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LETTER

Subsolidus phase equilibria in the RuO_2–ZnO–SiO_2 system

Marko Hrovat · Janez Holc · Sebastjan Glinšek

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Introduction

Thick-film resistors are made by screen-printing thick-film paste on insulating, mainly alumina, substrates. After printing and drying, the thick-film pastes are fired in a belt furnace. Thick-film resistor pastes consist basically of a conducting phase, a lead borosilicate-based glass phase and an organic vehicle. The organic material is burned out between 300 and 400 °C during the high-temperature processing. The ratio between the conductive and glass phases roughly determines the specific resistivity of the resistor. In most modern resistor compositions the conductive phase is either RuO_2 or ruthenates. The glass phase is based on the B_2O_3–PbO–SiO_2 glasses with the molar ratio of SiO_2/PbO approximately equal to 2. Some other oxides are also added as modifiers of the temperature coefficient of expansion and/or the glass-transition temperature [1–5].

The well-known European environmental legislation, i.e., the RoHS Directive (restriction of the use of certain hazardous substances), requires the elimination of the lead, or at least a minimising of the lead content in electrical and electronic equipment to below 0.1 wt.%—starting from July 2006. Thick-film materials are currently an exemption from the directive, but the producers of thick-film materials are already developing new material systems in accordance with the directive [6]. While there are many lead-free conductor and dielectric compositions available, the development of thick-film resistors with lead-free glasses is still mainly in the experimental stage. At least to the authors' knowledge, no commercially available thick-film lead-free resistor series with characteristics comparable to ''conventional'' resistors is on the market.

However, many ''experimental'' papers have reported on the preparation and investigations of the characteristics of lead-free thick-film resistors where the conductive phase is based, like with ''conventional'' resistors, on ruthenium oxide or ruthenates [7–11]. In the glass phase the lead oxide is often replaced with the zinc oxide [12–15]. Regardless of the very different melting points (T_m is 886 and 1,975 °C for PbO and ZnO, respectively) both oxides share similar characteristics. Both PbO and ZnO are classified as intermediate oxides, i.e., they can be either glass formers or glass modifiers. Some of the characteristics, i.e., the dissociation energy per MO_x, the coordination number and the single bond strength, are summarised in Table 1 [16].

The aim of this work was to investigate subsolidus phase equilibria (in air) in the RuO_2–ZnO–SiO_2 system. The results would indicate possible interactions between silica-rich glass with the addition of ZnO and the conductive phase (ruthenium oxide) in lead-free thick-film resistors.

The binary Zn_2SiO_3 compound exists in the SiO_2–ZnO system. The melting point of the eutectic on the ZnO-rich side is 1,507 °C, and on the SiO_2-rich side it is 1,432 °C [17, 18]. Morimoto et al. reported a synthesis at a high temperature of 1,400 °C and at a high pressure, and a characterisation of the binary compound $ZnSiOO_3$ [19]. Phase equilibria in the RuO_2–SiO_2 [5] and RuO_2–ZnO systems were studied by Hrovat et al. [20]. In both systems there is no binary compound and no liquid phase (eutectic) at temperatures up to 1,405 °C, the temperature at which RuO_2 decomposes (in air) to metallic ruthenium and oxygen.

For the experimental work, RuO_2 (Ventron, 99.9%), ZnO (Johnson Matthey, ultrapure), and SiO_2 (Riedel de

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M. Hrovat (✉) · J. Holc · S. Glinšek
Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia
e-mail: marko.hrovat@ijs.si

Table 1 Some of the characteristics of PbO and ZnO as intermediate oxides in glasses [16]

	Coordination number	Dissociation energy per MO_x (kJ/g-atom)	Single bond strength (kJ/g-atom)
PbO	2	607	305
ZnO	2	603	301

Haen, 99.9%) were used. The oxides were mixed in isopropyl alcohol, pressed into pellets, and fired up to five times in air with intermediate grinding. Three batches of samples were prepared for each composition. Samples in the RuO_2–ZnO–SiO_2 system were fired at 1,000 °C and in the ZnO–SiO_2 system they were fired at 1,200 °C. During firing the pellets were placed on platinum foils. The compositions of the relevant samples are shown in Fig. 2. The fired materials were characterised by X-ray powder-diffraction analysis using a Philips PW 1710 X-ray diffractometer with Cu K_α radiation. The X-ray spectra were measured from $2\Theta = 20°$ to $2\Theta = 70°$ in steps of 0.02°. A JEOL 5800 scanning electron microscope (SEM) equipped with an ISIS 300 energy-dispersive X-ray analyser (EDS) was used for the overall microstructural and compositional analysis. Prior to analysis in the SEM, the samples were sputtered with a carbon film to provide electrical conductivity and avoid charging effects.

