SIZE EFFECTS IN RUTHENIUM-BASED THICK-FILM RESISTORS: RUTILE VS. PYROCHLORE-BASED RESISTORS

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The size effect, namely the change of sheet resistance, R_s as a function of resistor length, has been investigated in layers whose conductive phase evolves from Pb-rich (Ru-deficient pyrochlores) to $Pb_2Ru_2O_{6.5}$ and finally to RuO_2 by increasing the firing temperature. It is found that Bi diffusion from the terminations is responsible for lower sheet resistance values in shorter resistors whatever the conductive phase is. On the contrary, Ag diffusion is responsible for lower sheet resistance values in shorter resistors only in the case of ruthenate conductive grains while the reverse is observed in RuO_2-based layers. Size effect can be suppressed with Pt/Au-based terminations provided that no Bi is contained and with Au-metallorganic-based contact provided that the peak firing temperature is not too high.

Key words: thick film resistors, size effects, electronic components

1. INTRODUCTION

The size effect in thick-film resistors, namely the change of sheet resistance, R_s as a function of the resistor length, 1 is of great concern for designers of hybrid circuits and their users, since it greatly affects the performance and reliability of these resistors, preventing, among other things, a precise design of the electrical properties of short resistors[1].

Several investigations have been published on these effects in Ru-based resistors, either in the form of RuO_2 or pyrochlore-type ruthenates.

At least two different causes of the size effect can be identified. The first one is associated with the change of shape (in particular thickness) of resistors when their length is varied. In this case the ratio between the actual resistance R and the aspect ratio (length 1/width w), does not represent the actual sheet resistance R_a, since the actual thickness is not constant for the whole set of resistors. Then R_s changes according to different 1, even if the resistivity of the material is constant into the resistive layer. This is usually a minor effect in Ru-based resistors, compared to the second source of size effects, namely a change of resistivity along the layer, associated with a compositional change.

The latter frequently occurs near the terminations due to interactions between the conductive layers and the resistive layers.

Different types of interactions can occur. A compound formation involving Pd-bearing terminations and pyrochlore-based resistors have been reported[2]. However, diffusive processes are probably the most important causes of size effect in Ru-based resistors.

At least two species have been identified as responsible for diffusive processes, namely Bi[3] and Ag[4-8]. Recently it has been shown[8] that Ag diffusion into RuO_2-based resistors exhibit very peculiar behaviours; in fact the silver diffusion coefficient is largely dependent on the surface area of RuO_2 particles (i.e. on RuO_2 grain size and concentration) as well as on the glass-matrix composition, and Al counterdiffusion occurs in resistors with an Al_2O_3-bearing glassy matrix due to either the glass formulation or diffusion from the alumina substrate. The Ag-Al interdiffusion is responsible for an "inverse" size effect, i.e. shorter resistors exhibit larger sheet resistance than longer resistors.

In this paper we will show that this peculiar phenomena are restricted to RuO_2-based systems (without any additive included, i.e. made of solely lead-silicate or boron-lead silicate glass frit and RuO_2 powders). Different behaviours are found in ruthenate-based resistors, since in this latter case a "direct" effect (i.e. lower sheet resistance in shorter samples) is observed, no matter the glass composition and interaction with the substrate, even if Ag largely diffuses into the resistive layers.

These results can allow us to elucidate the electrical transport in thick-film resistors.

2. EXPERIMENTAL

A. Samples and Method

This investigation was performed on resistive layers whose conductive phase evolves from Pb-rich (Ru-deficient) pyrochlores to $Pb_2Ru_2O_{6.5}$ and finally to RuO_2 by increasing the firing temperature. Preparation of the paste starts from powders obtained by precipitation of $RuCl_3$ on a Pb-containing glass of the percentage weight composition $SiO_2:PbO:B_2O_3 = 22:59:19$. The added $RuCl_3$ was equivalent to an amount of 3.8 wt% Ru (5 wt% RuO_2). Details of the preparation of the ink have been given previously[9] together with results concerning the evolution of the structural and electrical properties of the layers after heat treatment at various temperatures. For the present study, several inks were selected for the resistor terminations. Two Ag-bearing conductors were prepared with Pd and Ag powders in the relative ratio of 1 : 3 respectively. The composition of the glass bonding agent was the same as the glass frit used for the resistors. However, in one case (2120), a small quantity of (10 wt%) Bi_2O_3 was added to the glass as a flux. The Ag-free conductors were selected between the commercially available materials. 8081-A is a metallorganic Au-based ink. 9596 is a Pt/Au-based conductor with a glass bonding agent containing Bi. 5805 is a "fritless" Pt/Au-based ink which according to microprobe analyses, resulted free from Bi but with Mn and a small amount of Pb-rich silicate. Table 1 summarises the composition of the conducting materials either as known from preparation or derived from qualitative EDS analyses on dried inks (organic parts neglected).

