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THICK FILM RESISTORS ON DIELECTRICS

A thesis submitted by

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in partial fulfilments of the requirements for the

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This thesis is dedicated to a "simple country blacksmith" I once knew, whose philosophy I greatly admire.

THICK FILM RESISTORS ON DIELECTRICS

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ABSTRACT

This thesis investigates the viability of using thick film materials on a range of thick film dielectrics. They are usually formulated so as to be compatible with 96% alumina substrates. It is sometimes desirable, however, to deposit them on thick film dielectrics. This may produce both technical and commercial advantages. The electrical changes produced and the chemical interactions observed are discussed. It is concluded that viable systems are possible provided the materials are carefully selected. In particular, there is evidence that the presence of barium in a resistor material affects the conduction mechanisms. This means that, in cases where the dielectric contains barium, the effects on the properties of the resistors may be very marked.

It is observed , however, that ceramic filled dielectrics with a high content of glasses should form a satisfactory class of dielectric for use as an underlayer for thick film resistors. This conclusion appears to be in agreement with recently published commercial developments.

The thesis also discusses materials selection and the preparation of samples and gives detailed results of electrical tests. The figures include plots of the results of SEM/EDX analyses made on polished cross-sections of samples.

CONTENTS

Foreword

The experimental work on which this thesis is based was carried out as a collaborative investigation between the author, from Microelectronics Centre, Middlesex Polytechnic, Bounds Green, and various members of the Passives and Hybrids Division of Standard Telecommunication Laboratories, Harlow.

The investigation arose from a mutual interest in the manufacturing processes for thick film hybrid networks. In general, the experimental work, particularly sample preparation, was carried out at STL by the author and his colleagues, while the SEM/EDX work was done at Middlesex Polytechnic. Parts of the study, written jointly with Bharat Joshi and Anthony Winster, and with George Adie and Barbara Holodnik have previously been published.

The printing and firing equipment available at STL are in general of the same manufacture and of similar models to those at Bounds Green. This was of considerable value in comparison of samples and results from the two sites.

Scanning electron microscopy and elemental analysis facilities are available in both organisations. In general this aspect of the work was carried out at Middlesex Polytechnic, Enfield, except where separately acknowledged.

Chapter 1
INTRODUCTION

1.1 Thick Film Technology

Since the invention of the transistor and, later, the integrated circuit, there has been pressure on both passive components and interconnection technology to take full advantage of the size and power dissipation advantages these developments offer. The concept of a two dimensional plate similar to but more compact than a printed circuit board and also carrying integrated passive components forms an attractive approach as a complement to solid state devices (film circuits). A further stage in which surface mounted active or passive components can also be included is a logical development from this (hybrid circuits).

Initially, industrial effort concentrated on metal or metal compound films deposited under reduced pressure onto smooth substrates, usually glass or glazed alumina. This 'thin film' approach produced resistors of potentially much higher quality than is necessary for many applications and suffered from the disadvantage that it was easier to operate as a batch rather than continuous production. It also required individual substrate photolithography. As a consequence, a completely different two dimensional approach was developed. In this, 'thick film' technology, pastes containing a combination of glass frit and the electrically active component, 'pigment' are screen printed onto a ceramic substrate and subsequently fired to form an electrically active glaze. This thesis examines an extension of the basic concept of thick films in which there is an interface of a dielectric layer between the thick film conductors and resistors and the alumina substrate.

In an electronic system it is rarely possible to use integrated circuit components exclusively. It is almost always necessary to include in a design a number of additional components, both active and passive. To the equipment designer there are a several reasons why it may be advantageous to integrate these components in thick or thin film form.

a) Size and weight reduction

b) Improvements in uniformity of component shape, size and pin layout leading to manufacturing improvements and possible use of computer aids in design and manufacture.

c) Potential direct cost reduction compared with discrete component assemblies.

d) Potential indirect cost reduction compared with discrete assemblies.

e) Potentially improved system reliability both by a reduction in the number of discrete component interfaces (solder joints, welded and wrapped joints), and also by the use of film components of quality difficult to achieve with discretes.

f) A wider range of environmental conditions is often obtainable using film and hybrid circuits.

g) Precision and semi-precision resistors result from the virtually mandatory trimming of individual components.

Several authors have presented reviews of the thick film concept (1,2,3,4) and no further discussion is given here of this topic.

1.2 Thick Film Production Limitation

As described above, major motivation for the use of thick film hybrid circuits is provided by the potential for size reduction, reliability enhancement and economic competitiveness. Many of the most active thick film markets are in the aerospace or military electronics fields. Here, minimum size and weight and maximum reliability are of greater direct importance than unit cost. Typical hybrid circuit applications are for the interconnection of a large number of active devices with surface mounted capacitors and (usually) film resistors. Typical component counts of up to 50 are used on substrates in the range 2.5 cm^2 to 2.5 x 5 cm. Continuous circuit development including the introduction of more complex integrated circuits with higher pin counts puts pressure on the hybrid designer to maintain existing substrate size compatibility but to increase the actual component count and to obtain a similar yield. This pressure has an additional side effect, which is not discussed here, that of increased power density which calls for a thorough study of the thermal characteristics of the hybrid and its packaging (5).

A number of factors together tend to set a limit on the packing density achievable in a conventional hybrid. These include:

a) physical limitations of space available on a substrate for resistors, conductors and surface mounted components using normal high yield design rules.
b) power density and cooling modes.
c) inverse relationship between number of circuit components and yield.
d) acceptable 'throwaway value' for rejects or failures.
e) testability.

1.3 Methods of Increasing Packing Density

It is possible to go part way towards achieving high packing density by careful tightening of the design rules. For example, the conductor line/space figure may be reduced from a typical 250 micrometres to 200 micrometres overall and 125 micrometres in restricted areas and the crossover overlap to about 200 micrometres also. It is also possible to reduce resistor areas by increasing the trimmed power density 4 to 5 fold on each component. Similarly the minimum printed dimensions may be reduced from 1.0 mm to 0.5 mm but with a considerable loss of design accuracy and performance. Individual crossovers may be eliminated or combined by the use of multilayering techniques. The structure usually consists of two or more power planes with an insulator between them and several signal planes also isolated by dielectrics (6). Semiconductor dice are surface mounted onto conducting pads. Interconnections between layers are made by printed 'vias' through holes in the dielectrics. In general, multilayer structures have tended to contain active components only or active components plus surface mounted passives. However, many applications are now arising in which resistors are also needed in multilayer circuitry.

A number of alternatives may be proposed for combining resistors with multilayer hybrid structures. These include:

a) use of both sides of the substrate
b) use of chip resistors surface mounted
c) a mother board/daughter board assembly for the resistors
d) division of the substrate into areas for resistors and areas for multilayer interconnections
e) deposition of resistors onto the substrate and a build up of multilayers over them
f) deposition of the resistors onto the top dielectric layer.

Each of the above alternatives (a to f) has some disadvantages as well as advantages as discussed below.

a) A double sided substrate is a convenient space saving approach but interconnection round the edge may be difficult to achieve reliably and economically, while the surface flatness of the substrate may be distorted by the sandwich structure printed and fired onto it before the resistor. If the substrates are fired horizontally, either the dielectrics or the resistors may perform in a non-standard way because of being fired upside down. Special jigs are also needed to avoid interference with molten films during firing. It has been used industrially, especially in high packing density applications, although not normally with multilayers on one side.

b) Thick or thin film chip resistors are now widely used to obtain extended values and/or higher precision. They are very similar in handling to other surface mounted components and some may be soldered in place; others are wire bondable. They are at their most effective in small numbers. This approach has been used by Barlow in a medical application for a hybrid circuit (7).

c) A mother board/daughter board approach is not always a practicable way for combining resistors with multilayers, because of interconnection complexity and, in some cases, distance. The latter is a problem, especially at high frequencies. A variation on this idea is to use the daughter board on a printed circuit board holding both very close to the mother board.

d) A subdivision of the substrate into resistor and multilayer hybrid sections appears attractive at first sight. However, problems of level change can occur when moving between sections. This could lead to potential track breaks at the edge of the dielectric, but, more probably, to printing difficulties because screens do not normally have to conform to a height variation of 30 to 50 micrometres over a few millimetres in the horizontal direction. Hsu (8) discusses the effect of dielectric on the bow of a ceramic substrate and it would appear that the effects are markedly increased if only certain areas of the substrate are dielectric coated. Hsu's work is concerned with structures not containing resistors.

e) A deposition of resistors directly onto alumina followed by the building of a multilayer structure over the top has been discussed in detail by Motamedi-Azari (9,10,11). She describes the difficulties which arise. These include accessing the resistors and trimming them and also considerable chemical and mechanical mismatch between them and most dielectrics. In addition, resistor values are changed very markedly by a large number of successive firings. Her interest lay not in multilayer circuits with resistors, but in the manufacture and evaluation of the fully distributed RCnR filter shown in fig 1.1.

In practice she used a cascade series of firing temperatures to minimise the heat treatment of the first resistor. She used for her top layers materials originally developed for firing below 700°C on vitreous enamel coated steel.

Her work in the author's laboratory confirmed the view that this 'backward approach' would not be convenient for full multilayer structures. A slightly different approach was reported by Sugushita (12).

f) The simplest alternative in concept is to use a pre-completed multilayer structure as the substrate for resistor deposition which becomes the last layer to be printed and fired. This reduces the number of resistor firings to one and eliminates gross level changes. It is necessary to find sufficiently large flat areas for resistor deposition but this does not restrict layouts dramatically. Many dielectrics are either not flat when fired, often showing undulations at the separation of mesh wires in both directions or they may cause additional bow or camber on the substrate by differential expansion properties. Provided materials are selected carefully these problems can be overcome. However, most dielectrics do not react in the same way with resistors as do alumina substrates. Allington (13), and Vest (14), both discuss the effect of dissolved alumina on resistor properties. It is probable that some of the differences observed on dielectrics compared with alumina arise from this. In a greater part they also appear to arise from interface reactions which transfer constituents between layers. Stanbrook (6) reports the successful manufacture of a high speed telecommunication circuit using ECL dice on the top of a four layer interconnection system on which low value resistors were also printed. He showed that some thick film resistors can be successfully produced on dielectrics with only limited property changes. Pitt (15), Majithia (16), Rapeli (17,18) and others have all reported the construction of a lumped/distributed RCnR structure which requires resistors of two different sheet resistances deposited onto alumina for the lower value and onto a thick film dielectric for the higher value. They all encountered compatibility problems which rendered certain combinations of resistance and relative permittivity very difficult to use. In practice they found that low resistance inks were compatible with low permittivities but high resistances and high permittivities reacted very markedly to produce films whose sheet resistances were very different from those predicted. This format would also permit laser trimming, and successful results have been reported (ref 42, Chapter 2).

1.4 Thick Film Resistors on Thick Film Dielectrics

As a result of the earlier work reported by Stanbrook it was decided to examine the compatibility of resistors and dielectrics in more detail. The reasons for this study were twofold. The first was a continuing interest in lumped distributed RC networks and the second was the manufacture of high density resistor/multilayer circuits for a range of applications. This project became a joint study between the members of the Passive and Hybrids Group of

Standard Telecommunication Laboratories, Harlow and the Microelectronics Centre of Middlesex Polytechnic at Bounds Green, who shared a common interest in these structures. The work to be described here was carried out at both laboratories.

Chapter 2
THICK FILM MATERIALS

The purpose of this Chapter is to review some of the relevant aspects of thick film materials in the context of resistors deposited onto dielectrics instead of 96% alumina.

2.1 Substrates for Thick Film Circuits

Allington (13) has discussed in detail some interactions observed when thick film materials are fired on 96% aluminas. He has shown that there are quite noticeably different behaviours even when nominally similar materials are compared. Pitt (19) lists the composition, surface roughness and other properties of a representative range of 96 - 99% aluminas. In general they both conclude that a thick film substrate typically contains about 96% of alumina, while the residue consists of alkaline earth silicates and other traces. In some cases the main flux is based on calcium and in others on magnesium. Allington reports contamination effects due to interactions between the glass frits of conductors and substrate fluxes. He also shows that surface contaminants, eg Na^+ can have undesirable effects on film properties.

Table 2.1 taken from (19), lists some internationally produced substrates and their compositions. Table 2.2 (Allington) shows a wider list of flux components but does not distinguish their relative quantities. It must be assumed that not all are present in every make or type of substrate.

The data of Table 2.1 have been compiled from experimental measurements carried out at STL on the composition and surface topographies of a range of commercially available thick film substrates.

Allington also shows typical dimensional tolerances for alumina substrates; this is reproduced as Table 2.3.

Nakamura (20) has also examined the interface reactions between the glass of resistors and the alumina substrate. He investigated the effect of additives to the glass on film adhesion. Cattaneo (21) and co-workers in a similar type of investigation come to the conclusion that the substrate has only a limited effect on resistor conduction mechanisms except when piezo-electric effects are significant which cause tcr changes. This is in some conflict with the conclusions of Vest (14) and Pike and Seager (22), who both consider dissolved alumina near the interface to contribute considerably to the resistance and tcr. Wood (23) in an empirical study examines the substrate influences on a variety of thick film resistors from an engineering viewpoint.

Although the conclusions reported by these workers show some inconsistency, in general they indicate that the alumina substrate does have an influence on thick film properties. It is, however, more a second order effect. It would therefore be expected that a change from alumina to a composite dielectric surface could be capable of producing first order effects in some cases as indicated in Section 2.3.

2.2 Thick Film Conductors

Since thick film conductors may be required to be used with any of the following, soldering, ultrasonic or thermocompression wire bonding and eutectic or epoxy die bonding as well as resistor terminations, a wide variety has been developed often with subtly different compositions for specific applications. They are normally based on gold or silver with, where necessary, platinum and/or palladium additives to permit soldering. Coleman (24) has studied the effects of silver migration in thick film conductors and it can be seen from his results that silver containing conductors should not normally be used for high reliability applications or where humidity may be high. In this work a wide range of conductors has been used to be compatible with the selected resistors and this includes gold, platinum gold and palladium silver types.

Although multilayer thick film structures have been reported based on PdAg conductors the majority use gold either as fritted or reactively bonded films. The original concept of thick film conductors was as a glaze with a glass content which sank to the bottom of the metal film and acted as an adhesive to the substrate by wetting the pores of the alumina on firing. Crossland and Hailes (25) reported mechanisms of adhesion degradation in certain fritted conductors and the nature of the thick film conductor and its reactions with alumina have been examined further by Coleman in a wide ranging study (26). A continuation of this study (27) examines unfritted (reactively bonded conductors). Additives, such as copper, in the conductor react directly with the silicate in the substrate to form a bond. The constituents are specially processed so that they form a fine interface with the substrate. The film relies for its adhesion on the wetting of the two phases. In glazes there is a mechanical bond rather than the physical/chemical reaction found in unfritted conductors. Table 2.4 reproduces Coleman's analytical results for the compositions of a number of commercially available reactively bonded thick film conductors together with a control fluxed conductor. None of these conductors was used in this study.

Where possible, only conductors which were recommended as suitable by the manufacturer were used in these studies. In practice this meant gold for two of the resistor series and platinum gold for the third from one manufacturer, while a solderable palladium silver was supplied for a resistor series from another manufacturer. In general it was intended at the start, for simplicity, to attempt to ignore phenomena involving conductors but having no effect on resistors.

2.3 Thick Film Dielectrics

In its original concept the sole function of a thick film dielectric was to act as an insulating support for one conductor to bridge another. The first crossover dielectrics were simply lead borosilicate glasses similar to resistor cover glazes. They melted at temperatures well below that of the second conductor firing and resulted frequently in open circuits due to 'swimming' of the upper track. Two other types of dielectric for crossovers were developed, filled glasses and crystallising glasses and they are both currently used in thick film systems. The extension of the concept to the manufacture of capacitors is an obvious step beyond plain crossovers. Another obvious step is the building up of multilayer structures.

Linford (28) discusses thick film dielectrics in broad detail and presents a number of criteria for their properties, use and manufacture. Table 2.5 outlines his conclusions and adds further aspects.

In practice many crossover materials are in fact the same as those used for multilayer structures and further discussion below is limited to materials suitable for both these applications and omits capacitors as outside the context of this work.

Both thick and thin film technologies have been developed from their original concepts to a level where thick films have potential use in most applications where hybrids are viable while thin films have become limited to specialist applications which take advantage of their precision. The next sub-sections will examine the development of the two approaches and clarify their relationship.

2.4 Manufacturing Requirements for Thick Film Circuits Containing Resistors

Thick film hybrid circuits are used in a very wide range of applications and under an equally wide range of environmental stresses. Tables 2.6 and 2.7 illustrate in general terms the requirements for two very different classes of application.

The specific requirements listed for thick film resistors in Table 2.8 would apply also for applications where they are deposited onto a dielectric rather than alumina. Therefore an investigation into the use of resistor dielectric combinations must evaluate whether these targets are still achieveable and attempt an understanding of the causes of differences observed.

2.5 Thick Film Resistor Materials

2.5.1 Background

A simple study of the electrical conductivities of materials divides them roughly into three groups, Figure 2.1. Metals and degenerate semiconductors have bulk resistivity in the range 10^{-8} to 10^{-6} ohm metre. Associated with this is a large positive temperature coefficient in most cases. An intrinsic semiconductor with a small energy gap such as Ge has ρ_v close to 0.5 ohm metre while Si has been reported as 2500 ohm metre with strongly negative tcr's. The third group, insulators and near insulators have values of the order of 10^{10} to 10^{12} ohm metres.

If we consider the requirements of a thick film system, we see that, for a fired film thickness of 15 micrometres and a range of sheet resistances from 10 to 10^6 ohms square^{-1}, the bulk resisitivity to be achieved ranges from 1.5 x 10^{-4} to 15 ohm metres. However, in very general terms the observations above lead to the conclusion that low resistivity is associated with high positive values of tcr and the converse. A plot of tcr as a function of resistivity shows that most simple materials lie near a rough straight line. Watkins(29) has reviewed the temperature coefficients and resistivities of a number of common compound materials and points out that they also fit this relationship. He explains this in terms of Matthiessen's Rule.

$$\alpha_s \rho_s = \frac{d\rho s}{dT} = \frac{d\rho i}{dT} = \alpha_i \rho_i \qquad (2.1)$$

where ρ_i and α_i, are respectively the resistivity, and tcr of a pure material and α_s and ρ_s are the equivalents for materials whose intrinsic resisitivity has been enhanced by temperature independent mechanisms. This may occur in alloying, deformation of the pure material or by compound formation. Although the theoretical justification is extremely limited, it is possible to plot tcr vρ for a very large number of materials. A justification of the empirically derived Rule in terms of the additive nature of the components of resisitivity for metals only is given by Wert and Thomson(30) who state it in the form

$$\rho_{\text{total}} = \rho_{\text{temperature}} + \rho_{\text{impurities}} + \rho_{\text{deformation}} \qquad (2.2)$$

where it is implicit that the effects of lattice impurities and lattice structural distortions are both temperature independent. Fig 2.1 which has been derived from Watkins shows this crude relationship between temperature coefficient and bulk resistivity.

A useful film resistor material requires a tcr in the range ±100 ppm K^{-1} over a wide range of Rs values. It can be seen from the figure that this is unlikely to be possible with a single material. This immediately leads to using the implications of equation 2.1 in developing film resistor materials. An obvious way of enhancing ρ without changes to α is to add impurities or lattice distortions to the chosen conductor material. For thin films the effect of alloying chromium with nickel is to enhance the bulk resistivity by at least one order of magnitude and yet to allow the tcr to correspond to that of a single material of this new resistivity rather than that of either of the constituents. It can achieve ±100 ppm with a bulk resistivity permitting 300 ohms/square with a film thickness of 20 - 40 nm. This can be extended further by the use of composites of a conductor and an insulator such as Cr/SiO in thin films. Watkins shows that the basic concept of resistivity enhancement by dilution of conductor content is not in fact practicable unless there is a reaction between the constituents. He presents a curve which shows a sudden onset of conductivity when the conductor content reaches 20 - 40%, fig 2.2. In thin film technology this would restrict the range of values of sheet resistance obtainable because the steepness of the curve would make control of composition very difficult.

However, reactive dispersions of conductors and insulators including those based on Cr/SiO combinations(31-36) have been successfully used to provide extended ranges of sheet resistance. In contrast, the composite glass/metal/oxide compositions used in thick films do fulfill this reactivity condition as is discussed below and provide a controllable composition/sheet resistance relationship. However, the electrical properties of the product are extremely temperature sensitive. At low temperatures there is a negative tcr due to the dominance of semiconducting properties of the glassy matrix. Above a shallow minimum, -50 to +50°C approximately, the degenerate semiconductor used as the conducting phase is dominant and a positive, but non-linear tcr results. An R v T plot approximates to a shallow parabola.

2.5.2 Real Systems

In order to achieve the desired range of sheet resistance together with high stability of value with both temperature and time , it is necessary in the light of the discussion above to formulate glazes which have a wide range of ratios of 'conductive element' to 'glass-like' element. There are frequently additional trace components, such as CdO in the Du Pont 1100 series (37), to modify properties such as tcr, vcr or stability. A typical resistive glaze is a combination of a fluxing glass, usually based on lead borosilicate with controlled shape and size particles of a degenerate semiconductor such as ruthenium dioxide, iridium dioxide, bismuth and lead ruthenates and palladium oxide. Since thick film materials are commercial products there is restricted information available on their compositions and structure and, partly to avoid patent problems, their exact formulation varies from manufacturer to manufacturer. In addition to the major constituents, traces of further oxides are added as property modifiers as above. Coleman (37) has reported on the composition of two Du Pont resistor series, 7800 (Pd/PdO/Ag) and 1100 (bismuth ruthenate). His results for the 1100 series are replotted in Fig 2.3, together with a version of the curve for Watkins' idealised cermet. It can be seen that the composition curve for DP 1100 is much shallower, providing a relatively controllable system in contrast with the theoretical non-reactive mixture. His results for the two Du Pont series together are shown in Fig 2.4 where the percentage of conducting phase is plotted against sheet resistance. The 7800 series contains Pd and Ag in a ratio decreasing with increasing Rs and also the semiconductor PdO. [PdO is thermodynamically unstable and its composition may change from the stoichiometric during processing, rendering this type of resistor difficult to process.] The 1100 series contains Bi_2O_3 and RuO_2 in ratios which all approximate to $Bi_2Ru_2O_7$. It is believed from patent evidence that the compound is prepared in advance for use as conducting phase (38).

Coleman (39) has also reported on the chemical analysis of the Du Pont 1400 and HS 80 and Heraeus R4000B series of resistors. His results show that not only does the glass/conductor total ratio change within a series. but also the nature of each component is not constant.

For example, bismuth ruthenate, $Bi_2Ru_2O_7$ appears to be the major conducting constituent of 1411, 1421 and 1441, but in 1461 there is much less Bi_2O_3 than this composition demands and the phase is mainly RuO_2. The intermediate pastes 1431 and 1451 were not analysed. Traces were also found of alumina, approximately 1% throughout the series and cadmium also approximately 1% in 1411 to 1441 inclusive. The glass is probably a lead borosilicate although the boron content could not be evaluated quantitatively. A trace of silver was found qualitatively throughout the range and a significant quantity of Pt at 10 ohms/square with traces at 100 and 1000 ohms/square. In this series there appears to be a fairly consistent glass composition.

In contrast, DP HS 80 has a very marked spread of composition over its resistance range. The main conductor is RuO_2 throughout with traces of added Bi_2O_3 in the lower half up to a blend break at 1000 ohms/square. Above the break there is more Bi_2O_3 but still less then the stoichiometric ratio of 1·8:1. All members contained up to 1% of CuO and three of the lower set contained under 1% of Nb_2O_5. CaO , approximately 2%, was found here also. These last two were absent in the upper blend series. MnO was also present in quantities of 0.1 to 3% in five of the seven members studied. It was not possible to identify rare earth oxides although traces might be expected in some members. Except at 10 ohms/square 5 to 7% of alumina was also found. The glasses up to 10 kilohms/square appeared based on lead borosilicate while the two higher members appeared based on lead silicate glass.

The Heraeus R4000B series changed markedly with sheet resistance. The glasses appear to be based on lead/calcium borosilicate and the inks also contain alumina (1 to 6%, except 4001) and MnO_2 (1 to 2.5%, except 4050). CuO (1 to 2%) is also present in 4040 and 4050 and SnO (2 to 4%) was found in the three higher members. The conducting phase of the two lowest members was based on an AgPd alloy (not PdO) with added RuO_2 and above this contained BaO, suggesting the use of barium ruthenate as the phase, possibly with extra RuO_2.

A summary of these results into a calculation of the percentage composition of conducting and insulating phases yields the composite composition versus sheet resistance curves of Fig 2.5*.

*HS80 has two different compositions for 10000 ohms/square.

2.6 Resistors on Dielectrics

A number of authors (9,10,11,15,40,41,42) have reported sharp changes in resistance value on dielectrics compared with those on alumina fired under similar conditions. This is usually a decrease with filled glazes and an increase with crystallising materials. One of the objectives of this investigation was to investigate the causes of these changes. A very simple general hypothesis for resistors or filled glazes is that there is a transfer of insulating (glassy) phase between the films on firing due to the greater porosity and glass-poor nature of these dielectrics. The relatively small positive changes in value on crystallising glazes have been attributed by Kummer and Taitl (43) to differential expansion effects. The results of this investigation will show however that the picture is far more complex than the initial studies suggested. Other authors have discussed the laser trimming of resistors on dielectrics (44,45).

The data to be presented will show that there are marked differences in behaviour of resistors on filled and crystallising diectrics. In addition the reactions with dielectrics films are strongly dependent on both the conducting phase and the glass matrix.

Chapter 3

DESIGN OF THE INVESTIGATION

The basic philosophy of the project was to obtain experimental data on the behaviour of thick film resistors and dielectrics in direct contact. As described earlier, the resistors to be studied would be deposited on and not under the dielectric. Unpublished earlier work had shown that cofiring of resistors on dielectrics produced further destructive interactions, and, in common with normal industrial practice, the resistors in this investigation were all deposited onto prefired terminations and dielectrics or onto control alumina substrates also with prefired terminations.

Since the problem of interactions was one that was beginning to be apparent in manufacturing industry at the start of this work, for initial materials comparison the measurements were restricted to first order parameters, eg a comparison of as-fired sheet resistance on dielectric and alumina and to 'hot-side tcr', (25 to 125°C). In systems where the first measured parameters showed possible compatibility, a closer study of the comparative properties was made later.

$$\text{Let } D = \frac{\text{Sheet resistance on dielectric}}{\text{Sheet resistance on control substrate}} \qquad (3.1)$$

For a viable production system the value of D must approach unity in the optimum case or, less satisfactorily, be reproducibly higher or lower than unity. It must, also, ideally be unaffected by aspect ratio or length of track, film thickness and the limits of production control over printing and firing parameters. It must also be consistent over a typical substrate area. It is also desirable for the resistors on dielectric to have a coefficient of variation* of a similar order of value to that found on the control alumina.

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* $\sigma n/\bar{x}$

The work carried out in this investigation differs in two ways from widely used industrial practice. None of the systems studied here used any forms of overglaze on the resistor layer, although this is often employed as a protection, especially for the trimming stage. The second factor is that all resistors were examined and measured as fired and without any form of trimming. This was due mainly to the unavailability of laser trimming on site. However, since one of the objectives is an understanding of reactions occurring, the lack of a trim facility does not invalidate the work carried out here. Hain has reported the very successful use of laser trimmed resistors on dielectrics (45).

In a similar way we can define a pair of parameters, T_h and T_c, where the h refers to 25 to +125°C and the c to 25 to -55°C;

$$T = \frac{\text{Temperature Coefficient of Resistance on Dielectric}}{\text{Temperature Coefficient of Resistance on Control Substrate}} \qquad (3.2)$$

Since the resistance/temperature relationship of many thick film materials is roughly parabolic these parameters are subjective and overlook the actual non-linearities in these temperature ranges. They are only useful as a guide to the properties of the materials.

The parameters T_h and T_c are less directly useful than D where sign changes occur.

In practice, provided the resistor design rules are modified to take D into account, it is possible to use dielectrics which produce values of 0.5 to 1.5 approximately. Preliminary observations (46) and discussions with the manufacturers of various materials showed that in a given resistor series D is not constant but often decreases with increasing sheet resistance from near unity at 100 ohms square^{-1} to perhaps 0.5 at 100000 ohms square^{-1}. In some specific combinations, the variations were known to be much greater than this. A full evaluation of the usability of a given resistor series in combination with a specific dielectric must take into account the range of sheet resistances over which combinations are practicable. Preliminary studies had also shown that there were differences in the compatibility of filled and crystallising dielectrics and that high k capacitor glazes were particularly unsatisfactory since, in some cases, the glass was absorbed into the dielectric leaving the resistor as a silvery layer on its surface. For example, an EMCA resistor 4116 on a dielectric from Johnson Matthey was 15 ohms/square instead of 10^6 ohms/square on alumina.

Since production is a dynamic process, changes in materials, applications and specifications are continuously occurring and it is very easy to select materials for examination which become obsolete or obsolescent during the study. It was therefore decided to start with well established materials and to add in later some newer systems which appeared likely to become established as industrial standards. In a similar way, it was decided to use a number of well known commercially available alumina substrates and add others if relevant.

3.1 Selection of Materials

About a dozen major companies manufacture thick film systems either for in-house or for commercial use. At any given time each of these will have several different resistor series. The differences may be the result of manufacturing developments rendering older systems obsolescent or they may be designed for different qualities, costs or applications. This gives a potential choice from at least 50 different resistor series. Each of these will be compatible in some way with more than one conductor type and the choice here is dependent on application. Each manufacturer also produces a wide range of dielectrics, again for different applications. Even is it is assumed that the nature of the conductor is a second order effect, there are available commercially at any one time at least 30 each of resistor series and dielectric materials.

It is difficult to make an objective choice from nearly 1000 possible combinations and it was arbitrarily decided to use two manufacturers only whose products were well known in the Passives and Hybrids Division of STL and the Middlesex Polytechnic Microelectronics Centre. An initial decision was made to use two standard resistor series from one company and one from the other company. In practice, one seemingly well established product was withdrawn and superceded by a new development. This replacement was also included in some of the later studies. The conductors selected in all cases were recommended types for each series.

Similarly, dielectrics become modified during their production use and may appear in several allied guises for specific applications. A decision was initially made here that the small number of suitable dielectrics made by one of the manufacturers should be examined, concentrating on one specific product for the initial investigations. In practice, a new product from the second manufacturer was also examined because it reportedly showed very limited interactions with many different resistors.

Table 3.1 shows the resistor series selected for the investigation, together with a brief description. Table 3.2 shows the dielectrics together with their classification.

This reduction of available options still produces a large total number of possible combinations. Even treating 4019 and 4119 as one conductor leaves 15 resistors and four dielectrics. Of this possible total of about 60 only 45 to 50 figured in these investigations.

During the progress of this project the Du Pont Series 17 became only available on request for sale in the United Kingdom, although the work on it here was carried on from existing supplies. The Heraeus R4000B series was also changed in name and somewhat upgraded but not in a way that would invalidate the work reported here. This resulted from a takeover by Heraeus of Cermalloy and rationalisation of products which also made the new dielectric 9105HT available for study.

3.2 Resistor/Conductor/Dielectric Test Patterns

The three patterns used in this work are shown in Figure 3.1, Pattern A, Figure 3.1.a, on a 2 in square substrate is a standard STL design used to investigate the effect of aspect ratio on resistor properties. It produces six pairs of resistors all 1 mm wide and with lengths 0.5, 1, 2, 3, 6 and 10 mm. Two variants were used, firstly with both terminations and resistors on alumina acting as a control and, secondly, with a dielectric layer between the resistor/conductor pattern and the substrate. [One half also had additional conductor tracks passing under the insulator as can be seen in Figure 3.1.b.] Pattern B, Figure 3.1c is a standard Middlesex Polytechnic test pattern for resistors containing ten 5 x 1 mm resistors on alumina. The version used here was modified to have a dielectric layer under the five resistors on the left. However, a large proportion of the samples were made with Design C, Figure 3.1d. Of the 16 5 x 1 mm resistor stripes shown, the upper eight were on alumina and the lower eight on a dielectric. This pattern, unlike the others, could not be fully accessed by means of an edge connector without scribing and breaking. This was to enable it to be used with a computer measurement systems using probes. The upper resistors in the photograph on alumina were numbered from the left, 1 - 8 and similarly, the lower ones 9 - 16.

3.3 Manufacturing Processes

Except where specifically stated in the text all manufacturing procedures followed the outline given in Table 3.3.

3.4 Measurement Techniques

3.4.1 Resistance Value Measurements

Most of the resistance measurements were taken with the aid of a PDP11 minicomputer based data logging and presentation system. Substrates were either mounted in an edge connector or under a probe station to allow true four-wire resistance measurements to be taken by a five digit Fluke 8500A DVM. This system forms the centre of the overall data processing facility developed and used by the Passives and Hybrids Divsion of STL. In addition to the data logging, means and standard deviations of batch and/or substrate resistance measurements are produced by sub programs.

In some cases initial resistance measurements were made manually using hand held probes on the substrates and the results were also processed by hand. They were made using a Solartron 7040 digital multimeter.

3.4.2 Temperature Coefficient of Resistance Measurements

In a way similar to resistor data acquisition, both manual and automatic data processing wereused.

The resistance temperature curve of thick film cermets shows a rough similarity to a parabola with a shallow minimum near or below room temperature. In practice two very rough approximations can be made to a straight line, 'hot side' and 'cold side'.

The 'hot side' tcr is often reported as

$$tcr = [(R_{125} - R_{25})/R_{25} \times 100] \times 10^{6} \text{ ppm k}^{-1}$$

This does not take into account the noticeable non-linearity normally observed. However, it is a considerably easier measurement to take than the full cycling. It may be obtained either by extracting data from a full cycling curve or by spot measurements. Similarly, the 'cold side' value and the location of the shallow minimum may be found from plotted curves. No definition is given here because the exact temperature range would depend on the position of the minimum.

Using the data logging system described above, resistor measurements were taken in a temperature cycling chamber developed by Coleman (47). Readings on the substrate were taken by him over the temperature range $-70^{\circ}C$ to $+125^{\circ}C$. Examples of the results of cycling are given in Chapter 4.

For more rapid results a rough approximation to the hot side tcr may be obtained using probes connected to a digital voltmeter, in this case a Thurlby 5040, with readings taken at room temperature and on a temperature controlled hot plate set at $100^{\circ}C$ higher. The temperature was monitored using a dial thermometer. Prudhoe (48) has estimated using an infra red microradiometer, that the temperature fluctuation at $118^{\circ}C$ is $\pm 5^{\circ}C$. Taken together with estimated probing accuracy the overall accuracy on a nominal 100 ppm measurement for pattern C is ±25% at 100 ohms/square and ±10% at 1000 ohms/square. The above measurements are based on an assumption that there is a straight line relationship between R and T over the range $25^{\circ}C$ to $125^{\circ}C$. This means therefore that the results can be taken as a comparative guide only, and do not take into account any shift in the position of the minimum between different combinations of materials.

3.4.3 Electrical Noise

Electrical noise measurements were carried out on some of the samples using a QuanTech 315 noise meter. [QuanTech Laboratories Inc, Whippany, NJ 07981, USA] This instrument measures the noise index of resistors over the range 100 ohms to 22 megohms, which is within the range of values of samples produced in this investigation. According to power rating and resistance value the voltage applied during the test lies in the range 3 to 300 volts. The stated accuracy of noise measurements is ±5%.

Since the equipment was primarily designed for use with wire ended discrete resistors, modifications were made by Mrs. J.M. Wheeler of STL to enable it to be used with probes directly onto thick film resistor terminations. She has estimated that there is some loss of accuracy due to the nature of the contacts; a figure of ±2 dB, (±0.2 microvolts/V at 1 microvolt/V), on the noise index has been suggested by needle fluctuations on the instrument during measurements.

3.4.4 Voltage Coefficient of Resistance

Voltage coefficient of resistance becomes significant only at resistance values of the order of 10^5 ohms or greater, ie normally when Rs is 10^5 or 10^6 ohms/square in a resistor series. It was not considered necessary to make measurements of the change of vcr between resistors deposited on alumina and those on dielectrics in this investigation.

3.4.5 Measurement of Surface Characteristics

The measurement of thickness at both the dried and fired stages is a standard method of monitoring thick film manufacture. The commercial version of the surface profiling equipment used in most of this investigation was the Talysurf (Rank Taylor Hobson). Two models, T3 with vertical magnification of 1000 to 100000 times and T4 with 500 to 100000 have been used.

A Talysurf 4 was used for measurement of surface roughness of alumina substrates (42). CLA measurements are not very dependent on the flatness or levelness of the sample and consistent readings were readily obtained. However, for most applications in thick films it is necessary to measure one or, sometimes, two step heights across a resistor as the stylus moves from substrate to sample and possibly back to substrate again. There are several factors which cause the printed trace to be displaced from the horizontal and show vertical distortion. Some of these can be compensated, but this makes it necessary to use some subjective interpretation of the results. At low magnifications, x500 and, to a lesser extent x1000, the problem is not critical. However, a x2000 magnification is convenient for most standard thick films. This shows up very clearly any deviations from the horizontal. Interpretation then becomes subjective and, in some cases, impracticable. The main causes appear to be:

a) bow or camber in the substrate, often induced by expansion mismatch of dielectric films on the surface.
b) equipment badly set up and out of calibration
c) sample not parallel to stylus trace path
d) irregular datum line on substrate due to, for example, a dielectric film printed and fired before the film under investigation.

