JOURNAL OF MATERIALS SCIENCE 23 (1988) 3151–3155

Electrical properties of conductive materials used in thick-film resistors

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Layers of conductive oxide powders (IrO_2, RuO_2 and $Bi_2Ru_2O_7$) were prepared on alumina substrates by a thick-film technique. The films were fired at 875° C for different dwell times. The temperature dependence of resistance was measured in the range −196 to 850° C. SEM observations of the initial powders and the resistive layer surface after firing, as well as X-ray diffraction investigations, were carried out. The RuO_2 and IrO_2 oxides exhibit a high sintering ratio and the resistance of the fired layers increases with temperature as in the single crystal. The $R(T)$ curve for $Bi_2Ru_2O_7$ layers is in qualitative agreement with the polycrystalline material. The role of the grain surface area and the regions between the grains is dominant.

1. Introduction

Resistive inks are dispersions of submicrometre-sized conductive particles and glass frit in an organic binder. As a result of printing inks on to insulating substrates, drying and firing (usually at 850° C) thick-film resistors (TFRs) are obtained. They consist of conductive grains embedded in glass [1]. Air-fired TFRs are based on precious metal conductive oxides with rutile (IrO_2, RuO_2), pyrochlore ($Bi_2Ru_2O_7$) or perovskite structure.

During the firing process the material from the conducting grains diffuses into the glass, creating a deep impurity band. The conduction between conducting grains is dominated by hopping or tunnelling [2–7]. A sintering process between conducting grains may also occur. Sintering of RuO_2 grains has been confirmed by Vest [8, 9]. The TFRs may be modelled as a random network with percolative type conductivity [10–14], but the conduction model is still open to discussion.

The temperature dependence of the electrical resistivities of RuO_2 and IrO_2 monocrystals [15] and $Bi_2Ru_2O_7$ polycrystals have been published elsewhere [16]. Recently, the temperature dependence of $Bi_2Ru_2O_7$ single crystal as well as RuO_2 and ruthenate layers were measured [17, 18].

The main purpose of our experiments was to establish the electrical properties of conductive oxide powders in the form in which they occur in thick-film resistors. We examined the properties of IrO_2, RuO_2 and $Bi_2Ru_2O_7$ compounds screen printed on alumina substrates as resistors. For ink preparation, only powders of conducting materials and organic binder were used. The resistors were fired at 875° C for different dwell times. The resistance, temperature coefficient of resistance (TCR), as well as the temperature dependence of resistance, were measured over a wide temperature range (−196 to 850° C). Moreover, scanning electron microscope (SEM) observations of the resistive layer surface and an X-ray diffraction investigation were carried out.

2. Experimental details

Characterization of the materials examined is shown in Table I. The Brunauer–Emmett–Teller (BET) method was used to determine the powder surface area. The materials were mixed with an organic binder (ethyl cellulose in terpineol) to form the ink for screen printing. The ink was printed twice (drying in between) on 96% alumina substrate provided with prefired thick-film PdAg terminations. The test resistor geometry is shown in Fig. 1. The resistor was 0.6 mm wide and 370 squares long. The samples were fired at a peak temperature T_f = 875° C. The firing dwell times were 10 min, 1 and 5 h. The resistance of the layers was measured during the firing process typical for thick-film technology (dwell time 10 min). Test sample resistance and TCR were determined after firing. The resistance of the layers fired for 5 h at 875° C was measured over a wide temperature range (−196 to 850° C) in air. Measurements in the range 850 to 20° C were carried out in the oven during slow (60 min) cooling of the sample. The temperature dependence of resistance, in the range room temperature to liquid nitrogen temperature, was also measured in a different apparatus as the temperature fell.

SEM observations (SEM Cambridge 180) of the resistive layer surface were carried out. X-ray diffraction investigation (Dron 2) was used to establish the crystallite size in $Bi_2Ru_2O_7$ powder and thick-film sinter.

3. Results

The resistance of printed layers was measured during the firing process. The results are shown in Fig. 2. The steep temperature dependence up to 300° C is due to the removal of organic binder. Above 300° C (after 10 min in the furnace) there is no organic material in the layer. However, it can be seen that the value of film resistance after the whole temperature process is lower than the resistance level after removal of the organic binder.