TABLE 1

Composition of conductive layers used as terminations

Ink	Main Elements	Flux	Other constit.
2120	Pd:Ag = 1:3	Bi	Borosilicate glass
2130	Pd:Ag = 1:3	None	Borosilicate glass
5805	Pd:Au	None	Leadsilicate glass
8081-A	Au	None	None
9596	Pt/Au	Bi	Leadsilicate glass

Resistors were screen printed on Al_2O_3 substrates (Hoechst Ceram. Tec 708) with prefired terminations (prepared at T_f = 950 °C) and fired at different firing temperatures in the range 600–900 °C. The resistor patterns contain samples of fixed width (2 mm) and different lengths (from 0.5–10 mm) for the study of size effects.

Resistivity measurements were performed at 300 K using a Philips autoranging multimeter (PM 2528).

B. Analyses

Observations in scanning electron microscope (SEM) and analyses in energy dispersive spectroscopy (EDS) were performed with Philips PX 500 system equipped with a Si(Li) detector with Be window, enabling the detection of elements with Z > 10.

X-ray diffraction (XRD) measurements were performed using Cu K emission line (Ni filter) by means of a Philips PW 1700 diffractometer. XRD patterns were collected on samples etched in $HF:HNO_3:H_2O$ = 3:1:50 volume for 1 min in order to remove the glassy matrix and enhance the peaks of the crystalline phases. Areas under these peaks were measured in samples fired at various firing temperatures and, for reference, in powders of RuO_2 and $Pb_2Ru_2O_{6.5}$.

3. RESULTS

Samples prepared at lower temperatures (600–800 °C) exhibited the reflections corresponding to a cubic structure identified as a pyrochlore phase. However, the peak positions shift continuously in accordance with reduction of the lattice parameter from a_o = 10.6 Å in samples fired at 600 °C to a_o = 10.26 Å in samples prepared at 850 °C. Moreover, as the firing temperature increases from 700 to 950 °C two further effects are observed:

a) The pyrochlore height peaks (e.g. (222) peak near 2θ = 30 deg.) decrease by increasing the firing temperature; and

b) Weak and broad reflections of the RuO_2 rutile phase, (near 28.2 deg.) are observed first (T_f = 700 °C) which completely substitutes for pyrochlore phase at 950 °C.

