THE INTERACIONS OF CONDUCTIVE AND GLASS PHASE IN THICK-FILM RESISTORS DURING FIRING

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Abstract: Some thick-film resistors based on RuO_2, ruthenates or a mixture of RuO_2 and ruthenates, were evaluated. The resistors were fired at different temperatures to determine the influence of firing temperature on the electrical and microstructural characteristics. The microstructures of the thick-film resistors were analysed with scanning electron microscopy and energy-dispersive X-ray analysis. The temperature coefficients of resistivity, noise indices and gauge factors were measured as a function of firing temperature. After a long term high temperature firing ruthenate based conductive phase transform into RuO_2 coinciding with a significant increase of the temperature coefficients of resistivity and decrease of the resistance. Glass phase in thick-film resistors was analysed by EDS. All glass compositions are rich in SiO_2 with the molar ratio SiO_2 / PbO between 2 and 2.5. Subsolidus equilibria in the RuO_2 - PbO - SiO_2 diagram were determined with the aim to verify the interactions between conductive phase (either ruthenium oxide or ruthenate) and silica-rich glasses. The tie line between RuO_2 and $PbSiO_3$ indicates that the lead ruthenats are not stable in the presence of the silica-rich glass phase.

Interakcije med prevodno in stekleno fazo v debeloplastnih uporih med procesom žganja

Kjučne besede: debeloplastni upori, karakterizacija, rutenijev oksid, rutenati, fazni diagrami

Izvleček: Karakterizirali smo nekatere debeloplastne uporovne materiale na osnovi RuO_2, rutenatov ali zmesi RuO_2 in rutenatov. Uporte smo žgali pri različnih temperaturah, da bi ugotovili vpliv temperature žganja na električne in mikrostrukturne karakteristike. Mikrostrukture debeloplastnih uporov so bile preiskane z elektronskim vrstičnim mikroskopom in rentgensko analizo. Izmerili smo temperaturne koeficiente upornosti, indekse tokovnega šuma in faktorje gauge v odvisnosti od temperature žganja. Ugotovili smo, da v debeloplastnih uporih, žganih dolgo časa pri povišanih temperaturah, rutenat preide v rutenijev oksid. Pri tem se zelo zniža plastna upornost in poviša temperaturni koeficient upornosti. Stekleno fazo v debeloplastnih uporih smo analizirali z EDS (Energy Disspersive X-ray Analysis). Ugotovili smo, da so vsa stekla bogata na SiO_2 z razmerjem SiO_2 / PbO med 2 in 2,5. Preiskali smo fazna ravnotežja v sistemu RuO_2 - SiO_2 - PbO. Rezultati so potrdili, da rutenat ni stabilen v prisotnosti stekel bogatih na SiO_2.

Introduction

Thick-film resistors consist basically of a conducting phase, a lead-borosilicate-based glass phase and an organic vehicle. The organic material is burned out during the high-temperature processing. The ratio between the conductive and the glass phases roughly determines the specific resistivity of the resistor. In most modern resistor compositions the conductive phase is either RuO_2 or ruthenates; mainly, as reported in the literature, lead or bismuth ruthenates. The main change during firing is the transition from a mixture of glass grains and, usually, much finer grains of the conductive phase in a thick-film paste, into conductive chains through the sintered glass in the fired resistor. During the firing cycle all the constituents of the resistor paste react with each other and the melted glass also interacts with the substrate The resistors are only a relatively short time (typically 10 min) at the highest temperature (typically 850°C). Because of this the reactions between the constituents of the resistor material do not reach equilibrium so that the required characteristics of fired materials (e.g long-term stability, low noise indices and a low temperature coefficient of resistivity) are, in a way, a compromise as a consequence of this frozen non-equilibrium /1-5/. The aim of this paper is to present the results on some thick film resistor material, fired either at the required 850°C for 10 min or at higher firing temperatures for significantly longer times. The aim was to gain some insight into the changes in the electrical and microstructural characteristics, and gauge factors if the resistors are fired long enough at the high temperature to allow the reactions within the resistor to reach the equilibrium. Thick-film resistors with a nominal resistivity of 10 kohm/sq. (Du Pont 8039 and 2041, and Heraeus 8241) were evaluated. The conductive phase in 8039, 2041 and 8241 resistors is based on $(Bi_{2-x}Pb_x)Ru_2O_{7-x/4}$, a mixture of RuO_2 and $Pb_2Ru_2O_{6.5}$, and RuO_2, respectively /6,7/. Data on the conductive phase and the qualitative results of an energy-dispersive X-ray analysis (EDS) of the glass composition of the thick-film resistors are summarized in Table 1. All glasses contain, as main elements, lead, silicon and aluminum oxides. Boron oxide, which is also present in the glass phase, cannot be detected in the EDS spectra because of the low relative boron weight fraction in the glass and the strong

absorption of the boron K_α line during EDS analysis in the glass matrix.

