on alumina ceramics, were mounted in epoxy in a cross-sectional orientation and then cut and polished using standard metallographic techniques. A JEOL JSM 5800 scanning electron microscope (SEM) equipped with a LINK ISIS 300 energy-dispersive X-ray analyzer (EDS) was used for the microstructural analysis. Prior to analysis in the SEM, the samples were coated with carbon to provide electrical conductivity and to avoid charging effects.

Resistors fired for 10 min at 750, 850 and 950 °C, were also investigated by transmission electron microscopy. Samples were prepared from 3-mm discs that were cut from the Al_2O_3 substrates (on which the thick-film resistor layers were fired) using an ultrasonic cutting device. The disks were then ground from the substrate side, dimpled to 20 μm and thinned by ion erosion (Baltec ion mill) using argon ions at 4 keV and an incident angle of 10° to the specimen. The samples were examined at an operating voltage of 200 kV in a JEOL 2000 FX transmission electron microscope equipped with a Link AN 10000 energy-dispersive X-ray spectroscopy (EDXS) system with a UTW Si(Li) detector and in a JEOL 2010 F, FEG transmission electron microscope with a Link Isis EDXS system attached.

3. Results and discussion

3.1. Microstructural, EDS and XRD characterization

The microstructure of the dried surface of a 5093 resistor is shown in Fig. 1a. The larger grey particles are the glass phase. Micrometer- or sub-micrometer-sized white particles are the ruthenate phase, rich in ruthenium, gadolinium and bismuth. Because of the relatively small size of the grains present, the influence of the matrix on the EDS measurements could not be neglected. However, the ratio of these three elements indicates a composition of (roughly) $(Bi_{1/3}Gd_{2/3})_2Ru_2O_7$. The addition of Cu_2O to the paste (see Introduction) was confirmed by an element distribution analysis (mapping) on the surface of the dried 5093 resistor shown in Fig. 1b (mapping of Cu). The distribution of the copper oxide particles can be seen.

The microstructures of the cross-sections of the 5093 resistors fired for 10 min at 750, 800, 850 and 950 °C are shown in Figs. 2–5, respectively. In all the figures the alumina substrate is on the right. The 5093 resistor, fired at 750 °C, is densely sintered but the surface is relatively rough. The dark particles, seen in all the cross-sections, are rich in Si and Zr, and are presumably $SiZrO_4$. The white phase consists of ruthenate particles, rich in ruthenium, gadolinium and bismuth, again with a Bi/Gd ratio of around 1/2. The microstructures of the resistors that were fired at 800 °C are similar. However, a few-micrometers-thick layer of glassy phase, rich in alumina, appears at the interface between the resistor and the Al_2O_3 substrate. After an 850 °C firing, three distinct layers could be seen in the microstructure; the layer with small, sub-micrometer-sized round inclusions on the top (left side of Fig. 4), the middle layer with whitish areas in the glass phase