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LETTER

Subsolidus phase equilibria in the CaO-poor part of the RuO_2–CaO–V_2O_5 system

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Introduction

Thick-film resistor pastes consist basically of a conducting phase, a silica-rich, 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 thick-film resistor compositions the conductive phase is either ruthenium-oxide or electrically conducting pyrochlores; mainly lead or bismuth ruthenates [1–4] with resistivities of 40×10^{-6}, 150×10^{-6} and $270 \times 10^{-6}\ \Omega$ cm for RuO_2, $Bi_2Ru_2O_7$ and $Pb_2Ru_2O_{6.5}$, respectively [2, 5]. During the firing cycle the conductive phases of the resistor materials interact with the glass phase. The maximum firing temperature and time are typically 850 °C and 10 min, respectively.

As mentioned above, the glass phase in commercial thick-film resistors is based on lead borosilicates. The European environmental legislation, i.e., the RoHS Directive (RoHS—restriction of the use of certain hazardous substances or Restriction of the use of certain hazardous substances in electrical and electronic equipment), requires the elimination of lead, or at least a minimising of the lead content in electrical and electronic equipment to below 0.1 wt% [6]. Thick-film materials are currently an exemption from the directive [7], but in the near future further restrictions could be applied. Therefore, the producers of thick-film materials have already developed new thick-film material systems in accordance with the directive [8]. However, whilst there are many accessible lead-free conductor and dielectric compositions, no commercially available thick-film, lead-free resistor series with characteristics comparable to 'conventional' resistors is on the market, at least to the best of the authors' knowledge.

In the open literature there are many articles reporting on investigations of the characteristics of lead-free, thick-film resistor materials. If the bismuth ruthenates are used as a conductive phase in lead-free, thick-film resistors they decompose during firing due to the interaction with the silica-rich glasses [9, 10]. Some articles described the possible use of the electrically conducting $CaRuO_3$ perovskites (instead of lead- or bismuth-based ruthenate pyrochlores) as the conductive phase in 'experimental' lead-free, thick-film resistors and reported reasonably good results [11–16]. The $CaRuO_3$ perovskite has a resistivity of about $250 \times 10^{-6}\ \Omega$ cm at room temperature (rather similar to the $Pb_2Ru_2O_{6.5}$, see above) and a metal-like, positive and linear dependence of resistivity on the temperature [17, 18].

The low-softening-point, lead-free glasses developed for thick-film resistors have a tendency to crystallize during firing, which hinders the densification and results in rather porous layers [19]. The addition of up to 5 mol% of V_2O_5 to the glass phase prevents the crystallisation [16, 20].

The aim of this article is to evaluate the compatibility of $CaRuO_3$ as a conductive phase in lead-free, thick-film resistors with V_2O_5, which is added to the glass phase to hinder the crystallization. This could contribute to the development of lead-free, thick-film resistors. The aim of this study was to investigate the subsolidus phase equilibria (in air) in the CaO-poor part of the RuO_2–CaO–V_2O_5 system.

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Three binary compounds are reported in the RuO_2–CaO system: $CaRuO_3$, $Ca_3Ru_2O_7$ and Ca_2RuO_4. The $CaRuO_3$ perovskite compound can be synthesised at temperatures around or below 1000 °C, e.g., from ruthenium-oxide and calcium carbonate during solid-state reactions between 800 and 1000 °C [18, 21]. If prepared by a chemical route (e.g., co-precipitation from solutions), the required temperatures are around or below 600 °C [23, 24].

For the preparation of the other two binary compounds in this system, higher firing temperatures are required. Nakatsuji et al. [25] synthesised the Ca_2RuO_4 compound in a relatively inert atmosphere (99% Ar and 1% O_2) at temperatures between 1350 and 1380 °C. Jacob et al. [22] prepared Ca_2RuO_4 and $Ca_3Ru_2O_7$ compounds by firing appropriate mixtures of CaO and RuO_2 at 1360 and 1425 °C, respectively, in a pure oxygen atmosphere. Karpus et al. [26] grew single crystals of $Ca_3Ru_2O_7$ using flux techniques from a RuO_2, $CaCO_3$ and $CaCl_2$ mixture at the even higher temperature of 1480 °C. Munekaka and Sato [27] synthesised the pyrochlore $CaRu_2O_7$ by a hydrothermal route at a pressure of 150 MPa and a temperature of 600 °C under highly oxidising conditions. The ratio between the Ca and Ru cations is the same as for the $CaRuO_3$ perovskite. However, as the valence of ruthenium is 5+ this compound is not within the RuO_2–CaO system.