The results of the X-ray powder analysis of the relevant samples, fired in air at 1,000 °C in the RuO_2–ZnO–SiO_2 system and at 1,200 °C in the binary ZnO–SiO_2 binary system are summarised in Table 2. The nominal compositions of the samples and the phases identified after firing are included.

The microstructure of the fractured cross-section of the sample with the nominal composition 2 RuO_2 + SiO_2 + 2 ZnO, fired at 1,000 °C, is shown in Fig. 1. The material was poorly sintered, so a polished cross-section could not be prepared. The sample is a two-phase mixture of RuO_2 (smaller grains) and the Zn_2SiOO_4 (larger grains). Some of the RuO_2 and Zr_2SiO_4 grains are labelled ‘‘R’’ and ‘‘ZS’’, respectively. Based on the results obtained by XRD and EDS, a subsolidus RuO_2–ZnO–SiO_2 phase diagram, shown in Fig. 2, was constructed. No ternary compound was found in the system. The tie line is between RuO_2 and Zn_2SiO_4. The $ZnSiO_3$ compound was not detected under the described synthesis conditions. The results indicate that the RuO_2, as a conductive phase in PbO-free thick-film resistors, is compatible with the SiO_2 and ZnO components of the glass phase.

Table 2 Results of X-ray diffraction analysis of some compositions in the RuO_2–ZnO–SiO_2 system

Nominal composition	Phases identified
RuO_2 + SiO_2	RuO_2 + SiO_2
SiO_2 + 2 ZnO	Zn_2SiO_4
SiO_2 + ZnO	Zn_2SiO_4 + SiO_4
2 RuO_2 + SiO_2 + 2 ZnO	RuO_2 + Zn_2SiO_4
7 RuO_2 + SiO_2 + 2 ZnO	RuO_2 + Zn_2SiO_4
5 RuO_2 + 3 SiO_2 + 12 ZnO	RuO_2 + Zn_2SiO_4 + ZnO
RuO_2 + 2 SiO_2 + ZnO	RuO_2 + Zn_2SiO_4 + SiO_2

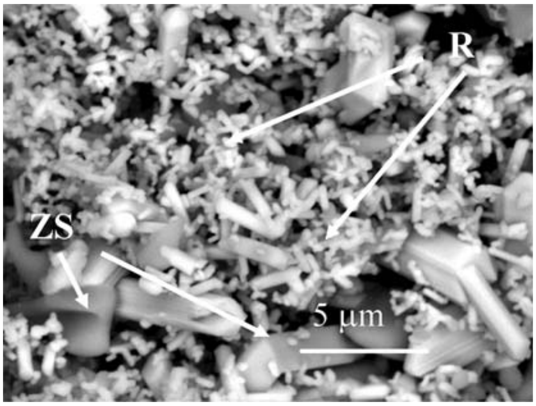

Fig. 1 Microstructure of the fractured cross-section of a sample with the nominal composition 2 RuO_2 + SiO_2 + 2 ZnO, fired at 1,000 °C. The material is a two-phase mixture of RuO_2 (smaller grains) and Zn_2SiO_4 (larger grains). The RuO_2 and Zr_2SiO_4 grains are labelled ‘‘R’’ and ‘‘ZS’’, respectively Back scattered electrons

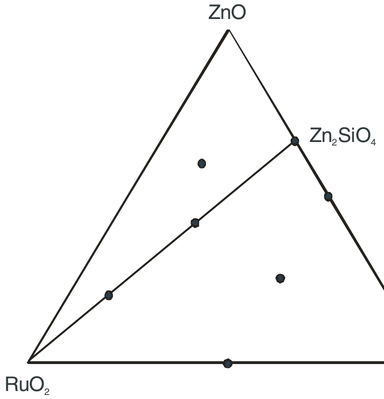

Fig. 2 The proposed RuO_2–ZnO–SiO_2 subsolidus phase diagram. The tie line is between RuO_2 and Zn_2SiO_4. The compositions of the relevant samples are denoted by circles

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