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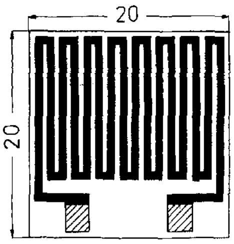


Figure 1 Test pattern. (Dimensions in mm).

The X-ray diffraction investigation showed no changes in microstructure: the average particle sizes before and after firing were the same and there was no evidence of new crystalline phases after firing. This means that the peak firing temperature used (875° C) was too low to cause microstructural changes (independent of dwell time). The decreasing resistance above 300° C can be explained by changes in macrostructure, such as densification of the layer, rearrangement of the conductive particles and sintering of the particles. These processes can be observed by SEM.

All sample sheet resistances and TCRs were measured after firing. The results are presented in Table II. The temperature coefficient of resistance was calculated from the equation

$$\mathrm{TCR} = \frac{R_{125} - R_{25}}{R_{25}\Delta T} \times 10^6 (\mathrm{p.p.m.}\,°\mathrm{C}^{-1})$$

where R_{25}, R_{125} are the resistances at 25 and 125° C, respectively, $\Delta T = 100$° C.

The investigated materials may be divided into two groups. The materials from the first group (IrO_2, RuO_2) exhibit very high positive TCR increasing with longer firing time. The second group samples ($Bi_2Ru_2O_7$) have negative TCR. The temperature coefficient of resistance became more negative with prolonged firing time for $Bi_2Ru_2O_7$ samples which contain an addition of CdO or glass. The $Bi_2Ru_2O_7$ grain size affects electrical properties of the test resistors. The sample with larger grain size exhibits a greater resistance and a more negative TCR. The difference is lower for longer firing time.

The resistance of the samples fired 5 h at 875° C was measured over a wide temperature range. The temperature dependence of resistance is shown in Figs 3 and 4. Our results are compared with the characteristics of monocrystals or polycrystals of these compounds taken from the literature. For layers with rutile structure oxides, the resistance increases over

TABLE I Characterization of the powders examined

Sample	Solid ingredient	Surface area, s_w ($m^2\,g^{-1}$)
A	100 wt % IrO_2	6.9
B	100 wt % RuO_2	26.9
C	100 wt % $Bi_2Ru_2O_7$ (unmilled)	0.82
D	100 wt % $Bi_2Ru_2O_7$ (milled)	4.93
E	95 wt % $Bi_2Ru_2O_7$ milled, 5 wt % glass	$s_{w,glass} = 0.7$
F	95 wt % $Bi_2Ru_2O_7$ milled, 5 wt % CdO	

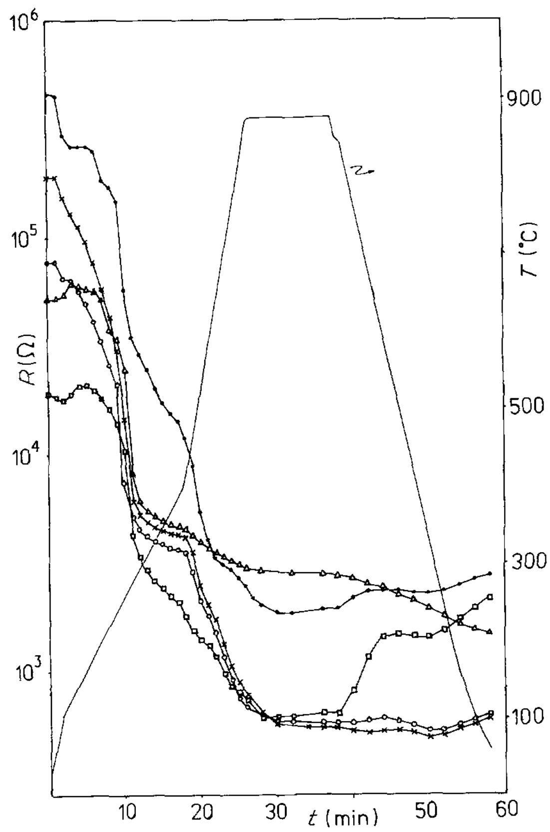


Figure 2 Resistance of the layers made from various oxides as a function of firing process time. (The temperature of the sample is shown on the right-hand axis.) (△) A, (□) C, (x) D, (○) E, (●) F.