Problems b) and c) are normally taken care of by regular manufacturer's maintenance and routine calibration using 2.5 micrometre scratch reference samples. Problems a) and d) are dependent on sample nature and may not always be overcome. In general, an objective analysis is only possible if the angle of the trace path is within approximately ±10% of the horizontal axis of the graph paper printout. Where possible, due to these problems, the readings reported are the mean of at least four or five separate readings. The horizontal magnification used in most measurements was x20, because of the greater speed compared with x100.

One major problem in results interpretation is the estimation of the base line of a print on dielectric. Most dielectrics show a regular undulation of the surface corresponding to the mesh pattern. The distance over which the pattern remains uniformly visible depends on the orientation of the trace to the mesh filaments but is often very clearly observed over several millimetres. One method of providing an average base line is to superimpose over the film trace an extrapolation of the surface trace which is hidden by the film. A straight line from the point of disappearance should then bisect the undulations and give an acceptable zero reference.

It is estimated that Talysurf film thickness measurements on alumina show an accuracy of ±10% (1.5 micrometres) at a mean of 15 micrometres.

Although the above comments are still valid in the context of the measurements reported in all the earlier investigations, new information has become available which may lead to the minimisation of the problems discussed above. It has not been possible to apply them retrospectively to earlier samples.

Close to the time of writing, a Tencor Instruments Alphastep 200 surface measuring meter became available and some fresh step height measurements were made. The problems reported above were visible here also, but it was possible to level distorted traces using the built-in software. In practice it was found that consistent reproducible results could only be obtained by restricting the horizontal movement of the stylus to the minimum necessary for observing reference points at each side of the film.

These points were then used for levelling the trace. Superimposition of levelled traces from adjacent resistors produced very close correspondence, compatible with the similarity in resistor values. If, however, as in the previous Talysurf measurements, several resistors were measured during one scan, the labelled traces could not be superimposed. It is therefore strongly recommended that single traces only are made on the thick film resistors in order to restrict the base line as above.

The Alphastep results showed clearly also that it is dangerous to use readings taken on a dielectric surface because of the subjective nature of the reference points. A resistor film of approximately 9.7 micrometres on alumina was estimated on the same substrate on a filled dielectric as from 7 to 11 micrometres in a series of repeated readings using different reference points. It is also strongly recommended that surface traces on dielectrics should not be used for calculation purposes but for illustration only. It is not possible to identify whether there are any significant thickness changes between resistors on alumina and dielectrics because of the surface topography. These observations made on the Alphastep appear valid also for the Talysurfs.

3.4.6 Optical Microscopy

Conventional optical microscopy techniques were used in the study of the reactions between resistor films and alumina substrates or thick film dielectrics. The standard presentation for convenience was chosen to be x125 on Polaroid prints.

3.4.7 Measurement of Chemical Composition

Joshi (42) reported the measurement of chemical compositions of DP 1730 and DP 1750 by both WDS (wavelength dispension spectrocopy) and EDS (energy dispersion spectroscopy). His specimens were scribed on the reverse side and cleaved. His results are not discussed further here.

Further work on samples of DP 1730 on alumina, DP 9950, DP 4032 and DP 9429 was reported by Adie (49) and by Holodnik (50). It was carried out using an ISI Super 3 System with a Link Systems 860 X-ray analysis package. The samples were scribed and cleaved as before but were this time polished at an angle of 30^o to the surface. Spot analyses for all elements above an atomic number of 9 were performed at regular intervals across the polished section. Depending on the nature of the sample and the exact angle of polishing, between approximately 10 and 20 scans were performed on each. Profiles were plotted of up to 14 elements in each scan. These were selected both from the preliminary examination of each specimen and, also from external evidence of film composition. The results computed by the instrument did not add up to 100% after calibration of the instrument.

Spears (51) has suggested that this is not solely due to the non-detection of light elements such as boron, which is known to be present in many of the materials. Normalisation was carried out as discussed in Chapter 6.

3.4.8 High Temperature Stability of Resistors

Although no electrical load tests were made during this research, three high temperature storage comparative stability tests were carried out on samples from the matrix experiment. These were:

a) 15 hours storage in air at 240°C for DP 1730 and DP 8031 on DP 9429 and alumina only.

b) Five cycles at 25 mm/min in air through a DEK 840 single zone thick film furnace with a peak of 300°C. This was carried out on samples of DP 8031, DP 1730, DP 1431 and Heraeus R4030B on DP 9950 and DP 4032, as well as on the control alumina, Kyocera A476.

c) For DP 1431 on DP 9950 only, the five cycles to 300°C were followed by storage at 300°C in the belt furnace with the belt stationary.

3.5 Experimental Investigations

The main experimental approaches are described in this section. In order to minimise the effect of processing differences on the results, each sub-section discusses only samples produced under comparable manufacturing conditions.

3.5.1 Aspect Ratio Effects

The physical dimensions of thick film resistors markedly affect their actual value under a given set of processing conditions. In summary, as track length is reduced, the electrical characteristics of the contacts begin to make a significant contribution. This results in resistors which apparently have a lower aspect ratio than expected if the length drops below 1 to 2 mm. At 1 mm the value may be 0.9 to 0.95 of the value at 2 to 3 mm length. For even shorter resistors the changes are more marked. The cause is not solely due to electrical contact effects, but is also due to end effects in very short length printed tracks where the paste, in effect, piles up over the contact edge (1). Temperature coefficient and stability also change for these shorter resistors. The initial investigation of this project 'took over' samples made using Pattern A and a selection of Du Pont 1400 and Series 17 resistor inks using gold conductors. Half the samples were printed onto Kyocera A476 96% alumina and the remainder onto Du Pont dielectric 9950. Resistance and selected temperature coefficient measurements were made using the data logger (Section 3.4.1). Film thicknesses were measured using a Talysurf 4.

3.5.2 The Effects of Film Thickness on Du Pont Series 17 Resistors

The purpose of this study using Pattern B was to examine the effect of print thickness on resistor properties on both alumina and test dielectrics. Since it was a widely made qualitative observation that resistor values on dielectrics were very often low with respect to those on alumina (parameter D above), a number of hypotheses were put forward as to the mechanism of this. One of the most obvious postulated that glass was directly leached from the resistor into the porous dielectric by capillary action. This study was aimed at producing evidence of volume resistivity changes as a function of film thickness on dielectrics using the alumina as a control. Film thickness variations were produced by a combination of changes in printing parameters, different mesh sizes and emulsion thickness and multiple printing. The results, (Chapter 4), show that there are a number of thickness dependant effects on both surfaces. The samples were all members of the Du Pont Series 17 (1721, 1731, 1751) on Coors ADS96 substrates.

3.5.3 The Effect of Film Thickness on a) Heraeus R4000B Resistors, and b) DP 1750.

In order to process automatically the large quantity of data produced by these investigations a new test pattern, C, was used. The resistors are similar to those of B but were in two rows of eight each on a one inch square substrate. The upper eight were always directly on alumina and a dielectric pattern was used in almost all cases to provide a base for the lower eight resistors. Existing computer probe cards required electrical connections corresponding to a row of eight resistors and a common connector on 0.100 in separation. For most of the work the substrate was not cut and measurements were made by probing only. If contacts via an edge connector became necessary for the resistors on alumina, the substrate could be diamond scribed and broken. The substrate used was Kyocera A476.

In this study a combination of the new screens and a more even distribution of samples on the substrate, together with an increase in sample number from each substrate led to a considerable improvement in resistor uniformity. Although the original purpose of this investigation was to attempt to verify the results of the work described in 3.5.2. for Du Pont 1750 ink, the Heraeus R4000B series was studied also. To vary the thickness, four different screens were used with parameter changes and multiple printing as required. The firing conditions described above were used. Three members of the R4000B series at 100, 1000 and

10000 ohms/square were studied, together with the repeated Du Pont 1750. The dielectric was DP 9950 as before. The Heraeus samples were supplemented by further data, 3.5.4 below, from a separate investigation. [In this set the DP 9950 was fired at 850°C not the normal 925°C]

3.5.4 Further Studies of the R4000B Series

Again using pattern C and, this time, a single 200 mesh stainless steel 13 micrometre screen and no deliberate variation of printing parameters, a repeat set of samples of R4020B, R4030B and R4040B was made in an attempt to confirm some marked differences in behaviour from Du Pont resistors on 9950 dielectric observed above. The samples processed were supplemented by a new sample of R4040B and the addition of the top of the range R4050B (100000ohms/square). In addition to 9950, a second dielectric, Heraeus/Cermalloy 9105 HT, was used. The substrate was Kyocera A476. The firing conditions were nominally as in Section 3.5.3.

3.5.5 1000 ohms/square Matrix

In order to obtain a wider view of the phenomena which occur when resistors are printed onto dielectric layers a matrix-like study of some selected combinations was made. To limit the size of the experimental work, a single nominal bottle value of 1000 ohms/square was used for all the resistors. Since it was necessary to use one set of parameters for all samples for the printing and firing, this means that the process conditions for some of the resistors, while close to nominal, were not optimised. Pattern C was used in this investigation also. The control substrate was Kyocera A476. The selected materials are tabulated in Table 3.4.

3.5.6 Comparative Study of a Range of Substrate Materials

An analysis of the results of two earlier investigations, 3.5.2 and 3.5.3, showed an unexpected anomaly between two substrate materials, Coors ADS96 and Kyocera A476. A wider study was therefore initiated to compare resistor properties on different substrates. Pattern C was again used and the control was, this time, the dielectric film Du Pont 4032, filled glaze. Sample numbers were very limited, in some cases to one substrate only, in order to compare as many different aluminas as possible. The resistor series, Du Pont HS80, marketed as a replacement/improvement for Series 17 was used over the nominal range 100 to 90000 ohms square^{-1}. The actual sheet resistance produced lay in the range 40 to 70% of nominal because of the selection of 23 micrometre emulsion and a 165 mesh stainless steel screen. The substrates and resistor materials used are tabulated below, Table 3.5. Chemical analysis and surface roughness measurements for all of these substrate materials were given above, Table 2.1. [The underlying dielectric was given two double wet prints with a drying stage between and then one standard 925°C firing.]

3.5.7 Study of Film Compositions and Interactions

Some of this investigation has previously been reported in a less detailed form by Joshi and co-workers (42). Initial observations using optical microscopy, of DP 1750 resistors on Kyocera A476 substrates had indicated the possibility of a mobile glass binder. These observations were extended by the use of electron microprobe analytical techniques to investigate the distribution of the active (ruthenium based) components within and between the thick film resistors and dielectrics or alumina substrate materials. Joshi's samples were selected from those prepared for the various investigations, 3.5.1. Those samples whose results are reported in detail in Chapter 4 were all taken from the matrix sequence, (3,5,5).

Chapter 4

EXPERIMENTAL RESULTS

4.1 Aspect Ratio Effects

Experimental measurements of sheet resistance value as a function of resistor track length/aspect ratio confirm that, like most resistor series, Du Pont 1400 and Series 17 show a significant drop in effective sheet resistance when the track length is reduced to 1 mm or less on alumina. The effect is small for 1421 and 1720 but is very marked for 1431, 1451, 1730 and 1750. The results are plotted in Figure 4.1a for 100 ohms/square, 4.1b for 1000 ohms/square and 4.1c for 100000 ohms/square. The samples were produced using designs A and B.

However, when the value of R_s on DP 9950 is also plotted against aspect ratio, the behaviour is generally different, the changes are much less and, in some case are non-existent. This is shown in Figure 4.2a and b where the value of the ratio, D, is plotted against aspect ratio for DP 1400 and Series 17 respectively. A line roughly parallel to the x axis indicates that the ratio is fairly constant and, looking at Figure 4.1, it can be seen that this means the size of the aspect ratio effect is similar on the two surfaces for 1421, 1431, 1451 and 1721. For 1731 and 1750 there is a rise in D for the short resistors. From Figure 4.1 it can be seen that since R_s drops on alumina, it must remain fairly constant on 9950. This is shown clearly for DP 1451 and DP 1750 only in Figure 4.3a and b.

Some of the samples produced using patterns A1 and A2 were temperature cycled by Coleman (47), over the approximate range -50 to +125°C using the data logging system described above. Figure 4.4 shows reproductions of four of his curves showing clearly the parabolic shape. Estimates of the tcr values were made, for DP 1451 and DP 1750 using curves not reproduced here, from the 'slopes' of the straighter portions over both the 'hot' and 'cold' sides of the curves. Using these results it is seen in Figure 4.5a and b that, like the resistance value, the tcr is not independent of aspect ratio. The estimated temperature coefficient of the resistors from Coleman's results, both hot (+25 to +125°C) and cold (+25 to -35°C) are plotted against aspect ratio in Figures 4.5a and Figure 4.5b for DP 1451 and DP 1750 respectively. For DP 1451 the tcr curves are lower on alumina than on DP 9950 but retain approximately the same shape. For DP 1750 there are marked differences between the two surfaces. The tcr on DP 9950 is very much less sensitive to aspect ratio than on alumina on the hot side. The differences are less marked on the cold side but in this case the DP 9950 values are lower than on alumina. This difference in behaviour with temperature is consistent with the different structures of the two resistor series. (DP 1400 is based mainly on bismuth ruthenate and most members of Series 17 on ruthenium dioxide

4.2 The Effect of Film Thickness on Electrical Properties of DP Series 17 Resistors

This early investigation used 60 substrates of Design B on which were printed 1720, 1730 and 1750 at five different thicknesses. Five of the ten resistors on each were deposited on Coors ADS96 alumina and the remainder on DP 9950 dielectric as described in Chapter 3. The results are tabulated in Table 4.1 and are presented in graphical form as part of the discussion of Chapter 5. There was a considerable scatter of results but they still clearly showed, however, that the volume resistivity ρ_v was not independent of thickness either on alumina or on DP 9950 and that the variations became more marked on moving from 1720 through 1730 to 1750. They also confirmed that, for this series of resistors, the values obtained of R_s on dielectric DP9950 differed sharply from those on alumina. The final pattern used in this research, Pattern C, was designed in an attempt to produce results of greater statistical significance than those obtained using B.

In these samples the measurement of film thickness showed considerable scatter which made it difficult accurately to identify real effects. For the next stage of the work, therefore, both the pattern and the substrate material were changed (4.3 below).

4.3 The Effect of Film Thickness on Electrical Properties of R4000B and DP 1750 Resistors

The results of investigation 4.2 indicated that, although there was definite evidence of a variation of fired bulk resistivity with film thickness in the higher members of Series 17 resistors, sample and measurement anomalies tended to make it difficult to identify this quantitatively. Therefore Design C was made and used in this follow up study. Kyocera A476 substrates were selected because of their improved surface characteristics. The initial purpose was to carry out an investigation of the resistivity/thickness characteristics of the Heraeus R4000B series for comparison with Series 17. In practice, the results of the two investigations were not directly compatible because of the pattern and substrate changes which led to very much more consistent results than previously. In order to confirm, if possible, trends observed earlier, DP 1750 only was also included here. The results are presented in Table 4.2.

4.4 Extended Study of Heraeus R4000B Series

In Section 4.3 above, three members of the Heraeus R4000B series were studied alongside a Du Pont resistor. Certain anomalies and gaps were observed. In an attempt to resolve and fill these, the range of inks used was extended to 100000 ohms/square and a second sample of the 10000 ohms/square material used. In addition, a

Heraeus/Cermalloy crystallising glass dielectric 9105HT was also used as a comparison with Du Pont 9950, on R4020B - R4040B inclusive only. The results are plotted in Figure 4.6 and confirm the trend of increasing values of D as R increases. They also show that this series behaves very similarly on 9105HT and 9950. In addition, a plot of D against sheet resistance on alumina for all samples of the R4000B series on alumina and 9950 regardless of preparation method and film thickness, Fig 4.7, shows a smooth transition in the value of D through all four series members investigated from values close to unity up to greater than four for R4050B.

4.5 Matrix Study of a Range of Resistor/Dielectric Compositions

This investigation provided the samples for the detailed EDS studies reported here, by Adie, Holodnik and Pitt (49) and by Holodnik and Pitt (50). Since the processing conditions were not optimised for all of the resistor systems used in this sequence, some show values on alumina which deviate a long way from the nominal 1000 ohms/square. Tables 4.3 to 4.6 show, the as-fired sheet resistance with the coefficient of variation in brackets for the four selected resistors. These figures are followed by the values on each of the three dielectrics in turn, together with the ratio of the mean on each dielectric to that on alumina (parameter D above), the tcr (20 to 120^{o}C) on each surface and the thermal stability.

Original measurements of the fired and unfired film thicknesses were made using a Talysurf 3 and were in the range 10.3 to 10.9 micrometres after firing. A repeat of the fired thickness measurements was made using an Alphastep 200 and this, with its software provisions and a horizontal travel restricted to 1.2 mm produced slightly lower figures which are more closely related to the true thickness. These four traces of resistors on alumina are shown in Figure 4.8, together with traces run on each of the three dielectrics. For comparison, the trace of DP 1730 on DP 4032 is also given although the true thickness is difficult to interpret and is not used. The dielectrics all show regular wavelike peaks due to the impression of the screen, despite the use of double wet prints in the processing. Table 4.7 presents the average film thicknesses estimated from these traces together with the shrinkage (final thickness/original thickness) observed on firing from Talysurf measurements. It was not realistic to attempt to identify film thickness changes between alumina and the dielectrics due to the undulating surfaces of the latter which prevented selection of a true base line.

4.6 Comparison Study of a Range of Alumina Substrates

As a result of the variations in sheet resistance of DP 1750 on Kyocera A-476 and Coors ADS 96 substrates reported above, it was decided to investigate whether similar differences occurred in other cases. Four members of the DP HS80 Series, 8021, 8031, 8041 and 8049, were printed and fired on to six different aluminas. The substrates, together with their chemical analysis and measured surface roughness are listed in Table 2.1. Dielectric DP 4032 was used as a control surface in this case only due to unavailability of DP 9950 at the time of printing. (The standard deviations of the CLA figures expressed as a percentage are given in brackets.)

Optical microscopy of the 24 combinations showed very little apparent difference. The photographs are not reproduced here. The slight horizontal movement of glass from the bulk resistor on to the bare alumina observed for DP 1750 on ADS 96 is present on all substrates for DP 8021, 8031 and 8041, although it is completely absent on 8049 (5.8 below). There is possibly a larger fringe of glass for all the lower value inks on ADS 995 than on any of the others(with the lowest alumina flux content). Despite the absence of a 'fringe' on alumina for DP 8049 the appearance of this glaze on DP 4032 showed no significant difference from the other resistors.

An examination of the spread of electrical results between the substrates also shows only marginal changes. These results are shown in Table 4.8 which compares the mean as-fired value on each substrate with that on DP 4032 used as a control. The actual values of sheet resistance are much lower than the nominal 'jar values' due to a mean film thickness of approximately 17 micrometres, (Talysurf 3 and Alphastep), caused by the use of a 165 mesh, 23 micrometres direct emulsion stainless steel screen. A 'value analysis' of both the spreads within a batch and the variations between alumina and dielectric for all 24 combinations shows virtually zero differences between five of the substrates and very slightly greater effects for Stemag. There is no correlation between this observation and the fringes seen under a high power microscope.

No investigation was made of the high temperature thermal stability on the various substrates but tcr measurements, from $22^{o}C$ to $122^{o}C$, were made on the samples. These, together with the mean values of R_s and a film thickness measurement made on Kyocera A476, are shown in Table 4.9. The tcr values in this table may not be compared with those in the Tables 4.3 to 4.6 because of the very much lower R_s due to the higher film thickness.

4.7 Physical Evaluation of the Interactions Between Resistors and Dielectrics

Initial observations using optical microscopy of DP 1750 resistors on Kyocera substrates and on DP 9950 dielectric had indicated the possibility of a mobile glass binder

Figures 4.9a and b show optical micrographs of the edges of DP 1750 resistors on alumina and on dielectric respectively. In (a) the edge on alumina is not well defined with indications of glass having flowed out of the resistor material for a short distance, possibly by capillary action, onto the substrate surface. By contrast, the resistor edge on DP 9950 is more clearly defined suggesting that any flow of glass out of the resistor may take place in a vertical rather than a horizontal direction.

These observations suggested that, as a first order approximation, at least, the value changes on dielectrics might be due to a change in the ratio of conducting phase to insulating phase. Joshi (42) showed that a glass transfer appeared to occur on both DP 1750 and DP 1730. An attempt was made to obtain more information by EDX techniques on this possible glass transfer.

The SEM/LINK system produced computerised printouts of the wt% detected of elements (as oxides if required) above the atomic number of 9. At each point on the sample cross-section values of the wt% present are printed for each selected oxide. In the composites a maximum of 12 were seen on one sample out of 14 elements detected overall. In the simpler cases as few as five or six were present. The processing of the raw data to compensate for the absence of, for example, undetected boron and the possible presence of voids and porosity, is discussed in Chapter 5.

Here, as an illustration of the nature of the results, Tables 4.10a and b show the analyses for two of the simpler cross-sections as a function of relative distance from the film surface towards the alumina substrate. They are respectively DP 1730 on alumina, M58A, and DP 9950 on alumina, M99D*. They are re-presented in Chapter 5 as average, normalised compositions. However, the results given there are for sample

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*See p46

M19A, DP 1730 on alumina, rather than M58A which were given here. The samples come from the same batch of printing and firing.

The deficiency in the total wt% recorded for readings 0.5 to 8.5 (which is the last reading before reaching the edge of the substrate) has a mean of 11.6%. This is very close to the estimate used for B_2O_3 in Chapter 5. The variation in deficit very roughly complements the RuO_2 content, suggesting that it may be confined largely to the glass matrix. This is further indirect evidence for an average boron figure of approximately 12% although from external evidence discussed in Chapter 5, it is not possible to equate the deficit with the B_2O_3 content

*The codings denote:

M = matrix experiment

58 etc = individual substrate number for a named resistor

A = alumina control section

D = named dielectric layer on alumina OR named resistor on that layer

Chapter 5

DISCUSSION

This chapter is divided into two parts. In the first an examination is made of the EDX scans of polished cross-sections of the samples together with other analyses available. In the second the electrical property differences observed between resistors on dielectrics and on alumina are reviewed. The following chapter is an attempt to discover whether there is any correlation between the electrical and analytical results discussed here.

5.1 Analytical Results

5.1.1 Data Processing

The raw results obtained from EDX analysis of cross-sections of resistor samples deposited on both alumina and dielectric and shown in extract form in Chapter 4, need re-arrangement and supplementing before full advantage can be obtained from the information. The data consists of sequences of spot elemental analyses taken at intervals across a cross-section polished at 30° to the surface. For each sample there are between 10 and 20 individual analyses each consisting of figures for 6 to 10 different detected elements. For a number of reasons these analyses do not normally add up to a true 100%,(51).

a) The samples contain elements of low atomic number not detected on the system used. Oxygen is the most important but its presence can be allowed for using a facility in the microscope's computer data processing system. It is calculated as the stoichiometric oxide of the element present if requested. Normally this is the most common oxide and in most of the cases here this agrees with the expected valency state. The oxides used were PbO, SiO_2, Al_2O_3, RuO_2, ZrO_2, TiO_2, ZnO, MnO, K_2O, CoO, MnO, CaO, CuO and BaO. Any deviation from these states would contribute to the error, although to a small extent. [MnO_2 would be the expected state here since it is added to the raw material, but the error is insignficant since the total content is of the order of 3.5%.]

Boron, calculated as B_2O_3 is not detected and in some samples, particularly resistors, is a significant absentee. External evidence for the boron content can be used to compensate. This has been done here (see below).

Fluorine, possibly as CaF_2 may also be present, but only in small quantities in some dielectrics and is unlikely to be a major source of error.

Nitrogen does not appear to be a major intentional constituent of thick films and many nitrides and almost all the nitrates would have decomposed at thick film processing temperatures. It has not been considered here.

Similarly, carbon remaining from incompletely burnt off organic vehicles may well be present although its compounds including most carbonates other than alkali metal or alkaline earths decompose before 850 - 900°C. However, in some materials containing these elements it may be present but undetected. The burning off of organics may, however, contribute to the errors by the presence of voids and porosities (see below).

Other light elements, Na, Mg, are detected but would only be present in traces, if at all in most thick film systems. The remainder, Li, Be and H, would not be expected to be present.

b) A post analysis calibration check found an error in the aluminium. All other elements were correctly calibrated. As a result in Chapter 4, the aluminium oxide content is too high and requires a constant calibration factor of 0.85 to correct it. This was not done there, but all discussions in this chapter take it into account, except where specifically stated.

c) The materials under examination are not always dense structures. Some of the dielectrics are very open and there is less solid material than expected in the regions being probed. This is likely to be one of the major causes of low aggregates. In some cases the recorded totals increase when a resistor is fired on top suggesting that some of the porosity is removed by the resistor's presence.

d) In a small number of cases in all types of material individual low aggregates were observed. These appeared from visual observations to be due to 'bubbles' in the film. Bubbles are normally associated with incorrect firing procedures which do not allow an even burn-off of the ethyl cellulose organic binder. They can also be associated with faulty drying when the volatiles are trapped below the surface.

For all of these reasons normalisation of results was carried out where possible. In general, this meant correction of the aluminium followed by obtaining, where possible, a figure for boron oxide. If these corrections produced a total very close to 100% no further changes were made. If, however, the figures were still very low, the recorded contents were normalised to (100% - the notional boron content).

These corrected figures were used to produce tables of average compositions across the cross-sections. In the composites a true interface does not appear to exist and as an arbitrary limit, the last reading at which the ruthenium dioxide content is significant is taken as the lower limit of the resistor. Similarly, where the SiO_2 figure drops to a very low value this is taken as the lower limit of the dielectric. The lack of sharpness of the interface is enhanced by some beam penetration through the shallow layers produced there by the 30° polishing. [In some cases, due to rounding and approximations, the normalised total is not exactly 100%, but is within ±1% of the target.]

An alternative method of presentation of the analytical results which would show materials interactions in more detail is to plot all the compositions as a function of distance across the polished section. This is very difficult to present as an overall comprehensible picture because, in the composites, up to a dozen different elements may be present in quantities of from 0.1 to 60%. As a result, only selections from these are presented here.

Although the nominal polishing angle was 30°, in practice it varied between samples. The individual film thicknesses also varied a little. In order to make comparison easier, the apparent differences in length of scan were eliminated by normalisation. An arbitrary 'thickness' of 10 cm was allocated to all film sections. This value was chosen as roughly corresponding to actual spot travel x SEM magnification. This meant that in practice, say for a resistor on a dielectric on alumina, the first reading was '1.0 cm' below the surface of the resistor. Measurements were then taken every 1 or 2 cm to 10 cm where this was the last reading that could be taken as resistor material. This point also corresponded to 0 on the dielectric. Beyond this, readings were also taken at 1 - 2 cm intervals up to the substrate interface which was given the dielectric reference 10 cm.

In two cases traces of sodium and sulphur were recorded, but were found to be due to contamination, perhaps finger prints on the sample and were eliminated. In addition, due to the complexity of the compositions, some of the elements present in small quantities were occasionally omitted from the analyses. These were mainly in the composites and were Cu, Mn and Ti. Occasionally silver from the earthing of the sample was detected, mainly in the analysis of the Heraeus samples, but was also eliminated before normalisation.

5.1.2 Discussion of the Average Analyses

The results of chemical analyses of certain thick film resistor series, DP 1400 and HS80 and Heraeus R4000B were made available by Coleman (52) (These are presented in tabular form in Chapter 2.) In the matrix investigation four resistors were used, DP 1431, 1730, 8031 and Heraeus R4030B. Analytical results are available for Heraeus R4030B and DP 8031, both of which have been studied electrically in this work. DP 1730 was not analysed but is of a composition very similar to 8031 which is derived from it, (Du Pont information). No analysis was available other than a qualitative spectrographic one for DP 1431, but detailed quantitative results of DP 1421 and DP 1441 gave an indication of its composition. From the HS 80 results for boron oxide a figure was estimated, rounded to a whole number of 12% of boron oxide in DP 1730. When converted to a figure for the glassy phase only this figure becomes 14%.

Table 5.1 shows the quantitative chemical analyses of DP 8031 and R4030B in the form (pigment + glass) expressed as a percentage and also shows the percentage composition of the glass itself. Table 5.2 presents an average of the chemical analyses of DP 1421 and DP 1441 in order to estimate the composition of DP 1431. Note that a trace of both Mg and Cu were detected qualitatively but not quantitatively. Also several attempts to quantify the significant boron content of the whole series were completely unsuccessful and this element has to be ignored in the analyses. In this case no normalisation, except to allow for the loss on ignition, has been made because of the absence of a boron figure. The pigment is $Bi_2Ru_2O_7$ in an approximately stoichiometric ratio.

No quantitative analyses were initially available from within STL, for any of the three dielectrics used but a published Bendix Report (53) gave an outline for both DP 9950 and DP 9429. These were used to obtain an estimate of the boron content for normalisation of the EDS results. DP 4032 is fairly similar to DP 9950 and an assumption was made that the figure for boron in DP 9950 would be used. Since it appears to be low in all three cases the error involved is not large overall. Table 5.3 shows the Bendix figures normalised to 100%. Their totals were very low and the analyses in some cases disagreed with both the literature and our EDX results. They can only be used as an indication of materials content.

Results were obtained at STL after this research has been completed, (J.M. Wheeler, (54,55)) for DP 9950, DP 9429 and two other dielectrics not examined here. Except for a slightly higher boron content than given by Bendix, her results were compatible with those given here for DP 9429. For 9950 the boron content was only given as the difference from 100% and not actually measured. With this reservation, the results were also compatible with those reported here. Table 5.3 also compares the results reported by Bendix with those of Wheeler.

Using the boron figures derived above, it is now possible to normalise the EDX results as described earlier. The results are given in graphical form. Figure 5.1a and b show the average compositions of DP 1730 and R4030B on alumina and of DP 9950 and DP 9429 both on alumina respectively. Figure 5.2 a, b, c and d show the changes observed in average composition when the two resistors are fired on the same two dielectrics. Results of the use of DP 4032 as a surface for resistors are only available for DP 1730 and not for R4030B. Accordingly, these analyses are presented separately as Figure 5.3a for 4032 alone and 5.3b for the differences in DP 1730 on DP 4032 with respect to alumunia. References (49) and (50) present the same data but in the original tabular form. As a result of the discussion above it is very difficult to put an absolute limit on the accuracy of these figures, but they appear to be self-consistent and have a relative accuracy of about 2.5% where the figures are comparable.

5.1.3 Discussion of the Cross-Section Analyses of DP 1730 and R4030B

As discussed above, the film thicknesses were all normalised to a notional value of 10 cm to allow for actual film thickness differences and for polishing angle discrepancies. The horizontal normalisation makes comparison between samples easier.

Analysis of the profile of the ruthenium content of DP 1730 on alumina across the cross-sections showed clearly the particulate nature of the films. Three samples were available for comparison, M19A, M58A and M99A, the control halves of the substrates used for analysis of interactions with DP 4032, DP 9429 and DP 9950 respectively*. The three analyses were normalised to 100% after correction of the alumina figure and allowing for the addition of 12% for B_2O_3. The means of the RuO_2 contents were, with number of readings in brackets: M19A 13.8% (20), M58A 11.2% (14) and M99A 10.4% (9). The mean for M19A was taken as the basis for Figures 5.1a and 5.2 c and d because it was compiled from the largest number of individual points. Figure 5.4 shows the three profiles. In M19A there are peaks right across the curve indicating that the probe hit the pigment rather than matrix on many occasions. M58A is similar but the peaks nearer to the substrate are less pronounced. In M99A the angle of polishing allowed only nine readings and the greater gaps left may have missed some of the peaks. Its much lower average value may be due to their absence. A similar plot could be made for R4030B on alumina from the six available analyses. This is not reproduced here.

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*See Section 4.7 for explanation of code.

The composite nature of the films is clearly illustrated for M19A by a plot of the PbO, RuO_2 and SiO_2 contents across the polished section. These oxides are also given as corrected and normalised contents. This is shown in Figure 5.5. The lines for lead oxide and silica follow one another very closely right across the section down to the substrate interface. The numerical value of the alumina is much more constant than for the other two and is also much smaller. Nevertheless the small fluctuations visible in the figure also follow those in the glass constituents except at the interface where they diverge due to the presence of the substrate. The three minor constituents are not plotted here due to their low value. However, although no firm conclusions can be drawn for copper, the zinc and manganese appear to change in the same direction as changes in the lead content and in the opposite direction to changes in the ruthenium dioxide. Figure 5.6 shows a similar plot for R4030B on alumina. Here it can be clearly seen that the barium content does not follow the ruthenium but, rather, the glassy phase.

This evidence suggests that fired Du Pont 1730 consists of small particles of, probably, pure ruthenium dioxide dispersed in a glass matrix which is based on a lead borosilocate glass which also contains 10 to 12% of alumina, 3% of manganese oxide, 2% of zinc oxide and under 0.5% of copper oxide. Since the earlier tables and figures suggest alumina content of about 7%, both in paste form and also on low alumina dielectrics, it is very probable that a considerable proportion of the oxide found here is dissolved from the substrate during the firing process.

For R4030B on alumina the evidence suggests that the barium ruthenate present in the paste (X-ray crystallography) has dissociated into RuO_2 and BaO.

raise the softening point to above 850°C. The dielectric film is very glassy suggesting that the added alumina fulfills the twin functions of ceramic filler and constituent of a high melting point glass phase.

b) DP 9950

This filled glaze appears more complex than DP 4032 and contains, in addition, ZrO_2 and a small amount of TiO_2. The ZrO_2 appears to be distinct from the glass phase and its peaks occur mainly at SiO_2 troughs. The Al_2O_3 appears to follow the SiO_2 closely but there is no real correlation between PbO and SiO_2.

It is possible that this is a glass system based on aluminium and calcium silicates and containing only small quantities of lead borosilicate. The ceramic filler appears to be based on ZrO_2 rather than an excess of alumina as seems to be the case for DP 4032.

The raw analyses of DP 4032 and DP 9950 differ sharply in one aspect, the apparent solids content recorded. In the case of DP 4032 it decreases from nearly 80% close to the surface to a steady value close to 60% in the bulk. For DP 9950 it starts at about 75% and rises to just under 100% declining to close to 90% except for one reading of 80%. These figures have been corrected for alumina content but no other modification has been made to the raw data.

The results of Figure 5.8 show these solid contents as a function of distance. They suggest that the structure of DP 4032 is much less dense than DP 9950, but that the surface may have less porosity, ie is

The former appears to behave in a particulate way, while the latter follows the glass matrix. Less alumina appears to have dissolved from the substrate than was the case for DP 1730. . The fired glass matrix would appear to be a mixture of lead silicate and calcium and barium alumino silicates, but is clearly very complex. X-ray analysis of the fired film did not show distinctly any crystalline phases except, probably, RuO_2.

5.1.4 Discussion of the Cross-Sectional Analyses of DP Dielectrics 4032, 9950 and 9429

Examination of plotted cross sections of the three dielectrics DP 4032, 9950 and 9429 fired on alumina shows reasonable homogeneity although it is possible to identify the ceramic fillers in the first two. These plots are complex and only the major constituents are shown in Fig 5.7 a, b and c respectively. The data show the calibration correction for alumina and are normalised to 10 cm in cross section. The compositions have not been normalised to 100%, nor do they allow for boron content.

a) DP 4032

The two major constituents of the glass, SiO_2 and PbO, follow one another very closely. The three minor constituents are CoO, CaO and K_2O and these are close to the limit of detection but possibly also follow the glass. The other major constituent, alumina, is clearly present, at least in part, as a filler and not as part of the glass system since its concentration changes in the opposite sense to the SiO_2. This glass appears to be a lead borosilicate with a considerable excess of SiO_2 with respect to PbO. The blue pigment is CoO. It is possible that the excess SiO_2 is present combined with part of the alumina, perhaps as mixed aluminium and calcium silicates. The excess silica would glassier in nature, than the bulk. For DP 9950, apart from the one low reading which may be due to a film defect, the structure appears denser in the bulk than at the surface. This is discussed further below in the context of a resistor on the top. Resistance changes with respect to alumina are slightly greater on DP 4032 compared with DP 9950 and this is compatible with greater porosity.

c) DP 9429

Also in Figure 5.8 is a plot of the apparent solids content of DP 9429 which lies between the other two, except for a void close to the substrate interface. (The estimated B_2O_3 content is 3%.) The constitution of this crystallising glaze is much more complex than that of the filled glazes. A number of tentative observations may be made regarding its structure from the raw data.

i) SiO_2, CaO and MgO appear to follow one another very closely.
ii) Lead is absent in this material.
iii) A plot of BaO and TiO_2 shows a wide variation in the wt % ratio of the two oxides, indicating that the phase $BaTiO_3$ is not a constituent of the fired film.
vi) The phase containing ZnO probably does not correlate with SiO_2 content.
v) There is some correlation between BaO and Al_2O_3.
vi) BaO does not peak with SiO_2 and is out of phase with MgO and CaO.
vii) There is a weak correlation between Al_2O_3 and SiO_2.

