Infrared absorption in thick film resistors

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Infrared absorption in polymer and glass-based thick film resistors has been measured between 400 and 1500 cm^{-1}. Sample structures are discussed on the basis of X-ray, Fourier transform–infrared and resistance–temperature data. It is shown that in polymer-based thick film resistors, the particulate phase is mostly responsible for the infrared absorption between 400 and 900 cm^{-1}, whereas the infrared absorption at higher wave numbers is related to the continuous phase. In glass-based thick film resistors, absorption is mostly determined by the highly doped glass. The results indicate that thick film resistors can be used as an absorbent coating in the 400–1500 cm^{-1} region by suitable selection of the continuous and particulate phases.

1. Introduction

Thick film resistors (TFRs) consisting of conducting and insulating phases have been known and widely used in the electronic industry for over 20 years [1]. TFRs are normally supplied as a "paste" which consists of submicrometre size conducting and nonconducting particles suspended in a viscous organic fluid. After printing the paste, organic solvents are removed during drying and the organic binders are burned out in the first stage of the heating. Maximum heating temperature is selected well above the glass transition temperature and thus the resultant TFR has a structure in which the particulate phase is randomly distributed in a continuous phase. Depending on the type of continuous phase, which is either some sort of glass or a thermosetting polymer, TFRs are classified as cermet and polymer types.

Electrical properties of TFRs are mainly determined by the volume fraction of the conducting phase [2]. It is known that some impurities are added to the paste in order to achieve low temperature and voltage coefficients of resistance. The energy level of such impurities lies deep in the band gap of the insulating phase and somehow affects the electrical conduction processes [3]. Together with these, low-resistive activation terms ranging from 0.1–10 meV [4, 5] suggest that these systems might have a strong electromagnetic absorption in the infrared and microwave regions.

The aim of this work was to investigate the infrared absorption properties of thick film resistors and to correlate them with their structural and electrical properties in an attempt to see if they could be used as absorbent coating in the infrared (IR) region.

2. Experimental procedure

Commercially available cermet and polymer thick film pastes (ESL 391x and RS1511x series,

respectively) having sheath resistivities of 10^2–$10^5 \, \Omega/\square$ were used in this work. Film samples with dimensions of 23 mm × 10 mm and 2.5 mm × 2.5 mm were screen printed on 96% alumina substrates for X-ray and resistance measurements, respectively. After printing, the samples were dried and cured under the conditions given in Table I. Cured samples were labelled as C2–C5 for cermet types and P2–P5 for polymer types. The thickness of the cured samples was measured by Talysurf-4 and found to be 25 ± 5 μm.

For IR measurements, bulk samples were prepared on 96% alumina substrates and cured under the same conditions as their film counterparts. Then, the samples were scraped out from the substrates and ground in an agate mortar. The mixture of KBr and the sample (1% by weight) was pelletized under vacuum by a pressure of 10 ton. IR spectra of homogeneous pellets were obtained using a BOMEM MB100 FT–IR spectrophotometer and are given in Figs 1 and 2 for polymer and cermet types, respectively.

A Rigagu-RadB automated X-ray powder diffractometer with copper anode and graphite monochromator were used for compositional investigations. XRDs were obtained with a scan speed of 1° min^{-1} in the continuous scan mode. The composition of the conducting phases was determined by comparing the spectrum with the standard data stored in the computer. The results are given in Fig. 3.

Resistance data were collected using an automated data work station. A closed-cycle helium refrigerator

TABLE I Curing conditions of thick film resistive pastes

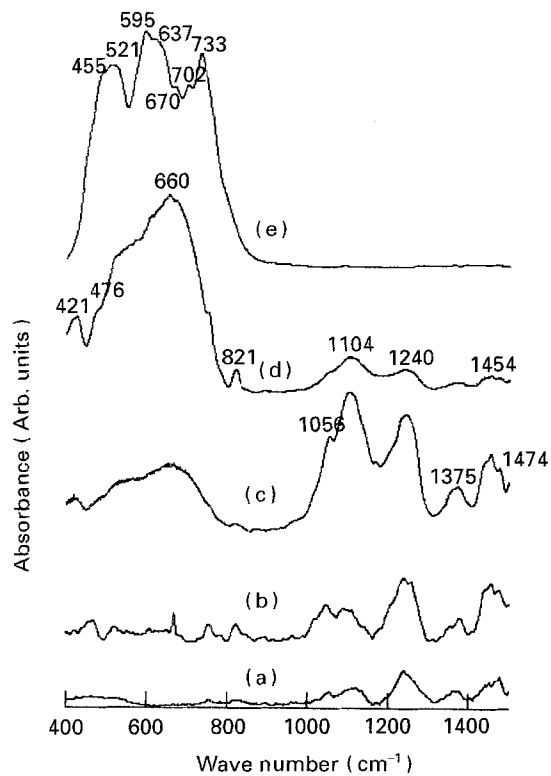| Type	Drying		Curing	
	Temp.(°C)	Time(min)	Temp.(°C)	Time(min)
Polymer	70	30	150	120
Cermet	150	30	850	10