Fig. 1a shows these results by comparing a segment of the XRD patterns of samples fired at different temperatures. An approximate evaluation of the relative fraction of pyrochlore converted in rutile phase was obtained through the ratio of area of the XRD patterns of the two phases taking into account the intensity of
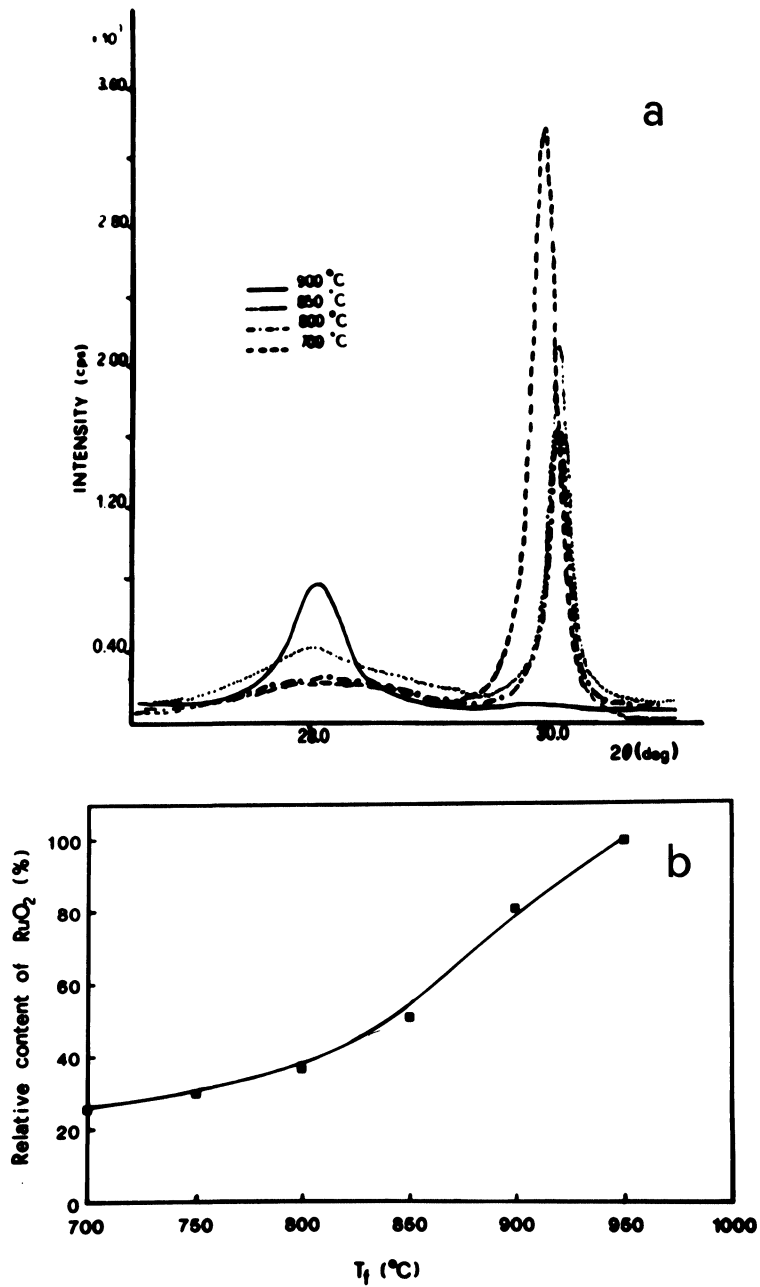
FIGURE 1   (a) The salient part of XRD patterns of Resistive layers fired at various peak temperatures. The correspondence between crystallographic planes and 2θ values is as follows: RuO_2 (110) $\rightarrow$ 28.135°; $Pb_2Ru_2O_{6.5}$ (222) $\rightarrow$ 30.15°. (b): Approximate relative content of RuO_2 evaluated from the normalized area of rutile/(rutile + pyrochlore) XRD reflections.

reflection of the reference powders. This approximate evaluation is reported in Fig. 1b. It is apparent that in samples prepared at 850 °C the conductive phase is made of about 50% RuO_2 and 50% pyrochlore grains.

Fig. 2 shows the size effect, namely the effect of resistor length, 1 on the effective sheet resistance, R_s of the samples fired at T_f = 850 °C and terminated with four different types of conductors. The direct effect, namely a lower effective sheet resistance for short resistors, is exhibited in the case of Ag-free terminations. The presence of Ag in the conductors is responsible for a great inverse effect, namely larger effective sheet resistance in the short resistors. It can be seen that Bi can only attenuate the consequence of Ag diffusion. The small variation of effective sheet resistance observed in resistors with "fritless" conductors is due to a geo-metrical effect. An increase of the peak firing temperature strongly enhances this behaviour (see Fig. 3 where the size effect of the resistors prepared at 900 °C is reported), particularly in the case of Bi-free Ag-bearing conductors.