These observations suggest that the fired film contains Ca and Mg silicates and probably Al silicates. There may be barium aluminate containing phases. It is not possible to identify any definite ZnO affinity.

5.1.5 Discussion of the Analyses of Resistors on Dielectrics

The complex interactions taking place after firing of resistors on dielectrics are difficult to display other than as colour transparencies. As a result, only selective discussion is made of the cross-section analysis, the main presentation of the results being the average analyses given in the previous section.

a) DP 1730 and DP 9950

The largest transfer of materials across the interface is that of PbO. This is plotted in Figure 5.9. These figures are all standardised to 10 cm cross-section as before and allow for normalisation of bulk and estimated B_2O_3 content as above. The average PbO content drops from about 30% in the resistor to about 10% over the course of the upper 40% of the dielectric film and settles down at this value. This is close to the original lead content of the material on alumina. The RuO_2 content also extends into the dielectric with between 1 and 2% across the whole section. (This is considerably higher than the the results of Prabhu et al who measured the saturation solubility of this oxide in a lead borosilicate glass (56). They found this to be less than 10 ppm at standard film firing temperatures. This implies that the 1 - 2% measured here is not in solution but is precipitated on the surface of glass or ceramic particles. However, they suggest that solubility laws imply a very much greater concentration in the glass matrix very close to the surface of the dispersed RuO_2 particles. If this is true, it has a considerable influence on the conduction mechanisms of thick film resistors.) Conversely, the alumina content of the resistor is considerably smaller than on an alumina substrate and it rises smoothly into the dielectric layer. A peak, 75% of the way into the dielectric may correspond to an undissolved alumina particle in the DP 9950.

b) DP 1730 and DP 9429

A similar plot of lead content, this time with BaO instead of alumina is made in Figure 5.10. As observed from the average figures above, there is an interchange of about 5 wt% of BaO and PbO between the resistor and dielectric films. A trace of RuO_2 is now present again in the dielectric. This film combination is the one in which the resistor value has risen approximately 40 times compared with its value on alumina and which now has an extremely negative tcr (-833 $ppmK^{-1}$).

Figures 5.11 a to d due to Adie (57) show SEM photographs at x15000 and x75000 magnification of coated samples of DP 1730 on DP 9950 and DP 1730 on DP 9429 respectively. In both cases the particulate structure can be seen indistinctly, but in b microcrystallites approximately 0.1 micrometres across are visible across the surface. Spot analysis on these crystallites has not yet been carried out, but provisionally it may be inferred that they are part of the devitrifying glass phase transferred into the resistor in exchange for lead during firing.

c) DP 1730 and DP 4032

A plot of the lead content across the profile of DP 1730 on DP 4032 produces a very similar shape to that on DP 9950 and is not reproduced here.

d) R4030B and DP 9950

The main difference between the R4000B series and DP series is the presence of BaO in the fired film. As stated above, the films on alumina appear to contain the barium, at least in part, in a phase which decreases in concentration when that of ruthenium increases. A similar observation may be made from an examination of Figure 5.12a. In the upper portions of the resistor, the lead and barium curves are roughly parallel; their peaks occur together at a trough in the ruthenium, approximately '2 cm' from the top; at approximately '2.6 cm' the peaks and troughs are reversed. As before, a small concentration of RuO_2 is present throughout the dielectric film, probably precipitated from the glass as suggested above, Some BaO has also diffused into the top 30% of the dielectric. However, none of these changes are large and are comparable with those taking place in DP 1730 and DP 9950. No evidence was found of association between Ba and Ti.

e) R4030B and DP 9429

Here the electrical changes were more marked than on DP 9950. The chemical changes shown in Figure 5.12b indicate a considerable loss of lead from the resistor into the top 60% of the dielectric. This lead, unlike in DP 9950, has not been replaced by barium, since the latter was already present in the Heraeus resistor. The affinity of lead and barium in the glassy phase can be clearly seen, as can the marked increase of the average RuO_2 content and the presence of sharper peaks than before. From Figure 5.2b the loss of lead content on DP 9429 was 7.5% compared with that on alumina.

5.2 Electrical Properties

It is desirable to produce, as in Chapter 2, a set of criteria by which to judge a combination of a series of resistors with a dielectric. These must include aspects of design and deposition values as well as component stability. These are discussed below.

a) Design and Firing Values

If no significant changes occur other than a reproducible change of sheet resistance when deposited on dielectric rather than alumina, a change of design sheet resistance may be all that is necessary. In this case the main factor would be parameter D and its reproducibility. It would appear unwise to attempt to do this unless it is in the range 1.0 ± 0.5 and, even then, only subject to other conditions below. A change of printing parameters to compensate for D by increasing or decreasing final thickness may be unsafe because the evidence of Joshi for the DP series 17 and of Chapter 4 for Heraeus R4000B suggests that D may often be thickness dependent. In addition it is not likely that the value of D will remain constant throughout a series.

b) Aspect Ratio Effects

For the DP 1400 series only (Chapter 4, (42) and Jalai (58)), it has been observed that the variation of effective sheet resistance with track length is completely different on DP 9950 compared with alumina. This was not investigated for other DP resistors except for DP 1750 which also showed differences.

c) Temperature Coefficient of Resistance

In many cases, following the trends set by Matthiessen's Rule, the product of Rs and α is approximately constant. This may mean a significant change in tcr, possibly outside an acceptable specification. (This approximation would be valid only if there is no change in the resistor other than an alteration in the conductor concentration and, also, only if Rs decreases and there is no change in the sign.

d) Noise Values

Noise values are difficult to measure accurately, especially for low resistance films where they may be close to the system noise. Nevertheless, significant changes may be important in some applications. Jalai reports noise measurements for 1421, 1431 and 1441 on alumina and 9950. His results suggest that the difference is small in this case. (See below)

e) Electrical Stability

In general, a total excursion tolerance, (covering time, on and off load stability, temperature range and post-trimming processing), of ±2 to ±3% is acceptable for thick film resistors on alumina. Similar figures are likely to be necessary on dielectric surfaces. In this work it was not possible to carry out electrical load tests. However, when the new Middlesex Polytechnic Microelectronics Laboratories became available, short term dry heat tests, originally intended for use as step stress analysis tests for Jalai were carried out. A convenient comparative test was to pass the samples through a 300°C cycle up to five times. The overall changes in all cases were very small, approximately ±0.1%. They showed, except for DP 8031 on DP 9429 which produces very high values of resistance on dielectric, very little difference between the surfaces.

An extension of the 300°C exposure to five hours in some cases shows that the differences were still not very significant. It is possible that a shorter exposure at say 450°C may also give a good guidance as to the relative stabilities on alumina and on dielectric.

A further possible electrical difference would be the sensitivity to severe humidity. Results from Jalai for DP 1421, 1431 and 1441 show that resistors on dielectric DP 9950 and on alumina show considerable changes after 215 hours at 85°C and 85% RH off load at 100 ohms/square but that the effect reduces with increasing sheet resistance, see below. This may be another parameter by which a successful resistor/dielectric combination needs to be judged.

From the above it is possible to draw up a table of 'acceptable' parameter variations for resistors on dielectrics and then to examine the groups of samples produced in this research to see whether they meet the criteria.

Table 5.4 shows one set of parameters by which the acceptability of a resistor system could be judged on a surface other than alumina.

Not all of these parameters have been investigated in all the combinations studied here. Where samples were available, as many as possible of these tests were carried out. The largest quantity of data is available for DP 1421, 1431 and 1441 on alumina and DP 9950 from tests made by and for Jalai.

The next sub-sections examine the properties of several combinations in turn.

In this discussion the dielectrics to be considered are reduced from the original four, DP 9950, 4032 and 9429 and Cermalloy 9105HT to DP 9950 only for all resistors. This is for the following reasons.

a) DP 4032

This dielectric performs in a very similar way to DP 9950 with all the combinations examined. In practice there appears very little advantage from its use because the parameter D is usually very slightly lower than for DP 9950. It is not likely to be widely used especially as a substrate for resistors.

b) DP 9429

This dielectric was only used in the matrix studies and gave very mixed results. These included a reduction in value to about 60% for Heraeus R4030B, a 20% rise for DP 1431 and very high values (see above) for DP 8031 and DP 1730. On account of the considerable mutual solubility of its constituents with those of the resistors it appears unwise to use it. It is not used as much as it used to be because it has been shown to be very porous.

c) 9105HT

This dielectric was used in conjunction with the R4000B series only and gave preliminary results which showed promise. Since it is a glass system there must be a possibility of constituent interchange in this case also. Its manufacturers (59) report very promising results under the R4000B series. Insufficient data is available from this investigation to discuss it further here.

d) DP 9950

At the start of this investigation this was one of the best established filled glass dielectrics available (42). It is still a much used material in production although Du Pont now market several further dielectrics for multilayer work. The largest quantity of information on dielectrics produced from this research concerns the behaviour of DP 9950 with various members of the DP 1400 Series 17 and HS80 families of resistors, together with Heraeus R4000B.

The following sections examine the behaviour of DP 9950 in conjunction with these resistors in turn.

5.2.1 DP 1400 Resistor Series and DP 9950 Ceramic Filled Glaze Dielectric

The information summarised here is taken from a number of the investigations of Chapter 4 and from the work of Jalai. Since not all samples were produced or tested under similar conditions, the information in Table 5.5 has to be somewhat generalised. As before, parameter D represents the ratio of sheet resistance on dielectrics to that on alumina.

A comparison of Tables 5.4 and 5.5 shows that the behaviour on DP 9950 is generally comparable with that on alumina. Provided further investigation shows that the ratio of values on the two surfaces is reproducible, it would be possible, on the basis of these figures, to use most of the members of the series on this dielectric. However, there must be reservations concerning the achievement of satisfactory values for DP 1451 and over the tcr and the effect of humidity for DP 1421 on the dielectric. (The considerable discrepancy of tcr on DP 9950 for the lowest member investigated may be related to the piezoelectric effects reported by Kummel (43).)

5.2.2 DP Series 17 and DP 9950

Less information is available from this research than for the 1400 series, but Table 5.6 displays the limited data obtained. Here again the combination of this series with DP 9950 gives promise of a satisfactory production system. (This will not actually be possible in practice, since Series 17 has been replaced by a very similar but higher stability product, HS80.) There are, as seen in Chapter 4, and as reported by Joshi, some differences between the two surfaces with respect to both aspect ratio effects and to the variation of bulk film resistivity with thickness. An attempt to identify any striation of the conducting phase in the glass matrix failed because there were too few analysis points on the cross-section. Adie, also, found no reproducible segregation of conductor for DP 1730 on any of the four surfaces he examined. The behaviour of DP 1720 is again anomalous, but this time the tcr on the dielectric is very high and positive instead of negative. This again suggests expansion mismatch. It is possible that this might make the full use of this series unacceptable.

5.2.3 HS80 and DP 9950

This series consists of two sections with a blend break. The lower half contains 8011, 8021 and 8041 and the upper half 8039, 8049 and 8059. (The two are not blendable although each sub-group is fully blendable internally.) As stated above, these samples were much lower in value than the nominal due to the use of a very high printing thickness. However, it can be seen from Table 5.7 that the value of 'D' for the three lowest members studied is acceptable. In these samples the values of tcr on alumina show more scatter than on dielectric although the latterare, in all cases, higher. (Unpublished industrial work has shown that this series at its specified thickness gives extremely promising results. The table gives provisional support to that observation.)

5.2.4 Heraeus R4000B and DP 9950

This resistor series is of a totally different construction from the three Du Pont families examined. A much larger wt % of RuO_2 is necessary for the same sheet resistance because there is much less lead present. The deficit in the glass content is made up in the fired state by barium oxide which has dissociated from the crystalline $BaRuO_3$ present in the unfired paste. However, like the other series, it appears to form the basis of a viable combination. A very unusual feature so far unexplained, which might limit its use is the curve of R_s v 'D', Figure 4.7, which suggests that there is a smooth relationship between value on alumina and the ratio, D, above about 5000 ohms/square, regardless of processing or thickness. The results are presented in Table 5.8.

Chapter 6

INTERPRETATION OF RESULTS

Two major effects of the interaction between thick film resistors and dielectrics may be identified. The first is a change of as-fired sheet resistance with respect to that on alumina, and the second is the change of slope of the R v T curve (tcr). Matthiessen's Rule, Chapter 2, implies that there may be a proportionality between bulk resistivity and tcr, provided that the change in resistivity is not brought about by a change in conduction mechanisms. In many cases the effect of a dielectric layer under the resistor appears to be to leach out some of the glass; in the examples studied the lead content in particular is affected. This causes the conducting phase composition to rise and the sheet resistance to reduce, at the same time making the tcr more positive. Figure 6.1 which is a replot of Figure 2.6 on different axes for the R4000B and DP 1400 series only, shows how composition changes might affect the values produced by a resistor series. A similar generalised curve for tcr cannot be drawn because there are tcr modifiers present which may be different for different series members. In some series, such as DP 17 and HS80, there are blend breaks where either or both of the conducting and glass phases are changed and the two halves become non-blendable.

It was originally suspected that the conducting phase might be unevenly distributed in the vertical cross-section of the resistor and that this effect could be more marked on a dielectric which absorbed some of the glass. There is some support for this in Figure 6.2 which shows, for the 10^5 ohms/square DP 1750, the variation of bulk resistivity with average thickness. These plots are not identical to the earlier ones of Joshi, although the measurements were made on similar samples. Here the film thickness and resistivity were calculated from the average film thickness across its total width as displayed by the Alphastep 200. These figures produce much smoother curves than from the earlier Talysurf data. The instrument also displays the value of W needed to give the true value of R_s rather than the nominal 5:1. This is significant for the very thick films. It may be seen that there appear to be two different effects of thickness on the resistivity. At very low thicknesses it is extremely high. This may be due either to a high alumina content dissolved from the substrate or to a reduction in conducting path density in the film due to its thinness. The minimum occurs below 10 micrometres film thickness and there is then a gradual rise as t increases further. Figure 6.3 shows analogous behaviour for the average hot side tcr.

These figures suggest that both on alumina and on DP 9950 there is some uneven distribution of particles in the thicker films. However, none of the EDX analyses gives clear support to this hypothesis. Joshi, with a few points available on his cross-sections of DP 1750 (10^5 ohms/square) did not identify any certain concentration of RuO_2 close to the interface on either alumina or DP 9950. An alternative explanation, supported by the similarities of the curves on DP 9950 and alumina, is that the cause of the rise is the solution of alumina from the surface below the resistor. This would agree with the work of the Pike and Seager (22).

The analyses reported in detail here were all for 1000 ohms/square, DP 1730 and Heraeus R4030B. Clear evidence of the particulate dispersion was present in both, but in neither case could it be concluded that there was a greater concentration of conductor close to an interface with either alumina or dielectric than elsewhere. (Three samples of DP 1730 on alumina gave contradictory results, two showing an irregular increase with depth while the third had its greatest RuO_2 concentration near the surface.) Figure 6.4 shows plots of the average content of RuO_2 as a function of position in the cross-section. These are based on six samples for R4030B and on the three samples above, for DP 1730. Although the figure shows some scatter of results, no definite trend is apparent in either case.

The initial hypothesis suggested that the reduction of R_s on filled dielectrics was caused not by uniform draining of glass from the resistor film, but rather of draining from layers close to the interface only. This could not be confirmed by the results of this work, so an alternative hypothesis became necessary. The previous chapters have shown that there are two major classes of resistor/dielectric combinations. These are:

a) Combinations in which the modifications of properties are relatively small and a useful product can result.

b) Combinations in which there are very large changes in the properties and no useful product can be made.

Work at Middlesex Polytechnic in the period 1975 - 79 prior to the start of this research had, in collaboration with both Du Pont and ESL, examined the effect of deposition of a number of different resistors on a small range of crossover/multilayer dielectrics. The results, in summary, show that both the bismuth ruthenate based DP 1300 series and the two ruthenium dioxide containing ESL series, 2800 and 3900, produce values of D less than unity on filled glazes, eg ESL 4901. In contrast, on crystallising dielectrics ESL 4608CFB M2 and DP 9429 the ratio is in the range 1.2 - 1.5 (6,15,60). Unpublished work by Moran (61) on distributed filters also reported small rises in value on crystallising glazes. These appear to be examples of an intermediate class of reaction. No further studies of the ESL materials were carried out during this research, but the DP 1431/DP 9429 combination reproduced the earlier results when included in the matrix combinations. The earlier work, first on distributed notch filters, and later, on the fabrication of very high speed digital multilayer circuits for BTRL, provided the initial motivation for this programme of research.

Since there are many different pigments used with a range of modifiers and a wide choice if glass matrices for both resistors and dielectrics, it is not possible to cover all combinations in this discussion. Tables 6.1 and 6.2 respectively, show some of the constituents in thick film resistors and dielectrics. Not all these were present in the films analysed in this research.

The greatest value changes observed here were of two types:

a) A reduction to approximately 50% of nominal alumina value on some filled glasses for high R_s materials. In these cases the tcr shift was generally positive and of the same order of magnitude. No major compositional differences appeared in all the cases where D was less than 1. This suggests, in general terms, that the reduction in value is due to a loss of glass from the matrix rather than to a change in conduction mechanisms.

b) A considerable increase in value, D ranging from 1.2 to 40, on crystallising dielectrics. A major cause of this appears to be an exchange of lead and barium oxides in the glass phases. In the examples examined here the tcr changes did not show Matthiessen's Rule compatibility with the R_s changes. The addition of BaO to DP 1730 and HS 8031 was accompanied by large values of D. R4030B already contains BaO and the changes were less but the tcr became more negative. An additional factor in the high values of D observed may be the absorption of titania from a crystallising dielectric. It is not possible from the evidence presented here to identify a separate titania contribution to the large changes. However, Rzasa and Potencki (62), have recently shown that the DP 1400 series resistors on titania filled glasses show very high values compared with alumina and, also, sharply negative tcr. These combinations were used by them as temperature sensors.

The above study leads to a general conclusion that viable systems of resistors on dielectrics are unlikely to be obtained using crystallising dielectrics because of constituent interchange. However, filled dielectrics appear only to be affected by a limited draining of glassy phase from resistor to dielectric. New materials provided by many manufacturers for specific use as an underlayer for resistors appear to be developments of the earlier materials such as DP 9950, DP 4032 or ESL 4901 discussed in this research. They are described as dense and glassy ceramic filled dielectrics. This indicates that they have been designed to absorb the absolute minimum of the glass from the resistor. If these claims can be shown to be correct, resistors on dielectrics will now become a much more viable economic propostion. The high glass content of these materials has the effect also of acting as a barrier to moisture in multilayer structures.

Chapter 7
CONCLUSIONS

This Chapter summarises the main observations and conclusions drawn from this work. These conclusions cover commercial, electrical and materials aspects of the interactions between thick film resistors and dielectrics.

7.1 Commercial

a) The variation between different alumina substrates is sufficiently small to be absorbed in the laser trimming without changes in design.

b) With appropriate recalibration of the design process and a careful control of print thickness all the resistor series examined here may be used with the filled glazes, DP 4032 and DP 9950, although there may be some degradation of properties at low sheet resistances.

c) Crystallising dielectrics appear in general to be unsuitable substrates for most thick film resistors.

d) Before setting up a production process for resistors on dielectric it is essential that a careful evaluation should be made which includes all the series members to be used as the reactions may vary significantly through a series.

7.2 Electrical

a) In general the changes on crystallising dielectrics are large and affect both value and tcr. These changes are often inconsistent with Matthiessens's Rule and imply a change in the conduction mechanisms.

b) On ceramic filled glasses the changes are often small decreases in value and similar increases in the hot side tcr. This is compatible with Matthiessen's Rule, implying that the main effect of the combination is to alter the dilution of the conducting phase in the glass matrix.

7.3 Materials Interactions

a) In all cases studied an interchange of constituents occurs.

b) On filled glasses the main mobile constituent is usually lead oxide. The small changes of conductor/matrix ratio are the changes consistent with Matthiessen's Rule.

c) Small traces of RuO_2 were found throughout dielectric layers suggesting that the glass matrix in the resistor may be saturated with the conductor and be a major contributor to the observed electrical properties on alumina.

d) The property modifiers, ZnO, CuO, MnO_2 etc, diffuse similarly to the lead and silica suggesting that they too are part of the matrix rather then the conducting phase.

e) Small traces of the minor constituents of the dielectrics have been found throughout the resistor layer suggesting that CaO, CoO. MgO and K_2O are part of the glass phase. Traces of ceramic were sometimes found in the resistor layers implying that some at least also dissolves in the glass matrix as well as remaining in particulate form.

f) The changes on crystallising glasses are of two kinds; firstly an increase in the conductor/matrix ratio as on filled glasses, but possibly larger in value and, secondly, an interchange of barium and lead oxides. This is associated with the changes incompatible with Matthiessen's Rule.

g) An analogous interchange of glass between conductors and dielectrics may affect either the solderability or the adhesion (61). This presents a potential reliability hazard.

h) No definite evidence has been found on either alumina or on dielectrics to confirm an uneven vertical distribution of the conductor within the matrix, in the combinations studied here.

Chapter 8
RECOMMENDATIONS FOR FUTURE WORK

1. Analyses of DP 1431 on various surfaces need to be carried out to try to identify how the interactions of a bismuth ruthenate resistor differ from those based on ruthenium dioxide or barium ruthenate.

2. The SEM/EDX analyses should be extended to a wider range of sheet resistances.

3. A study of the conduction mechanisms of resistors on both alumina and dielectrics should be made using both computer modelling and low temperature measurements.

4. The current research has not made any examination of the effect of resistor overlayers on the electrical properties of dielectrics. This should be carried out on samples of dielectrics both underneath and near to the edge of resistor films.

5. The new commercial dielectrics designed as resistor underlayers should be examined.

6. Piezo-resistive effects associated with the bending of resistor on alumina and dielectrics should be examined to see whether they can add to the information on conduction mechanism changes (63).

7. Reactive ion beam etching of films on alumina and dielectrics should be carried out both to provide samples for SEM/EDX analyses and also to attempt to obtain irect information on the variation of film bulk resistivity with thickness.

8. Further studies should be made of the ageing behaviour of selected combinations and controls, both on and off load.

9. The effect of laser trimming on the resistors should be examined in order to see whether the work of Firmstone and Hain is applicable to materials from other manufacturers.

10. Since the preparation of the majority of samples for this work, Du Pont have lowered the recommended temperature for firing DP 9950 from 925°C to 850°C. The effect of this on resistors fired on top needs to be investigated.

11. In many resistors materials, small quantities of zinc and manganese oxides are present. It is possible that they have some effect on vcr at high values of R_s. They also are leached from the resistor with the glass matrix on DP 9950. Possible changes in vcr should be examined.

12. Much data remains to be analysed from the SEM/EDX investigation. Further information should be obtained on the movement of the minor constituents between films.

Since completion of the practical work (1984) additional associated studies have been carried out by the author and co-workers, Ref. 50, 63, and

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Chapter 10

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Table 2.1 Chemical Analysis (wt%) and Surface Roughness (micrometres) for Various Alumina Substrates

	Substrate Type						
	Alsimag 614	Coors ADS 96	Kyocera A-476	Narumi AT 396	Stemag	Coors 99.5	Rosenthal
Al_2O_3	94.67	95.10	95.25	95.05	97.31	99.18	96.70
SiO_2	2.98	2.33	3.38	3.30	1.71	0.52	0.96
CaO	0.20	0.01	0.02	0.04	0.84	0.07	0.48
MgO	2.15	1.94	1.35	1.61	0.14	0.23	1.83
CLA (μm)	0.53 (7.5)	0.75 (12.9)	0.42 (17.0)	0.80 (10.0)	0.55 (22.0)	0.19 (13.0)	0.79 (7.3)

Table 2.2 Chemical Composition of Typical 96% Alumina Thick Film Substrates (Allington)

Alumina Al_2O_3	96%
Flux Components 4%	4 %
MgO	
Na_2O	
CaO	
K_2O	
ZrO_2	
Fe_2O_3	

Table 2.3 Substrate Dimensional Tolerances

Camber	4μm/mm
Thickness	±10% but not less than ±100μm
Width and Length	±1% but not less than ± 100μm
Surface Finish	0.4 to 1.0μm CLA

Table 2.4 The Composition of Reactively Bonded Gold Conductors

Ink Type	Major Elements	% Composition	
		Cu	Cd
Cermalloy S4399	Cu Ge	0.32	-
Du Pont 9500	Cu Cd	0.83	0.18
Du Pont 9791	Cu Cd Pb Si Bi	0.19	0.72
E-0 6990	Cu Cd	0.70	0.34
EMCA 3264	Cu Cd Bi	0.70	1.23
Englehard T2888	Cu Cd Bi	0.62	0.50
ESL 8880	Cu Cd	0.49	0.30
Plessey C5700	Cu	0.67	-
Du Pont 9260	Pb Si	-	-

Table 2.5 Desired Features of Thick Film Dielectrics

Feature	Crossovers	Multilayers	Capacitors
Relative Permittivity	Minimum	Minimum	10 - 2000 reproducibly
Thermal expansion coefficent	To match that of substrate		
Surface Finish (fired	As smooth and dense as possible		
Pinhole free	Vital in all cases		
Geometry retention during multiple processing	Important	Extremely critical	Important
Chemical compatibility in contact with conductors	Vital in all cases		
Chemical compatibility with resistors	No	If possible	Rarely possible or necessary

Table 2.6 Thick Film Technology Requirements for Military/Aerospace Products

Portion of Technology	Specific Limiting Parameters
Environmental Specification	Conforming to MILSPEC, NASA or similar standards and may include: storage temperature -65 to +150 to 200°C operation temperature -55 to +150°C individual device failure rates 10^{-7} hr^{-1} at 150°C
Circuit Specifications	Selected parameter chip devices for surface mounting. Package screening and burn-in Resistor tolerances: as trimmed ±0.1%[+] end of life ±1 or 2%[++]
Packing Density	25 - 50 components in^{-2}, (4 - 8 cm^{-2})
Package Dissipation	2 - 3 W in^{-2}, (0.3 - 0.5 cm^{-2}) over operational range
Package Cost Targets	Typically £100
Size Range	Typically 1 x 1 sq in to 2 x 2 sq in (2.5 x 2.5 to 5 x 5 cm) approximately

[+] closest realistic target tolerance obtainable

[++] depending on specific applications and environmental specifications.

Table 2.7 Thick Film Technology Requirements for Consumer/Automotive Products

Portion of Technology	Specific Limiting Requirements
Environmental	a) Consumer operation and storage -10 to +50°C typical individual device failure rates 10^{-6} hr^{-1} at 50°C b) Automotive Depends on application but will lie between the military and consumer extremes
Circuit Specifications	Mainly packaged devices for surface mounting, but also some chip devices. In general neither specially selected or closely toleranced. Package screening and burn-in not required. Resistor tolerances As trimmed 0.5% End of Life 5 - 10%
Approximate Packing Density	10 - 20 components in^{-2} (2 - 3 cm^{-2})
Package Dissipation	2 - 3 W in^{-2} over temperature range
Package Cost Targets	Hybrids = £2 - 3 Networks = £0.50
Size Range	Typically 0.5 in sq to 2 in sq (12.7 to 50.8 mm)

Table 2.8 Production Requirements for Thick Film Manufacture

Substrates	High purity (96%) alumina with specified dimensional tolerance. Size range (Imperial) 0.25 to 4 in rectangular or square. Also non-rectangular shapes and sometimes holes.
Conductors	Screen printable with high yield for 0.125 mm line and space upward. A choice of wire/die bondable or solderable materials, preferably usable for both without change. Where migration is not a problem, Ag containing materials for low cost, otherwise Au containing. Compatibility with resistors, dielectrics, packaging methods and surface mounting components.
Resistors	Value range 1 - 10^7 ohms Sheet resistance range 10 - 10^6 ohms/square Temperature coefficient of resistance ±100 ppm K^{-1} Operational temperature -65 to +150°C Target tolerance ±1% Voltage coefficient of resistance 200 ppm/V mm for Rs = 10^4 ohm Printability on and compatibility with substrates, dielectrics and conductors Quantech noise: from -35 dB at Rs = 100 to +5 dB at Rs = 10^6 ohms/square
Dielectrics	Permittivity: low (10) Compatible with all types of conductors Pinhole and porosity free Compatible with resistor processing
Packaging	Both hermetic and plastic methods

Table 3.1 Resistor Series within the Investigation

Manufacturer	Resistor Series	Conductors	Members Investigated
Du Pont	1400[1]	Au, 4019 and 4119	1421 10^2 ohms sq^{-1}
			1431 10^3
			1451 10^5
			1461 10^6
	17[2]		1721 10^2
			1731 10^3
			1750 10^5
	HS 80[2]	PtAu 4596	8021 10^2
			8031 10^3
			8041 10^4
			8049 10^5*
Heraeus	R4000B[3]	PdAg C1206	R4020B 10^2
			R4030B 10^3
			R4040B 10^4
			R4050B 10^5

[1] Bismuth ruthenate based

[2] Ruthenium dioxide based

[3] Alkaline earth ruthenate based

* Blend break

Table 3.2 Dielectrics within the Investigation

Manufacturer	Dielectric	Type	Comments
Du Pont	9950	Filled	General purpose multilayer
	4032	Filled	Similar
	9429	Crystallising	Similar
Cermalloy (Heraeus)	9105HT	'True Glass'	Similar; a glass ceramic with high softening point

Table 3.3 Manufacturing Procedures

Artwork	Rubylith master (x10) reduced to x1 on glass high resolution plates
Screens	
type	presensitised Dek Direct
mesh	stainless steel at 45^{o} to squeegee travel
tension	not recorded
emulsion thickness	9, 13 or 23 micrometres
Printing Parameters	
printer	Dek 1200
squeegee speed	5 cm/sec
snap off 1 mm	
squeegee pressure	not normally recorded
substrate hold	mechanical (no vacuum)
levelling	10 minutes
drying	oven, 125^{o}C, 15 minutes
Firing Procedure	
furnace (i)	BTU 6-zone, air firing
cycle time	conductors/dielectrics : 52 minutes resistors: 54 minutes
profile	conductors/dielectrics : peak 930, 10 minutes over 900^{o}C resistors: 10 minutes at 850^{o}C
furnace (ii)	BTU 4-zone, air firing. see text for details

Table 3.4 Materials Used in 'Matrix Investigation

Resistors	Conductors	Dielectrics
Du Pont 1400 : 1431	Du Pont Au : 4019	Alumina : Kyocera, 96% A476
Du Pont Series 17 : 1730	Du Pont Au : 4019	Du Pont : 9950 (filled)
Du Pont HS80 : 1831	Du Pont PtAu : 4596	Du Pont : 4032 (blue, filled)
Heraeus R4000B : R4030B	Heraeus PdAg : C1206	Du Pont : 9429 (crystallising)

Table 3.5 Materials Used in the Comparative Study

Substrates	
Alsimag 614	
Coors ADS96	
Kyocera A476	
Narumi AT396	
Stemag+	
Coors ADS995*	
Rosenthal Rubalit 708	
Conductor	
Du Pont Pt/Au 4596	
Dielectric	
Du Pont 4032	
Resistor Materials and Nominal Sheet Resistance	
Du Pont HS 80	
8021	100 ohms sq^{-1}
8031	1000 ohms sq^{-1}
8041	10000 ohms sq^{-1}
8049	90000 ohms sq^{-1}

+No further data available

*Marketed primarily for thin film use

Table 4.1 The Effect of Film Thickness on Volume Resistivity and Sheet Resistance for Series 17 on Al_2O_3 and 9950

Resistor Material	Mean Film Thickness μm	Properties on Alumina		Properties on DP 9950		Ratio of Rs	Ratio of Rv
		Rs ohms sq^{-1}	Rv ohm m	Rs ohms sq^{-1}	Rv ohms m		
1720	9.8	146	0.0014	124	0.0014	0.85	1.01
	10.0	132	0.0012	105	0.0011	0.80	0.92
	10.9	129	0.0014	98.9	0.0011	0.77	0.79
	17.4	72.5	0.0011	58.6	0.0011	0.81	0.98
	23.5	43.9	0.0011	37.4	0.0008	0.85	0.73
1730	11.7	2220	0.026	1820	0.02	0.82	0.76
	12.5	1500	0.018	1320	0.017	0.89	0.91
	12.6	1790	0.022	1490	0.019	0.83	0.86
	21.5	710	0.014	640	0.016	0.90	1.16
	33.8	570	0.019	520	0.017	0.91	0.89
1750	12.4	180 k	2.210	77 k	0.980	0.43	0.44
	13.5	132 k	1.810	66 k	0.880	0.50	0.49
	13.6	152 k	1.970	70 k	0.970	0.46	0.49
	24.0	78 k	1.870	40 k	0.970	0.51	0.52
	30.0	48 k	1.390	26 k	0.780	0.54	0.56

(The values of sheet resistance and bulk resistivity have been corrected for considerable spreads of width beyond the nominal 1 mm, particularly noticeable in the thicker films.)

Table 4.2 The Effect of Film Thickness on Volume Resistivity and Sheet Resistance of R4000Band DP 1750 on A476 and DP 9950

All figures are corrected for actual track widths; (values of CV are given in brackets)

Resistor Material	Mean Thickness	Properties on Alumina		Properties on 9950		Ratio of Rs	Ratio of Rv
		Rs ohms sq^{-1}	Rv ohms m	Rs ohms sq^{-1}	Rv ohms m		
R4020B	4.8	282 (3)	1.35×10^{-3}	263 (3.9)	1.29×10^{-3}	0.93	0.95
	9.5	153 (3.8)	1.45×10^{-3}	146 (4.3)	1.31×10^{-3}	0.95	0.90
	10.0	128 (3.3)	1.27×10^{-3}	120 (5.8)	1.20×10^{-3}	0.94	0.94
	9.9	133 (1.6)	1.33×10^{-3}	123 (4.5)	1.21×10^{-3}	0.93	0.91
	16.8	72.6 (1.9)	1.22×10^{-3}	68 (4.7)	1.17×10^{-3}	0.94	0.96
	26.3	49.5 (1.6)	1.30×10^{-3}	49.5 (3.6)	1.29×10^{-3}	1.01	0.99
R4030B	5.0	2209 (3.7)	1.10×10^{-2}	2032 (5.4)	1.00×10^{-2}	0.92	0.92
	12.0	973 (3.3)	1.14×10^{-2}	854 (5.6)	1.05×10^{-2}	0.88	0.92
	12.5	942 (1.3)	1.16×10^{-2}	826 (4.5)	1.04×10^{-2}	0.88	0.90
	21.3	523 (3.5)	1.10×10^{-2}	515 (2.5)	1.11×10^{-2}	0.98	0.95
	29.3	397 (2.5)	1.15×10^{-2}	366 (2.6)	1.09×10^{-2}	1.00	0.95
R4040B	5.9	23.9 k (5.1)	0.143	46.5 k (10.5)	0.266	1.92	1.86
	11.4	10.8 k (3.8)	0.130	14.1 k (5.2)	0.162	1.23	1.25
	11.8	10.3 k (2.1)	0.128	13.8 k (2.8)	0.163	1.26	1.27
	12.1	9.87 k (2.6)	0.125	12.3 k (6.3)	0.148	1.18	1.19
	22.0	5.23 k (1.8)	0.121	5.77 k (1.8)	0.127	1.05	1.05
1750	6.4	411 k (7.2)	2.63	229.5 k (7.1)	1.47	0.56	0.56
	11.4	103 k (3.7)	1.18	82.4 k (3.6)	0.94	0.80	0.80
	12.4	98.4 k (3.1)	1.22	75.6 k (8.1)	0.95	0.77	0.78
	20.0	59.0 k (2.9)	1.18	32.7 k (3.3)	0.66	0.55	0.56
	30.4	39.8 k (2.3)	1.22	24.5 k (2.1)	0.75	0.62	0.61
	38.9	32.1 k (3.9)	1.25	20.5 k (3.8)	0.80	0.64	0.64

Table 4.3 DP1431

	Alumina	DP 9950	DP 4032	DP 9429
Sheet resistance (ohms sq^{-1}) (CV%)	1413 (1.7)	664 (4.7)	599 (1.5)	1699 (4.4)
Ratio to Value on Al_2O_3	1	0.47	0.43	1.19
tcr (22-122°C) ppm K^{-1}	+64	+139	+200	+93
Thermal Stability a) 5 cycles to 300°C	-0.02%	+0.04%	-	-
b) Further 5 hours at 300°C	+0.32%	+0.43%	-	-
Film Thickness (micrometres)	10.4	-	-	-

Table 4.4 DP 1730

	Alumina	DP 9950	DP 4032	DP 9429
Sheet resistance (ohms sq^{-1}) (CV%)	1372 (3.0)	1085 (4.3)	1034 (3.3)	54709 (6.7)
Ratio to Value on Al_2O_3	1	0.79	0.75	39.9
tcr (22-122°C) ppm K^{-1}	+49	+74	+33	-833
Thermal Stability a) 5 cycles to 300°C	-0.08%	+0.10%	-0.08%*	-
b) Further 5 hours at 300°C	-	-	-	+0.24%
Film Thickness (micrometres)	9.8	-	-	-

*excluding one positive change in 16 samples (+0.17% on 5th cycle only.