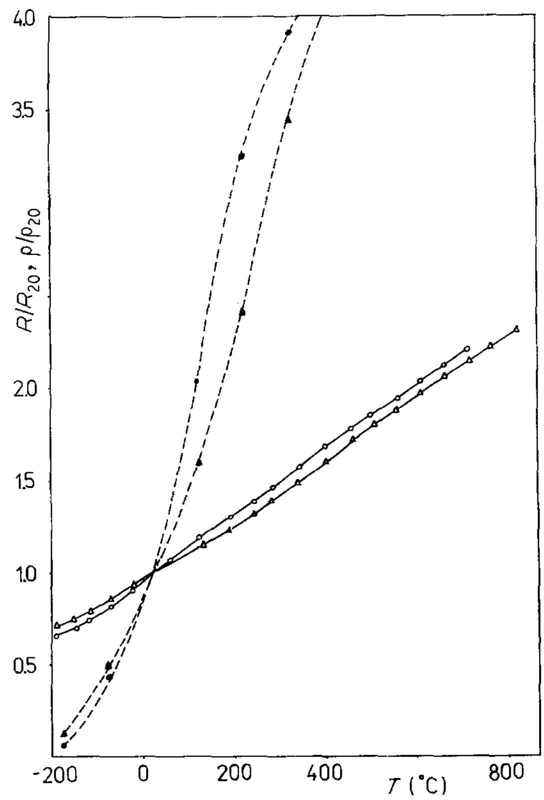


Figure 3 Normalized resistance against temperature plot for conductive oxides with rutile structure. (▲) IrO_2 single crystal [15]; (△) sample A (875° C, 5 h); (●) RuO_2 single crystal [15]; (○) sample B (875° C, 5 h).

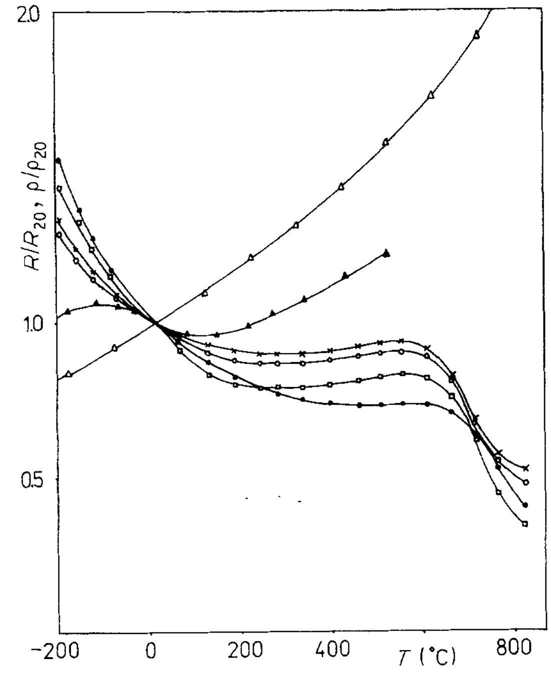


Figure 4 Resistance against temperature plot for thick-film sinters, polycrystal and monocrystal of bismuth ruthenate. (△) $Bi_2Ru_2O_7$ single crystal [17]; (▲) $Bi_2Ru_2O_7$ polycrystal [16]; (□) sample C (875° C, 5 h); (x) sample D (875° C, 5 h); (O) sample E (875° C, 5 h); (●) sample F (875° C, 5 h).

the whole temperature range almost linearly; however, the magnitude of the temperature sensitivity of these thick-film sinters is six to eight times less than for single crystals.