The effect of the peak firing temperature as a consequence of Ag diffusion into the resistors is shown in Fig. 4. Here, it is interesting to note that at lower tem-
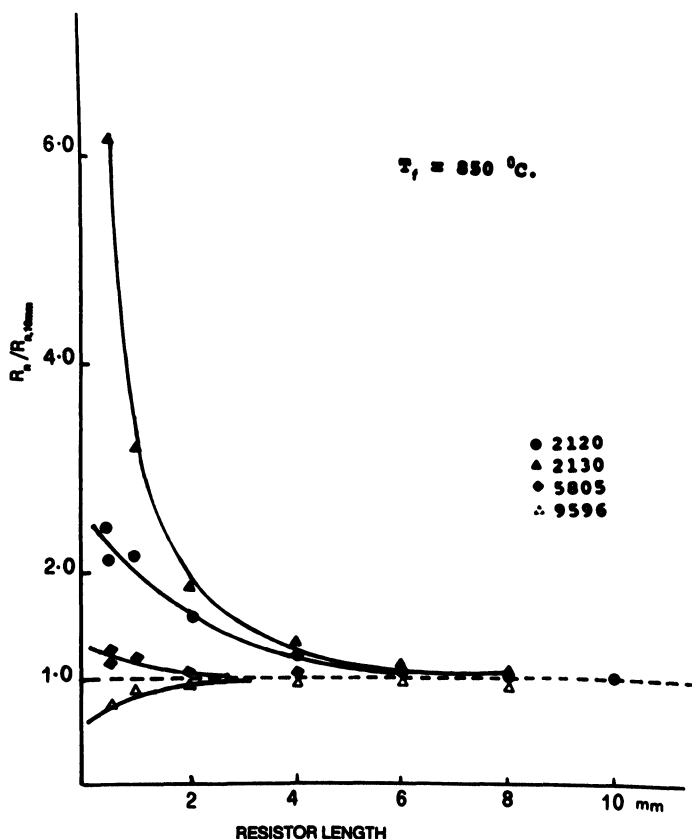

FIGURE 2   Normalised Sheet Resistance vs. Resistor length for the resistor with four different ter-minations (Note: T_f = 850 °C).
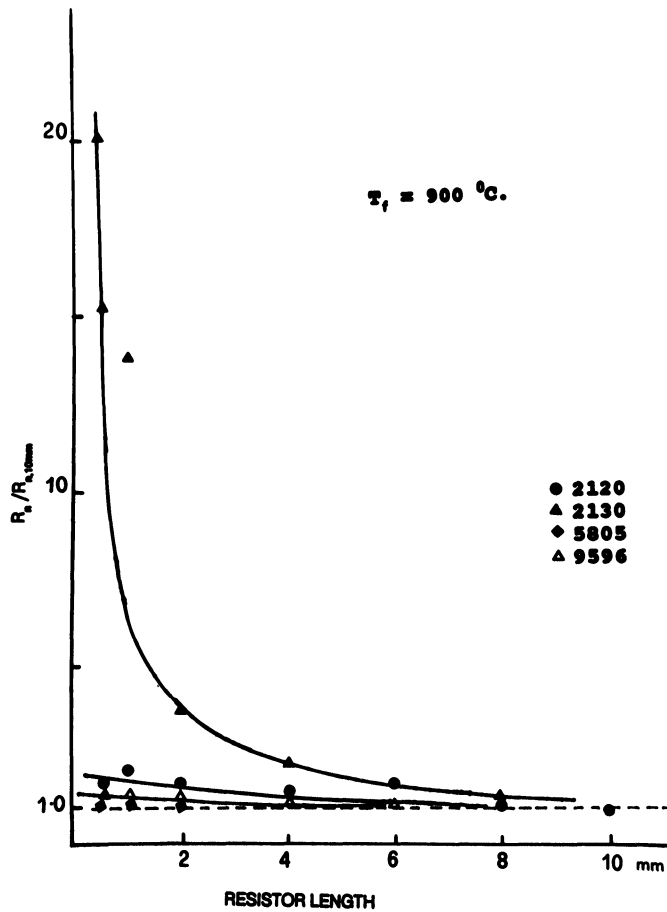
FIGURE 3   Normalised Sheet Resistance vs. Resistor length for the resistor with four different terminations (Note: $T_f = 900$ °C).

peratures ($T_f < 750$ °C) a direct effect is observed, while at higher temperatures ($T_f > 800$ °C) the inverse effect is observed. This peculiar consequence of Ag diffusion should be related to a change of microstructure of the resistive layer, as explained later.

The consequence of Bi diffusion is quite different from that of Ag diffusion as shown in Fig. 5. Here as temperature increases the direct effect becomes more pronounced.

