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Phase equilibria in the RuO_2–Bi_2O_3–CdO–Nb_2O_5 system

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Interactions between the conductive phase in thick-film resistor materials (RuO_2 and $Bi_2Ru_2O_7$) and TCR modifiers (CdO and Nb_2O_5) were studied. Phase equilibria in the RuO_2–Bi_2O_3–CdO, RuO_2–Bi_2O_3–Nb_2O_5 and RuO_2–CdO–Nb_2O_5 systems were examined. The lines in the systems were established. The existence of a solid solution of composition $Bi_{2-x}Cd_xRu_2O_{7-x/2}$ was confirmed.

1. Introduction

Thick film resistor materials consist basically of a conductive phase, a glass phase and an organic vehicle which evaporates and burns out during the firing process. In contemporary thick-film resistors, the conductive phase is usually either RuO_2 or a ruthenate, usually $Bi_2Ru_2O_7$ [1–3]. Thick-film resistors, prepared only from a mixture of the conductive and glass phases, possess a relatively high positive-temperature coefficient of resistance (TCR). To decrease TCR, small amounts of so-called TCR modifiers, i.e. semiconducting oxides with negative TCR, are added. Typical TCR modifiers are CdO and Nb_2O_5 [4–6].

The aim of this work was to obtain some insight into possible interactions between the conductive phase in thick-film resistors and the TCR modifiers, CdO and Nb_2O_5. Phase equilibria in the RuO_2–Bi_2O_3–CdO, RuO_2–Bi_2O_3–Nb_2O_5 and RuO_2–CdO–Nb_2O_5 ternary systems will be presented.

The CdO–Nb_2O_5 phase diagram with binary compounds $CdNb_2O_6$ and $Cd_2Nb_2O_7$ was presented by Roth [7]. The compounds melt at 1435 and 1410° C, respectively. Phase equilibria in the Bi_2O_3–CdO system were studied by Jager and Kolar [8]. Binary compounds in this system are Bi_2CdO_4 which decomposes at 650° C into $Bi_{10}Cd_3O_{18}$ and CdO; $Bi_{10}Cd_3O_{18}$, which melts incongruently at 690° C; and $Bi_{12}CdO_{19}$, which also melts incongruently and is stable between 625 and 725° C. In the Bi_2O_3–RuO_2 system [9] the binary compound $Bi_2Ru_2O_7$ dissociates at temperatures around 1250° C into Bi_2O_3 and RuO_2 which decomposes at temperatures over 1350° C into ruthenium and oxygen. A solid solution between $Bi_2Ru_2O_7$ and CdO with formula $Bi_{2-x}Cd_xRu_2O_{7-x/2}$ was reported by Bouchard [10] for x between 0 and 1, and by Schuler and Kemmer-Sack [11] for x between 0 and 0.9. Five binary compounds exist in the Bi_2O_3–Nb_2O_5 system [12]. Three of them ($Bi_2Nb_{10}O_{28}$, $Bi_2Nb_2O_8$ and $Bi_{10}Nb_6O_{30}$) are stable under 1000° C while the other two ($Bi_8Nb_{18}O_{57}$ and $Bi_2Nb_{12}O_{33}$) are stable at temperatures over 1000° C. No data were found on the RuO_2–CdO and RuO_2–Nb_2O_5 systems.

2. Experimental procedure

For experimental work, Bi_2O_3 (Merck, extra pure), RuO_2 (Fluka, extra pure), CdO (Koch, 99.99%) and Nb_2O_5 (Koch, 99.9%) were used. Samples were mixed in ethyl alcohol, pressed into pellets and fired (with intermediate grinding) in air. During firing pellets were placed on platinum foils. Compositions of relevant samples are shown in Figs 1, 3 and 4. The results were evaluated by X-ray powder diffraction analysis, differential thermal analysis, scanning electron microscopy and energy dispersive X-ray spectroscopy (EDAX).

3. Results and discussion

The phase diagram of RuO_2–Bi_2O_3–CdO is presented in Fig. 1. In the RuO_2–CdO system there is neither a binary compound nor liquid phase (eutectic) at temperatures up to 1000° C, where the sublimation of CdO is already noticeable. Solid solutions of $Bi_{2-x}Cd_xRu_2O_{7-x/2}$ for $0 < x < 0.9$ were synthesized. For values of x over 0.9, beside solid solution, samples always contained RuO_2 and CdO, which is in agreement with Schuler and Kemmer-Sack [11].