Table 1. Conductive phase and qualitative results of EDS microanalysis of elements detected in glass phase of thick-film resistors /17/.

Resistor	Conductive phase	Ma in elements	Other elements detected
8039	ruthenate	Si, Pb, Al	Zr
2041	RuO 2+ ruthenate	Si, Pb, Al	Mg, Zn, Ca, Ba
8241	RuO 2	Si, Pb, Al	Zn, Cu

The X-ray analysis of conductive phase in investigated thick film resistors will be given. The change of conductive phase (from ruthenate to the ruthenium oxide) at high firing temperatures, depending on the composition of glass phase will be discussed.

Experimental

Thick-film resistors with dimensions 1.6x1.6 mm^2 were printed on 96% alumina substrates and fired for10 min at 850°C and for 6 hours at 950°C. The resistors were terminated with a Pd/Ag conductor that was prefired at 850°C. Cold TCRs (from -25°C to 25°C) and hot TCRs (from 25°C to 125°C) were calculated from resistivity measurements at - 25°C, 25°C, and 125°C. Current noise was measured in dB on 100 mW loaded resistors by the Quan Tech method (Quan Tech Model 315-C). Gauge factors (GFs) were measured. The resistors were examined by X-ray powder-diffraction (XRD) analysis A JEOL JSM 5800 scanning electron microscope (SEM) equipped with an energy-dispersive X-ray analyser (EDS) was used for the microstructural analysis.

Results and discussion

Sheet resistivities, cold (-25°C to 25°C) and hot (25°C to 125°C) TCRs, noise indices and gauge factors of the investigated thick-film resistors that were 10 min at 850°C and 6 hours at 950°C are shown in Table 2.

After firing at 950°C for 6 hours, the resistivities of all the resistors significantly decreased to around 5% of the resistivities after firing at 850°C for the 2041 resistors, and to 1% or less for the 8039 and 8241 resistors. The GFs of all the resistors, as well as the sheet resistivities, decreased with increasing firing temperature. The TCR values of the resistors after firing at the "normal" temperature of 850°C are below $100x10^{-6}/K$. After firing for 6 hours at 950°C the absolute values of the TCRs of the 8039 and 8241 resistors increased significantly. The noise indices decrease with increased firing temperature. The 2041 resistor material has the lowest noise, around or under -20 dB, regardless of the firing temperature.

X-ray diffraction (XRD) spectra of ruthenate-based "equilibrated" resistors showed that at higher firing temperatures the ruthenate decomposes forming RuO_2, while the conductive phase in RuO_2-based resistors stays unchanged. This is shown in Figs. 1.a, 1.b and 1.c for 10 kohm/sq. Du Pont 8039 and 2041 thick film resistors, and Heraeus 8241 thick-film resistors, respectively /6/. As mentioned before, the 8241 resistor is based on RuO_2 and the 2041 material is based on a mixture of (mainly) ruthenate and RuO_2. The resistors were fired for 10 min at 850°C and for 6 hours at 950°C. After 6 hours of firing at 950°C the ruthenate peaks of the 8039 resistors disappear while the spectrum of RuO_2 based 8241 resistors remains unchanged. Presumably because of the interaction with the molten glass the ruthenate decomposes.

The decomposition of the ruthenate phase in the ruthenate-based 8039 resistor after high-temperature firing and the formation of RuO_2 was confirmed with SEM. Microstructures of the 8039 resistors that were fired for 10 min at 850°C and for 6 hours at 950°C are as an example in Figs. 2.a and 2.b. The microstructure of the 8039 resistor, fired at 850°C (Fig. 3.a) consists of light sub micrometer-sized particles of a conductive phase in a grey glass matrix. The dark particles are $SiZrO_4$. After 6 hours firing

Table 1: Sheet resistivities, cold and hot TCRs, noise indices and gauge factors of the thick-film resistors, fired 10 min at 850°C and 6 hours at 950°C

Resistor	T firing (°C)	Resistivity (ohm/sq.)	Cold TCR (10-6/K)	Hot TCR (10-6/K)	Noise (dB)	GF
8039	850	7,3 k	50	90	-14.3	11.0
	950, 6 h	37	1845	1810	-29.9	1.5
2041	850	6.6 k	-35	20	-23.3	11.0
	950, 6 h	280	-90	-85	-32.0	7.0
8241	850	5.4 k	20	60	-4.5	15.5
	950, 6 h	36	1950	1990	-25.5	2.0

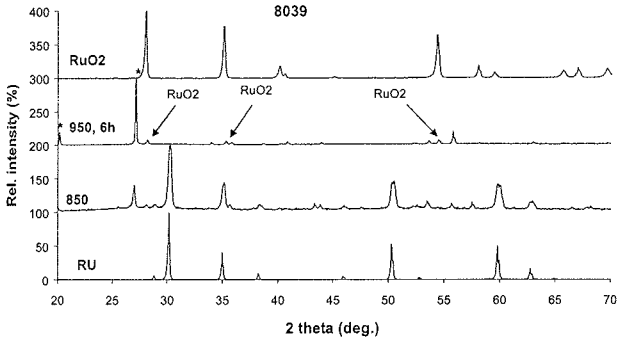

Fig. 1a: XRD spectra of 2039 thick-film resistor, fired for 10 min at 850°C and for 6 hours at 950°C. Spectra of ruthenate (RU) and of RuO_2 (RuO2) are also included.