Figure 1 IR absorption spectra of polymer thick film resistors and TiO$_2$. (a) P2, (b) P3, (c) P4, (d) P5, (e) TiO$_2$.
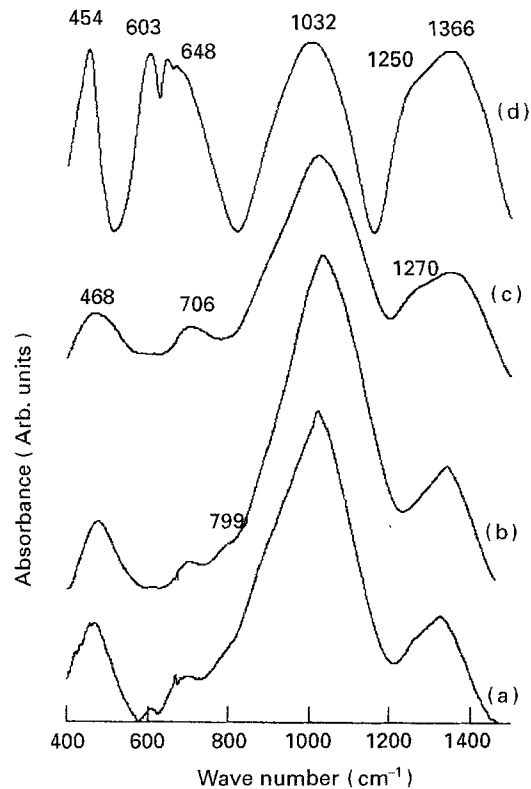
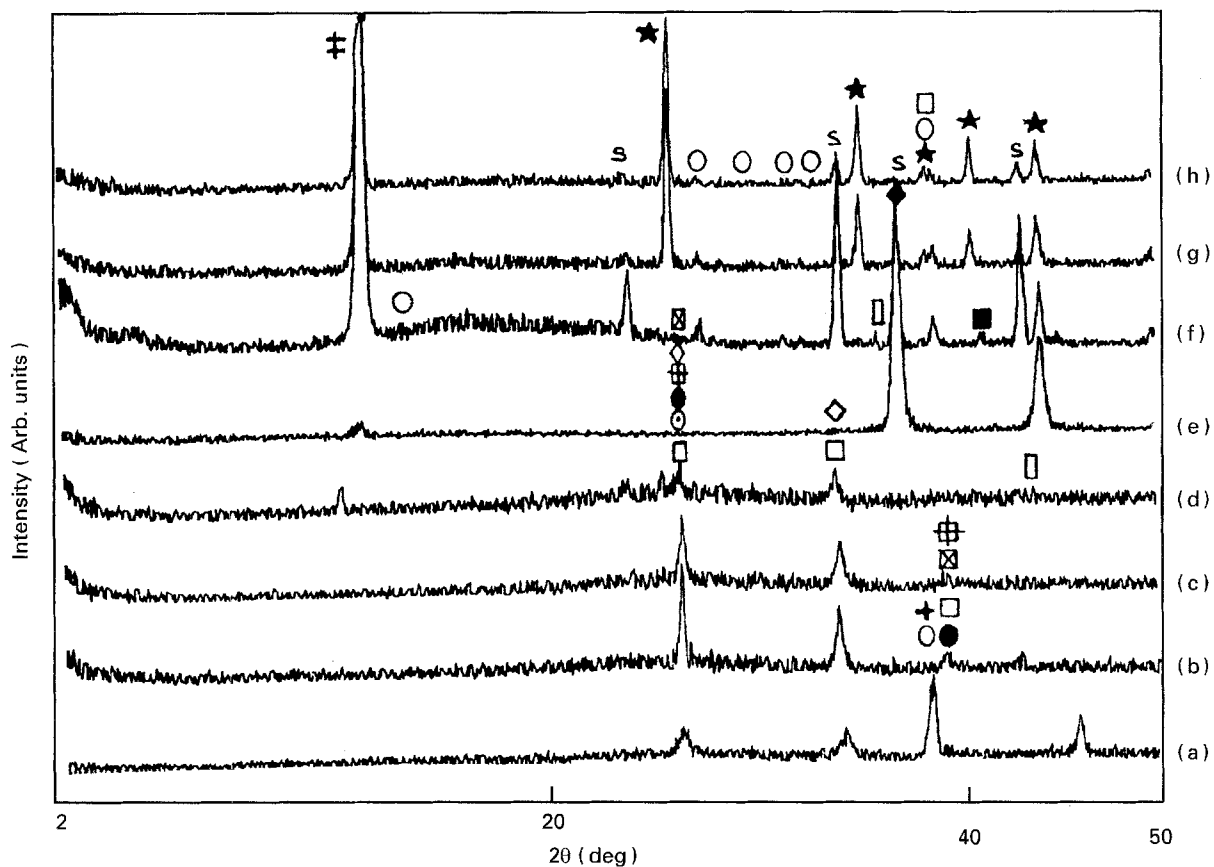*Figure 2* IR absorption spectra of cermet thick film resistors. (a) C2, (b) C3, (c) C4, (d) C5.