In order to remove almost completely the size effect both Bi and Ag have to be absent in the conductive layers as in the case of 5850 (Pt/Au terminations). In fact in this case, the sheet resistance does not change more than ± 15% which is the usual scattering of sheet resistance values due to variation of the thickness and aspect ratio as well as inhomogeneity of thick film resistors.
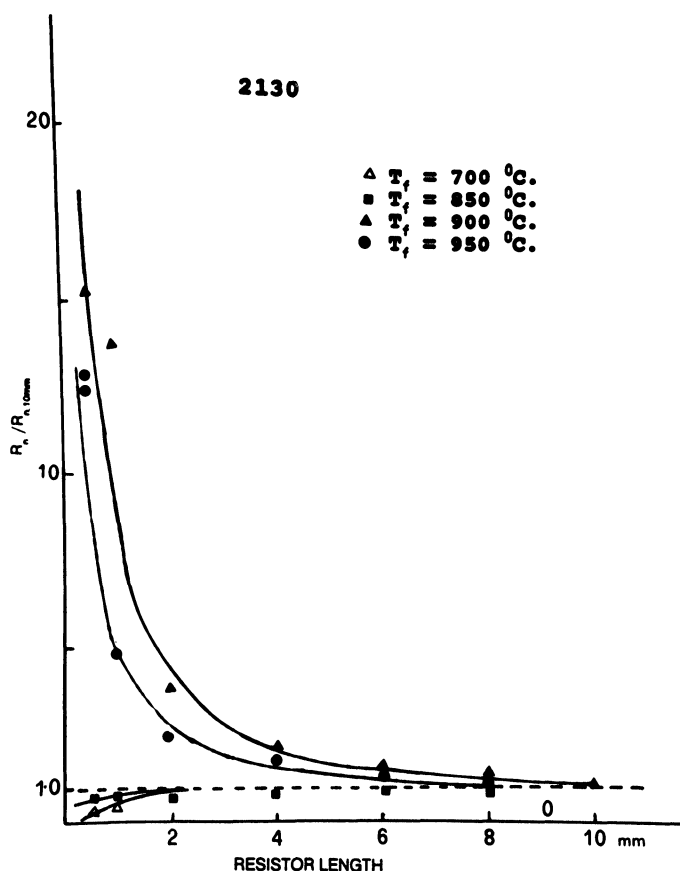
FIGURE 4   Variation of Normalised Sheet Resistance with Resistor length for the resistor terminated with 2130 and fired at different peak temperatures.

Our attempts to avoid the size effect with the use of metallorganic Au-based terminations were unsuccessful for T > 800 °C. In fact, this conductor has a poor compatibility with the resistive material as well as with the alumina substrate at high temperature in agreement with the recommendation of the manufacturer who suggests a peak firing temperature in the range 625–850 °C with an optimum at 825 °C. Fig. 6 illustrates this property. It can be seen that the region where the resistor and the conductor overlap is affected by intermixing of the two types of layers. Consequently, a good low resistive contact can not be formed (see Figs. 6a & b). The metallic layer suffers from lack of contact also far from the resistor. The presence of voids are observed in samples prepared at T_f = 850 °C (see Fig. 6c) while the formation of disconnected islands results from heating at higher temperatures (Fig. 6d). This finding suggests strong driving forces for nucleation and weak interface between gold and alumina. As a consequence, resistance of the metal lines increases with the firing temperature.
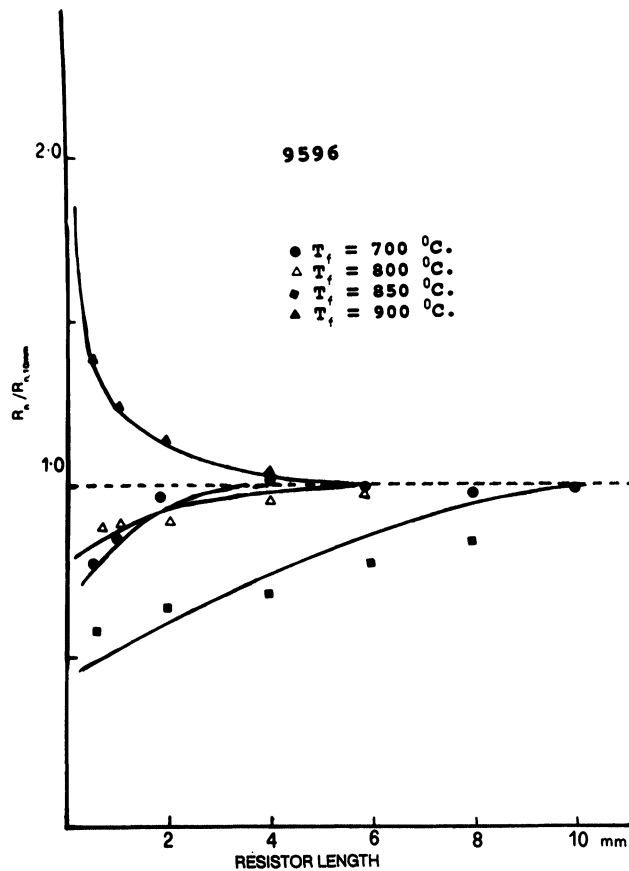
FIGURE 5   Variation of Normalised Sheet Resistance with Resistor length for the resistor terminated with 9596 and fired at different peak temperatures.