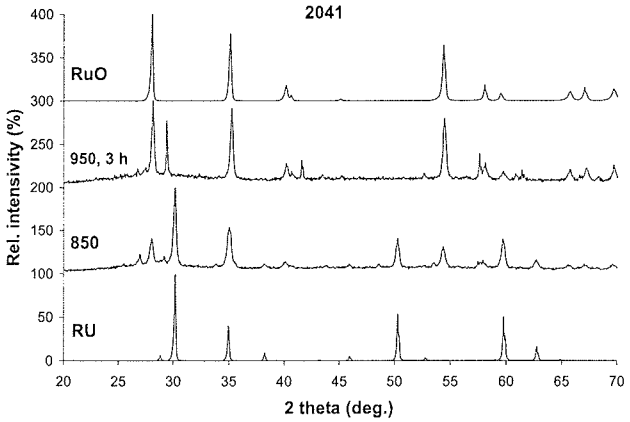

Fig. 1b: XRD spectra of 2041 thick-film resistor, fired for 10 min at 850°C and for 6 hours at 950°C. Spectra of ruthenate (RU) and of RuO_2 (RuO_2) are also included.

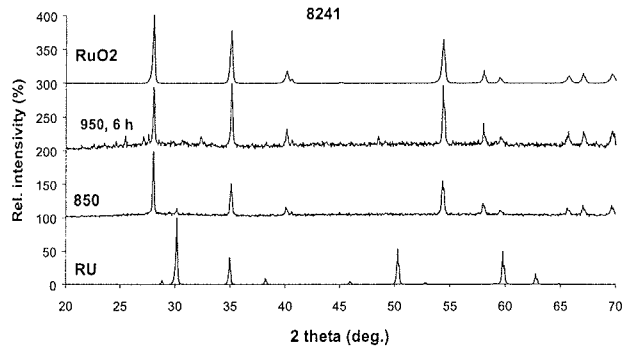

Fig. 1c: XRD spectra of 8541 thick-film resistor, fired for 10 min at 850°C and for 6 hours at 950°C. Spectra of ruthenate (RU) and of RuO_2 (RuO2) are also included.

at 950°C the ruthenate particles in the 8039 resistor have nearly all disappeared.

Adachi and Kuno /8,9/ studied high-temperature interactions between $PbO-B_2O_3-SiO_2$ glasses and $Pb_2Ru_2O_{6.5}$

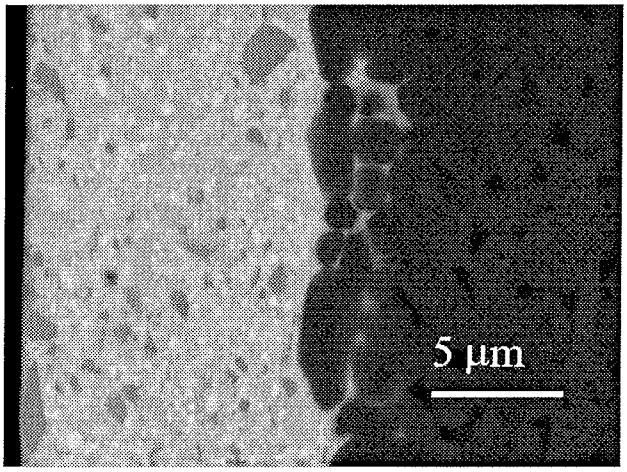

Fig.2a: Microstructure of a cross-section of the thick-film resistor 8039, fired for 10 min at 850°C. Alumina substrate is on the right. Light particles are conductive phase - $(Bi_{2-x}Pb_x)Ru_2O_{7-x/4}$.