Table 4.5 DP 8031

	Alumina	DP 9950	DP 4032	DP 9429
Sheet resistance (ohms sq^{-1}) (CV%)	1169 (3.6)	984 (7.0)	910 (3.9)	56175 (7.9
Ratio to Value on Al_2O_3	1	0.84	0.77	48.2
tcr (22-122°C) ppm K^{-1}	+65	+121	+62	-850
Thermal Stability a) 5 cycles to 300°C	-	-	-	-
b) Further 5 hours at 300°C	-	-	-	+0.26%
Film Thickness (micrometres)	10.0	-	-	-

Table 4.6 Heraeus R4030B

	Alumina	DP 9950	DP 4032	DP 9429
Sheet resistance (ohms sq^{-1}) (CV%)	1000 (1.7)	930 (3.4)	924 (2.6)	629 (2.7)
Ratio to Value on Al_2O_3	1	0.93	0.92	0.63
tcr (22-122°C) ppm K^{-1}	+54	+99	+69	-19
Thermal Stability 5 cycles to 300°C	-0.056%*	+0.005%	+0.035%	+0.11%
Film Thickness (micrometres)	11.3	-	-	-

*excluding one positive change in 48 samples (+0.1%) on 5th cycle only.

Table 4.7 Film Thickness

Resistor Material	% Shrinkage (Talysurf 3)	Average Thickness (μm) (Alphastep 200)
DP 1431	57	10.4
DP 1730	54	9.7
DP 8031	50	10.0
R4000B	52	11.3

Table 4.8 Comparison of Sheet Resistance Values (ohms/square) of HS80 on Alumina and DP 4032 for a Range of Alumina Substrates

	HS 80 Ink Member			
	8021	8031	8041	8049
Alsimag 614	59.8	422	5.84 k	67.2 k
Rosenthal 315	56.0	428	5.62 k	66.0 k
Kyocera A-476	58.6	425	5.98 k	63.2 k
Narumi AT 396	59.2	410	5.74 k	64.5 k
Stemag	59.9	429	5.64 k	68.8 k
Coors ADS 995	59.8	433	6.00 k	69.5 k
Mean Al_2O_3	58.9	425	5.64 k	66.5 k
DP 4032 (Control surface)	59.6	381	5.11 k	29.0 k

Table 4.9 Comparative tcr Readings on a Range of Alumina Substrates

	8021	8031	8041	8049
Mean R_s (Al_2O_3) (ohms sq^{-1})	58.9	425	5637	66533
Film thickness (μm) Alphastep 200	15.2	19.2	16.0	17.9
Mean tcr (Al_2O_3) ppm K^{-1} (22 - 122°C)		+118	+132	+29
tcr (ADS 995)	+118		+135	+29
tcr (A476)	+118		+126	+33
tcr (AT396)	+112	+21	+130	+30
tcr (614)	+114		+20	+27
tcr (Stemag)	+125		+150	+22
tcr (R315)	+124		+132	+33
tcr DP 4032	+126	+113	+154	+111

Table 4.10a Tabulated Raw Analysis Data for M58A, DP 1730 on Alumina (Wt%)

Relative Distance (cm)	Al_2O_3	SiO_2	PbO	RuO_2	MnO	CuO	ZnO	Deficit	Total
0.5	11.4	25.0	34.0	8.0	2.8	0.3	1.7	17.0	100
1.0	10.6	23.0	28.5	24.0	2.7	0.3	1.7	9.2	100
1.5	11.5	25.8	34.7	13.0	3.0	0.5	2.0	9.5	100
2.0	10.5	25.4	33.1	16.5	2.8	0.3	2.0	9.4	100
2.5	10.5	24.5	31.7	19.4	3.0	0.3	1.8	8.6	100
3.0	11.4	26.4	35.7	12.8	2.9	0.5	1.9	8.4	100
4.0	10.6	23.8	33.4	17.8	2.8	0.7	2.2	8.3	100
5.0	11.4	25.8	36.3	9.5	2.9	0.3	2.0	11.8	100
6.0	11.7	25.3	36.1	11.5	3.2	0.3	1.8	10.1	100
7.0	12.0	23.6	36.5	9.4	3.3	0.2	2.3	12.7	100
7.5	12.8	25.5	37.0	4.2	3.6	0.5	2.0	14.4	100
8.0	12.7	24.2	38.5	4.3	3.5	0.5	2.1	14.2	100
8.5	13.0	23.6	35.0	5.0	3.3	0.4	2.3	17.4	100
9.0	23.5	21.3	28.0	3.6	2.3	0.3	1.8	19.2	100
9.5	63.0	12.9	14.2	0.1	1.2	0.1	0.8	8.5	100
10.0	93.5	1.5	0.4	0	0	0	0.2	4.4	100

The only change made from the printed data is a calibration of the alumina figure by a constant factor of 0.86.

Table 4.10b Tabulated Raw Analysis Data, M99D, for DP 9950 on Alumina (Wt%)

Relative Distance (cm)	Al_2O_3	SiO_2	PbO	K_2O	CaO	ZrO_2	TiO_2	Deficit	Total
0.5	13.2	28.2	6.5	0.6	9.5	13.0	0.2	28.8	100
1.0	13.1	42.0	14.3	1.5	9.2	6.8	0.2	12.9	100
1.5	16.9	42.2	10.5	1.1	8.7	12.2	0.3	8.1	100
2.0	17.5	42.7	9.2	0.8	10.6	16.1	0.2	2.9	100
2.5	18.9	41.7	9.8	0.7	9.8	14.8	0.2	4.1	100
3.0	28.0	44.5	7.1	0.7	9.4	9.7	0.2	0.4	100
4.0	14.3	42.1	14.0	0.8	11.6	10.6	0.5	6.1	100
5.0	12.9	37.5	12.0	1.1	9.7	27.2	0.5	-0.9	100
6.0	16.9	40.5	9.8	1.0	9.5	10.6	0.2	11.5	100
7.0	14.5	38.9	9.2	1.0	9.6	5.4	0.2	21.2	100
7.5	19.1	42.0	6.7	0.6	10.7	11.5	0.1	9.3	100
8.0	15.7	38.6	10.2	0.7	11.7	13.6	0.2	9.5	100
8.5	15.4	33.6	6.7	0.4	11.6	21.7	0.2	9.4	100
9.0	18.0	39.5	6.8	0.6	11.9	12.3	0.2	11.6	100
9.5	18.3	39.8	5.3	0.6	12.2	11.6	0.2	12.0	100
10.0	22.8	39.7	7.1	0.6	1.6	10.0	0.3	10.9	100

The calibration factor of 0.86 has again been applied to the alumina figures from the raw data.

Table 4.10a Tabulated Raw Analysis Data for M58A, DP 1730 on Alumina (Wt%)

Relative Distance (cm)	Al_2O_3	SiO_2	PbO	RuO_2	MnO	CuO	ZnO	Deficit	Total
0.5	11.4	25.0	34.0	8.0	2.8	0.3	1.7	17.0	100
1.0	10.6	23.0	28.5	24.0	2.7	0.3	1.7	9.2	100
1.5	11.5	25.8	34.7	13.0	3.0	0.5	2.0	9.5	100
2.0	10.5	25.4	33.1	16.5	2.8	0.3	2.0	9.4	100
2.5	10.5	24.5	31.7	19.4	3.0	0.3	1.8	8.6	100
3.0	11.4	26.4	35.7	12.8	2.9	0.5	1.9	8.4	100
4.0	10.6	23.8	33.4	17.8	2.8	0.7	2.2	8.3	100
5.0	11.4	25.8	36.3	9.5	2.9	0.3	2.0	11.8	100
6.0	11.7	25.3	36.1	11.5	3.2	0.3	1.8	10.1	100
7.0	12.0	23.6	36.5	9.4	3.3	0.2	2.3	12.7	100
7.5	12.8	25.5	37.0	4.2	3.6	0.5	2.0	14.4	100
8.0	12.7	24.2	38.5	4.3	3.5	0.5	2.1	14.2	100
8.5	13.0	23.6	35.0	5.0	3.3	0.4	2.3	17.4	100
9.0	23.5	21.3	28.0	3.6	2.3	0.3	1.8	19.2	100
9.5	63.0	12.9	14.2	0.1	1.2	0.1	0.8	8.5	100
10.0	93.5	1.5	0.4	0	0	0	0.2	4.4	100

The only change made from the printed data is a calibration of the alumina figure by a constant factor of 0.86.

Table 4.10b Tabulated Raw Analysis Data, M99D, for DP 9950 on Alumina (Wt%)

Relative Distance (cm)	Al_2O_3	SiO_2	PbO	K_2O	CaO	ZrO_2	TiO_2	Deficit	Total
0.5	13.2	28.2	6.5	0.6	9.5	13.0	0.2	28.8	100
1.0	13.1	42.0	14.3	1.5	9.2	6.8	0.2	12.9	100
1.5	16.9	42.2	10.5	1.1	8.7	12.2	0.3	8.1	100
2.0	17.5	42.7	9.2	0.8	10.6	16.1	0.2	2.9	100
2.5	18.9	41.7	9.8	0.7	9.8	14.8	0.2	4.1	100
3.0	28.0	44.5	7.1	0.7	9.4	9.7	0.2	0.4	100
4.0	14.3	42.1	14.0	0.8	11.6	10.6	0.5	6.1	100
5.0	12.9	37.5	12.0	1.1	9.7	27.2	0.5	-0.9	100
6.0	16.9	40.5	9.8	1.0	9.5	10.6	0.2	11.5	100
7.0	14.5	38.9	9.2	1.0	9.6	5.4	0.2	21.2	100
7.5	19.1	42.0	6.7	0.6	10.7	11.5	0.1	9.3	100
8.0	15.7	38.6	10.2	0.7	11.7	13.6	0.2	9.5	100
8.5	15.4	33.6	6.7	0.4	11.6	21.7	0.2	9.4	100
9.0	18.0	39.5	6.8	0.6	11.9	12.3	0.2	11.6	100
9.5	18.3	39.8	5.3	0.6	12.2	11.6	0.2	12.0	100
10.0	22.8	39.7	7.1	0.6	1.6	10.0	0.3	10.9	100

The calibration factor of 0.86 has again been applied to the alumina figures from the raw data.

Table 5.1 Normalised Chemical Analyses of Heraeus R4030B and DP HS 8031

Constituents	R4030B Paste	HS 8031 Paste
% Conducting phase (as RuO_2)	15	12.5
% Glassy phase	85	87.5
Glass content %		
PbO	30	49.0
SiO_2	30	24.0
Al_2O_3	9	7.0
B_2O_3	5	13.0
MnO	3	4.0
ZnO	-	-
CuO	-	1.0
SnO	4	-
Nb_2O_5	-	1.0
Bi_2O_3	Tr	-
BaO	15	-
CaO	4	-

Tr trace, - not detected

Table 5.2 Estimated Composition of DP 1431 by Chemical Analysis

Constituents	Wt%
Bi_2O_3	15.6*
RuO_2	8.6*
PbO	38.1
SiO_2	21.2
Al_2O_3	1.0
CdO	0.9
Pt	0.1
Ignition Loss	5.1
Total	90.6

Ratio Bi_2O_3: RuO_2 1.82 : 1

MgO, CuO and B_2O_3 were all detected qualitatively only

Table 5.3 Normalised Chemical Analyses of DP 9950 and 9429 (Bendix) Compared with Chemical Analyses at STL

Constituent	9429 Bendix	9429 STL	9950 Bendix	9950 STL
BaO	23.0	26.0	-	-
PbO	-	-	12.5	11.0
SiO_2	34.0	30.0	45.0	39.0
B_2O_3	3.0	5.0	2.0	11.0*
CaO	5.0	5.0	16.0	12.0
Al_2O_3	8.0	10.0	19.0	16.0
MgO	1.0	2.0	0	1.0
TiO_2	15.0	10.0	6.0	1.0
ZnO	9.0	11.0	-	-
ZrO_2	Tr	-	-	11.0
Ta_2O_5	1.0	-	-	-

Tr trace, - not detected *by difference

Table 5.4 Acceptable Resistor Parameters on a Dielectric

Parameter	Acceptable Limits
R_s	Alumina value ±50% (Value reproducible by ±20%)
tcr	±100 ppm unless alumina values are outside this
200 hours: 85°C, 85% RH	2% max or not greater than twice change on alumina
5 off load cycles to 300°C	Not greater than ±0.25%
1000 hours on load 125°C	Not greater than 1%
Noise	Not greater than on alumina
Aspect ratio effects	Not greater than on alumina

Table 5.5 Composite Behaviour of DP 1400 Series on Alumina and DP 9950

A = alumina D = dielectric

Parameter	Surface	1421	1431	1441	1451	1461
R_s (ohms/sq)	A	76	840	7010	148 k	1.03 M
	D	74	590	5100	64 k	0.55 M
Parameter 'D'		0.97	0.70	0.73	0.43	0.53
Hot tcr (ppm K^{-1})	A	+1180	+64	+80	+55	+80
	D	-240	+140	+90	+110	+150
200 hrs 85°C/85% RH	A	+1.35%	+0.04%	+0.09%	-	-
	D	+1.62%	+0.17%	+0.13%	-	-
Thermal cycling	A				-	-
(300°C)	D				-	-
Noise (dB)	A	-22	-21	-12	-	-
	D	-18.5	-22.5	-14	-	-

Table 5.6 Composite Behaviour of DP Series 17 on Alumina and DP 9950

Parameter	Surface	1720	1730	1750
R_s (ohms/sq)	A	130	1372	110 k
	D	108	1085	55 k
Parameter 'D'		0.83	0.79	0.5
Hot tcr (ppm K^{-1})	A	+140	+49	+56
	D	+180	+74	+102
Thermal cycling	A	-	+0.08%	-
(300°C)	D	-	-0.10%	-

Table 5.7 Composite Behaviour of DP HS 80 Series on Alumina and DP 4032

Parameter	Surface	8021	8031	8041	8049
R_s (ohms/sq)	A	59	425	5600	67 k
240°C, 24 hours	A	-	+0.01%	-	-
Parameter 'D'		1	0.9	0.9	0.4
Hot tcr (ppm K^{-1})	A	+120	+20	+130	+30
	D	+126	+113	+150	+110

Table 5.8 Composite Behaviour of Heraeus R4000B Resistors on Alumina and DP 9950

Parameter	Surface	R4020B	R4030B	R4040B	R4050B
R_s (ohms/sq)	A	122	1000	9900	110 k
	D	114	940	11800	480 k
Parameter 'D'		0.94	0.94	1.2	4.4
Hot tcr (ppm K^{-1})	A	-	+54	-	-26
	D	-	+99	-	-32
Thermal cycling	A	-	-0.06%	-	-
	D	-	+0.005%	-	-

Table 6.1 Constituents of Thick Film Resistor Pastes

Conducting Phase	Glass Phase	Property Modifier
Ruthenium Dioxide	Lead Oxide	Zinc Oxide
Bismuth Ruthenate[a]	Silicon Dioxide	Copper Oxide
Lead Ruthenate[a]	Boron Oxide	Cadmium Oxide
Calcium Ruthenate	Calcium Oxide[b]	Manganese Dioxide
Barium Ruthenate	Barium Oxide[b]	Titania
Palladium	Alumina[c]	Tin Oxide
Palladium Oxide		
Silver		
Platinum		

a: pyrochlore structures
b: these may be used in the paste in the form of a ruthenate which dissociates into the oxides on firing.
c: in some cases the film alumina content is very much higher than that of the paste due to solution from the alumina substrate during firing. This change is notably less on most of the dielectrics studied here.

Table 6.2 Constituents of Thick Film Dielectrics

Glass Phase	Crystalline Additives
Lead Oxide	Alumina
Boron Oxide	Zirconia
Silicon Dioxide	Titania
Calcium Oxide	
Barium Oxide	
Zinc Oxide	
Cobalt Oxide[a]	
Potassium Oxide	

a: coloured pigment, others are also used as traces to give permanent colours to dielectrics.

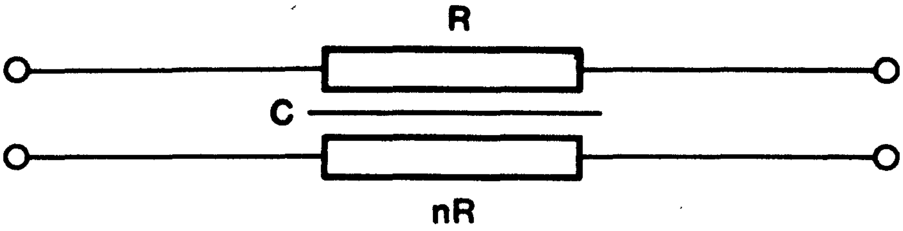


Fig.1.1 Fully distributed R CnR filter

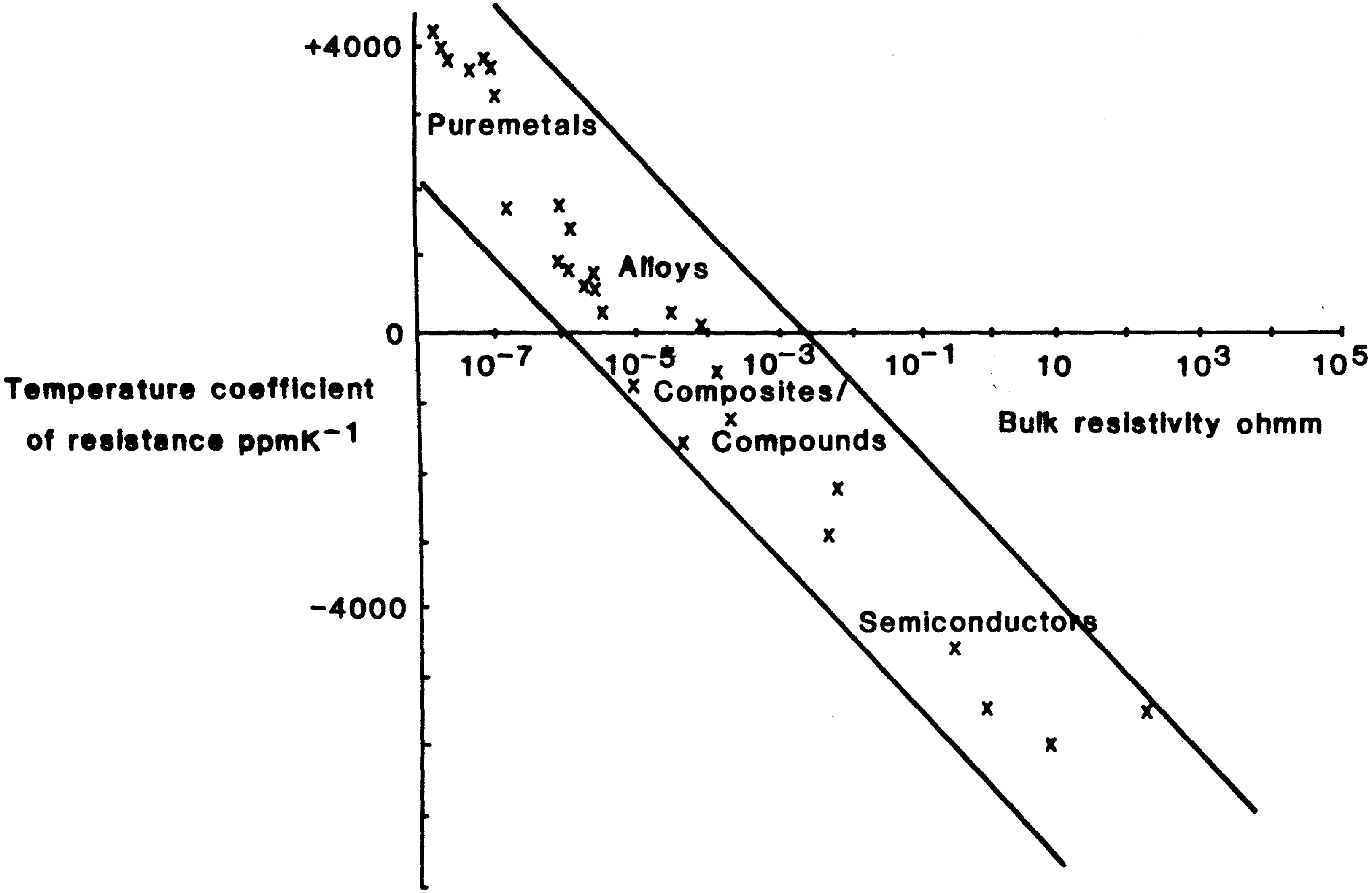


Fig.2.1 TCR and resistivity (after Watkins 1971)

AW7639-2

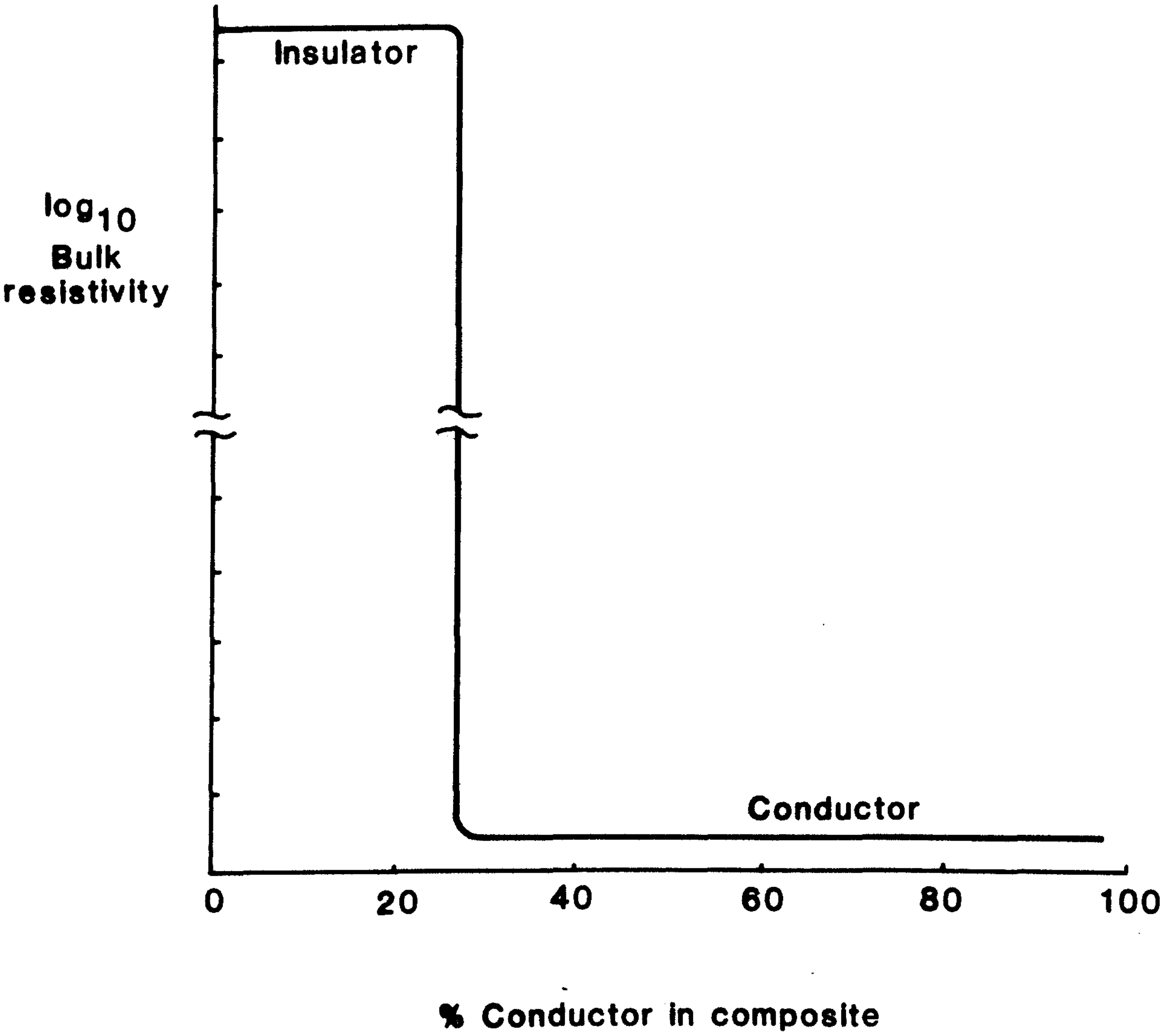


Fig.2.2 Schematic variation of resistivity with composition for a non-interactive composite (After Watkins 1971)

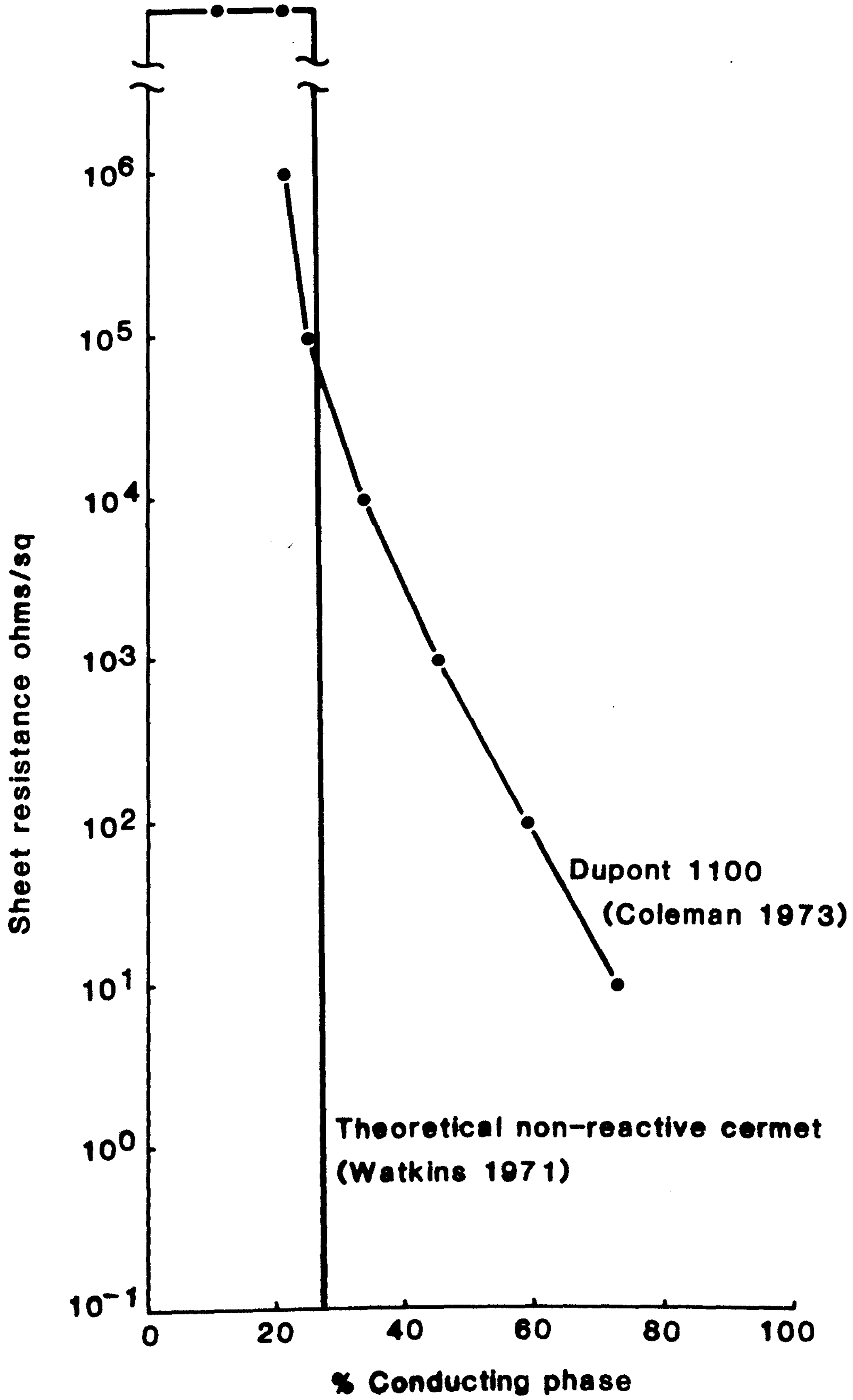


Fig. 2.3 Reactive and nonreactive cermets

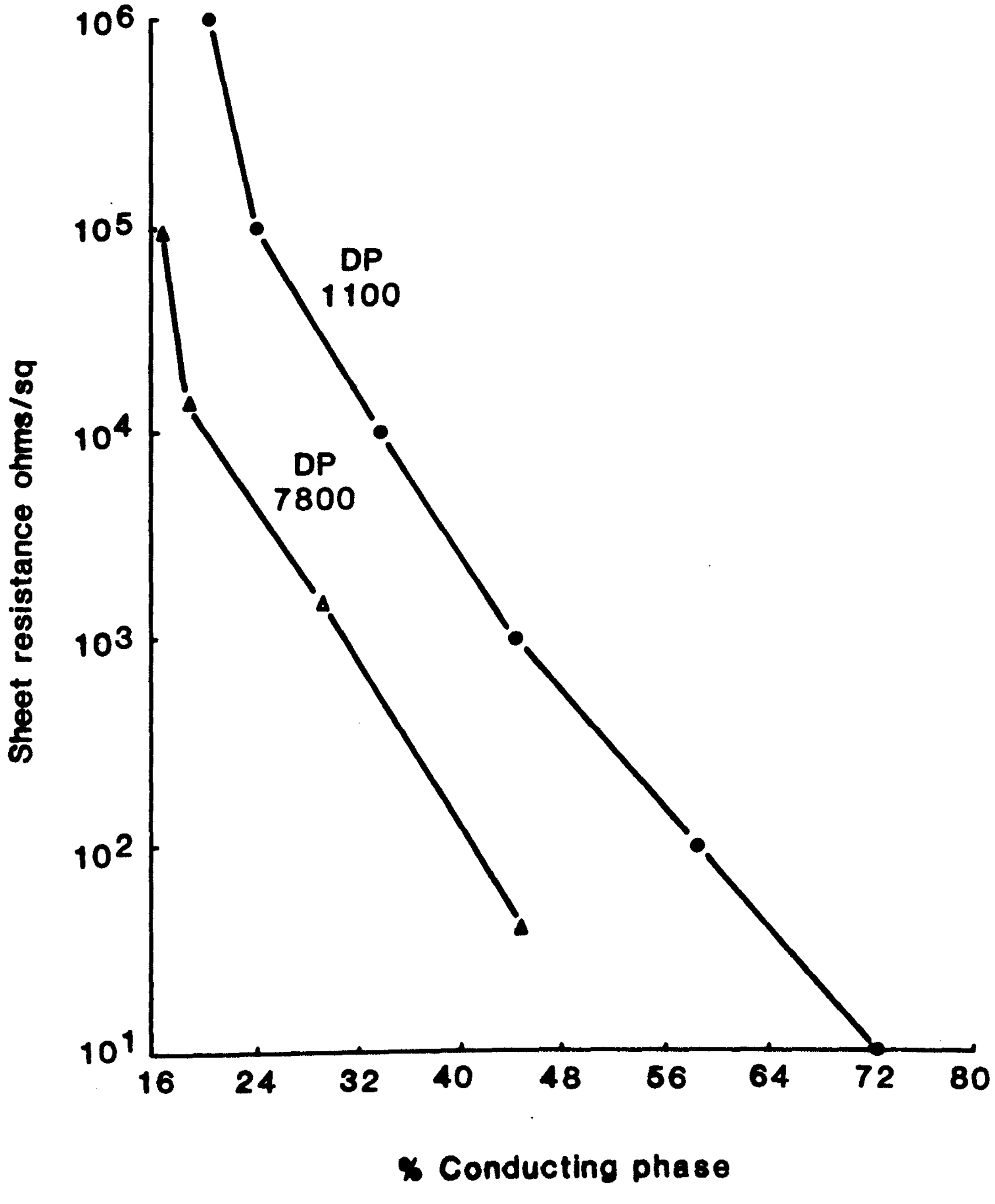


Fig. 2.4 % Composition Dupont 7800 and 1100 glazes

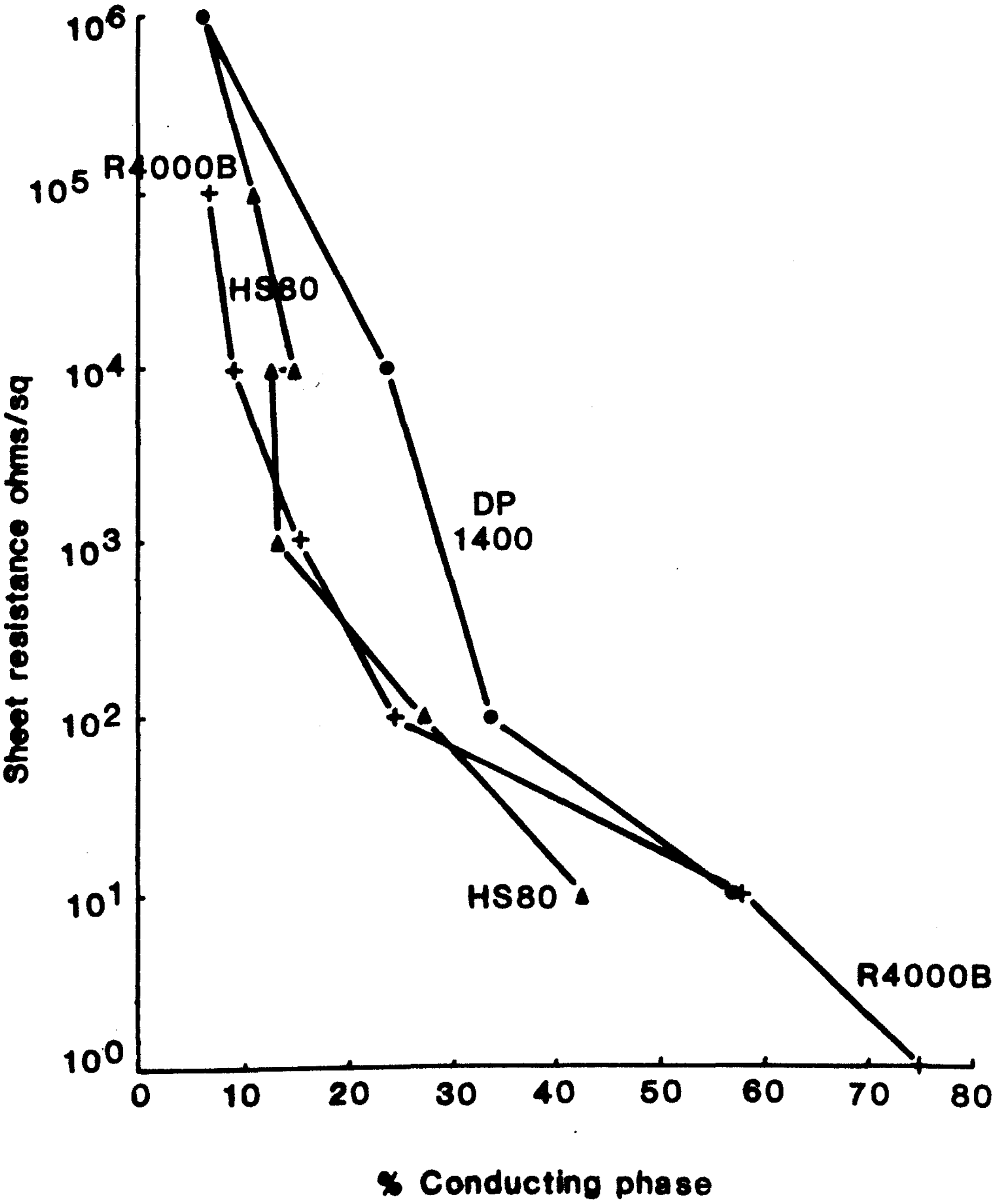


Fig. 2.5 % Composition DP1400, HS80 and R4000B

a) Design A: 2in x 2in x 0.025in
Test pattern without dielectric

b) Design A: 2in x 2in x 0.025in
Test pattern with dielectric
and underlying conductors

c) Design B: 0.5in x 1in x 0.025in
Test pattern with dielectric
covering left half of substrate

d) Design C: 1in x 1in x 0.025in
Test pattern with dielectric
covering lower half of
substrate