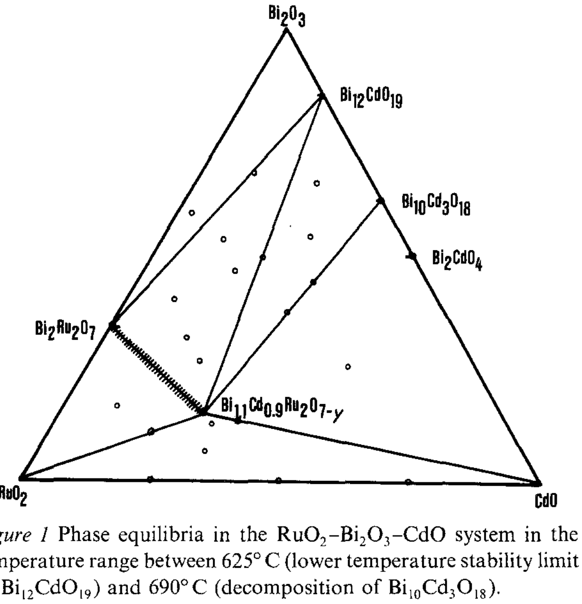

Figure 1 Phase equilibria in the RuO_2–Bi_2O_3–CdO system in the temperature range between 625° C (lower temperature stability limit of $Bi_{12}CdO_{19}$) and 690° C (decomposition of $Bi_{10}Cd_3O_{18}$).

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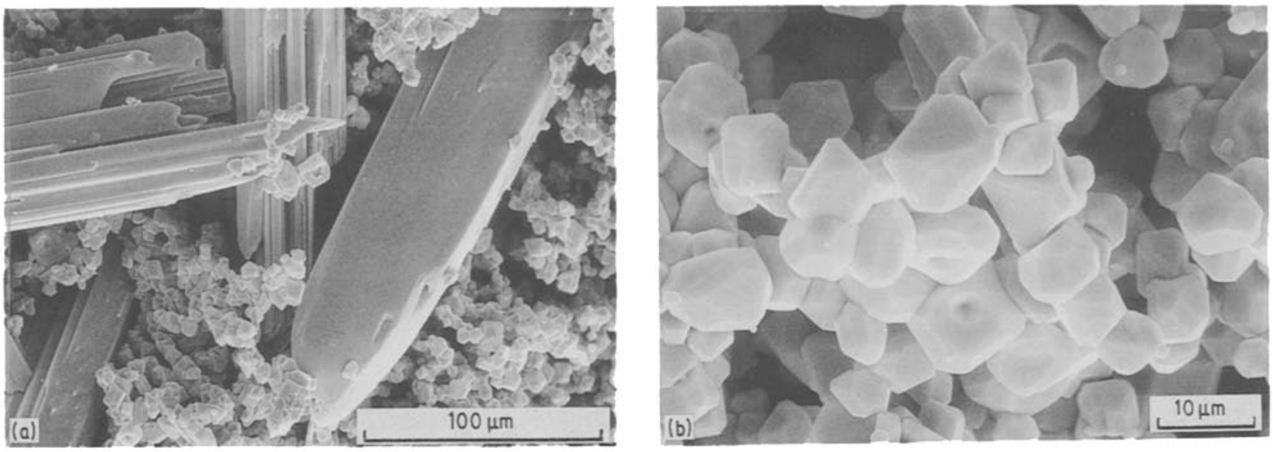

Figure 2 (a) $Bi_{2-x}Cd_xRu_2O_{7-x-2}$ solid solution, fired above 1200° C. Because of sublimation of CdO, the microstructure is a mixture of large, elongated RuO_2 crystals and smaller $Bi_2Ru_2O_7$ grains. (b) $Bi_2Ru_2O_7$ grains.

At temperatures over 950° C, CdO begins to sublime from the solid solution and completely evaporates at higher temperatures. The microstructure of $Bi_{2-x}Cd_xRu_2O_{7-x/2}$ fired at temperatures over 1200° C (Figs 2a and b) displays a mixture of large, elongated crystals of RuO_2 and smaller grains of $Bi_2Ru_2O_7$.

The tie lines are between solid solution-RuO_2, solid solution-$Bi_{12}CdO_{19}$, $Bi_{1.1}Cd_{0.9}Ru_2O_{6.55}$–$Bi_{10}Cd_3O_{18}$ and $Bi_{1.1}Cd_{0.9}Ru_2O_{6.55}$–CdO. The phase equilibria, as shown in Fig. 1, are accurate at temperatures between 625° C (lower temperature stability limit of $Bi_{12}CdO_{19}O$) and 690° C (decomposition of $Bi_{10}Cd_3O_{18}$).

The phase diagram of RuO_2–Nb_2O_5–CdO is presented in Fig. 3. In the CdO–Nb_2O_5 system both compounds reported by Roth [7], i.e.$CdNb_2O_6$ and $Cd_2Nb_2O_7$, were synthesized. In the RuO_2–Nb_2O_5 system there is no binary compound. Formation of the liquid phase (eutectic) was not detected up to 1350° C, which is the temperature of dissociation of RuO_2 into ruthenium and oxygen. No ternary compound was found. Tie lines are between RuO_2–$Cd_2Nb_2O_7$ and RuO_2–$CdNb_2O_6$.