4. DISCUSSION

The described experiments have shown how complex the size effect can be. In fact, the same resistive layer on the same substrate exhibits a behaviour depending on the composition of the terminations but also an inversion of the effect itself by changing the firing temperature. This latter is due to silver diffusion. If we reasonably assume that the diffusion of elements from the termination does not affect the conductive phase transformation in the resistors, we can include all the observed effects in a single picture, according to the following statements:

   i) Bi diffusion is responsible for a decrease of resistance in RuO_2 as well as in ruthenate-based resistors[3].

   ii) Ag diffusion is responsible for a decrease of resistance in ruthenate-based resistors[5] as well as in RuO_2-based systems, provided that the latter are free from aluminium[8]; and
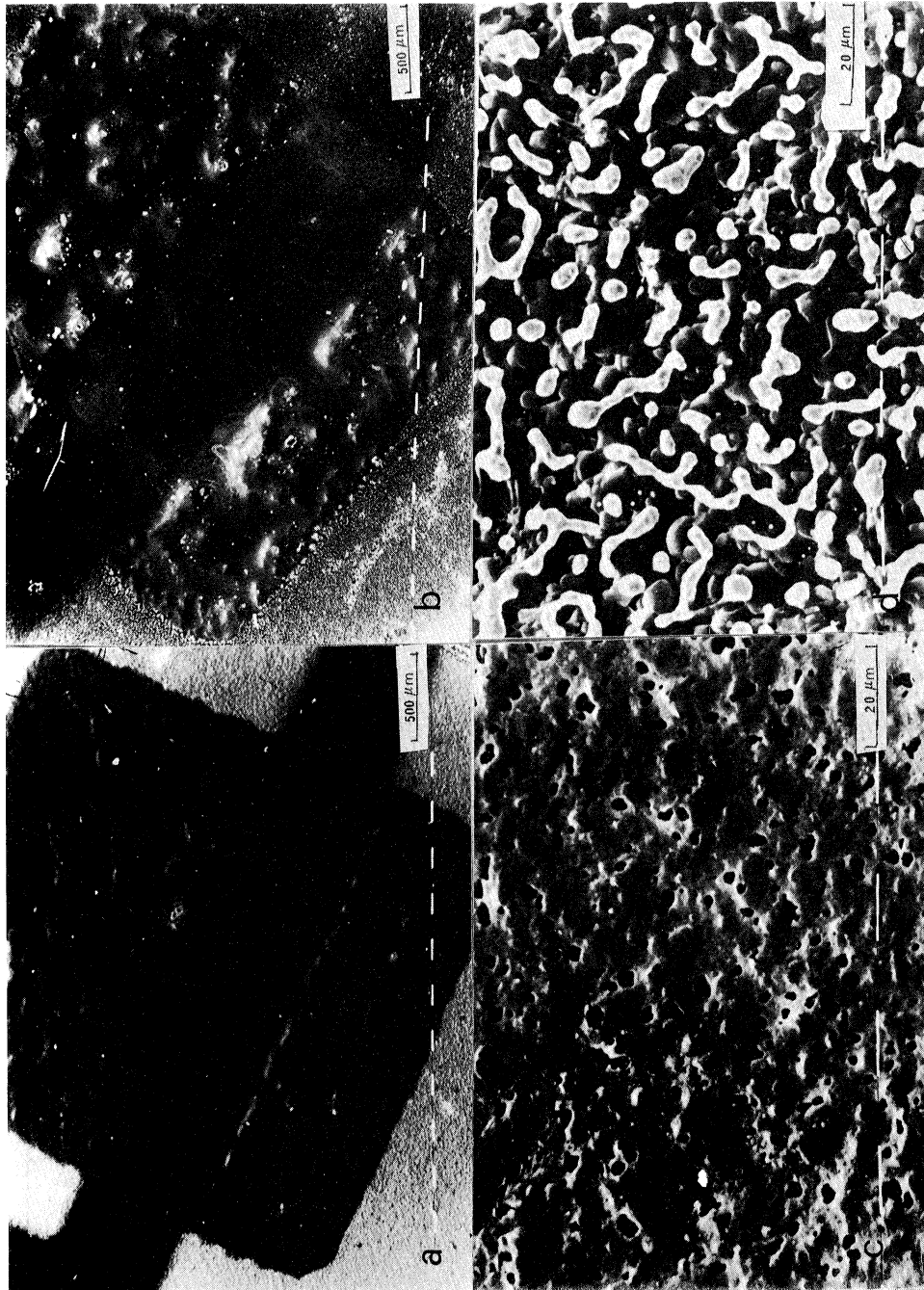
FIGURE 6   SEM micrographs of: a) and b) the resistor terminated with Au-metallorganic-based conductive layers; a): T_f = 850 °C. b) T_f = 1000 °C. c) and d) the surface of the metal layer fired at T_f = 850 °C (c) and T_f = 1000 °C (d).