Fig.3.1 Test pattern designs

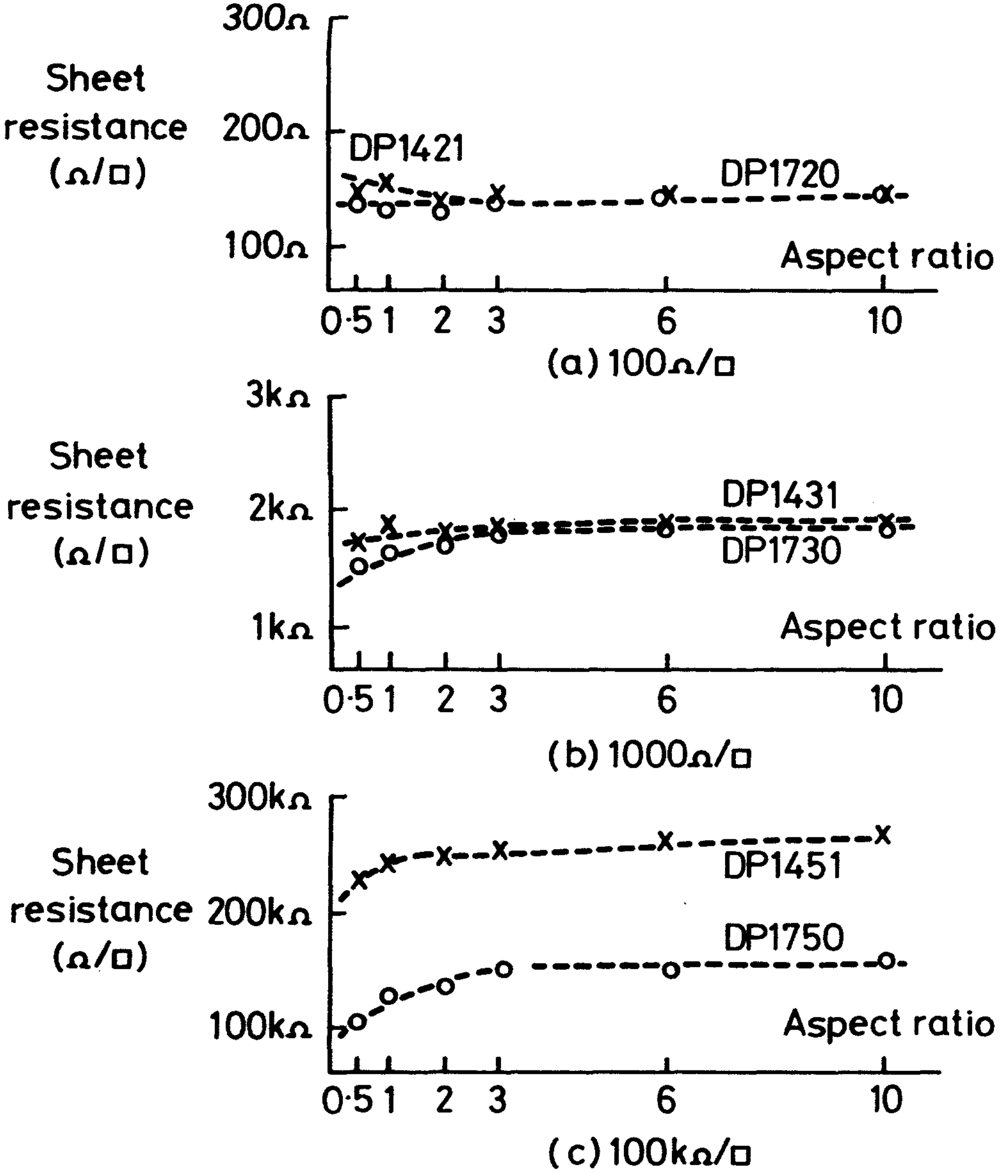
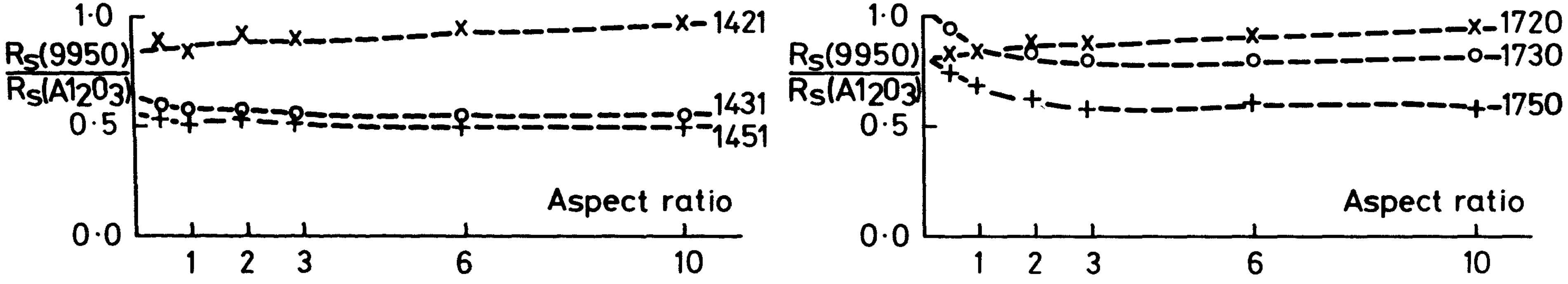


Fig. 4.1 Variation of sheet resistance with aspect ratio: Du Pont 1400 and Series 17 resistors on Kyocera A476 substrates

AW 5845-1

AW 5845 1



(a) Du Pont 1400

(b) Du Pont Series 17

Fig.4.2 Variation in ratio of sheet resistance of DuPont 1400 and Series 17 resistors on Du Pont 9950 dielectric to that on Kyocera A476 substrates

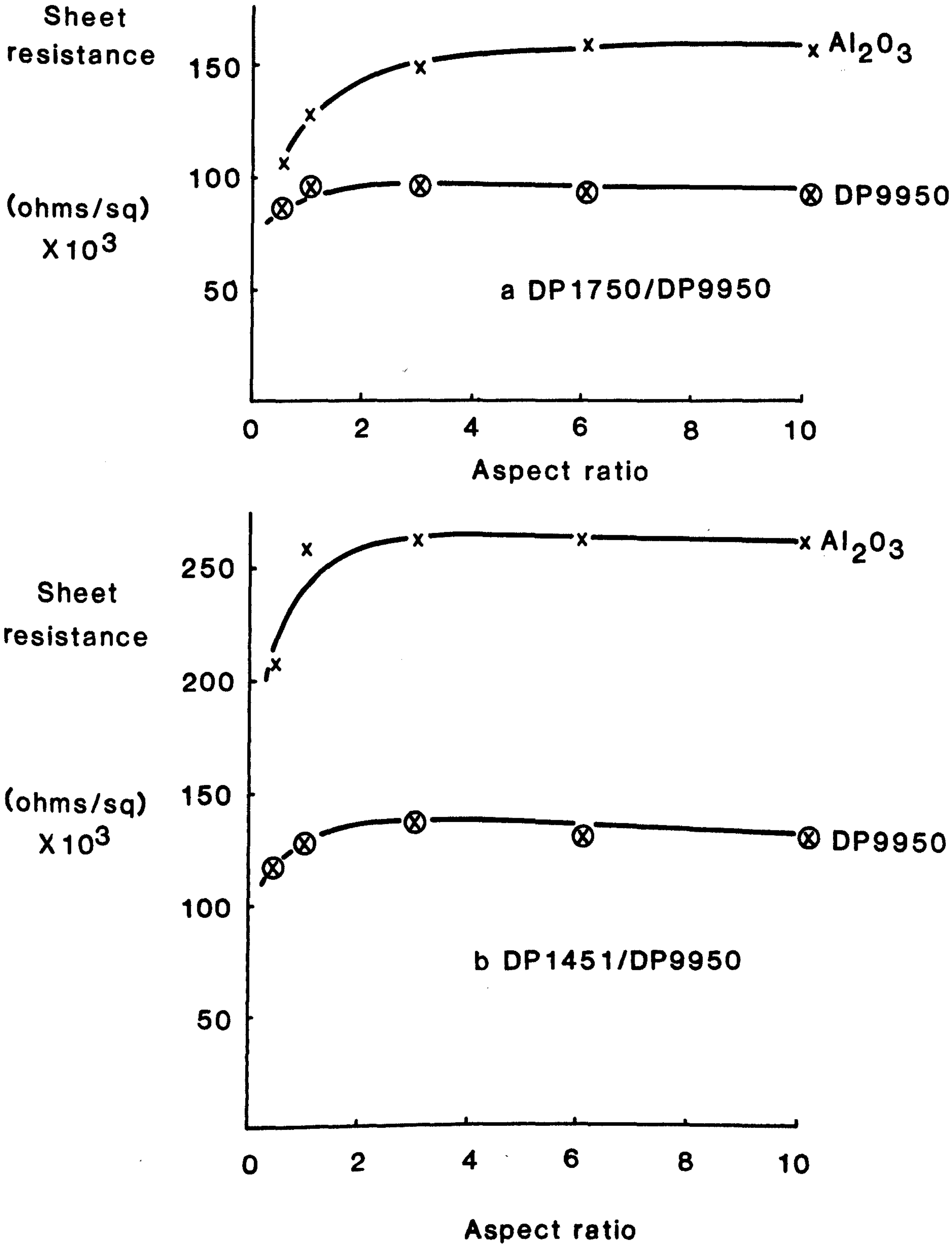


Fig.4.3 Sheet resistance as a function of aspect ratio for DP1451 and DP1750 on DP9950 and Al_2O_3

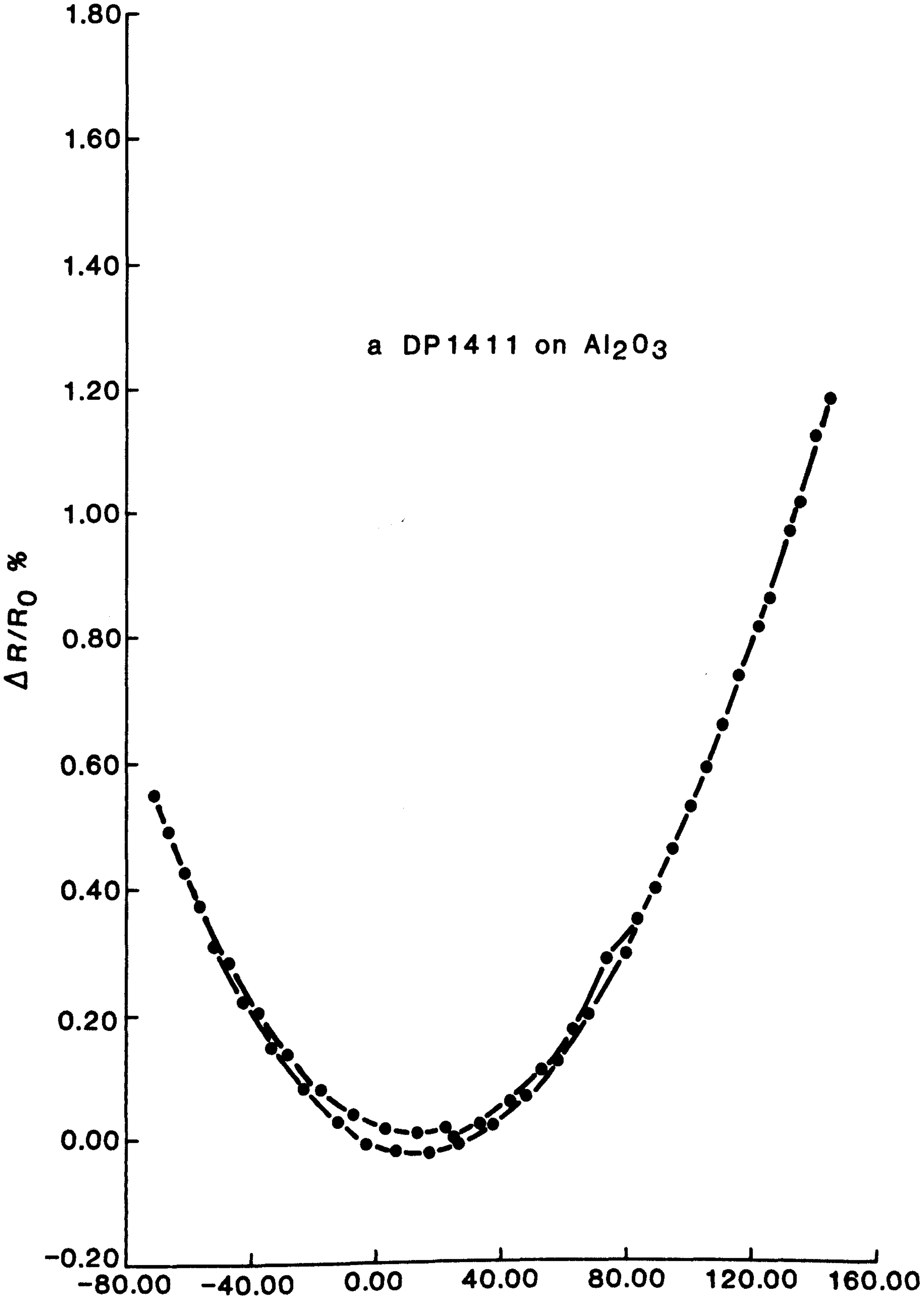


Fig. 4.4a Change in resistance value as a function of temperature. [After Coleman]

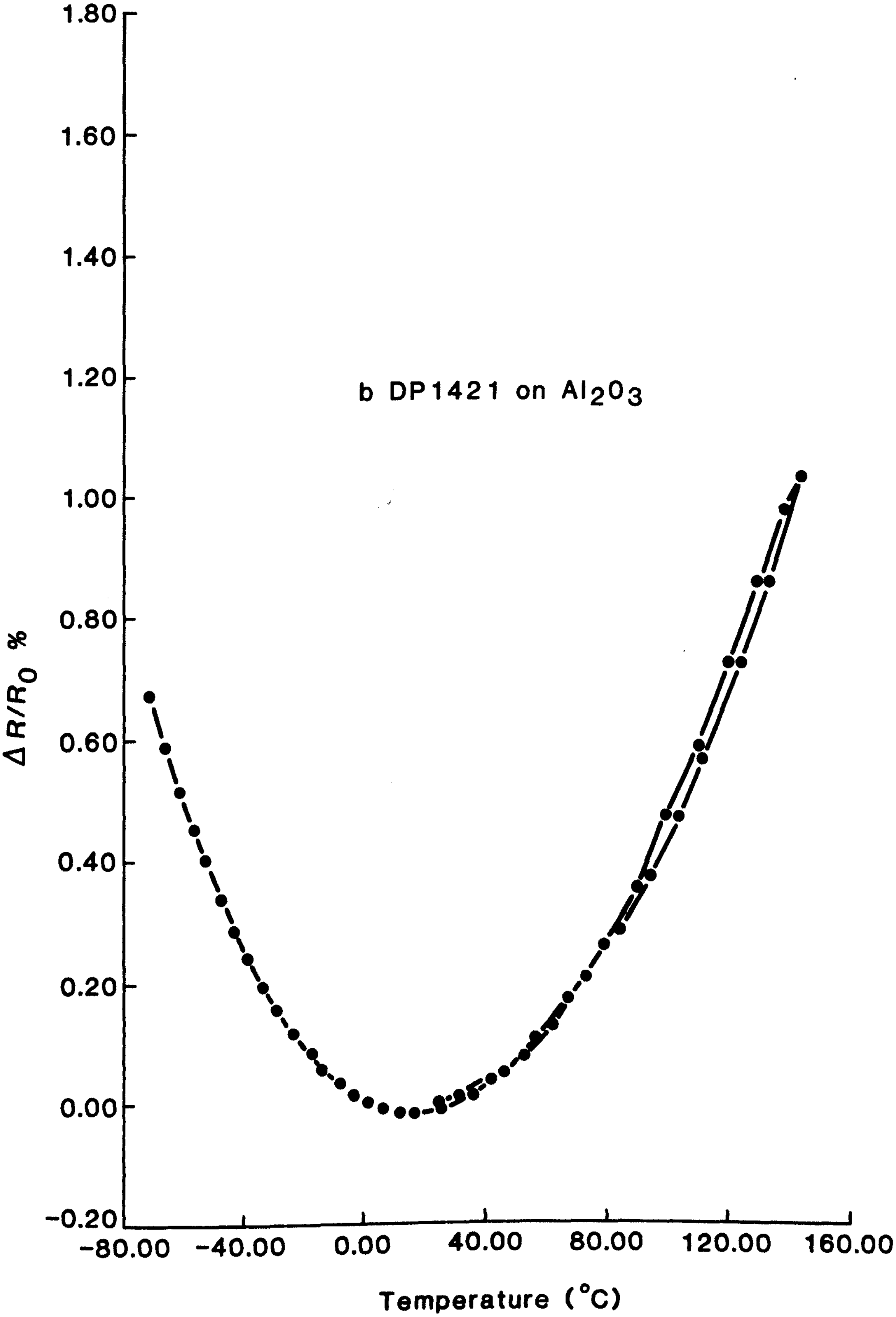


Fig.4.4b Change in resistance value as a function of temperature. [After Coleman]

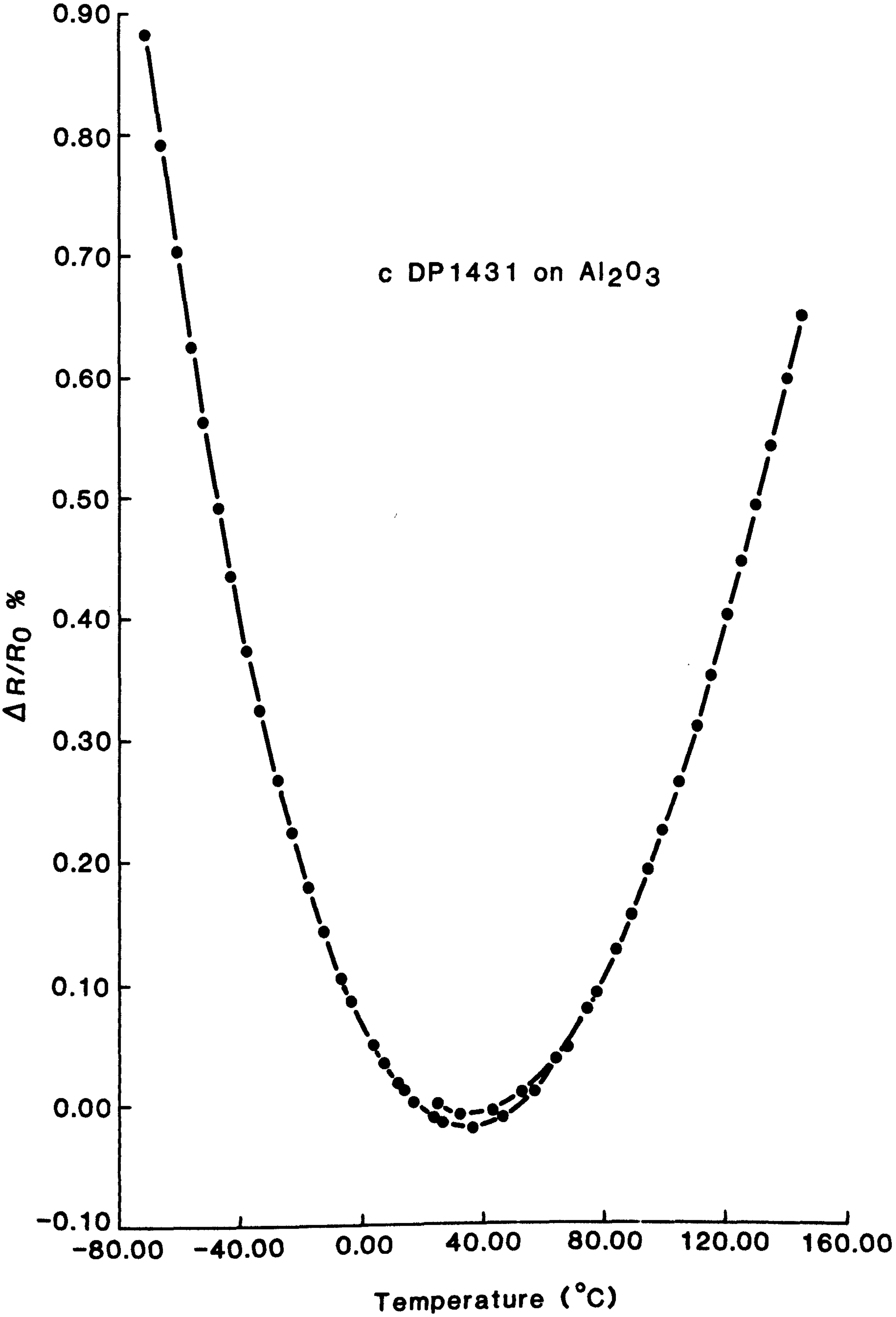


Fig.4.4c Change in resistance value as a function of temperature. [After Coleman]

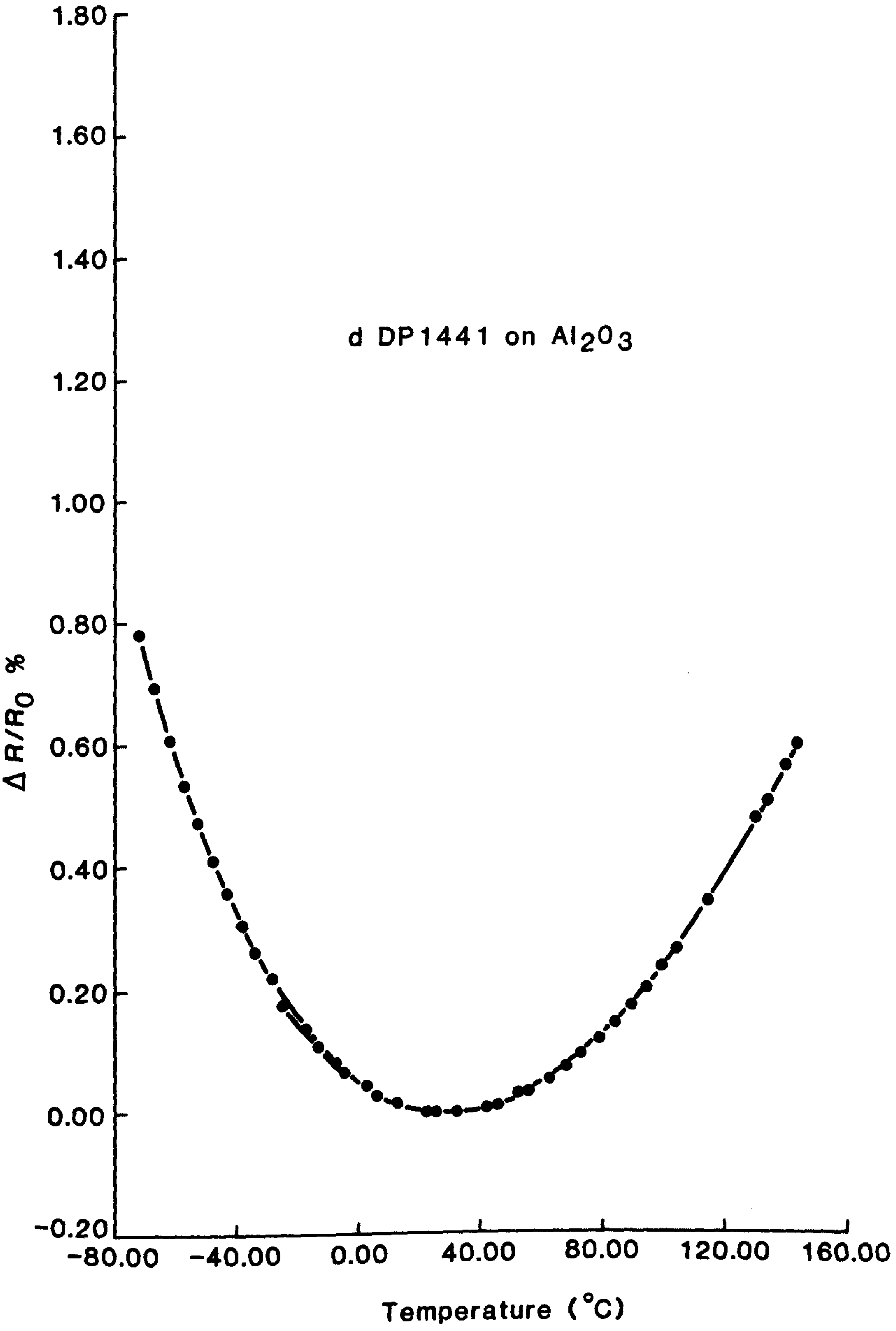


Fig. 4.4d Change in resistance value as a function of temperature. [After Coleman]

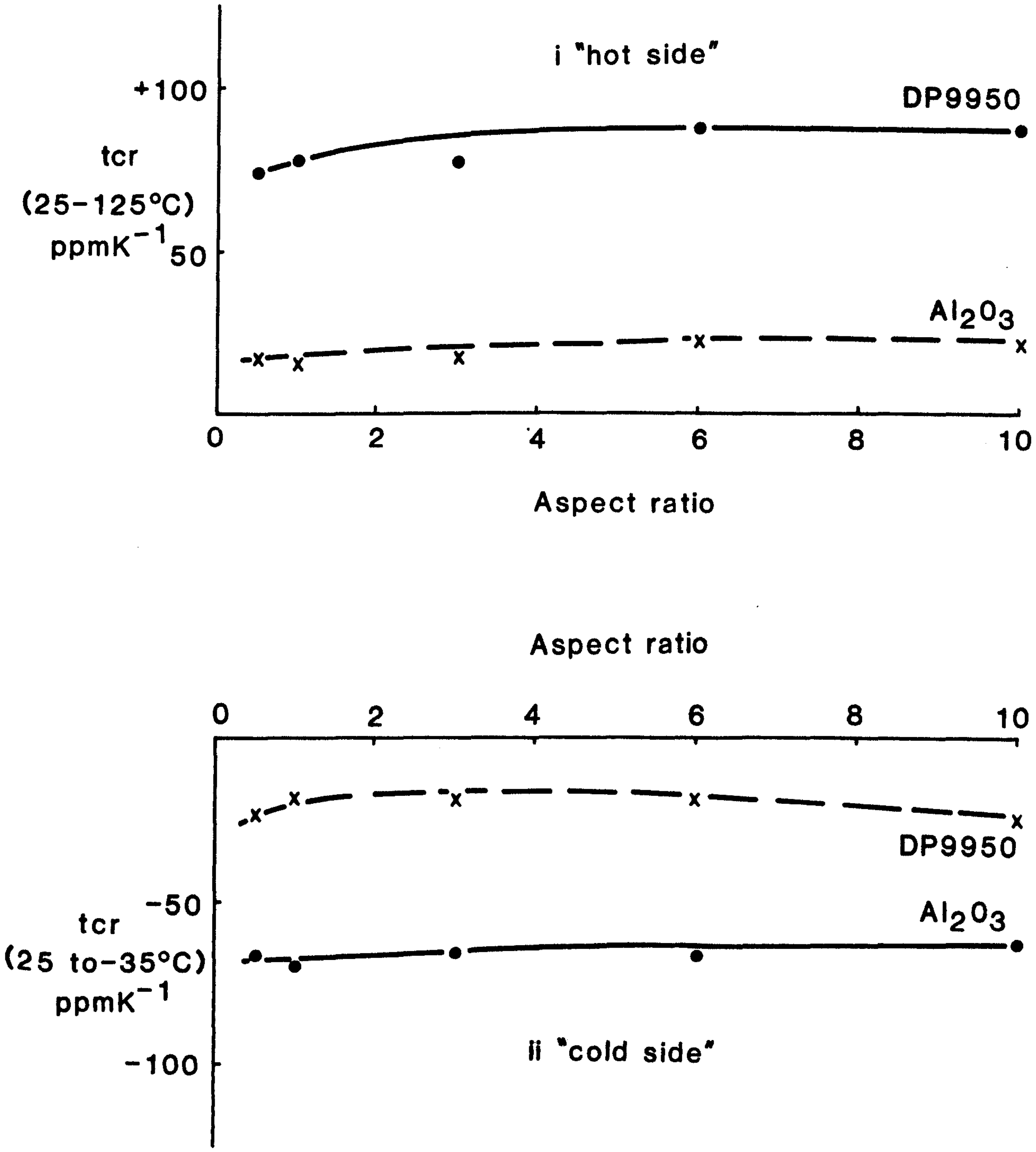


Fig. 4.5a tcr as a function of aspect ratio for DP1451 on DP9950 and Al$_2$O$_3$

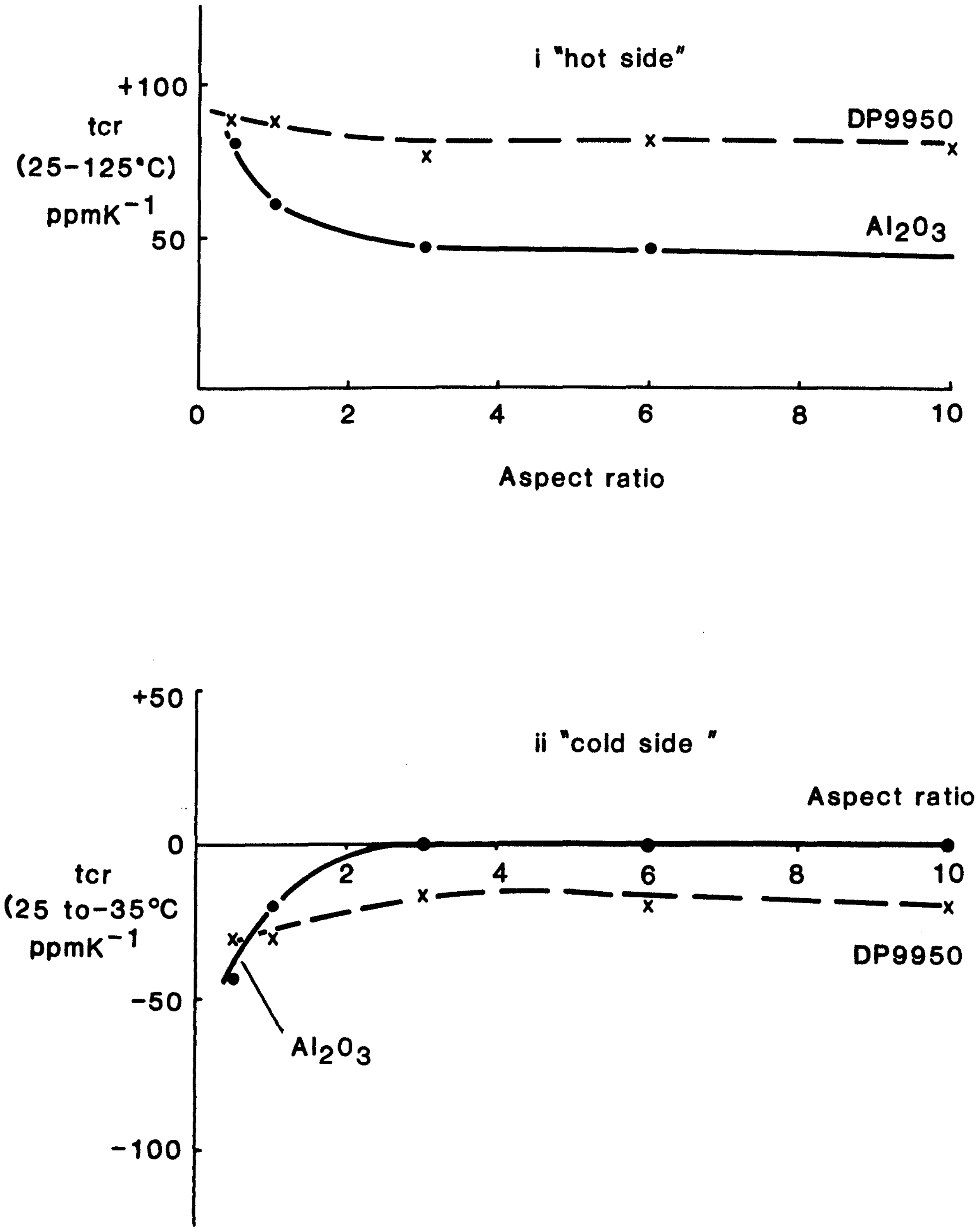


Fig.4.5b tcr as a function of aspect ratio for DP1750 on DP9950 and Al_2O_3

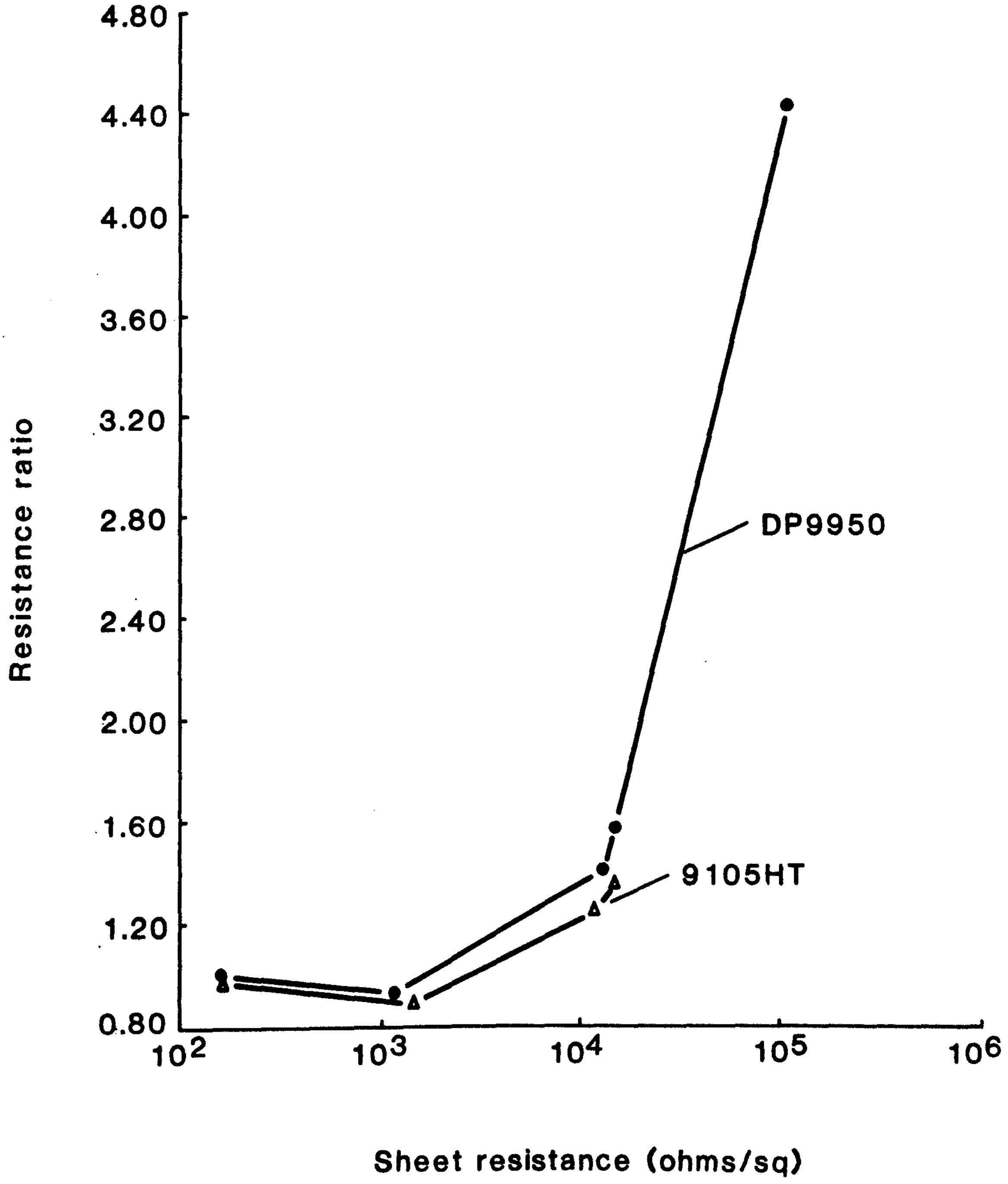


Fig. 4.6 The ratio of the resistance of R4000B on dielectric to alumina as a function of Rs for DP9950 and 9105HT