The phase diagram RuO_2–Bi_2O_3–Nb_2O_5 is presented in Fig. 4. No ternary compound was found in the system. In the Bi_2O_3–Nb_2O_5 system, three binary compounds, stable under 1000° C ($Bi_2Nb_{10}O_{28}$, $Bi_2Nb_2O_8$ and $Bi_{10}Nb_6O_{30}$), were synthesized. Tie lines are between RuO_2–$Bi_2Nb_{10}O_{28}$, RuO_2–$Bi_2Nb_2O_8$, RuO_2–$Bi_{10}Nb_6O_{30}$ and $Bi_2Ru_2O_7$–$Bi_{10}Nb_6O_{30}$.

The results of phase equilibria investigations indicate possible reactions between the conductive phase in thick-film resistor materials and TCR modifiers, i.e. CdO and Nb_2O_5. When RuO_2 forms the conductive phase in a resistor material, then neither CdO nor Nb_2O_5 react, nor do they form new compounds with it. When the conductive phase is $Bi_2Ru_2O_7$, CdO is incorporated into the pyrochlore structure of bismuth ruthenate, resulting in $Bi_{2-x}Cd_xRu_2O_{7-x/2}$ solid solution. The "displaced" Bi_2O_3 could react with CdO, but more likely dissolves in the glass phase, which is a component part of thick-film resistor materials. Nb_2O_5 also reacts with $Bi_2Ru_2O_7$ resulting in RuO_2 and one of the compounds between Bi_2O_3 and Nb_2O_5.

It should be mentioned, however, that the results described are a very idealized picture of what is really happening during firing in actual thick-film resistor materials. Resistor materials are complex systems composed of glasses with different compositions, a conductive phase and TCR modifiers, all of them reacting with each other during the firing. Also, due to the relatively short time at the highest temperature (usually 10 min at 850° C), the reactions in resistor

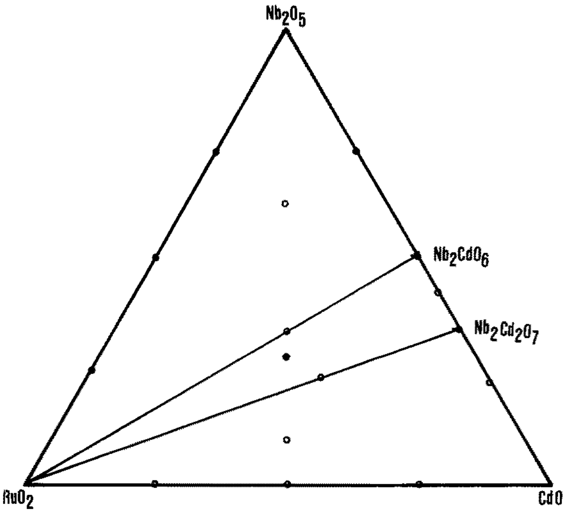

Figure 3 Phase equilibria in the RuO_2–Nb_2O_5–CdO system in the temperature range up to 1000° C.

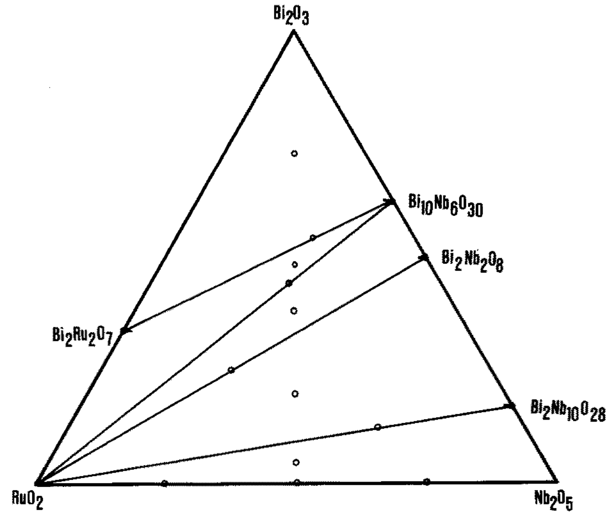

Figure 4 Phase equilibria in the RuO_2–Bi_2O_3–Nb_2O_5 system in the temperature range up to 1000° C.

material do not reach equilibria. Nevertheless, the results obtained indicate the direction of reactions during firing.

4. Conclusion

Phase equilibria in RuO_2–Bi_2O_3–CdO, RuO_2–Bi_2O_3–Nb_2O_5 and RuO_2–CdO–Nb_2O_5 systems were investigated. Tie lines in ternary phase diagrams were established. In the RuO_2–Bi_2O_3–CdO system there is a $Bi_{2-x}Cd_xRu_2O_{7-x/2}$ solid solution for x values between 0 and 0.9. The results indicate possible interactions between the conductive phase in thick-film resistor materials and TCR modifiers. If the conductive phase is RuO_2, CdO or Nb_2O_5 do not react with it. In the case of $Bi_2Ru_2O_7$ as the conductive phase, reaction with CdO results in the solid solution $Bi_{2-x}Cd_xRu_2O_{7-x/2}$, while the result of reaction with Nb_2O_5 is RuO_2 and one of the Bi_2O_3/Nb_2O_5 compounds.

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