CONDUCTIVITY OF THICK FILM (CERMET) RESISTORS AS A FUNCTION OF METALLIC PARTICLE VOLUME FRACTION*

G. E. Pike

Sandia Laboratories, Albuquerque, NM 87115

ABSTRACT

Thick film resistors (TkFR) are composites of metallic particles embedded in a glass matrix. Conduction is through interconnected particle chains. For each of five systems studied the conductivity varies over many decades with particle volume fraction v_m . It follows a power law dependence, $G = K(v_m - v_{m,c})^t$, where K , $v_{m,c}$ and t are constants for a given system. There are two interesting features of this relation for TkFRs: $v_{m,c}$ is very low (0.02 or less) and t is rather high ($3 < t < 7$). These values of $v_{m,c}$ and t are in apparent disagreement with percolative systems in which $v_{m,c}$ is much higher and the critical exponent $t \sim 1.6$. Nevertheless, a model is proposed for which the conductance is indeed governed by percolation. This model takes explicit account of the resistor formation process and the observed microstructure. It is essentially a modified bond percolation model in which the metallic particles are partial bonds in the lattice connecting the interstices of the relatively larger, close-packed glass particles.

INTRODUCTION

The term thick film resistor (TkFR) refers to a class of resistive materials, used widely in the electronics industry, which are prepared according to a well established technology.¹ Preparation starts with an "ink" composed of glass and metallic powders suspended in a viscous organic fluid. The glass powders for the TkFR's discussed in this paper are 1 to 10 μm particles of various lead borosilicates. The metallic particles are either RuO_2 or $\text{Bi}_2\text{Ru}_2\text{O}_7$ and they are submicron. The organic fluid is present mainly to permit the mixture to be screen printed onto an alumina substrate, after which it is air dried at an elevated temperature. Finally the printed substrate is slowly fired (heated) to a temperature well above the glass transition temperature (typically 30°C per min. until a final temperature near 850°C is reached). The finished resistor is 10 to 20 μm thick and has a dark, glassy appearance. However, selectively removing a few microns of glass with an acid etch reveals a network of connected metallic particles as shown in Fig. 1 for a $\text{Bi}_2\text{Ru}_2\text{O}_7$ TkFR.²

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FORMATION AND STRUCTURE

Vest and co-workers have made an extensive study of the microstructure formation processes in TkFRs.³⁻⁵ They find that the microstructure evolves in a series of steps. As the temperature T increases, the first change from a powder mixture is the initiation of sintering between adjacent glass particles. Neck growth proceeds by Newtonian viscous flow. This occurs at $T \sim 500^\circ\text{C}$ where the metallic particles can be neither wet significantly by the glass nor sintered together. Constrained to be on the surface of the glass, these smaller particles are pushed into pores and channels between the glass particles as the glass sintering goes to completion. At some higher temperature the glass begins to wet the metallic particles with the result that surface tension draws adjacent metallic particles closer together. Finally at the highest temperatures the still solid metallic particles begin to sinter by the liquid-phase process, which involves a thin interparticle layer of molten glass. Once this stage has been achieved, the essential features of the TkFR are relatively unchanged by either higher firing temperatures or times.^{3,6}

Fig. 1

ELECTRICAL

Although most commercial TkFR systems have compositions which are highly proprietary, there are some studies in which compositional information is available.^{2,3,6,7} From these we have obtained results for the dependence of sheet conductivity, G , on the volume fraction of metallic particles v_m (relative to glass plus metallic particles; i.e., the organic volume was not considered). Figure 2 shows the results for two RuO_2 TkFR systems plotted as $\log G$ vs $\log (v_m - v_{m,c})$. For the data of Ref. 7 the value of $v_{m,c}$ was taken to be zero. However, for the results of Ref. 3, $v_{m,c}$ was chosen as 0.021. This is close to the v_m value that Vest claims is a lower limit for making reproducible TkFRs with his system,³ and it also yields a very linear graph. For each system illustrated in Fig. 2 the composition and size distribution of both the glass and metallic particles was constant for all points; the change of v_m alone is responsible for the many decade variation of (sheet) conductivity. Similar results are seen in Fig. 3 for some $\text{Bi}_2\text{Ru}_2\text{O}_7$ TkFRs. The D-1200 and D-1400 are

Fig. 2

Fig. 3

commercial systems for which analysis of the principle constituents has been performed.^{2,6,8} The D-Proto was custom formulated from $\text{Bi}_2\text{Ru}_2\text{O}_7$ and $\text{PbO}(\text{SiO}_2)_2$ plus a standard organic.^{2,6,8} For all these systems $v_{m,c}$ was taken to be zero. As in Fig. 2, these data seem to accurately obey a dependence of the form

$$G = K(v_m - v_{m,c})^t \quad (1)$$

where the least-squares determined values of t are shown in the figures.