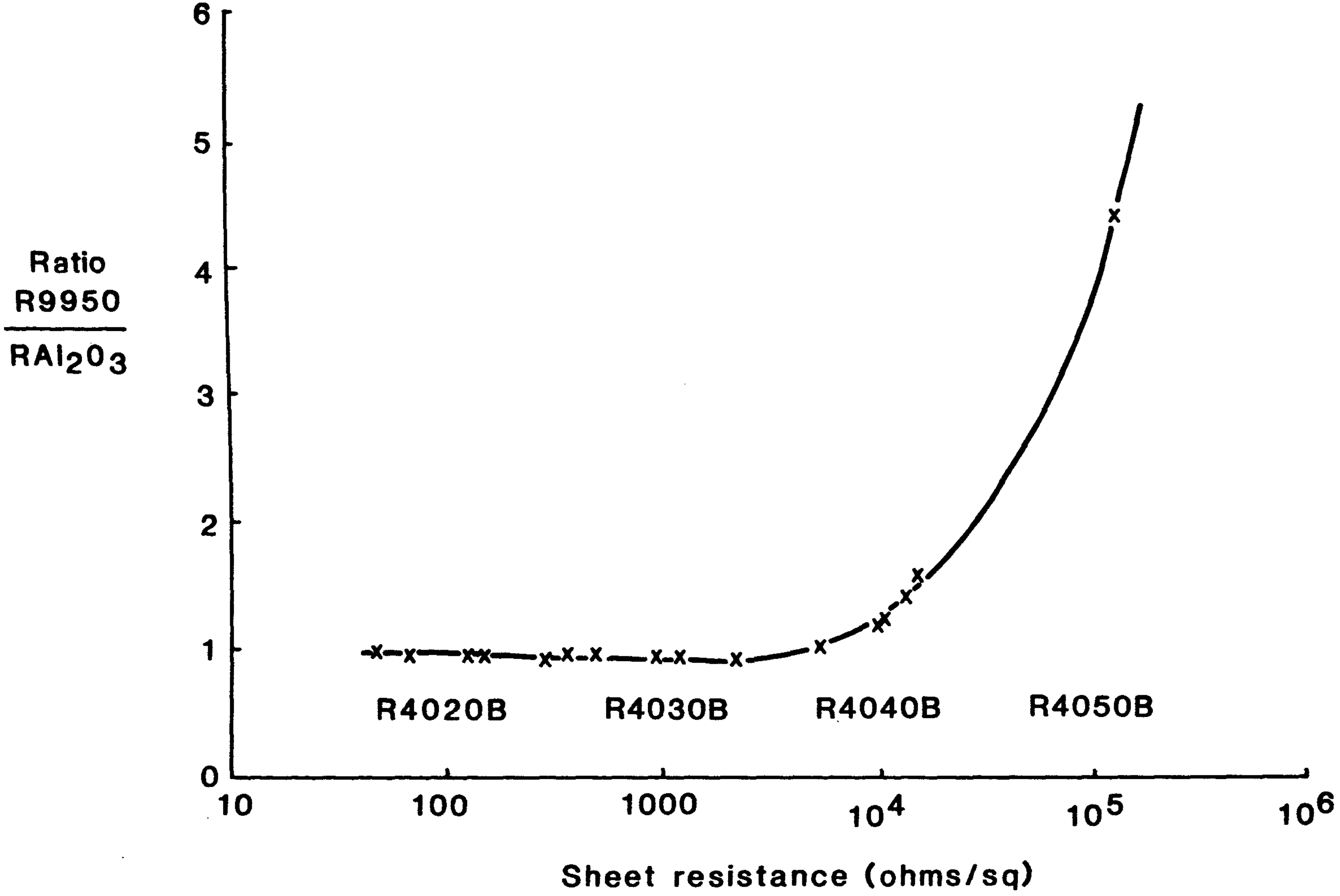
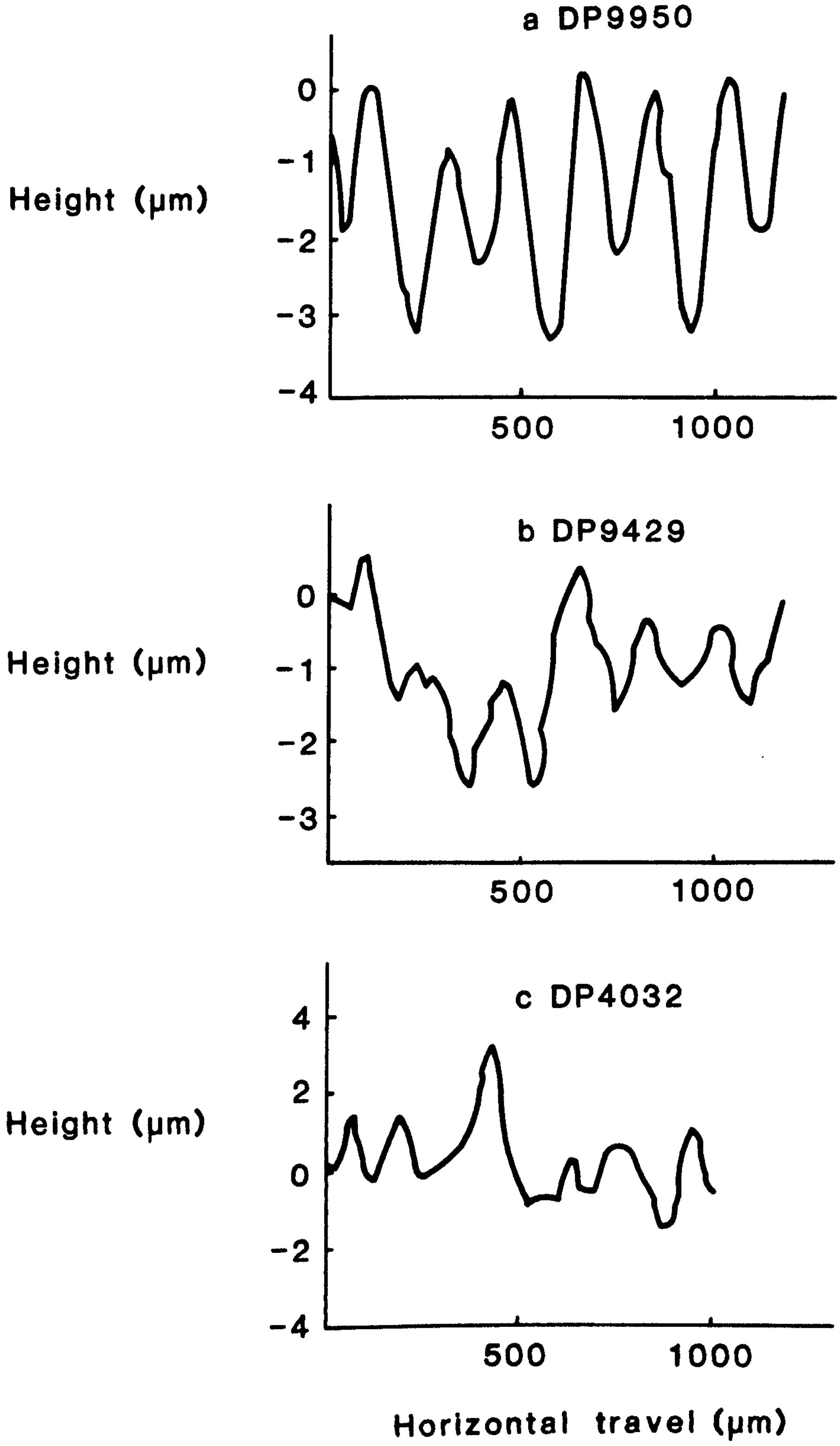


Fig.4.7 Value of ratio D as a function of Rs for R4000B series on 9950 (all samples)



ig. 4.8 Surface traces transcribed from Alphastep 200 prints (All surfaces fired onto Kyocera A476 alumina unless stated otherwise)

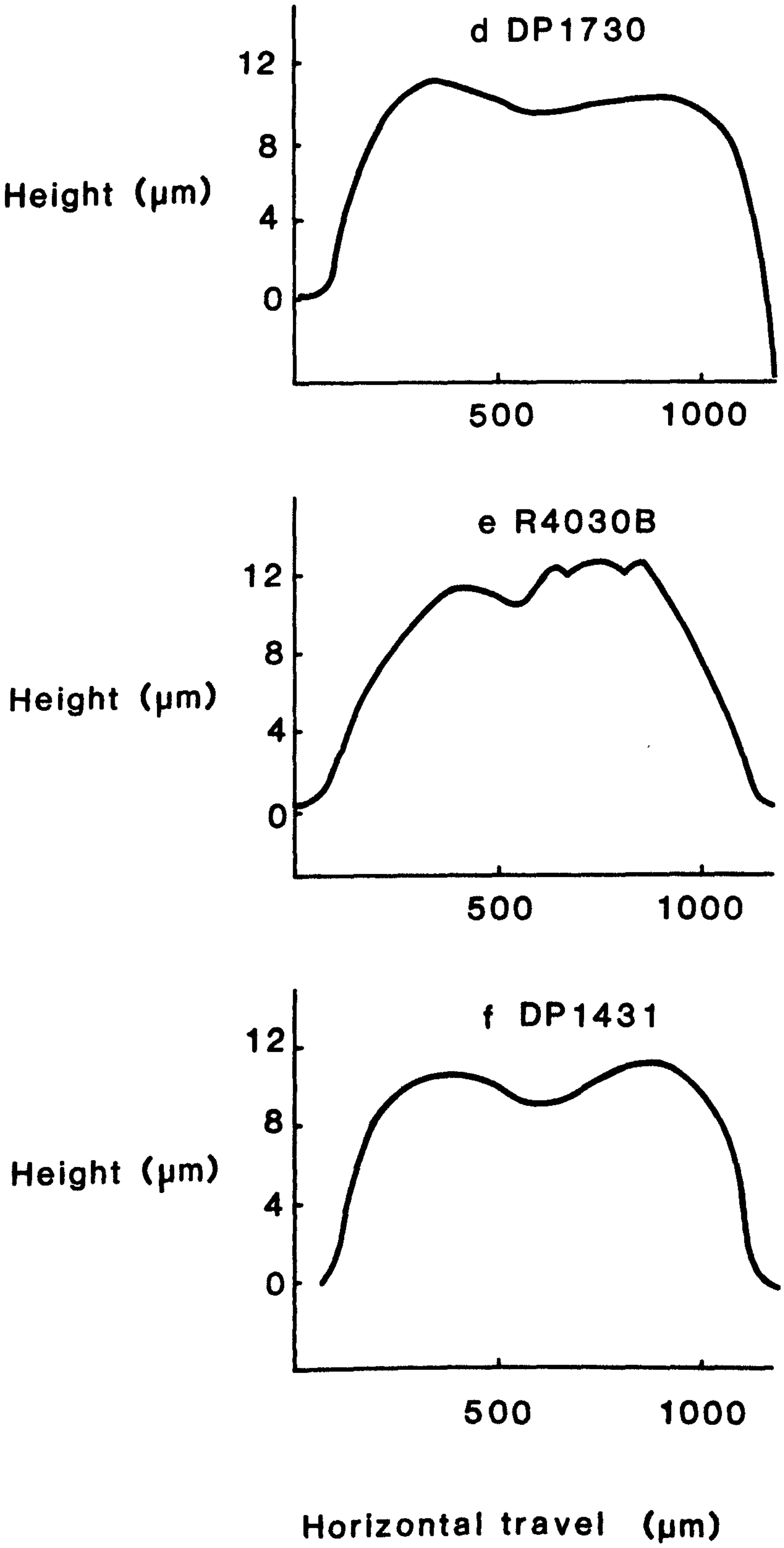


Fig.4.8 Surface traces transcribed from Alphastep 200 prints (All surfaces fired onto Kyocera A476 alumina unless stated otherwise)

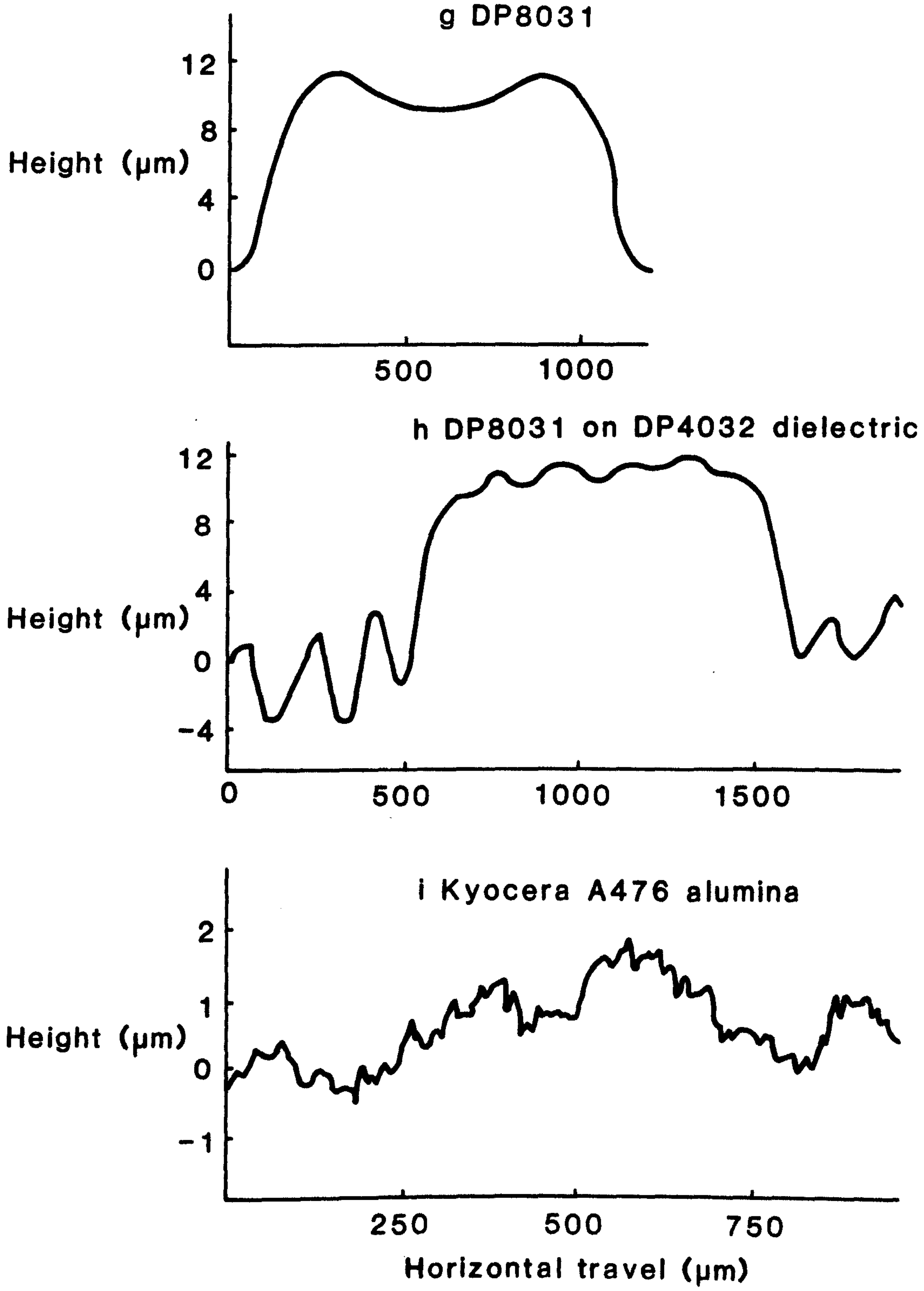
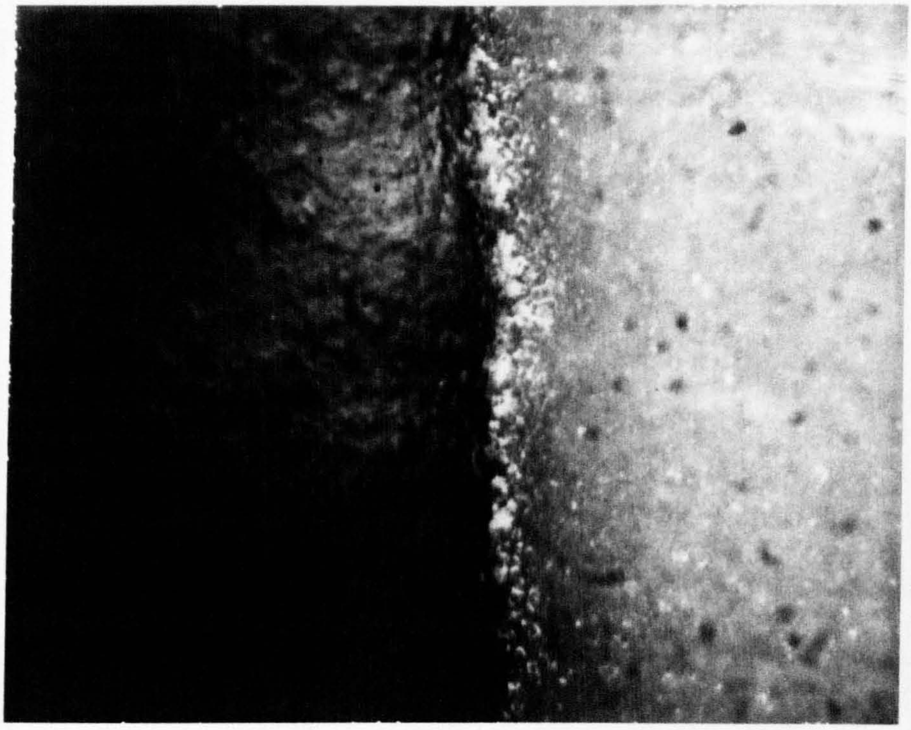
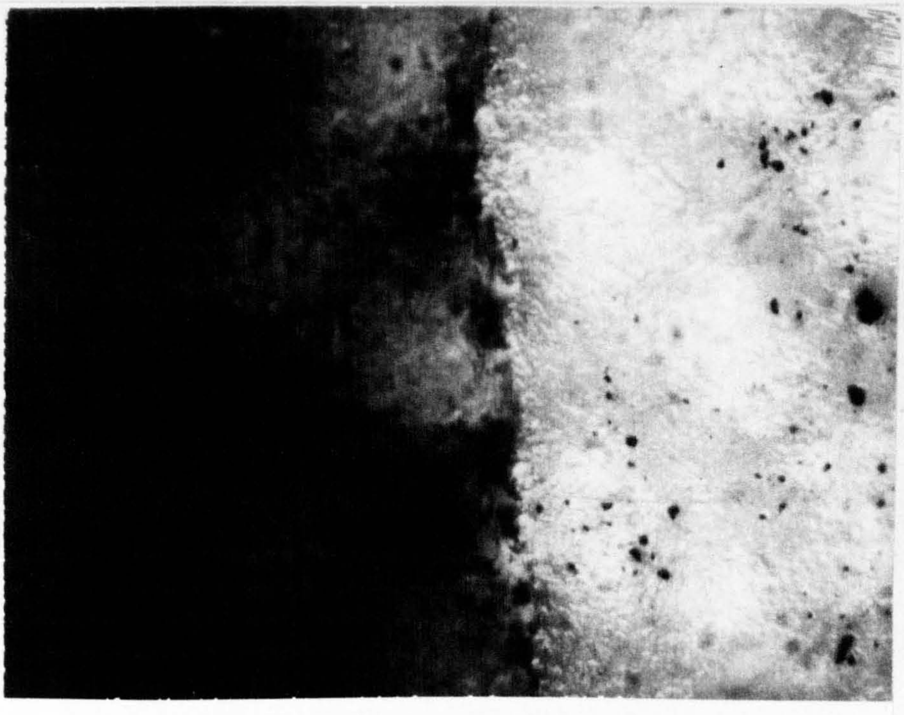


Fig.4.8 Surface traces transcribed from Alphastep 200 prints (All surfaces fired onto Kyocera A476 alumina unless stated otherwise)



(a) DuPont 1750 on Kyocera A476 (x 125)



(b) DuPont 1750 on DP9950 dielectric (x 125)

Fig.4.9 Optical micrographs of DuPont 1750 resistors indicating bleed-out of glass binder on alumina substrate

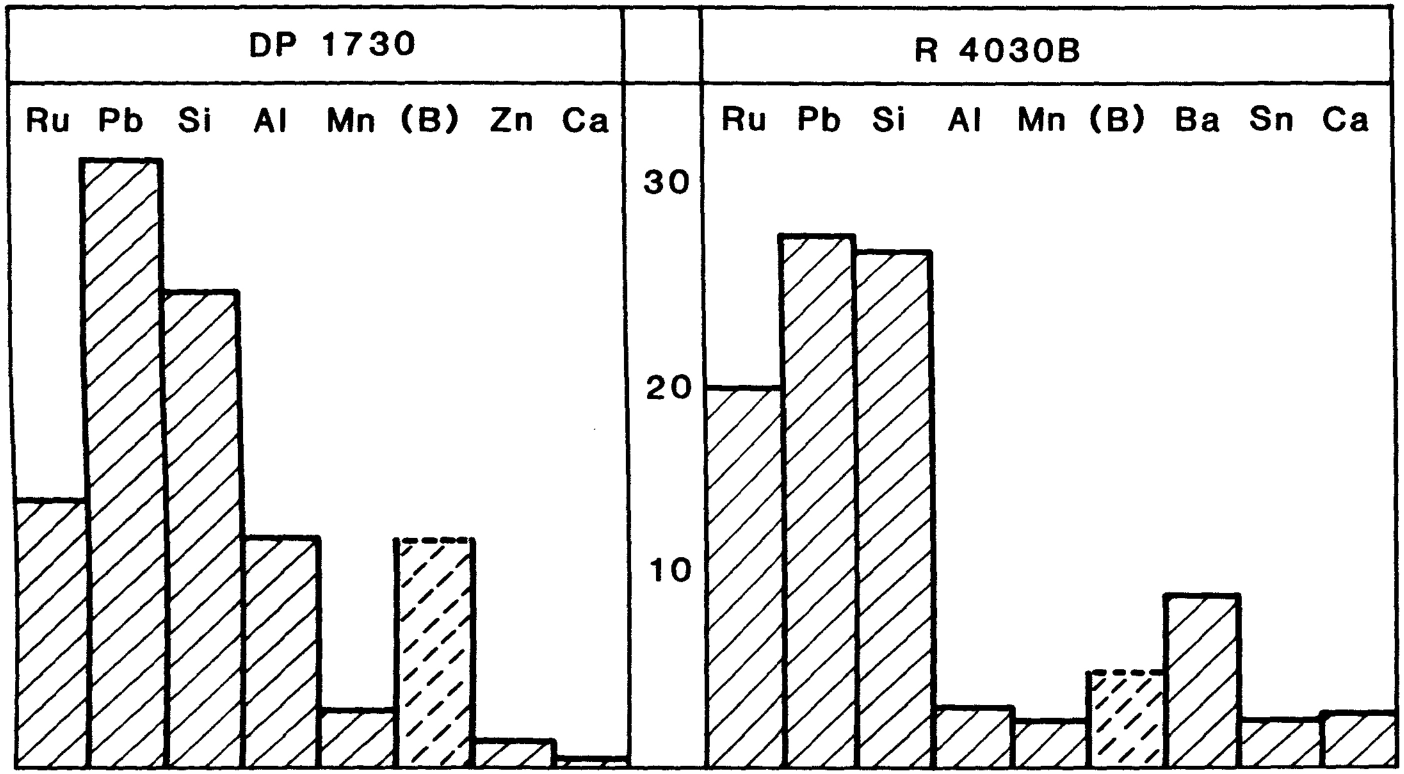


Fig. 5.1a % concentration of element in fired film as oxide, using EDX analysis. (On 96% alumina) [R4030B also showed < 1% of Ti]

AW 7381-1

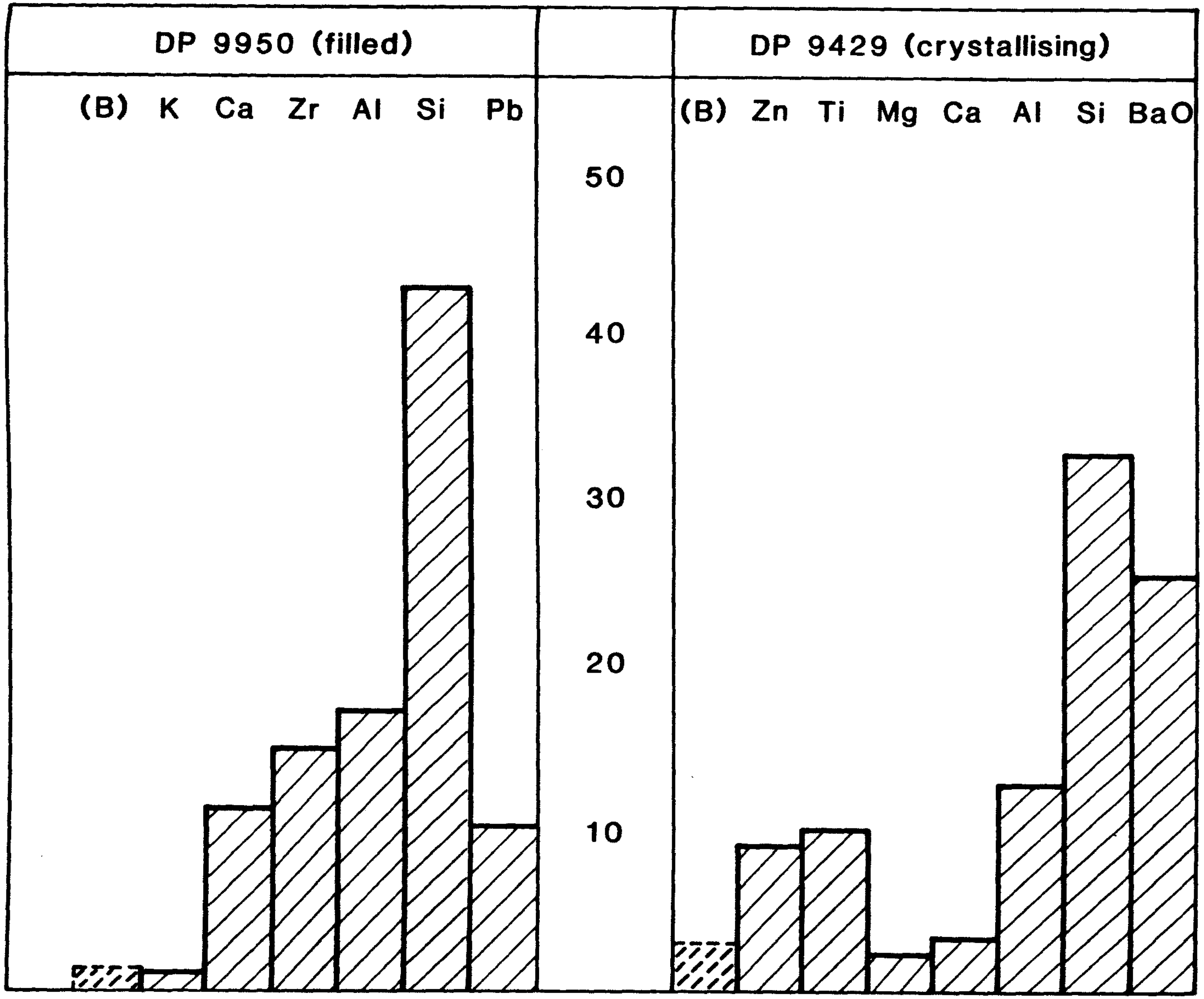
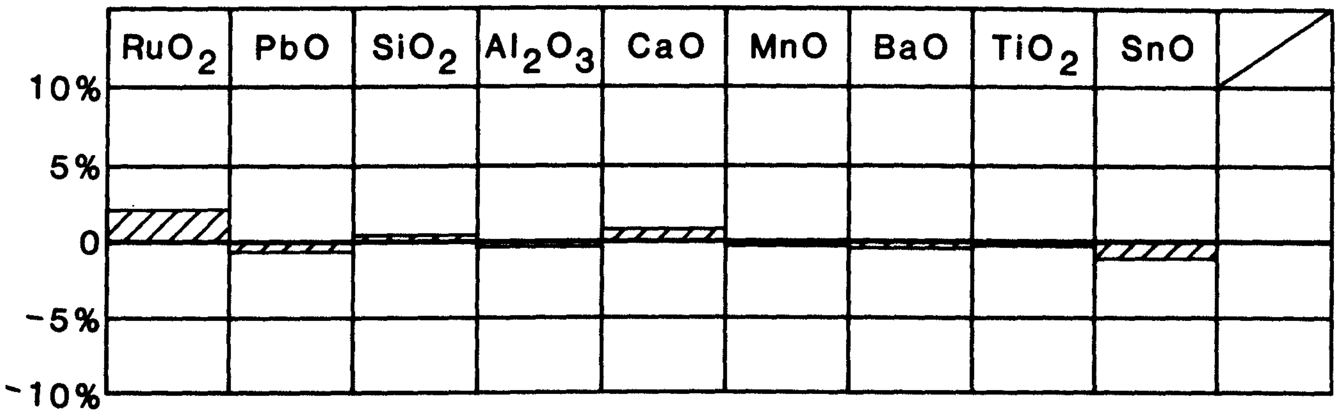
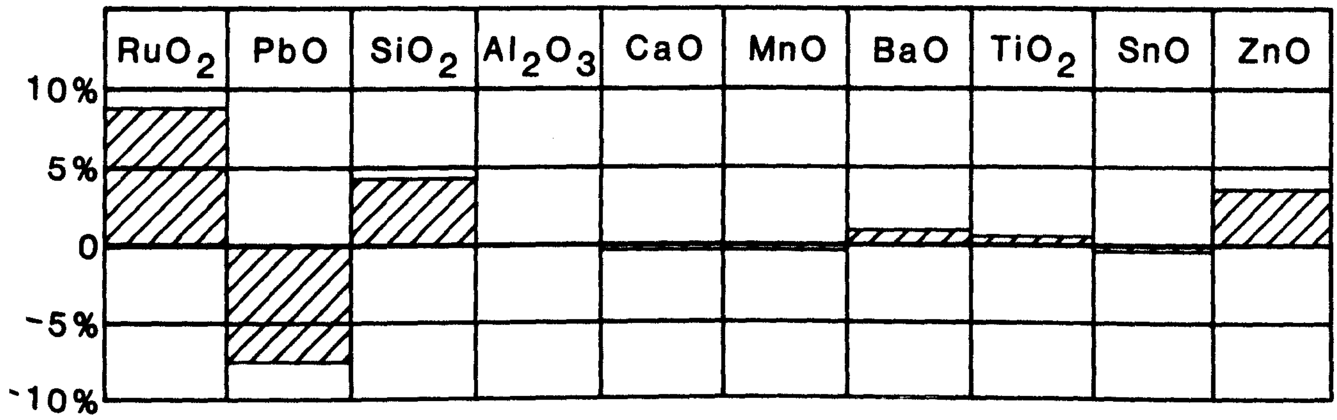


Fig. 5.1b % concentration of element in fired film as oxide, using EDX analysis. (On 96% alumina)

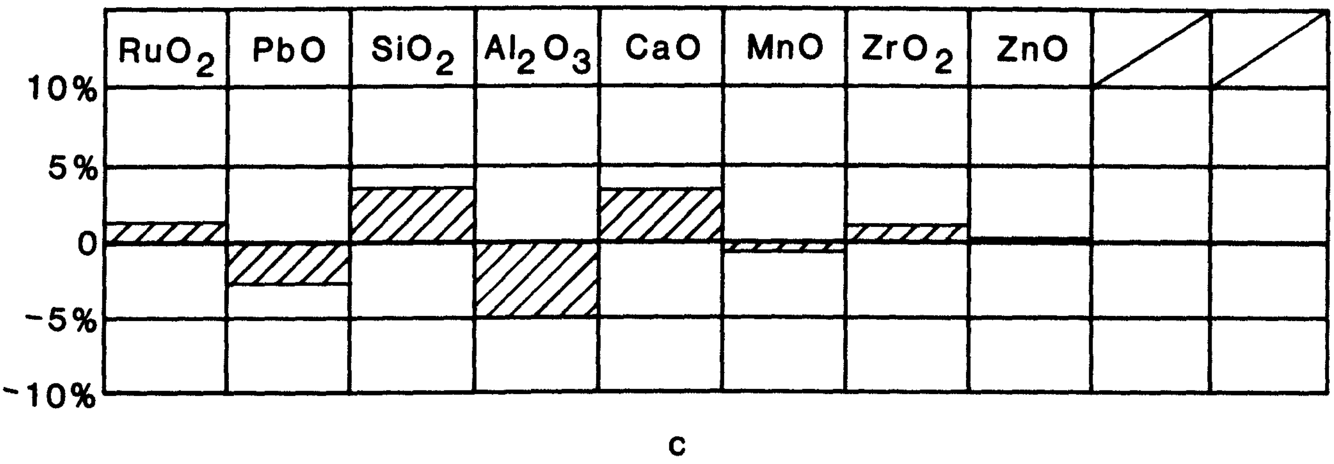


a



b

Fig. 5.2 Changes in resistor composition when fired on dielectrics compared with Kyocera A376 alumina
a) R4030B/DP9950
b) R4030B/DP9429



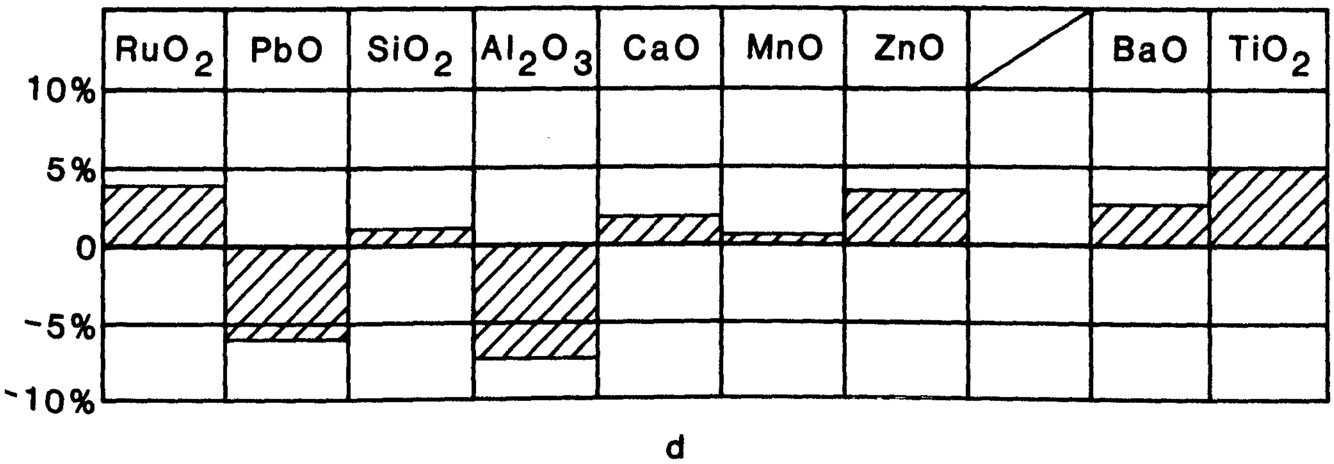


Fig. 5.2 Changes in resistor composition when fired on dielectrics compared with Kyocera A376 alumina
c) DP1730/DP9950
d) DP1730/DP9429

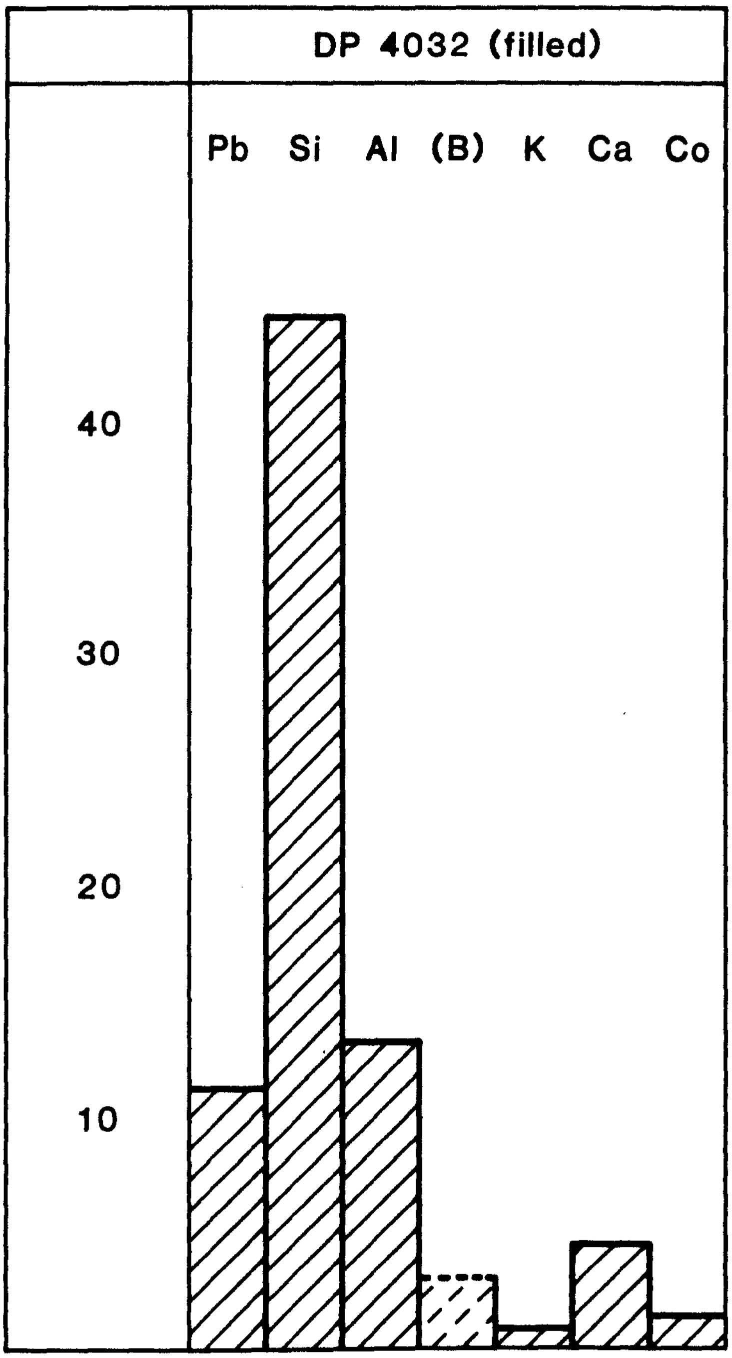


Fig. 5.3a % concentration of element in fired film as oxide, using EDX analysis (on 96% alumina)