Figure 3 X-ray powder diffractograms of the samples. (a) C2, (b) C3, (c) C4, (d) C5, (e) P2, (f) P3, (g) P4, (h) P5. s Substrate, (★) TiO$_2$, (□) RuO$_2$, (◇) PtO$_2$, (○) Cd, (■) Al$_3$Ti, (◆) TiCl, (●) Ag$_2$S, (‡) MoS$_2$, (⊠) PdTi, (⊞) PtTi, (☉) CuInSe$_2$, (+) Pt$_3$Pd$_2$Sn$_2$, (⊕) PtIn, (⊡) CdTi.

and a cryostat were used in cooling the samples and the temperature was measured by a calibrated silicon diode connected to a temperature control unit (Lake-Shore DRC-91CA). The overall error in temperature measurements was better than $\pm$ 0.5 K. Because the room-temperature resistances of the samples were higher than 100 Ω, a two-probe technique was employed in measuring all resistances, using a Keithley 617.

3. Results and discussion

3.1. X-ray analyses

From the XRD results given in Fig. 3d and f, it is seen that the cermet and polymer types have broad peaks centred at 28° and 18°, respectively. This indicates that polymer and cermet systems contain different types of amorphous phases, as expected. Except for the substrate peaks (labelled s in Fig. 3), the others are associated with particulate phases and/or impurities. For the samples P4 and P5, peaks are identified as TiO_2, MoS_2 and cadmium peaks, Fig. 3g and h; whereas for P3, peaks correspond to MoS_2 and to some metallic alloys of cadmium, titanium, iron, silver, manganese, tin, silicon, aluminium, Fig. 3f. In sample P2, the composition of the particulate phase was identified as cadmium and Cd/Ti alloy with a small amount of MoS_2, Fig. 3e. It should be noted that cadmium appears in all polymer TFRs. These results are rather surprising, because they suggest a reverse structural picture of what is commonly known for polymer TFRs in which the conducting particles are distributed over an isolated polymeric phase [5].

XRDs of C3 and C4 are quite similar, Fig. 3b and c. Their peaks indicate the existence of some palladium, platinum, titanium, cadmium and silver alloys and RuO_2, whereas the peaks for C5, Fig. 3d, mainly refer to lead, cadmium, aluminium and silicon alloys with some amount of RuO_2 and PtO_2. C2 mainly consists of platinum, palladium, indium and tin alloys as well as some RuO_2.

3.2. Resistance measurements

The temperature dependence of normalized resistances of polymer TFRs given in Fig. 4 shows that activation terms of P2, P3 and P4 are quite similar, despite the fact that their resistances are different by one or two orders of magnitude. An abrupt change in the activation term of P5 ($\sim$ 10.65 meV for P5 and $\sim$ 4.42 meV for P4, between 250 K and 73 K) suggests that the volume fraction of the conducting phase of P5 is very close to the percolation limit.