An important aspect of the TkFR systems illustrated in Fig. 3 is that they all have the same conduction mechanism, and this mechanism is the same for each value of v_m plotted.^{2,6} It has recently been shown that conduction through these TkFRs is along the sintered chains of metallic particles. The major impedance there is due to electron tunneling through the thin, interparticle glassy layer remaining from the liquid-phase sintering.^{2,6} These conclusions were based on extensive electrical transport measurements on the TkFRs and on the metallic particles extracted from the fired resistors. The most important of these measurements were the temperature and electric field dependence of conductivity and the thermopower. As an example of uniform behavior we show in Fig. 4 the temperature dependence typical of all systems (including the RuO_2 systems, but the data for these are not as complete). The details of this behavior have been fully discussed elsewhere;^{2,6} the important points for the present discussion are that the conductivity does not vary significantly over a large temperature range, and that each resistivity composition eventually develops a slightly metallic (G decreases) variation as T increases.

DISCUSSION

The functional dependence of Eq. (1) is reminiscent of that for conduction in a resistor lattice just above the percolation

Fig. 4

threshold,^{9,10}

$$G = K'(p - p_c)^t, \quad (2)$$

where p is the fraction of bond positions occupied by a resistor. However if one identifies v_m with p , then the values of $v_{m,c} < 0.02$ are considerably smaller than the published value of $p_c = 0.25$ for the simple cubic (sc) lattice⁹ or $p_c \sim 0.10$ to 0.15 for various degrees of bond correlation on this same lattice.^{9,10} Also regardless of correlation the value of $t \sim 1.6$ seems to characterize the 3-D resistor lattices while the TkFRs exhibit values of $3 < t < 7$.^{9,10} Nevertheless, since the TkFR conductivity is increasing much faster than v_m , and since the conductivity at all values of v_m is controlled by chains of sintered metallic particles, it seems that connectivity changes among chain segments must be largely responsible for the conductivity variations. Since this is exactly the situation in resistor networks for $p \gtrsim p_c$, one should ask whether the values of $v_{m,c}$ and t for TkFRs can be reconciled with p_c and t for the networks.

Recall that during formation the smaller metallic particles could not penetrate the larger glass particles, and that the glass sintering squeezed the metallic particles into pores and channels. Assume, for a rough estimate of $v_{m,c}$, that the glass particles sinter into cubes of side l_1 with the spherical metallic particles of diameter l_2 constrained to occupy rectangular channels of dimensions $l_1 \times l_2 \times l_2$ along the cube edges (see Fig. 5). Then the fractional

volume of the channels is

$$v_2 = 3\ell^2 - 2\ell^3 \quad (3)$$

where $\ell = \ell_2/\ell_1$. These channels form a sc lattice and the probability that a channel is completely occupied by $1/\ell$ adjacent metallic particles (i.e., a bond is complete) is

$$p = [v_m/(0.5v_2)]^{1/\ell} \quad (4)$$

where the factor of 0.5 is due to spherical particles in a rectangular channel. For the TkFR systems discussed here ℓ is 0.1 to 0.2, so taking $\ell = 0.15$ and $p_c = 0.25$ and using Eqs. (3) and (4) one finds $v_{m,c} \sim 0.025$. Thus the condition that the metallic particles are a priori excluded from a large volume of the TkFR material permits a small amount of them to span the material as connected chain segments, each $\sim 1/\ell$ particles long.

The model described by Eqs. (3) and (4) can only hold for very small v_m since v_2 is quite small and v_m would equal $0.5v_2$ for $v_m \sim 0.03$. At this value, $p = 1$ and no more particles could fit in the channels. This is clearly unphysical since the channels do in fact accommodate whatever v_m is present in the ink. Thus v_2 is some function of v_m , and substituting p from Eq. (4) into Eq. (2) is not straightforward. Furthermore if p is nearly unity and the channels simply swell as v_m increases, then connectivity would be unimportant for $v_m > 0.03$ and the conductivity would simply be proportional to v_m . This, of course, is not observed. Since large, connectivity-related changes in the conductivity can only occur for $p_c \lesssim p$,⁹ p must remain near p_c even though v_m changes from 0.05 to 0.60 (in the extreme case of Ref. 7). A completely satisfactory explanation of how this can happen has not yet been developed. However, one possibility is that the connectivity of the channels, and hence the maximum value of p , is mainly determined by the process of glass sintering. That is, because of different sized glass particles some fraction of the initially open channels sinter closed and exclude the metallic particles before the particles in the chain segments are sufficiently bonded together. In this case increasing v_m primarily increases the occupied cross-section of the channels, a few additional channels are occupied, and p is nearly constant. There is some SEM evidence for this.⁶ The required functional form of p would have to

Fig. 5

be $p_c + K v_m^n$ with $n \sim 2$ for Eq. (2) to describe the TkFR data. How this form could arise is not known. However, it is not likely to be a form intrinsic to all glass powder mixtures since the TkFR systems are not arbitrary as to the composition and size distributions of both the glass and metallic particles.

Although the detailed reasons for the large conductivity changes of TkFRs over a wide range of v_m are not known, this paper has demonstrated that this behavior is common to several systems, that connectivity changes dominate the conductivity variations, and that small volume fractions of metallic particles can reasonably be expected to form chain segments spanning the TkFRs.

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Fig. 1 SEM of a slightly etched, $10^6 \Omega/\square$ D-1200 TkrR.

Fig. 2 Sheet conductivity G vs RuO₂ volume fraction v_m .

Fig. 3 Sheet conductivity G vs Bi₂Ru₂O₇ volume fraction v_m .

Fig. 4 Normalized conductivity vs temperature for the D-proto system.

Fig. 5. Simple model for estimating v_m .