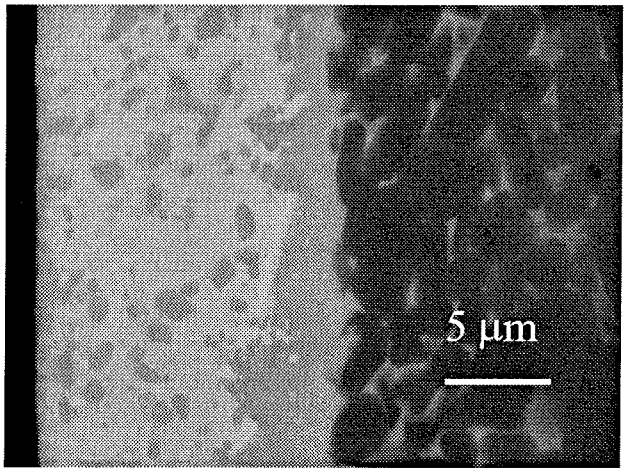

Fig. 2b: Microstructure of a cross-section of the thick-film resistor 8039, fired for 6 hours at 950°C. Alumina substrate is on the right. After firing at 950°C the ruthenate particles in the 8039 resistor have nearly all disappeared.

or RuO_2. They showed that in glasses poor in PbO the $Pb_2Ru_2O_{6.5}$ disappears and the RuO_2 is formed while for PbO-rich glasses the RuO_2 reacts with the PbO from the glass and forms $Pb_2Ru_2O_{6.5}$. Their results are summarised in Fig. 3. Three regions are marked in the $PbO-B_2O_3-SiO_2$ phase diagram. In the first region in the silica rich part of diagram ruthenates decomposes into RuO_2. In third region (PbO rich) ruthenates are stable while RuO_2 reacts with glass forming $Pb_2Ru_2O_{6.5}$. In glasses with roughly 1/1 SiO_2 / PbO ratio (second region) the RuO_2 and the ruthenate coexist.

To confirm these findings, the subsolidus ternary phase diagram of the RuO_2 - PbO - SiO_2.system was investigated. The glass phase in different commercial thick-film resistors was analysed by SEM and the PbO/SiO_2 ratio was

determined. All analysed glass compositions are rich in SiO_2 with the molar ratio SiO_2 / PbO between 2 and 2.5. The molar ratio SiO_2 / PbO in glass phases of thick-film resistors is also graphically shown as a short bold bar near SiO_2 in the PbO-poor part of the RuO_2 - PbO - SiO_2 system in Fig. 4. The PbO-rich part of phase diagram, which was not investigated, is shown with dotted lines. No ternary compound was found in the system. There is no binary compound between RuO_2 and SiO_2. The tie lines are between $Pb_2Ru_2O_{6.5}$ and $PbSiO_3$, and between RuO_2 and $PbSiO_3$. The results therefore indicate that the lead-ruthenate-based conductive phase in thick-film resistors is indeed unstable when in contact with the silica-rich glass phase, as shown by dashed lines in Fig. 4.

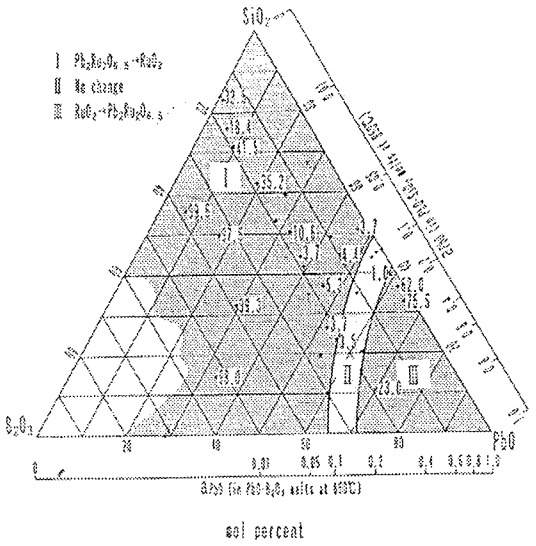

Fig. 3: The PbO-B_2O_3-SiO_2 system (after Adachi and Kuno /8/). Lead ruthenate is stable in the region III and unstable in the region I.

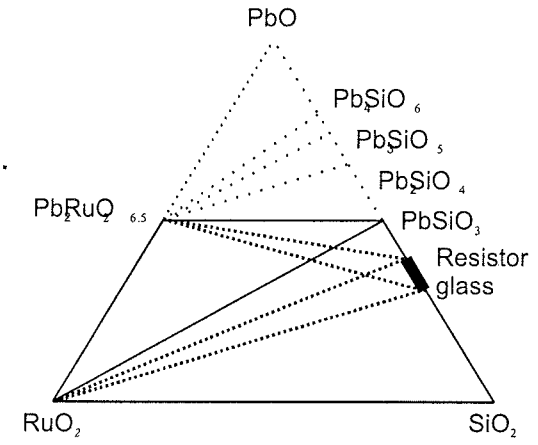

Fig. 4: The proposed subsolidus ternary phase diagram of the PbO-poor part of the RuO_2 - PbO - SiO_2. The molar ratio SiO_2 / PbO in glass phases of some thick-film resistors is shown as a short bold bar near SiO_2 in the PbO-SiO_2 system.

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