iii) The resistance of RuO_2-based resistors containing aluminium, either due to its presence in the glass frit or interdiffusion from the substrate increases as a consequence of silver diffusion.

In this frame work, a qualitative explanation of the results concerning the size effect in these resistors can be easily given. With reference to Fig. 2, the direct effect observed with 9596 terminations is closely related to the previous point (i) regardless of the composition of the conductive phase inside the resistor. On the contrary, the effect given by Ag-bearing conductors requires that RuO_2 grains are present in a considerable quantity (in accordance with the result shown in Fig. 1b), as well as the presence of aluminium diffused from the substrate. Evidence of considerable interactions between the glass and alumina have been reported[10].

An increase of the firing temperature means an increase of diffusivity for Bi, Ag and Al as well as a further transformation of the conductive phase into RuO_2. Consequently, according to point (ii), the direct effect due to Bi diffusion is enhanced with 9596 terminations and similarly the reverse effect due to Ag diffusion is more evident according to point (ii) as in fact observed in Fig. 3. The results of Fig. 4, where terminations based on Ag without Bi are considered, can be realised according to the correlation between the Ag diffusion and its consequence and according to the nature of the conductive phase in the resistor. In fact, at lower temperatures (700–750 °C) interactions between glass and alumina have already taken place concurrently with Ag diffusion in the resistors; the direct effect is observed in agreement with the presence of the conductive grains mainly consisting in a ruthenate phase. As far as temperature increases and ruthenate is transformed into RuO_2 inverse effect becomes evident. Here the absence of Bi in the terminations as well as the identity of composition of the glass in the conductive and resistive layers warrant that an inversion of the size effect is exclusively related to the phase transformation of the conductive grains in the resistor.

Finally, the results of Fig. 5 support the contention that Bi is responsible for the direct effect whatever the conductive phase in the resistors.

It is interesting to note that the diffusion of Bi partially suppresses the effect of Ag diffusion. Other elements (e.g. Mn) are even more effective in suppressing the inverse effect. These are the same elements usually introduced in RuO^2-based resistors for the control of the Temperature Coefficient of Resistance (TCR)[11–12]. This is the reason why the inverse size effect is rarely observed in the commercial pastes.

5. CONCLUSIONS

The electrical properties of ruthenate- and ruthenium dioxide-based resistors exhibit some similarities but also some important differences[13–14]. The size effect due to silver diffusion from terminations seems to be one of the most striking distinctive features. Reverse size effects were already observed occasionally[6] e.g. in silver terminated commercial resistors and systematically found in our RuO_2-based model systems[8] while the direct size effect was always found in ruthenate-based resistors[5].

However, this investigation is the closest we have come to show that the con-

sequence of silver diffusion (and related Al interdiffusion[8]) on electrical properties is dependent on the nature of the conductive phase. In fact, we have found an inversion of the size effect in a single system, by changing "only" (or mainly) the conductive phase from Pb-pyrochlore in RuO_2 while the glass matrix remains essentially the same (except for the minor changes due to the exchange reactions giving rise to the phase transformation itself).

Further investigations are required to understand in which way silver is located into the microstructure of the Ru-based resistors (bond state with glass and/or the conductive grains) in model resistors which give simpler systems and hopefully offer a possibility to clarify the behaviour of these very complex resistors.

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