In the CaO–V_2O_5 system three binary compounds are reported, i.e., CaV_2O_5, $Ca_2V_2O_7$ and $Ca_3V_2O_8$ [28, 29]. All three decompose incongruently at the melting: CaV_2O_5 at 778 °C, $Ca_2V_2O_7$ at 1015 °C and $Ca_3V_2O_8$ at 1380 °C.

In the ruthenium-oxide–vanadium-oxide system the binary compound Ru_2VO_6 exists [30, 31]. However, note that this compound is not part of the RuO_2–V_2O_5 system as the valence of the vanadium is 4+.

Experimental

For the experimental work, RuO_2 (Ventron, 99.9%), $CaCO_3$ (Alfa Aesar, 99.95%) and V_2O_5 (Riedel–de–Haen, 99.9%) were used. The starting chemicals were mixed in different ratios in isopropyl alcohol, pressed into pellets and calcined at 650 °C, i.e., below the melting point of V_2O_5 (680 °C). During firing the pellets were placed on platinum foils. The pellets were then ground and fired at higher temperatures, depending on the compositions, but always below the melting points of the oxides or the binary compounds present. The compositions of the samples and the firing temperatures are listed in Table 1. The samples were fired three times with intermediate grinding.

The fired materials were characterised as powders by X-ray powder-diffraction analysis using a Philips PW 1710 X-ray diffractometer with CuKα radiation. The X-ray spectra were measured from $2\Theta = 20°$ to $70°$ in steps of 0.02°. The cross-sections of the samples were investigated by X-ray powder-diffraction analysis and with a JEOL 5800 scanning electron microscope (SEM) equipped with a link ISIS 300 energy-dispersive X-ray analyser (EDS), which were used for the overall microstructural and compositional analyses. Before the analysis in the SEM, the samples were coated with carbon to provide electrical conductivity and to avoid charging effects. The microstructures of the samples were studied by back-scattered electron imaging using compositional contrast to distinguish between the phases that differ in density (average atomic number *Z*). As the samples were 'poorly' sintered at these relatively low temperatures, polished cross-sections could not be prepared and therefore the pellets were broken and fractured cross-sections were observed.

Table 1 Results of the XRD analysis of the relevant compositions in the RuO_2–CaO–V_2O_5 system

No.	Nominal composition (mol%)	*T* fir. (°C)	Identified phases
1	55% CaO + 22.5% RuO_2 + 22.5% $VO_{2.5}$	1000	$CaRuO_3 + Ca_3V_2O_8$
2	50% CaO + 25% RuO_2 + 25% $VO_{2.5}$	950	$RuO_2 + CaRuO_3 + Ca_2V_2O_7$
3	35% CaO + 55% RuO_2 + 10 $VO_{2.5}$	950	$RuO_2 + CaRuO_3 + Ca_2V_2O_7$
4	42% CaO + 30% RuO_2 + 28% $VO_{2.5}$	1000	$RuO_2 + Ca_3V_2O_8$
5	25% CaO + 58% RuO_2 + 17% $VO_{2.5}$	1000	$RuO_2 + Ca_3V_2O_8$
6	33.3% CaO + 33.3% RuO_2 + 33.3% $VO_{2.5}$	760	$RuO_2 + Ca_2V_2O_7$
7	40% CaO + 20% RuO_2 + 40% $VO_{2.5}$	760	$RuO_2 + Ca_2V_2O_7$
8	37% CaO + 18% RuO_2 + 45% $VO_{2.5}$	650	$RuO_2 + Ca_2V_2O_7 + CaV_2O_6$
9	28% CaO + 29% RuO_2 + 43% $VO_{2.5}$	760	$RuO_2 + Ca_2V_2O_7 + CaV_2O_6$
10	25% CaO + 25% RuO_2 + 50% $VO_{2.5}$	760	$RuO_2 + CaV_2O_6$
11	15% CaO + 35 RuO_2 + 50% $VO_{2.5}$	760	$CaV_2O_6 + Ru_2VO_6$
12	15% CaO + 15% RuO_2 + 70% $VO_{2.5}$	650	$V_2O_5 + CaV_2O_6 + Ru_2VO_6$

Firing temperatures are included

Results and discussion

The results of the X-ray powder analysis of the relevant samples in the RuO_2–CaO–V_2O_5 system are summarised in Table 1. The nominal compositions of the samples and the phases identified after firing are given. The firing temperatures are included. The numbers of the samples correspond to the numbers marked on the diagram of the RuO_2–CaO–V_2O_5 system are given in Fig. 2.