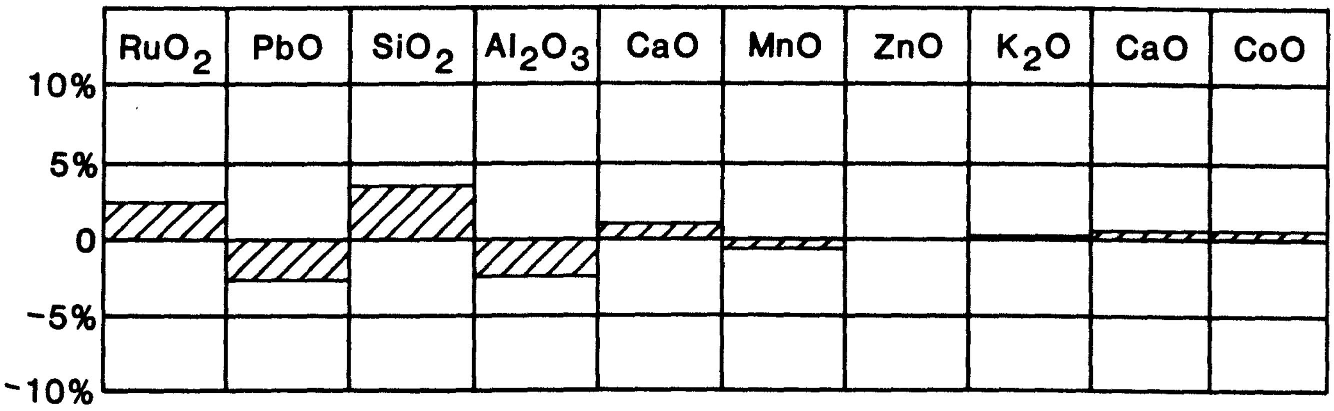
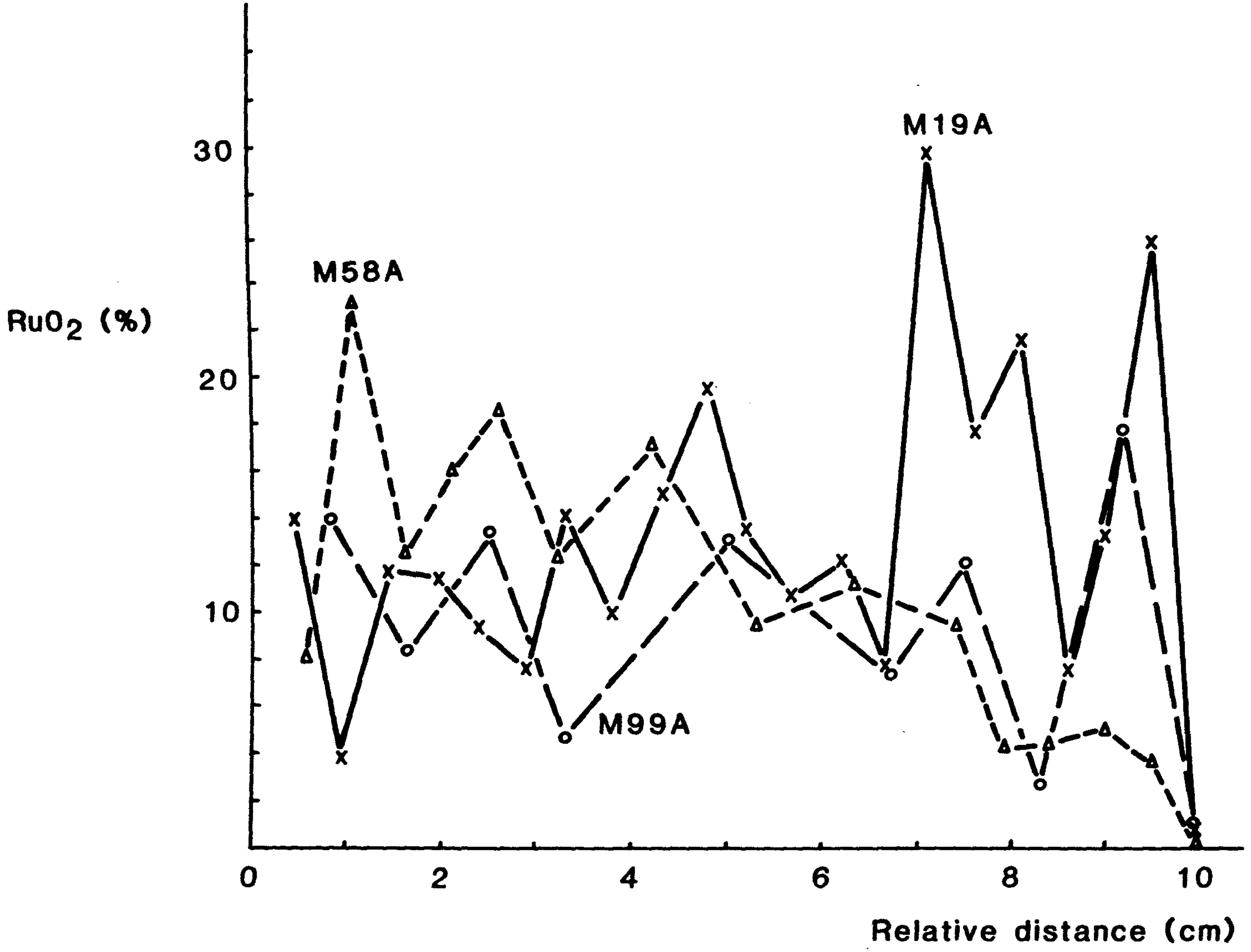


Fig. 5.3b Changes in resistor composition when fired on dielectrics compared with Kyocera A376 alumina
DP1730/DP4032



ig. 5.4 RuO_2 content v distance for M19A, M58A and M99A (normalised and corrected), DP1730 on Al_2O_3

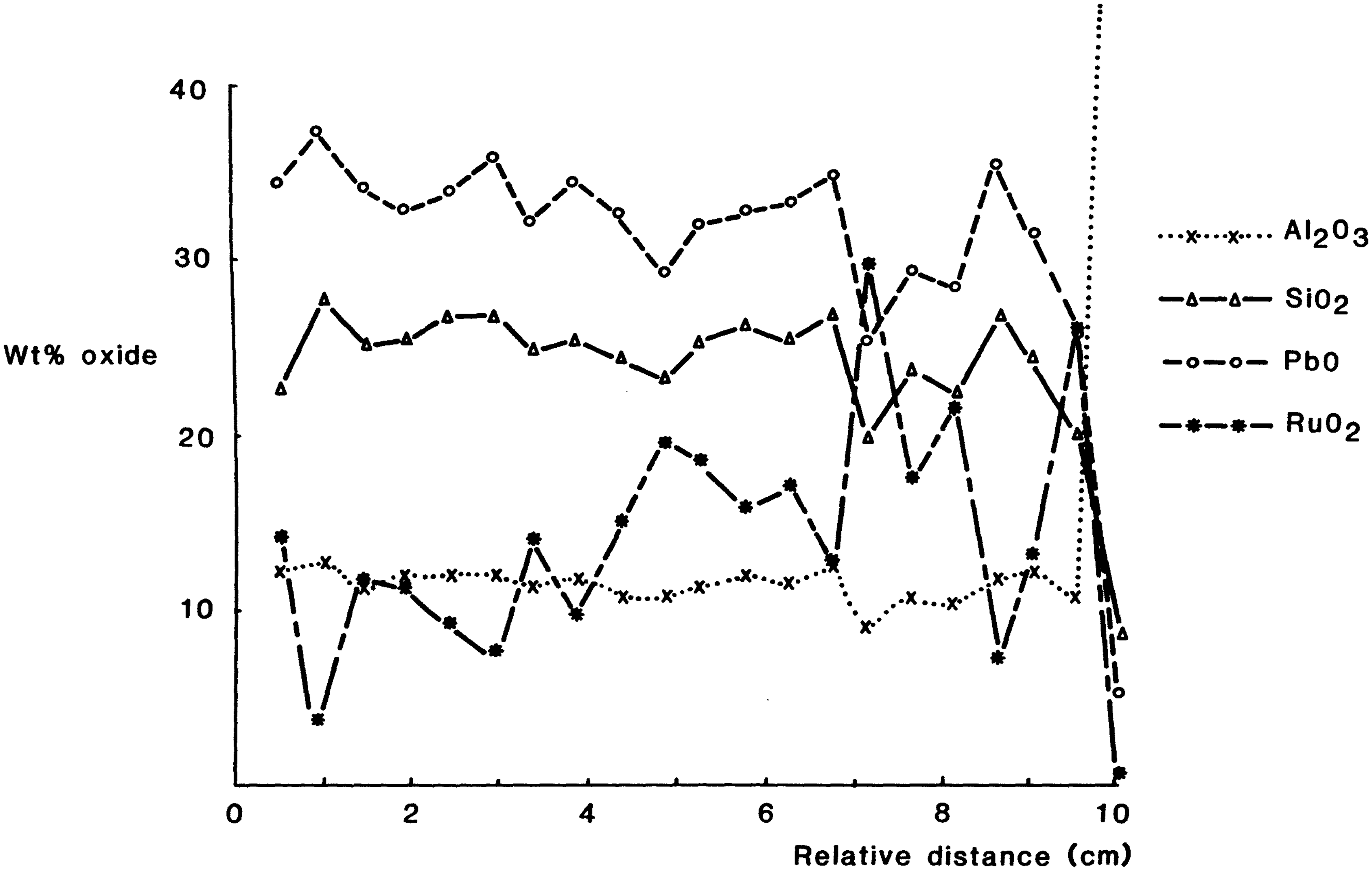


Fig. 5.5 Distribution of constituents in M19A, DP1730 on Al_2O_3

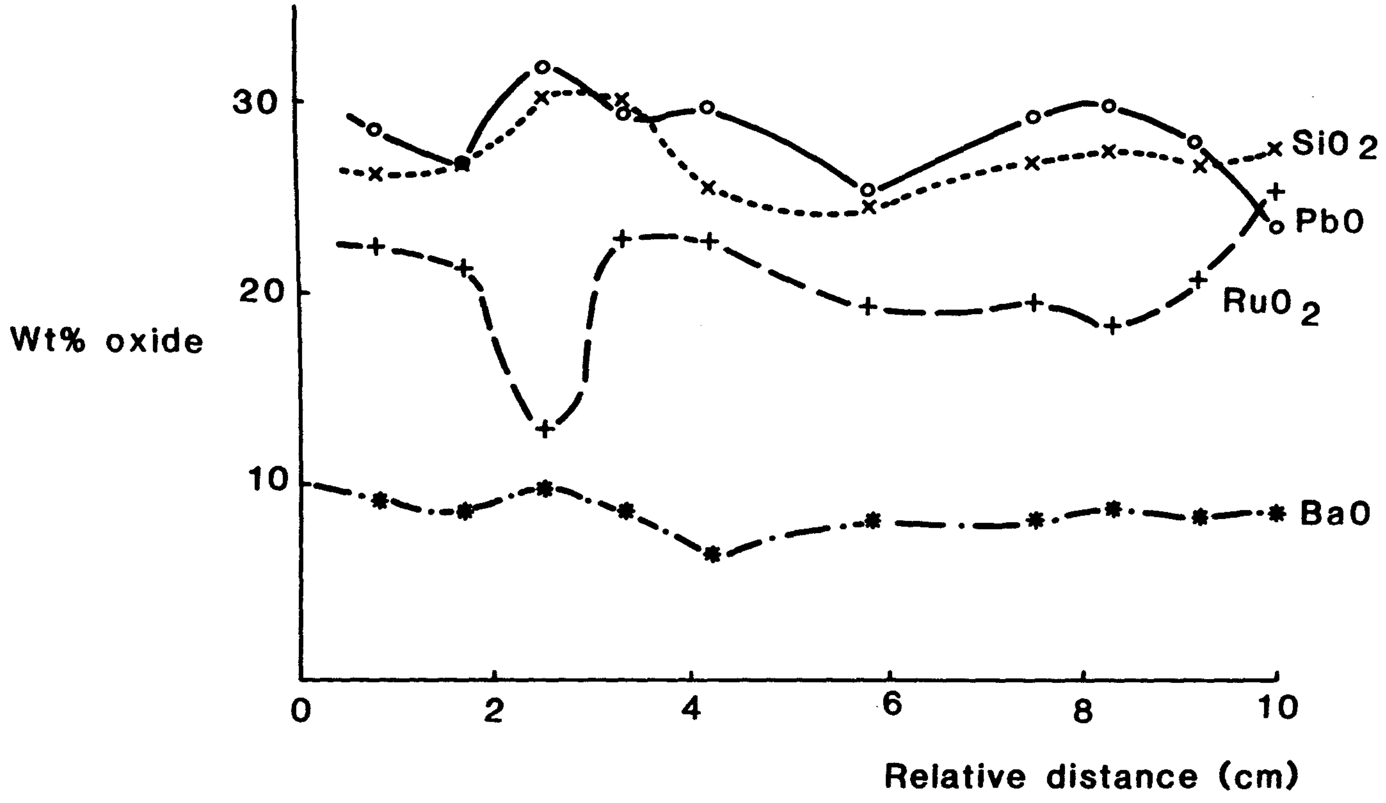


Fig. 5.6 Distribution of constituents in M78, R4030B on Al_2O_3

AW 7639-28

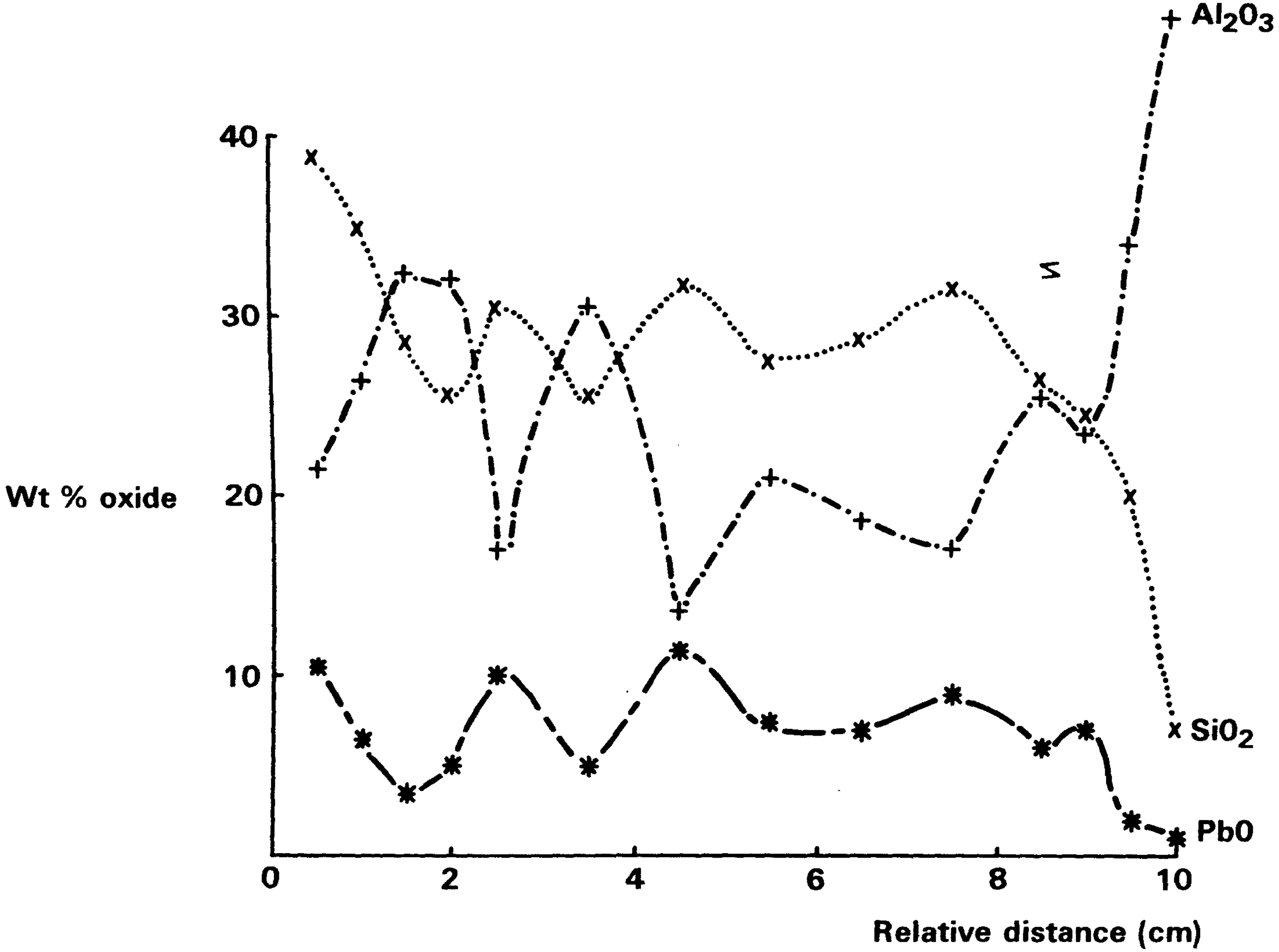


Fig.5.7a Distribution of constituents in M19D, DP4032 on Al_2O_3

AW 7639-29

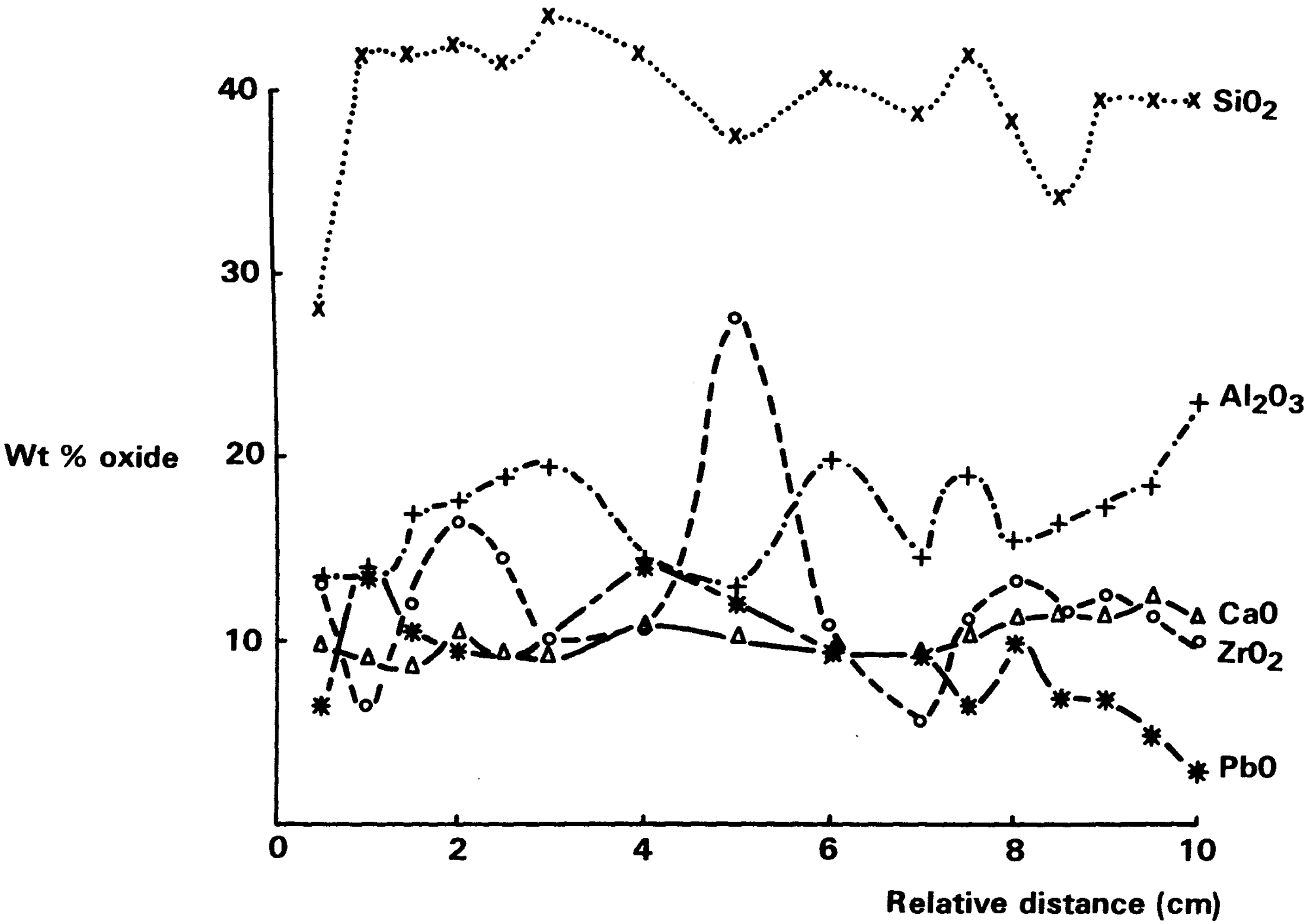


Fig.5.7b Distribution of constituents of M990, DP9950 on Al_2O_3

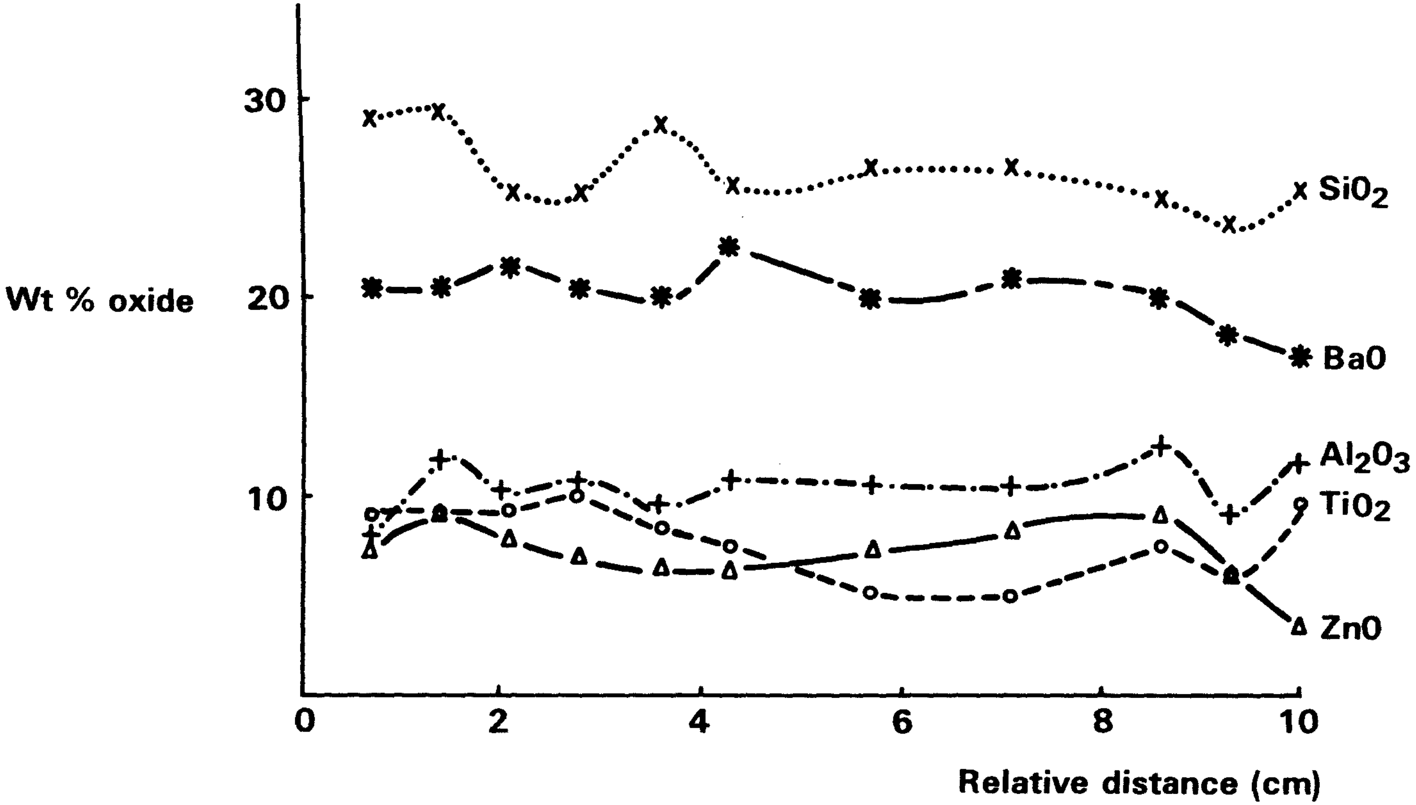


Fig.5.7c Distribution of constituents in M58D, DP9429 on Al_2O_3

AW 7360-4

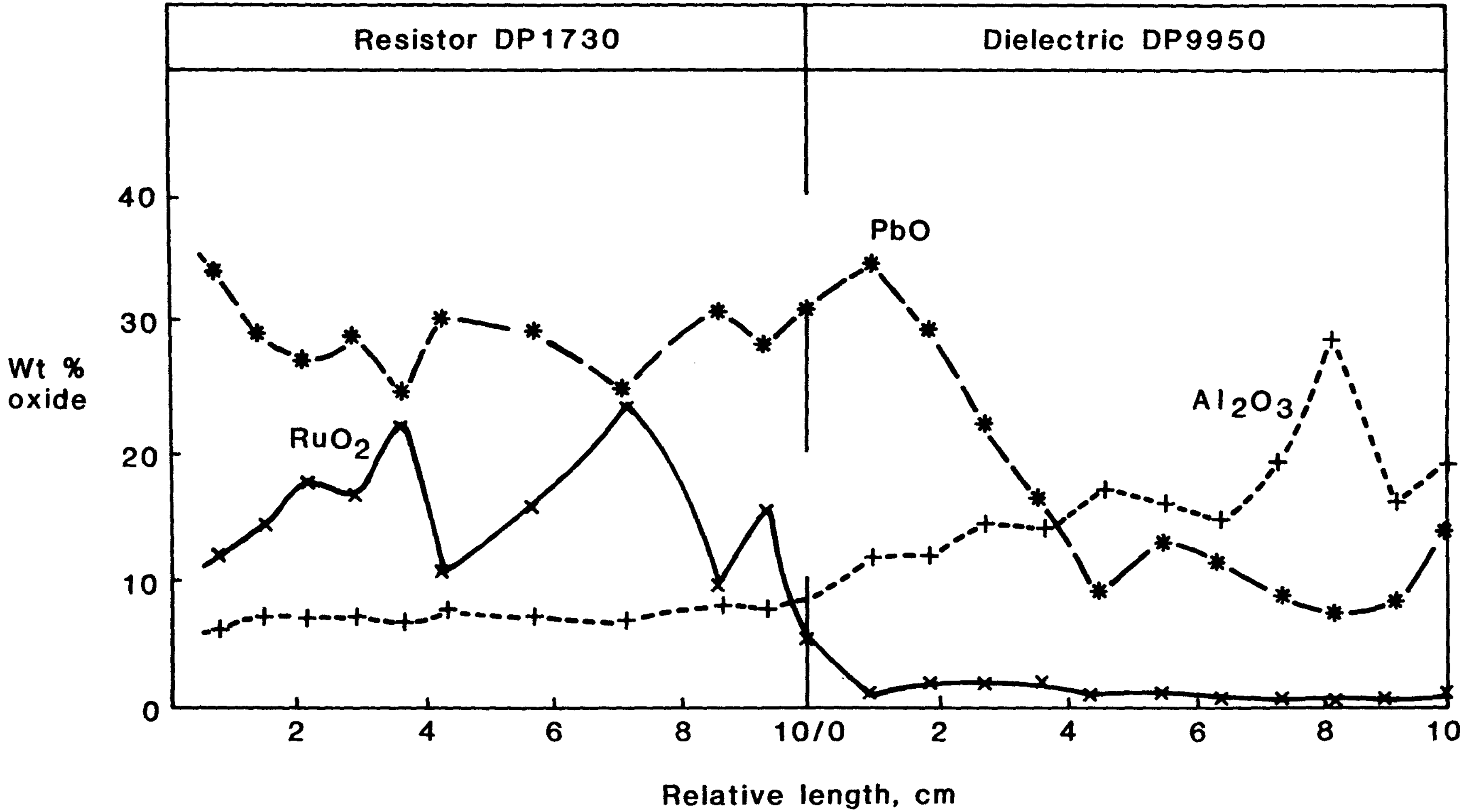


Fig. 5.9 Cross section analysis of DP1730 on DP9950 showing ruthenium, lead and aluminium oxides