In the light of the low-temperature dependence of resistance and the XRD results it can be stated that the conducting alloys with low resistance and positive temperature coefficients had been used to modify these features of the conducting polymeric phase in P2. In P3, MoS_2 seems to have partly replaced the conducting alloys to increase the resistance. However, its activation term remains the same, probably due to cadmium inclusion. In P4 and P5, TiO_2 and MoS_2 have completely replaced the conducting alloys and
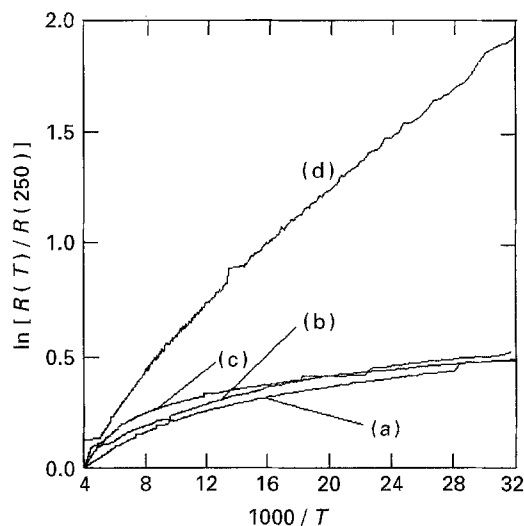
Figure 4 Normalized logarithmic resistance versus $1000/T$ graphs of polymer thick film resistors. (a) P2, (b) P3, (c) P4, (d) P5.
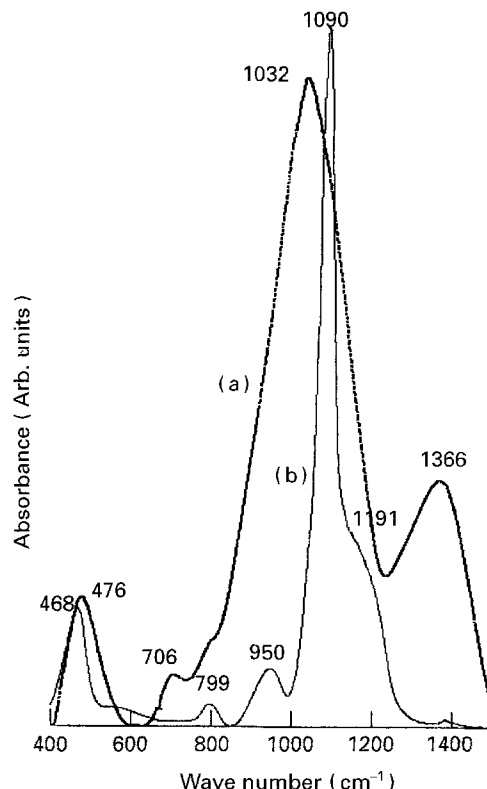
Figure 5 IR absorption spectra of (a) C3 and (b) paste of C3 after it was washed with solvents and reacted with acids.

increased the resistance by decreasing the volume fraction of the conducting polymeric phase while temperature coefficients are retained by cadmium substitution.

For cermet TFRs too, no correlation exists between the average activation terms and the resistances, Fig. 6. Resistances and the activation terms in cermet TFRs seem to be related to the type and amount of particulate phase in a much more complex way than they do in the polymer case.
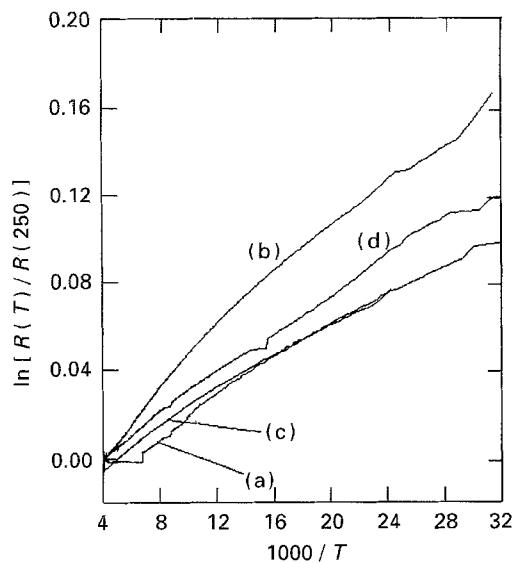
Figure 6 Normalized logarithmic resistance versus $1000/T$ graphs of cermet thick film resistors. (a) C2, (b) C3, (c) C4, (d) C5.

3.3. Infrared analyses

IR absorption of polymer TFRs can be inspected in two spectral regions; one being between 400 and 900 cm^{-1} and the other being between 900 and 1500 cm^{-1}, Fig. 1. Peak intensities increase regularly within the first region while a steady decrease is observed in the second region as the resistances increase. This suggests that the bands within the second region can be attributed to the continuous polymeric phase while the bands within the first region are ascribed to particulate phase.