The microstructure of the fractured cross-sections (backscattered electrons) of the sample with the compositions 25% CaO + 58% RuO_2 + 17 $VO_{2.5}$ fired at 1100 °C (sample no. 8) is shown in Fig. 1. The lighter grains are RuO_2 and the darker grains are $Ca_3V_2O_8$.

Based on the results obtained with the XRD and EDS, a subsolidus RuO_2–CaO–V_2O_5 phase equilibria in the CaO-poor part of the diagram, shown in Fig. 2, was constructed. The CaO-rich part of the phase diagram, which was not investigated, is shown with dotted lines. No ternary compound was found. The tie lines are between $CaRuO_3$ and $Ca_3V_2O_8$, RuO_2 and $Ca_3V_2O_8$, RuO_2 and $Ca_2V_2O_7$, RuO_2 and CaV_2O_6, and Ru_2VO_6 and CaV_2O_6. However, because the Ru_2VO_6 compound is not a part of the RuO_2–CaO–V_2O_5 system (the valence of vanadium is 4+) the tie line between Ru_2VO_6 and CaV_2O_6 is shown as a dashed line. The results, therefore, indicate that the calcium-ruthenate-based conductive phase in thick-film resistors could be unstable when in contact with the V_2O_5 if the latter is added to a lead-free glass phase to prevent the crystallisation during firing.

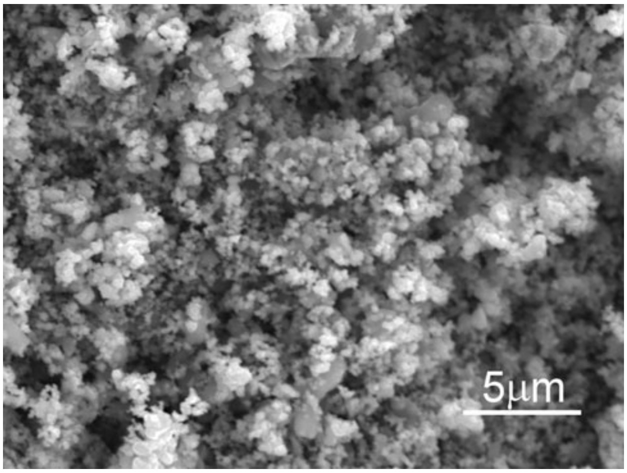

Fig. 1 The microstructure of the fractured cross-section (backscattered electrons) of the sample with the composition 25% CaO + 58% RuO_2 + 17 $VO_{2.5}$ fired at 1100 °C (sample no. 8)

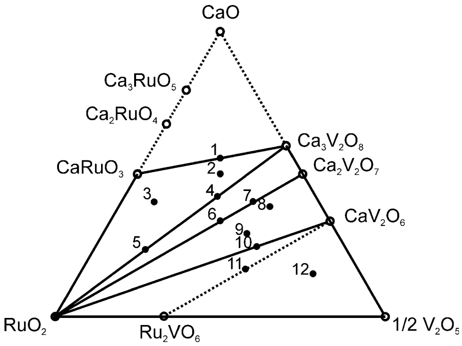

Fig. 2 The proposed subsolidus ternary phase diagram of the CaO-poor part of the RuO_2–CaO–V_2O_5 system. The tie lines are between $CaRuO_3$ and $Ca_3V_2O_8$, RuO_2 and $Ca_3V_2O_8$, RuO_2 and $Ca_2V_2O_7$, RuO_2 and CaV_2O_6, and Ru_2VO_6 and CaV_2O_6

Conclusions

Subsolidus equilibria in the CaO-poor part of the RuO_2–CaO–V_2O_5 diagram were studied by X-ray powder-diffraction analysis, SEM and energy-dispersive X-ray analysis. No ternary compound was found in the system. The tie lines are between $CaRuO_3$ and $Ca_3V_2O_8$, RuO_2 and $Ca_3V_2O_8$, RuO_2 and $Ca_2V_2O_7$, RuO_2 and CaV_2O_6, and Ru_2VO_6 and CaV_2O_6.

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