A differently shaped $R(T)$ curve was obtained for bismuth ruthenate layers. Qualitative agreement of $R(T)$ dependences of our films and a polycrystalline sample of $Bi_2Ru_2O_7$ is observed. Up to about 200° C a decrease of resistance is found, then an insignificant increase appears up to 600° C; then the resistance distinctly decreases. These results and their discrepancy with $Bi_2Ru_2O_7$ single crystal (which is typical for the metallic behaviour), suggest the predominant importance of grain surface properties (for example the ability to sinter) and of the regions between them. Intrinsic transport properties of bismuth ruthenate are masked. A small addition of glass (5 wt %) causes only a greater resistance change with temperature, whereas the same addition of CdO creates more pronounced changes of the normalized resistance curve. This is a result of the chemical interaction between $Bi_2Ru_2O_7$ and CdO [19].

SEM observations of unfired powders and the test layer surface after 5 h firing at 875° C (Fig. 5) were carried out. IrO_2 and RuO_2 grains in the fired layer exhibit a very high sintering ratio. The individual grains are hard to see. This is in good agreement with the electrical properties.

Sharp edged $Bi_2Ru_2O_7$ grains in the powder are changed to rounded ones in the fired layer. Some appear to be sintered together. The addition of glass does not change the picture. The same amount of CdO creates a visible change in the appearance, confirming the chemical reaction between $Bi_2Ru_2O_7$ and CdO.

4. Discussion

The investigated materials might be divided in two groups, according to their properties in the form of thick-film resistors. Rutile structure compounds (RuO_2 and IrO_2) belong to the first group, while pyrochlore ($Bi_2Ru_2O_7$ and bismuth ruthenate with additives) forms the second group.

During the firing process the decrease in resistance with increasing temperature is much faster for $Bi_2Ru_2O_7$ than for IrO_2 samples. This might be explained by the difference in thermal expansion linear coefficient, α. The $Bi_2Ru_2O_7$, IrO_2 and 96% Al_2O_3 substrate α coefficients are equal to 11.5 p.p.m. $°C^{-1}$ [20], 5 p.p.m. $°C^{-1}$ [21] and 7.9 p.p.m. $°C^{-1}$ [22], respectively. The contact resistance between two conducting grains decreases with increasing temperature while $\alpha_{grain} > \alpha_{substrate}$, and increases in the case $\alpha_{grain} < \alpha_{substrate}$.

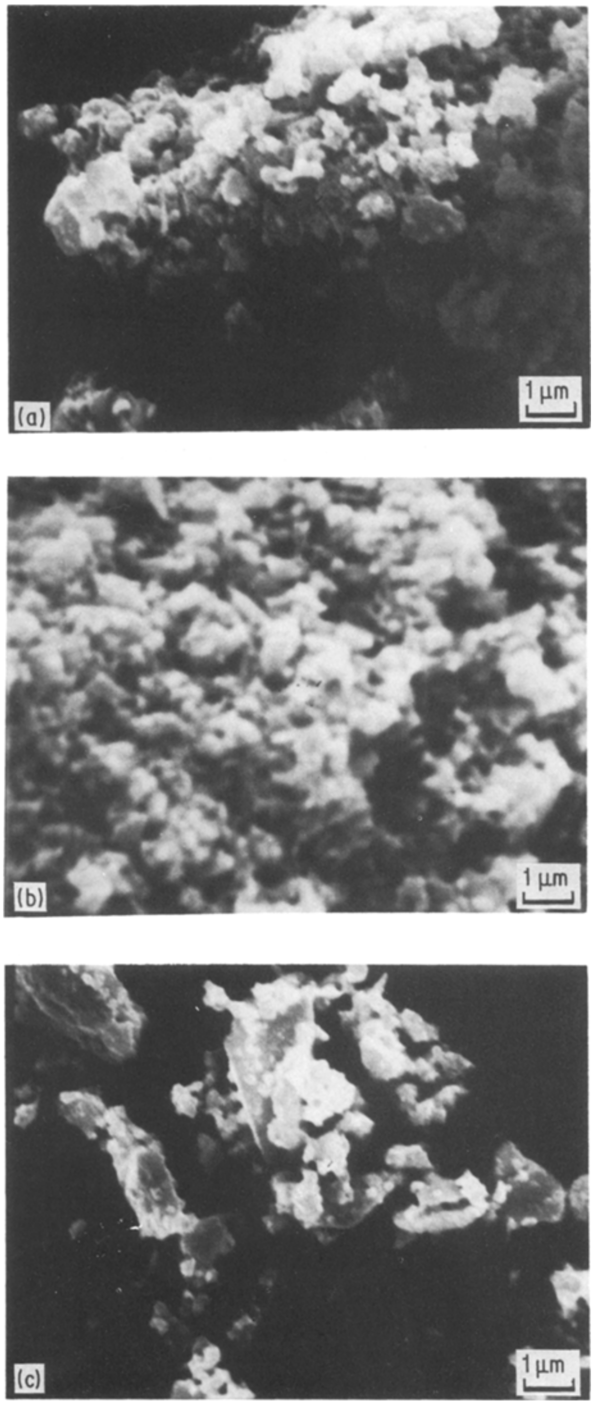
RuO_2 and IrO_2 grains exhibit a very high sintering ratio, which influences the electrical properties of the test resistors. The almost linear increase of resistance with temperature is similar to single-crystal properties. However, the magnitude of the temperature sensitivity of the thick-film sinters is six to eight times lower.