The spectra of the P4, P5 and pure TiO$_2$ are very much alike between 400 and 900 cm^{-1}, Fig. 1, indicating the presence of TiO$_2$ in these samples. The spectra of P2 and P3, however, indicate the scarcity of oxides. These findings are consistent with the XRD results given above.

IR absorption spectra of the cermet TFRs, Fig. 2, look relatively simple and the bands are broader than those of the polymer TFRs. The bands at 1032 and 1366 cm^{-1} are common for all cermet TFRs. Furthermore, C4 and C5 exhibit shoulders at 1270 and 1250 cm^{-1}, respectively. Differences among bands essentially appear at low frequencies, i.e. C2, C3 and C4 yield the same bands at 706 and 468 cm^{-1}, whereas C5 gives bands at 648, 603 and 454 cm^{-1}.

In cermet TFRs, band intensities do not appear to depend systematically on the resistances, and the bands arising from the glass and the particulate phases seem to overlap, which is not observed in the case of polymer TFRs. Hence it is difficult to ascertain from which phase the peaks originate. In an attempt to identify the bands that arise from the glass phase, the following procedure was employed: paste of C3 was first washed with various organic solvents to remove the organic constituents of the paste. The remaining mixture was then reacted with various acids and aqua regia to remove the particulate phase. After rinsing carefully with distilled water, the IR absorption spectrum of the residue was taken. As can be seen from Fig. 5, the band at 476 cm^{-1} was slightly affected by

the acid treatment and shifted down to 468 cm^{-1} whereas the bands at 1366 and 706 cm^{-1} completely disappeared. Therefore, we conclude that the bands at 1191, 1090, 950, 799 and 468 cm^{-1} are essentially associated with the glass phase and the bands at 1366 and 706 cm^{-1} are associated with the particulate and/or impurity phase. In fact, similar bands at 430 and 1030 cm^{-1} have been observed in the reflectance spectra of SiO$_2$ which were associated with the rocking modes of Si–O–Si angle and the stretching modes of Si–O–Si complex, respectively [6].

These results indicate that in cermet TFRs, the components of the particulate phase have been selected from glass-forming elements, so that the glass could be highly doped. In glasses, absorption properties may drastically be changed by the level of doping, and the intrinsic properties could be suppressed. In this respect, IR absorption in cermet TFRs has a more complex nature than that of polymer TFRs in which the absorption in the insulating and the particulate phases seems to compete with each other as their volume fraction varies.

The sharp increase in the absorption of P5 between 400 and 900 cm^{-1}, however, cannot be explained by the absorption of the constituents because the increase in the volume fraction of the constituents could not be as high as this sharp increase suggests as evinced by comparison of the resistances of P4 and P5 (10^4 and 10^5 $\Omega/\square$, respectively).

The temperature dependence of resistors given in Fig. 4 clearly indicates that the volume fraction of the constituents in P5 is close to the percolation threshold, P_c. An increase in the IR absorbance of discontinuous systems near P_c is predicted both by the effective medium approach [7] and the scaling theory [8]. Although the long wavelength limit is satisfied, the effective medium approach still fails to explain the details because it treats the sample as a homogeneous medium [9]. In the scaling theory, however, two different length scales are used; one for being the inhomogeneity represented by the coherence length and the other being the measuring probe represented by the anomalous diffusion length. Near P_c, the coherence length becomes very large, thus the length scale of the measuring probe becomes comparable to or shorter than the length scale of the sample inhomogeneity. Therefore, the local IR response strongly depends on the position of the incident light.

Testing the validity of these two approaches for the IR absorption in TFRs is beyond the scope of this work. Such an attempt should also consider the mechanisms such as the capacitive coupling of the conductive islands [8] and the magnetic dipole absorption [10], both of which are known to be important for the IR absorption of discontinuous systems near P_c.

Extending the absorption range to the microwave region may require the use of the rotational properties of the molecules. The use of weakly bonded solids, such as the fullerenes as the particulate phase, may be helpful because the molecular rotations in fullerenes are not significantly restricted by the strength of the molecular interactions and/or the molecular symmetry [11, 12].

4. Conclusion

From the X-ray diffraction and IR absorption data of polymer and glass-based TFRs, it was found that particulate phase is mainly responsible for the absorption within the 400–900 cm^{-1} region, whereas the continuous phase is effective at higher frequencies.

TFRs may potentially be used as IR absorbents and offer frequency tunability by proper selection of the phases.

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