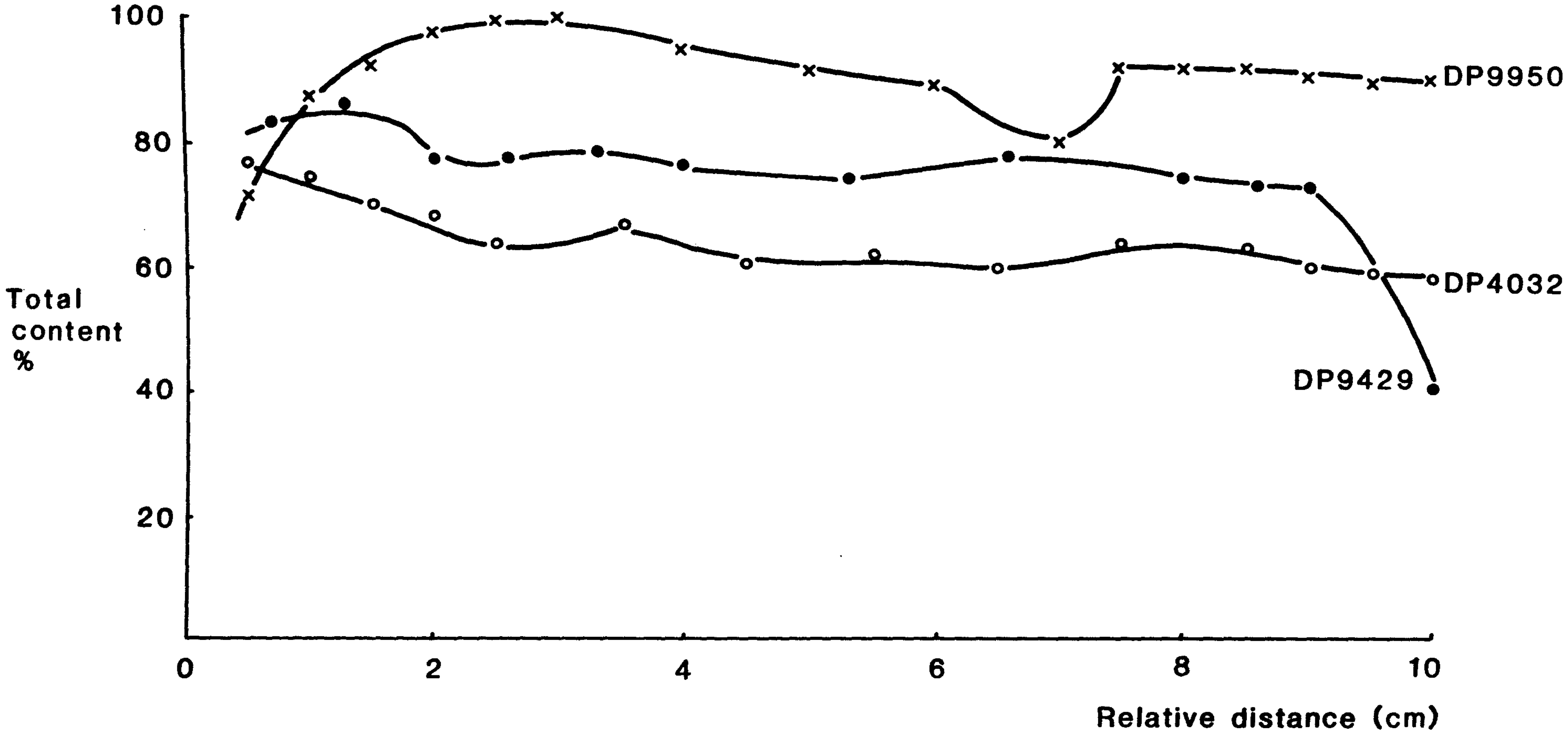


Fig. 5.8 Apparent solids contents for DP4032, DP9950 and DP9429

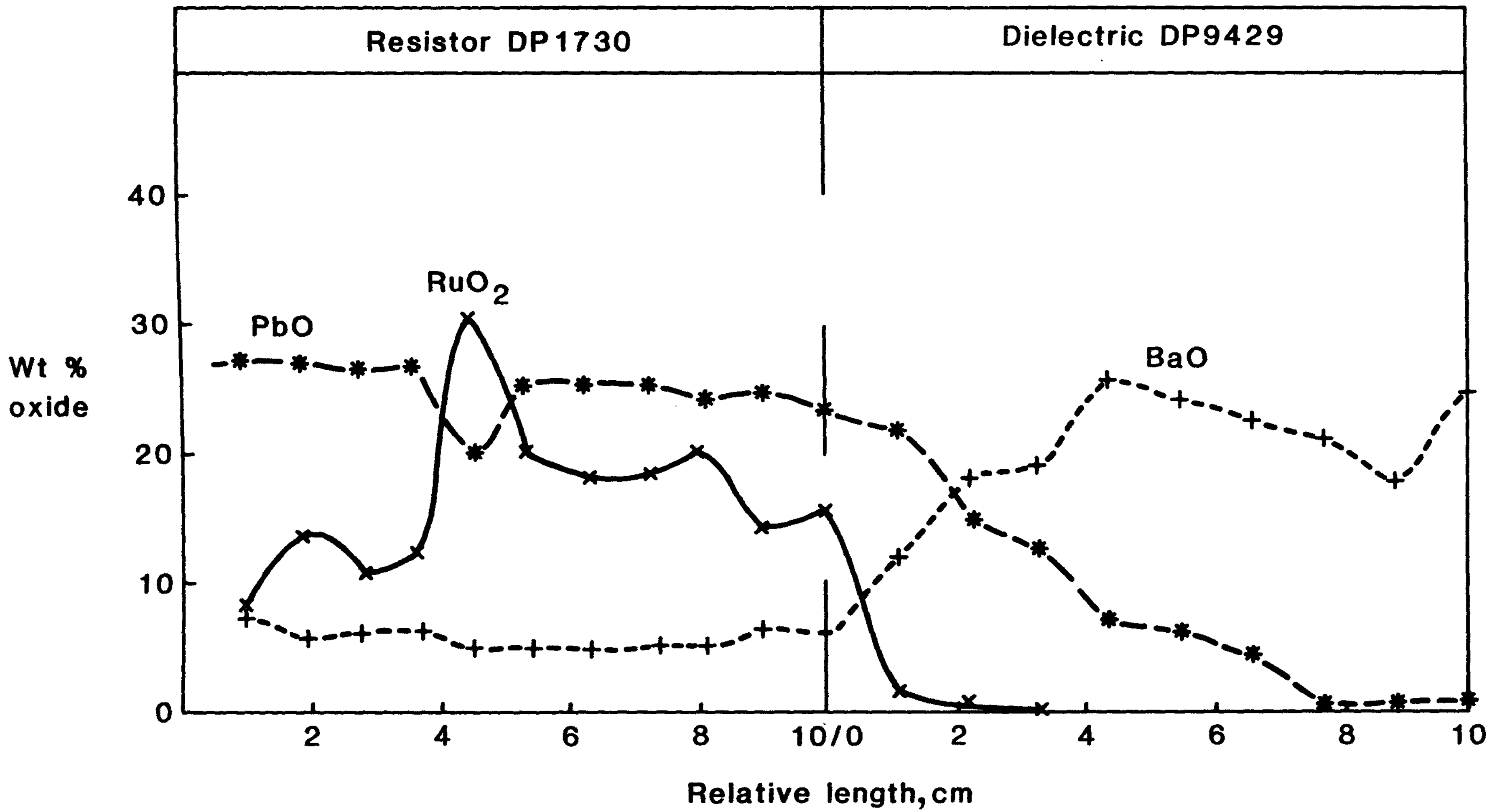
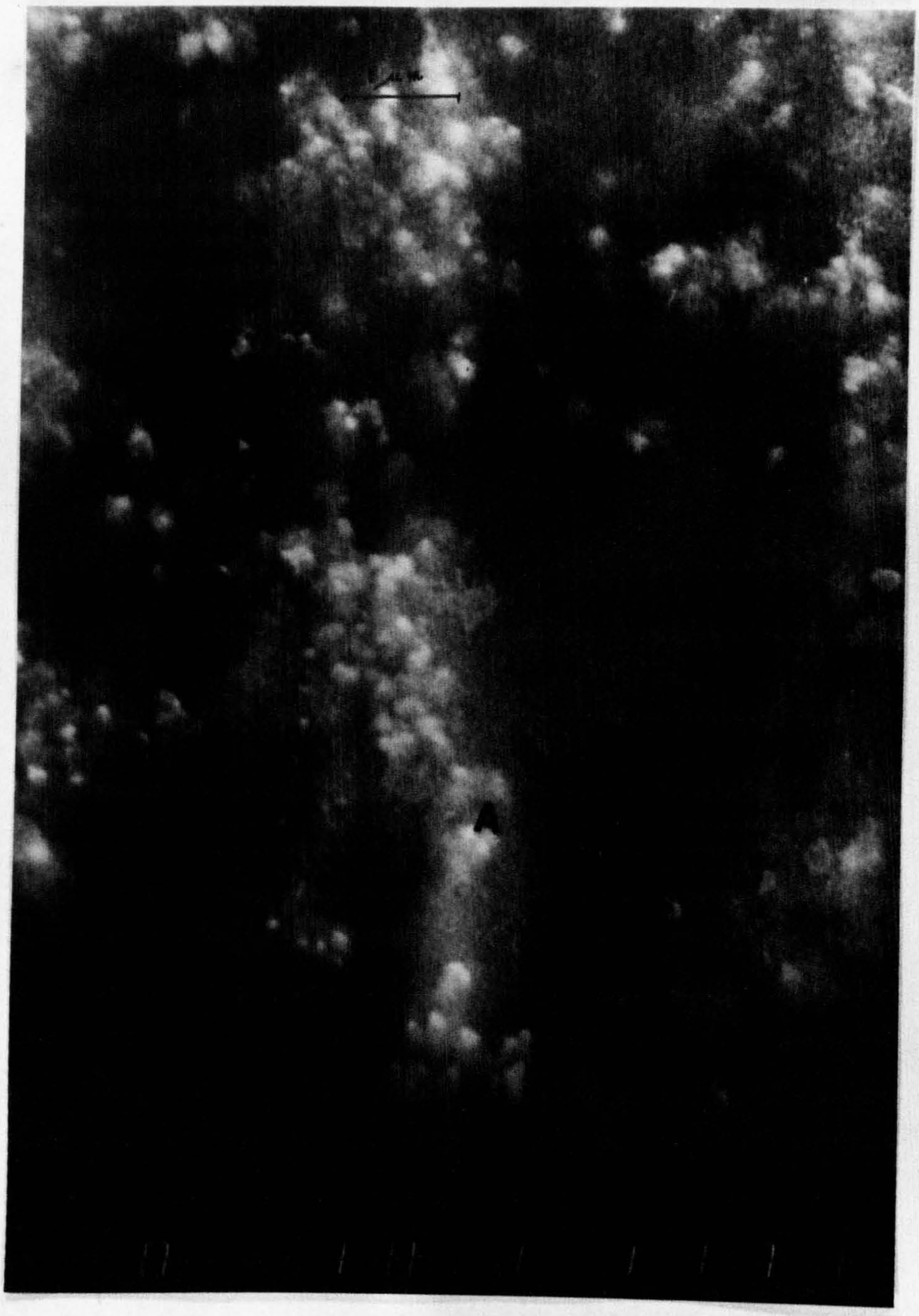
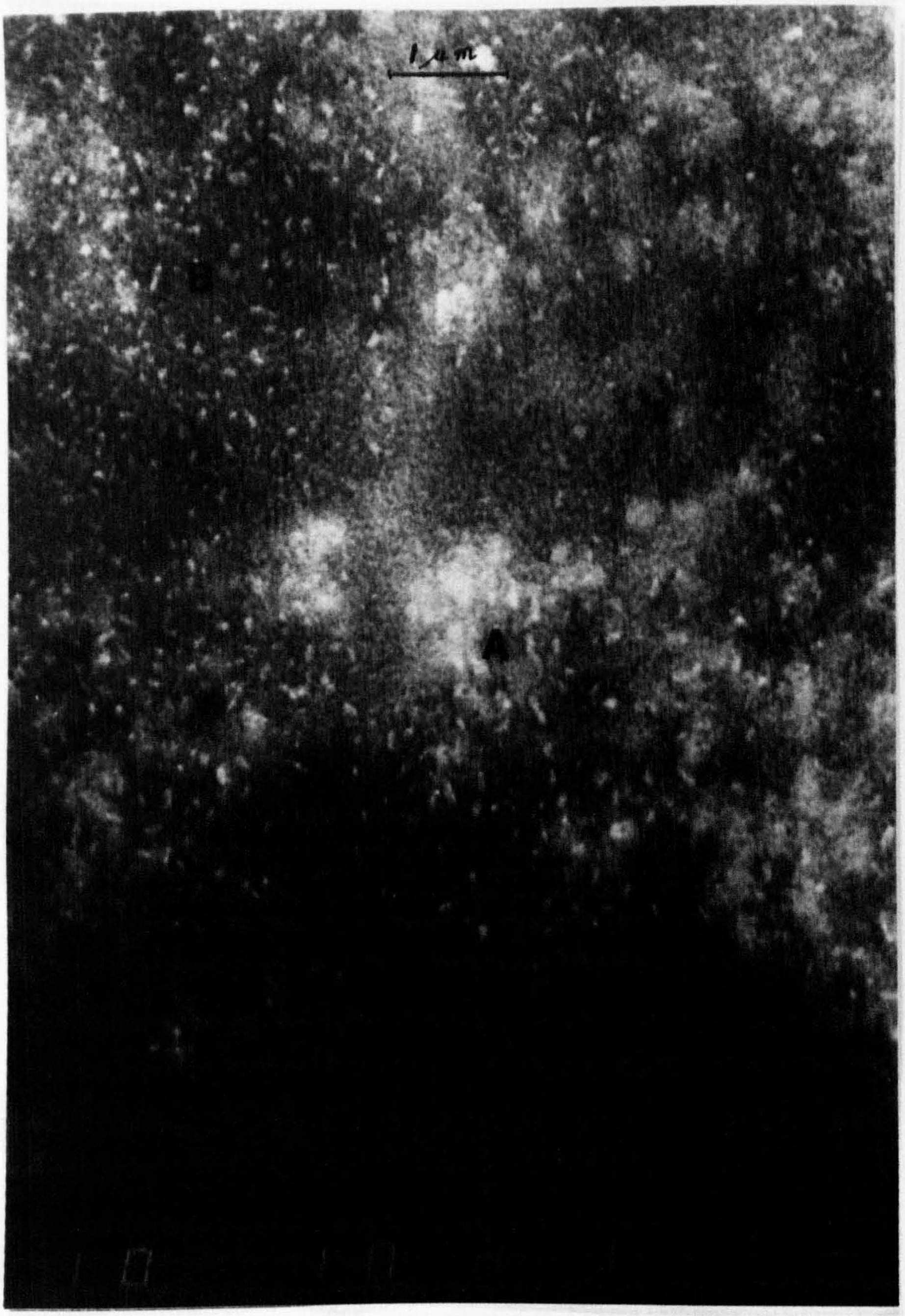


Fig. 5.10 Cross section analysis of DP1730 on DP9429, showing ruthenium, lead and barium oxides. Readings of less than 1% are shown as zero for clarity. The actual lead concentration does not fall to zero throughout the dielectric layer, but is in the range 0.2–0.6% approximately



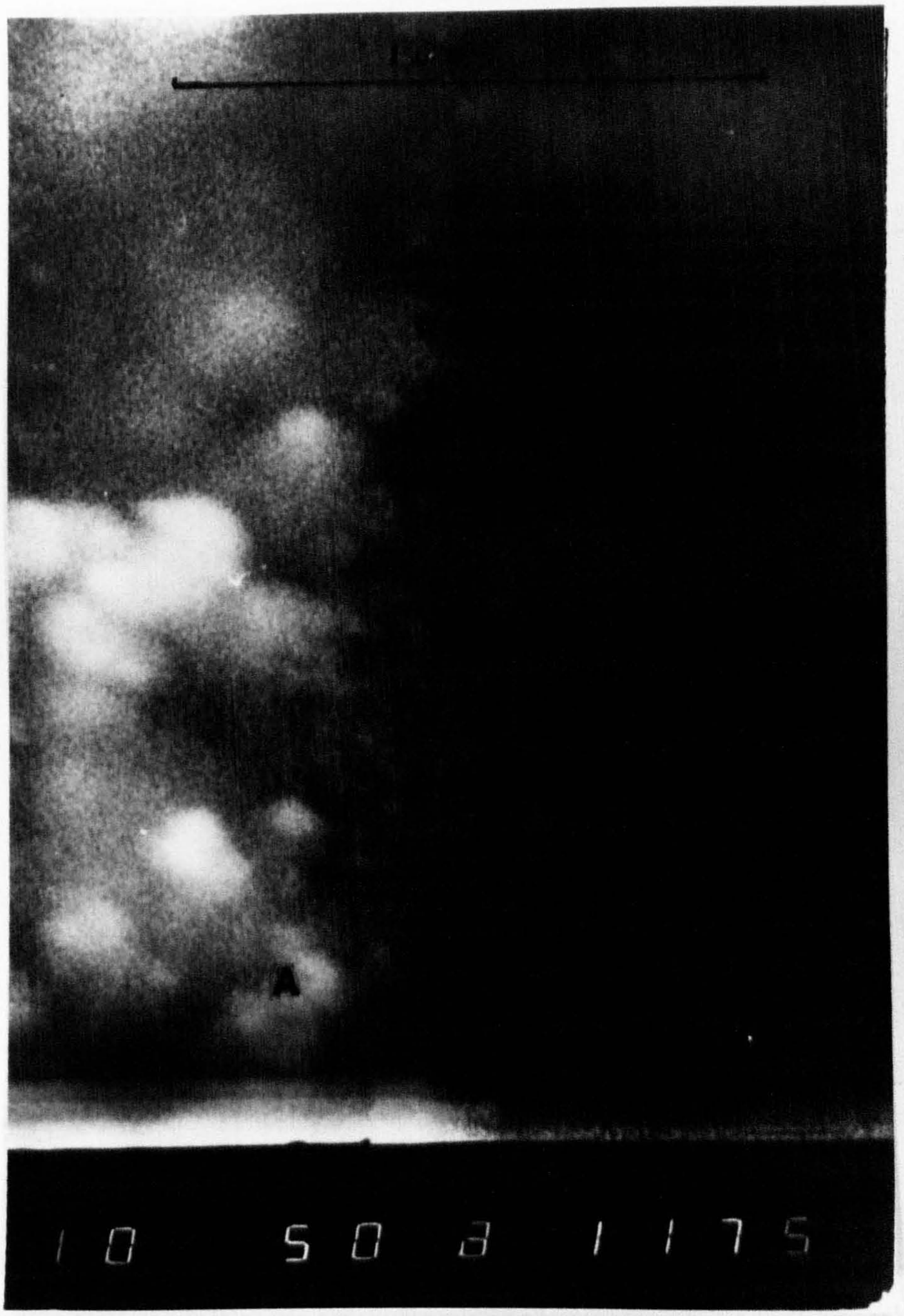
M55A 100kV SEM x 15000

Fig. 5.11a DP1730 on alumina, x 15000.
Feature A only is visible



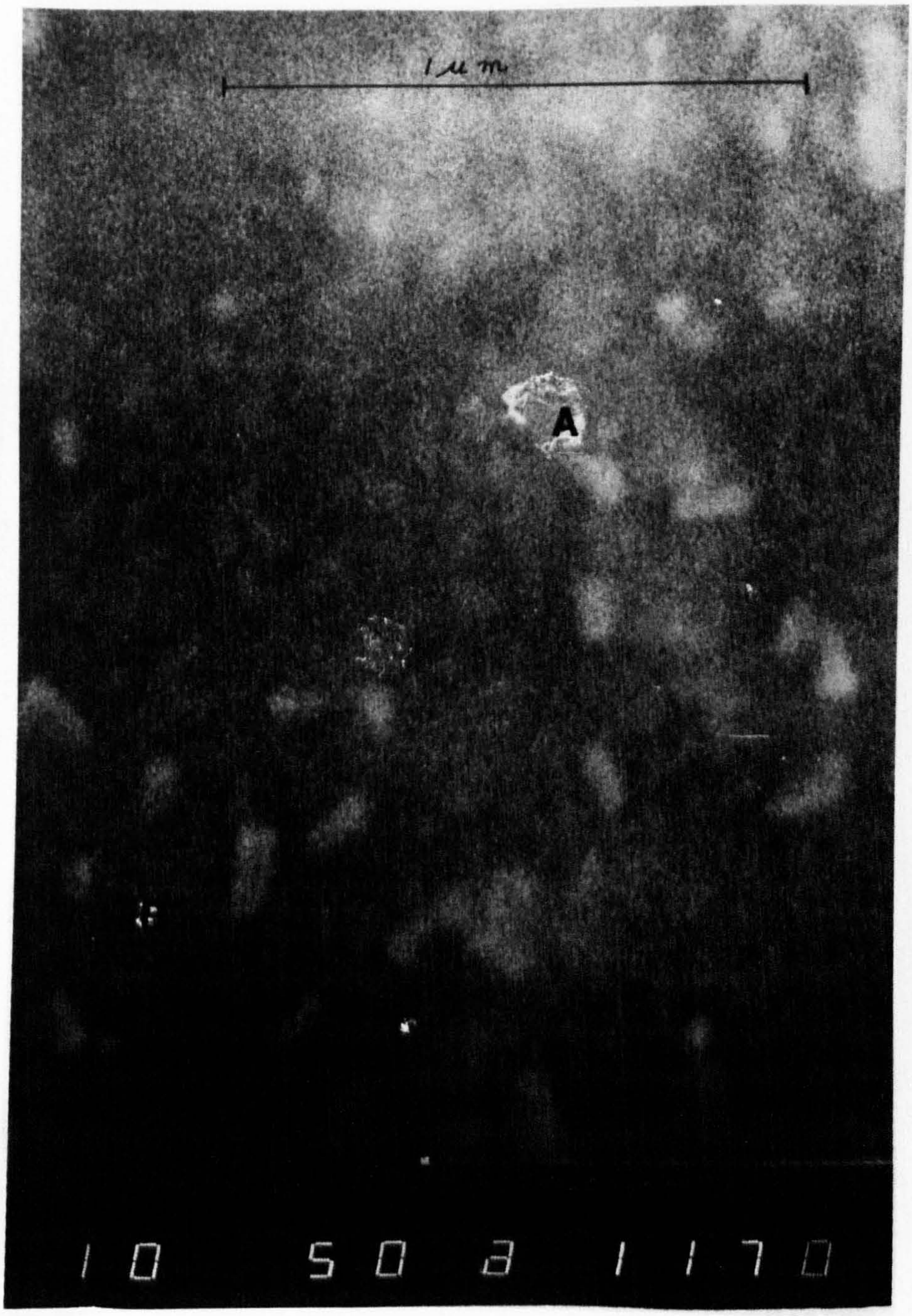
M55D 100kV SEM x 15000

Fig. 5.11b DP1730 on crystallising dielectric DP9429, x 15000. Features A and B are both present



M55A 100kV SEM x 75000

Fig. 5.11c DP1730 on alumina, x 75000. Only feature A is visible



M55D 100kV SEM x 75000

Fig. 5.11d DP1730 on crystallising dielectric DP9429, x 75000. Features A and B are both present

AW 7360-5

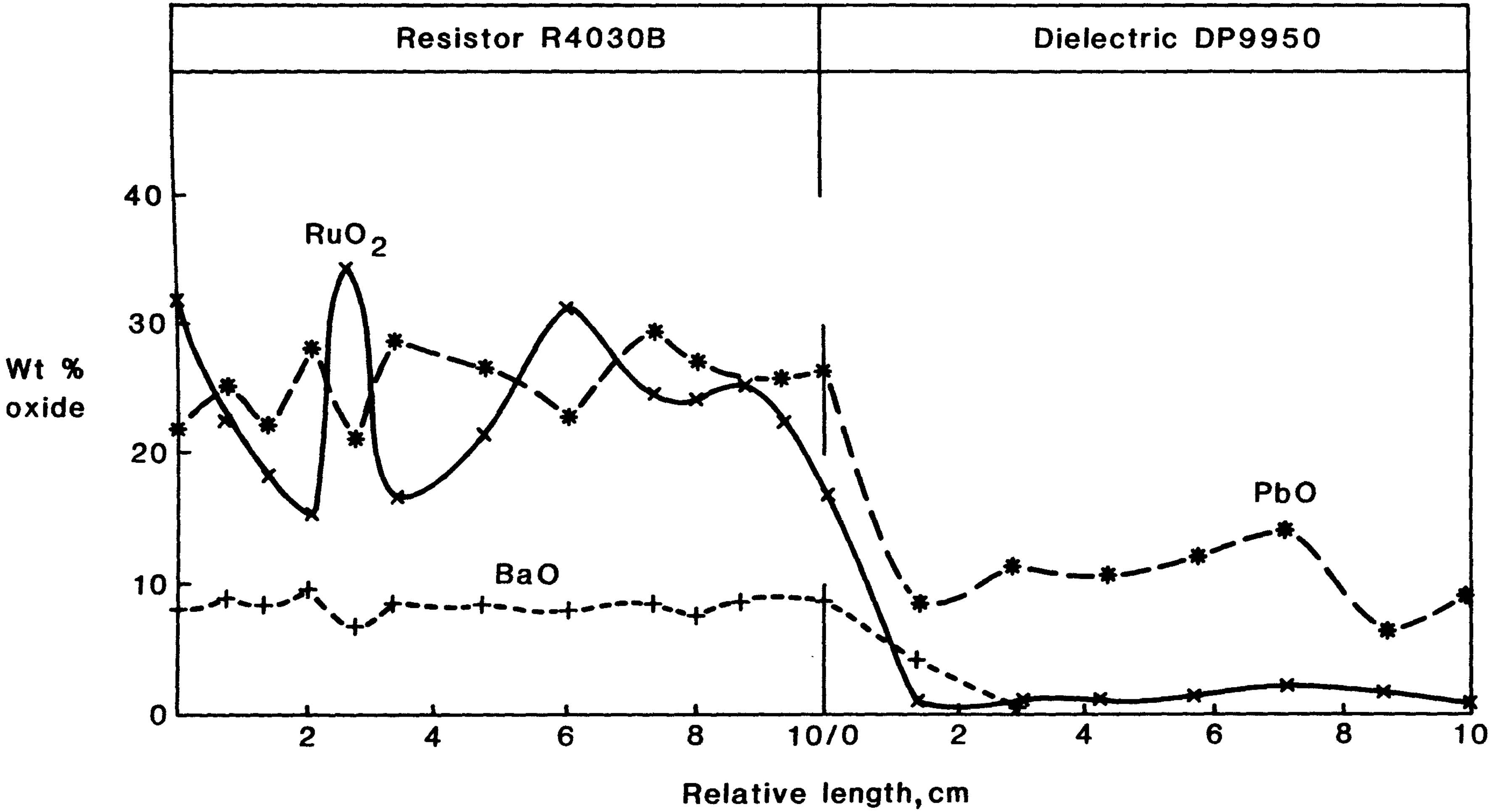


Fig. 5.12a Cross section analysis of Heraeus R4030B on DP9950 showing ruthenium, lead and barium oxides

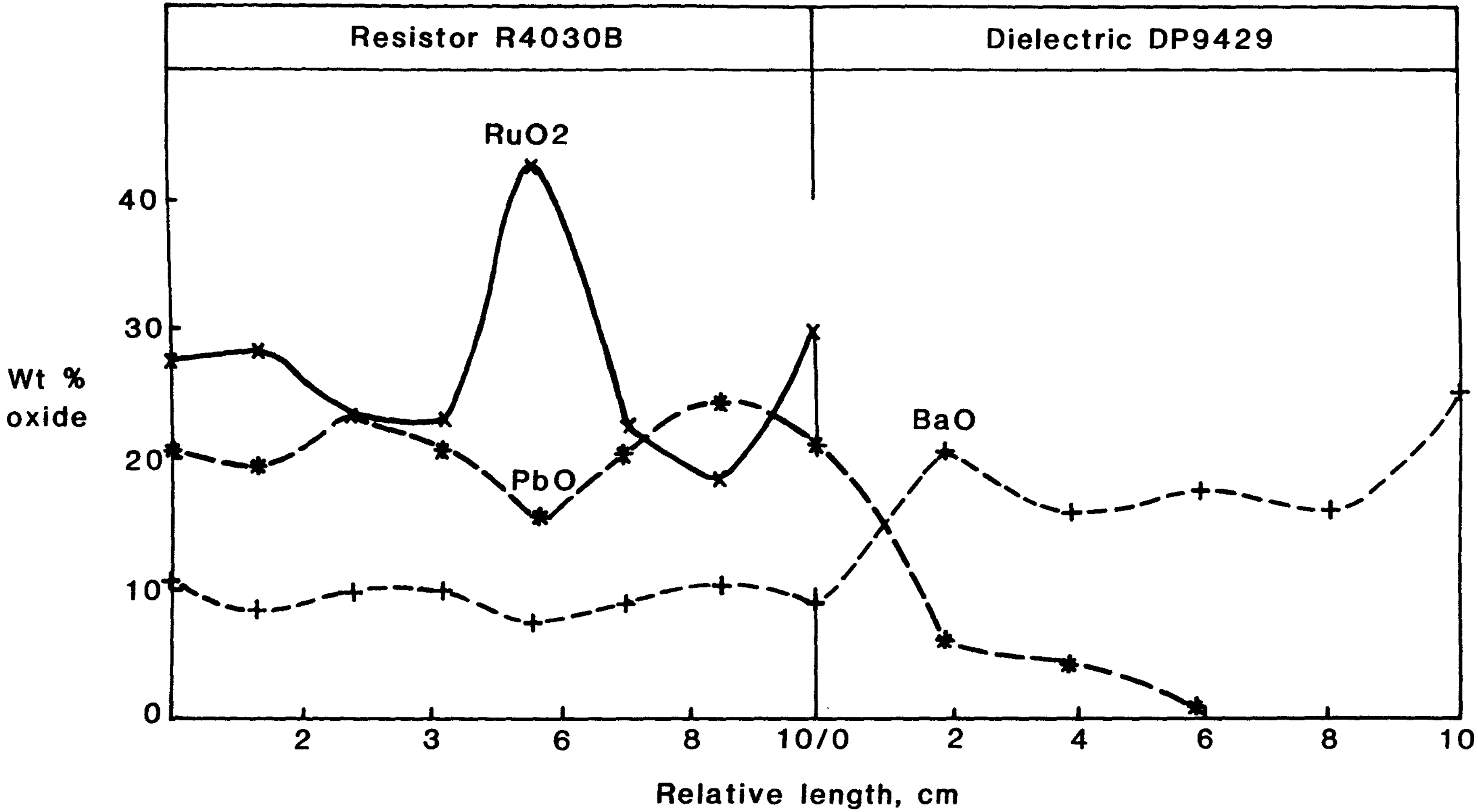


Fig. 5.12b Cross section analysis of Heraeus R4030B on DP9429 showing ruthenium, lead and barium oxides. Although, for clarity, the concentration of ruthenium throughout the dielectric and of lead in the lower portion are both shown as zero, their measured concentration there lies in the approximate range 0.2-0.6%

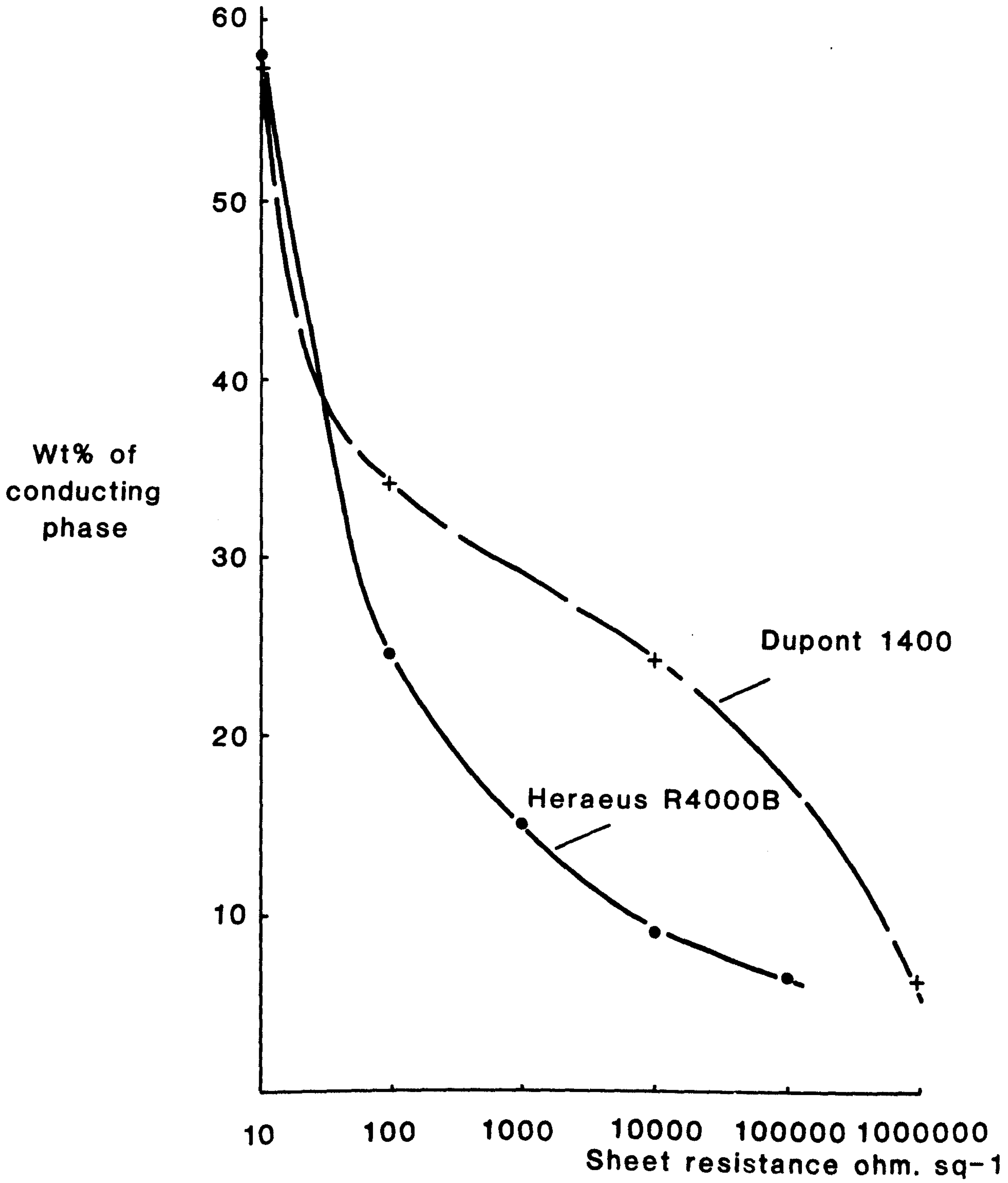


Fig. 6.1 Conductor content of solid phase of two thick film resistor pastes as a function of nominal sheet resistance

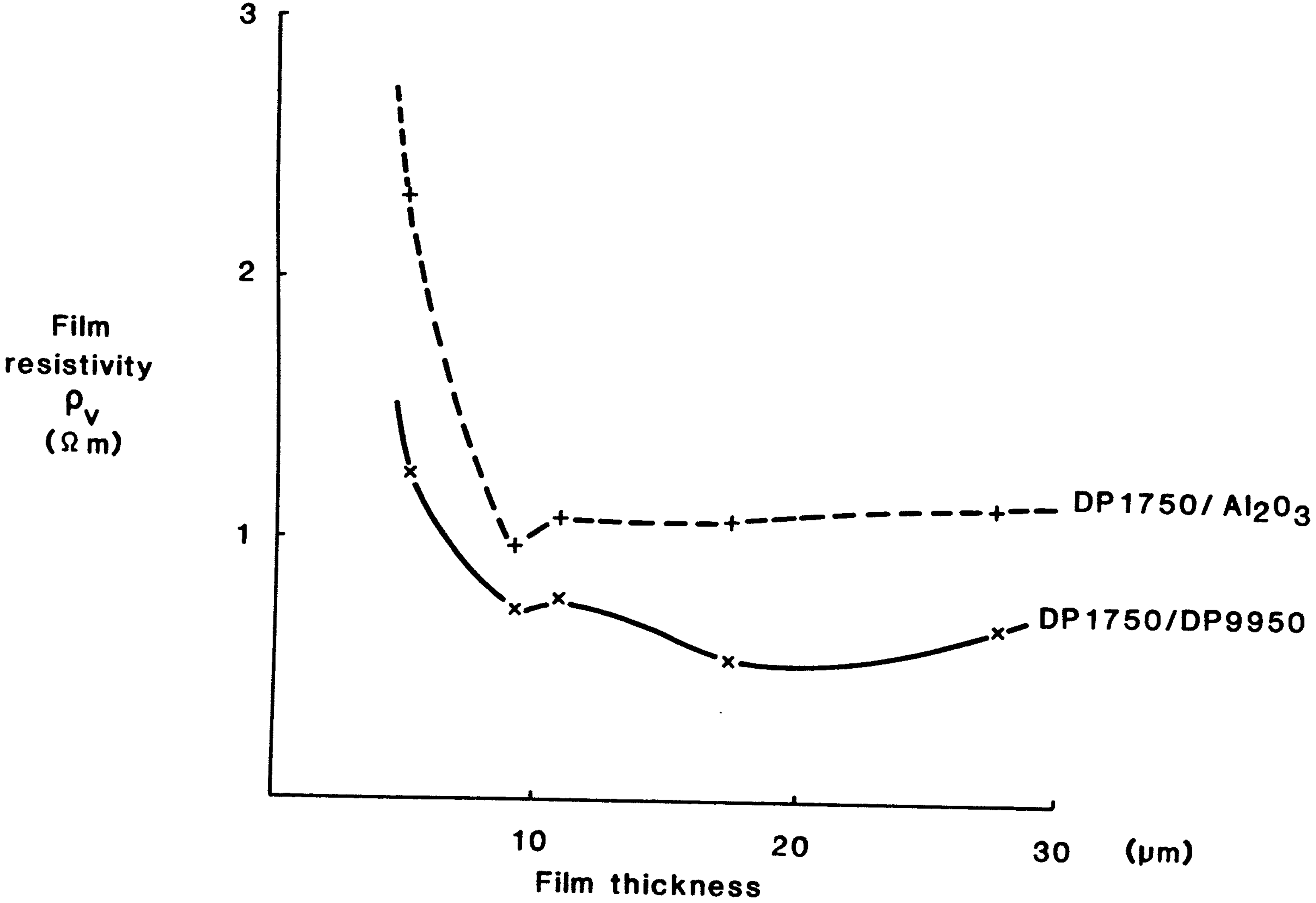


Fig. 6.2 The effect of fired film thickness on the bulk resistivity of films of DP1750 on DP9950 and alumina

AW7639-21

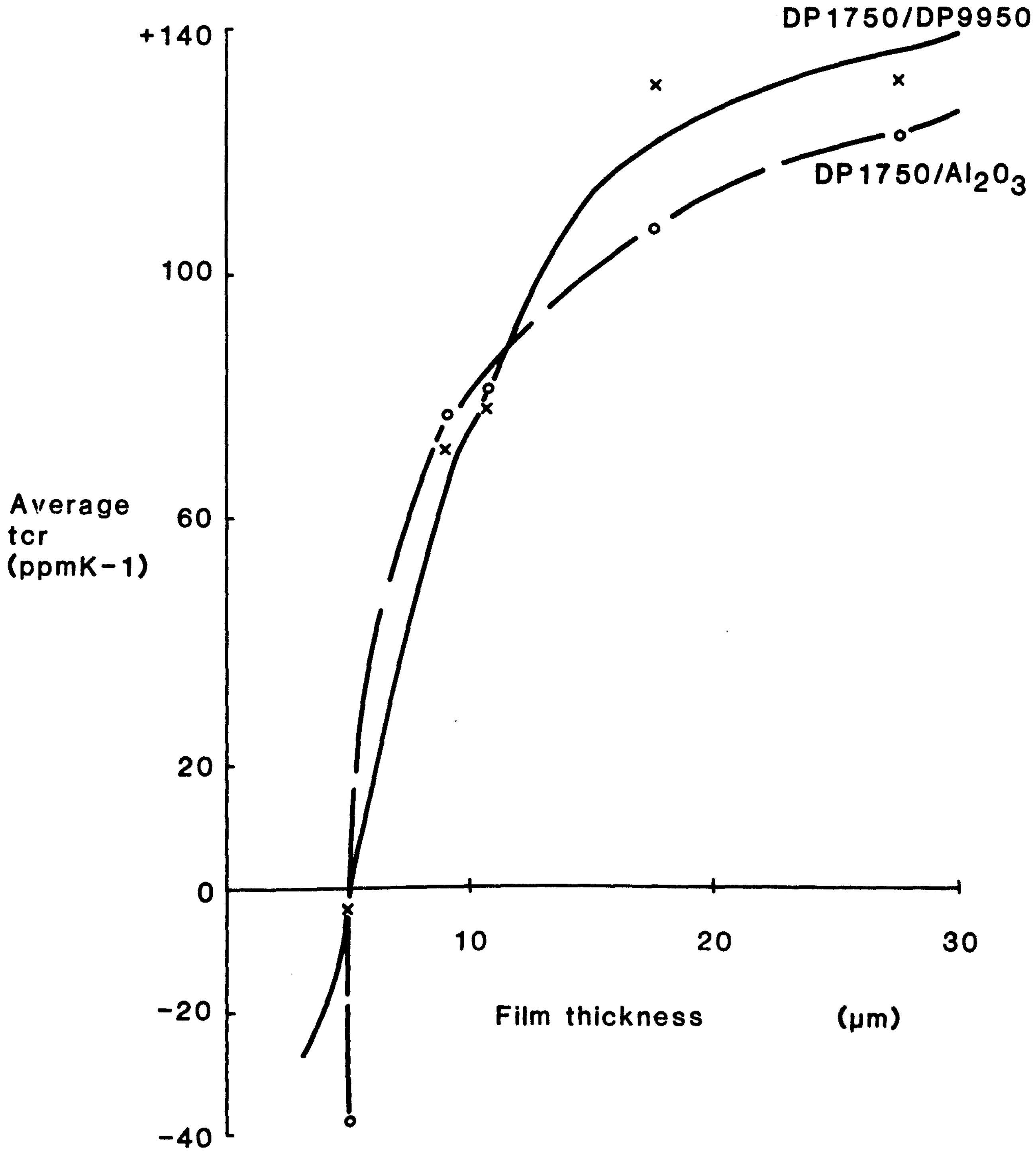


Fig. 6.3 Hot side tcr (20–120 °C) as a function of film thickness for DP1750 on DP9950 and alumina

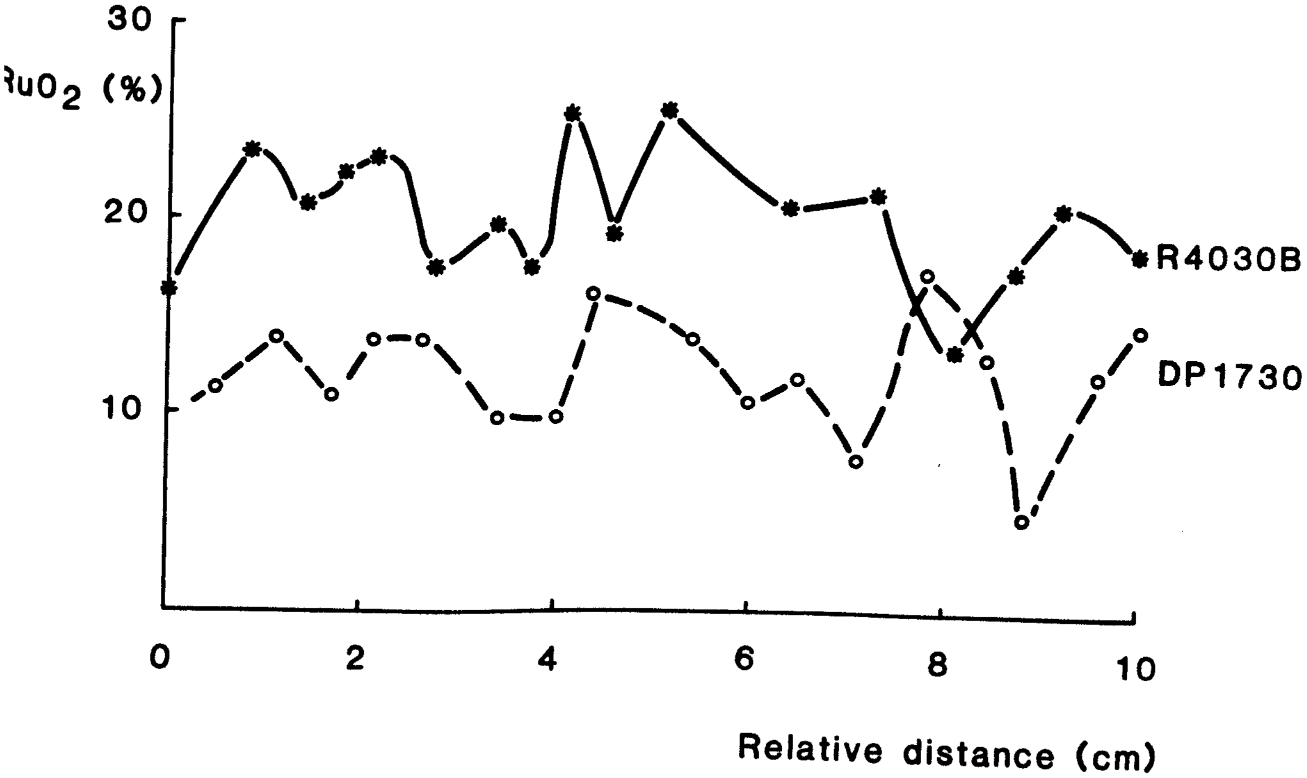


Fig. 6.4 Average RuO$_2$ content (Wt%) across cross section for resistors on alumina

6 samples for R4030B
3 samples for DP1730