A different shape of the $R(T)$ curve was obtained for bismuth ruthenate layers. The curve is in qualitative agreement with the polycrystalline sample. The discrepancy with single crystal characteristic suggests the dominant role of the grain surface as well as of the regions between the grains. However, SEM observation shows that some of the grains appear to be sintered together. It is evident that sharp-edged $Bi_2Ru_2O_7$ grains in the powder are changed to rounded ones in the thick-film sinters.

A small addition of glass (5 wt %) to $Bi_2Ru_2O_7$ causes only a slight change in properties. The same addition of CdO brings about considerable changes of the $R(T)$ curve as well as in the SEM picture. This is

TABLE II Test resistor sheet resistance and temperature coefficient of resistance (TCR). Samples fired at 875° C at various dwell times (film thickness ~ 40 μm)

Sample	Dwell time					
	10 min		1 h		5 h	
	$R_□$ (Ω/□)	TCR (p.p.m. $°C^{-1}$)	$R_□$ (Ω/□)	TCR (p.p.m. $°C^{-1}$)	$R_□$ (Ω/□)	TCR (p.p.m. $°C^{-1}$)
A	2.4	1550	2.0	1890	1.7	1950
B	95.5	1620	130	1840	76.2	2150
C	6.9	−600	5.2	−577	4.1	−528
D	1.7	−349	2.4	−269	3.0	−476
E	2.3	−131	4.8	−300	3.6	−361
F	8.3	−705	5.0	−755	6.9	−980



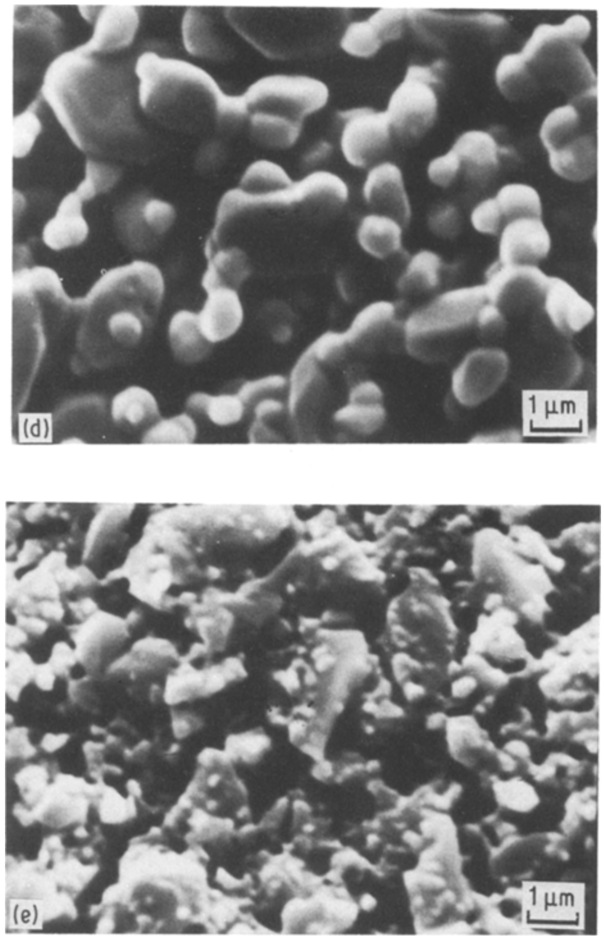


Figure 5 Comparison of initial conductive oxide powders and the surface of thick-film sinters. (a) RuO_2 powder, (b) surface of RuO_2 sinters, (c) powder of milled $Bi_2Ru_2O_7$, (d) grains at the surface of thick-film sinters prepared from milled $Bi_2Ru_2O_7$, (e) surface of sinters based on milled $Bi_2Ru_2O_7$ and CdO.

due to chemical interaction between $Bi_2Ru_2O_7$ and CdO.

The results of our investigation should be useful in modelling the electrical properties of thick-film resistors [23]. The TFR conduction model is still open to discussion.

References

1. T. V. NORDSTROM and C. R. HILLS, *Int. J. Microel.* **3** (1980) 14.
2. G. E. PIKE and C. H. SEAGER, *J. Appl. Phys.* **48** (1977) 5152.
3. N. C. HALDER, *Electroc. Sci. Technol.* **11** (1983) 21.
4. M. PRUDENZIATI, A. RIZZI, P. DAVOLI and A. MATTEI, *Il Nuovo Cimento* **20** (1983) 697.
5. S. DEMOLDER and A. VAN CALSTER, Proc. Conf. on Noise in Physics Systems, North-Holland Publ., Amsterdam (1986) p. 145.
6. A. KUBOVY and O. STEFAN, *Thin Solid Films* **135** (1986) L9.
7. L. GOLONKA and M. ŁUKASZEWICZ, in Proceedings of the Conference on Electronic Properties of Metal/Non-Metal Microsystems, Szklarska Poręba (Poland), September 1987, Technical University Wrocław (1987) p. 205.
8. R. W. VEST, "Conduction Mechanisms in Thick Film Microcircuits", Purdue Research Foundation, Final Technical Report, ARPA order no. 1642 (1975).
9. P. PALANISAMY, D. H. R. SARMA and R. W. VEST, *J. Amer. Ceram. Soc.* **68** (1985) C-215.
10. G. E. PIKE, in Proceedings 1st Conference on the Electrical Transport and Optical Properties of Inhomogeneous Media, Columbus, September, 1977. AIP Conf. Proc. no. 40, New York (1978).
11. P. J. S. EWEN and J. M. ROBERTSON, *J. Phys. D* **14** (1981) 2253.
12. E. LISTKIEWICZ and A. KUSY, *Thin Solid Films* **130** (1985) 1.
13. A. DZIEDZIC, L. GOLONKA and B. LICZNERSKI, in Proceedings 7th Czechoslovak Conference on Electronics and Vacuum Physics, Slovak Acad. Sci., Bratislava (1985) p. 855.
14. B. LICZNERSKI, in Proceedings 5th European Hybrid Microelectrics Conference, Stresa, ISHM Europe, Stresa (1985) p. 389.
15. W. D. RYDEN, A. W. LAWSON and C. C. SARTAIN, *Phys. Rev. B* **1** (1970) 1494.
16. R. J. BOUCHARD and J. L. GILLSON, *Mater. Res. Bull.* **6** (1971) 669.
17. B. REHÁK, PhD thesis, University of Chemical Technology Pardubice (1984).

18. B. REHÁK, M. FRUMAR and L. KOUDELKA, *J. Mater. Sci. Lett.* **3** (1984) 1011.
19. L. C. HOFFMAN, *Ceram. Bull.* **63** (1984) 572.
20. S. PASZCZYŃSKI, PhD thesis, Technical University Rzeszów (1978).
21. I. TAITL, *Hybrid Circuits* **1** (1982) 24.
22. M. L. TOPFER, "Thick Film Microelectronics" (Von Nostrand Reinhold, New York, 1971) p. 42.
23. A. DZIEDZIC, in Proceedings of the Conference on Electronic Properties of Metal/Non-Metal Microsystems, Szklarska Poręba (Poland) September, 1987, Technical University Wrocław (1987) p. 199.

Received 29 June
and accepted 16 December 1987