ELECTRONIC CERAMICS

EDITED BY
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Preface

A seminar on electronic ceramics organised by IBC in 1989 provided the initial stimulus for the present publication. The seminar was concerned with the current status of electronic ceramic technology and possible future trends both for the relevant technology and market opportunities. The seminar demonstrated once again that electrical ceramic components continue to dominate the commercial applications of technical ceramics and that this situation will continue for the forseeable future. This optimistic outlook for electronic ceramic contrasts with the more realistic and somewhat pessimistic projections now prelevant for the application of structural ceramics for mechanical engineering applications.

As participants at the seminar wished to have a written record of the proceedings the speakers were requested to provide an expanded version of their oral contributions to provide an up-to-date review of both scientific and technological aspects of their particular subject. Most of the speakers accepted this invitation and the various chapters in this publication now provide an authoritative and useful review of various topics in the area of electronic ceramics.

The first two chapters are concerned with the relatively mature technology of varistor and positive temperature coefficient resistor devices. Both chapters incorporate comments about developments associated with new configurations, including surface mounted components, and the possible introduction of chemically prepared powders. A complete chapter, prepared by Dr. D.L. Segal, is devoted to this latter topic, and indeed the key role of powder preparation and processing is emphasised in all the chapters.

Chapters on high frequency ceramic dielectrics, magnetic ferrites and pyroelectric ceramics provide useful reviews of the many electronic engineering applications which are dependent upon the behaviour of these materials. These contributions also demonstrate how technological advances are dependent upon a clear understanding of the basic scientific principles involved in the optimisation of the relevant properties. The very important question of reliability and quality control is addressed in the article concerned with multi-layer capacitors, whilst the topic of selection between competing materials is considered in the chapter on electromagnetic windows. The final chapter summarises the role of ceramic materials in fuel cells and batteries and suggests that the ceramic solid oxide fuel cell and sodium sulphur battery will have a major role in addressing the scientific and technological challenges arising from global constraints on future energy use.

The editor wishes to thank all those who participated in the preparation of this book, and hopes that the contents of the various chapters will provide insight and stimulation for what is still the most exciting branch of technical ceramics.

B.C.H. Steele

Contents

Chapter 1

Present and Future of Zinc Oxide Varistors

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ABSTRACT

Zinc oxide varistors are solid state suppressors widely applied to limit voltage surges in the range from low voltages (5 V) to high voltages (up to 1 MV). The non-ohmic property is controlled by the grain boundary barrier. The manufacturing process, the effect of additives, the microstructure, the electrical properties are described. Some examples of applications are reviewed. The future trends of zinc oxide varistors in the field of technology and component configuration are discussed.

1. INTRODUCTION

Electronic and electrical circuits can be subject to severe impulse voltage transients generated by lightning, switching and electrostatic discharge accumulated on the human body. As a solution the designer can over-specify the circuit or incorporate protection. The economic balance generally leans towards protection: it authorizes the reduction of component costs by specifying moderate ratings.

Various kinds of transient suppressors are used: silicon carbide, zener diode, spark gap and zinc oxide varistor.

This chapter describes the structure, manufacture, electrical properties and applications of zinc oxide varistors. The future trends of this technology are also discussed.

2. CHARACTERISTICS OF THE ZnO VARISTOR

The ZnO varistor has a very steep non-linear voltage–current curve and therefore can support widely varying currents over a narrow voltage

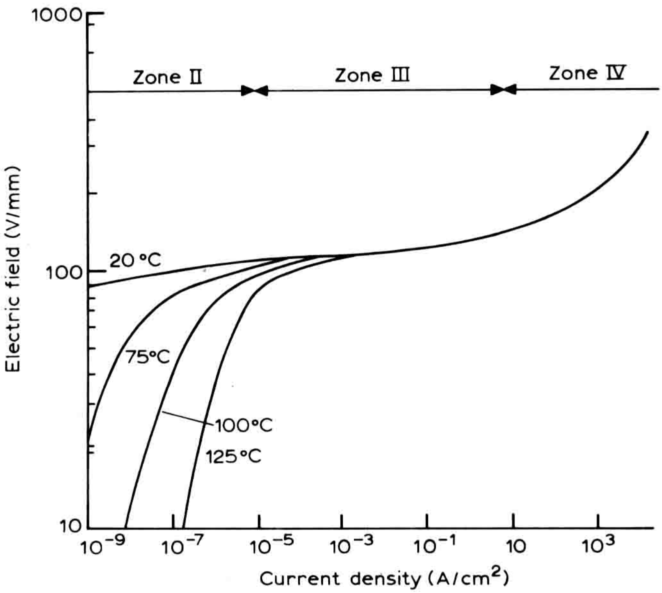

Fig. 1. *V–I* static characteristics of a ZnO varistor.

range (a factor of 10^{11} while the voltage varies by about a factor of approximately three) as shown in Fig. 1. This phenomenon is termed the varistor effect and was discovered by Matsuoka[1] in 1968.

At low voltages, the varistor looks like an open circuit. Beyond the breakdown voltage V_b, it becomes a short circuit protecting the component or the device that it shorts.

A more complete examination of the relationship between current and voltage leads us to observe four zones, each of them being characterized by a particular conduction mechanism.

2.1 Zone I: Ohmic Region

In this zone, the relationship between current and voltage is *linear*. Current density values are a few nA/cm^2 or less. This region is not used in practical applications.

2.2 Zone II: Pre-breakdown Region

This zone (known as the leakage region) is particularly important for applications. It corresponds to the region of varistor operation in the absence of all overvoltages. Generally the current is governed by a thermo-ionic emission process which results in a weak non-linearity.

As can be observed, the leakage current increases with temperature. For example, from room temperature to 125°C the current increases from 1 μA/cm² to 100 μA/cm². In other words the leakage current is thermally activated and, as will be shown later, limits the electrical performances of ZnO varistors.

2.3 Zone III: Breakdown Region

The breakdown region corresponds to the essence of varistor action: the current is a highly non-linear function of the applied voltage and can be described by the empirical law:

$$I = KV^{\alpha}$$

where α is the non-linear coefficient (>1) and K a constant depending on geometry and manufacturing process. The higher the value of α the better the protection. However α is not a constant and varies with voltage; α achieves its maximum near 1 mA/cm², as shown in Fig. 2.

Another interesting and important feature of the breakdown region is that it is relatively insensitive within reasonable limits to temperature, chemical composition and processing.

The origin of the non-linearity is attributed to the presence of electro-

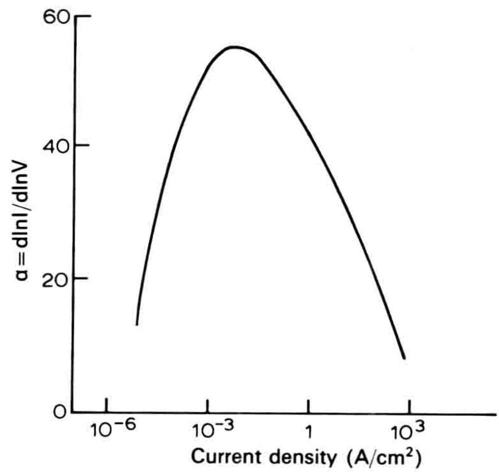

Fig. 2. Non-linear coefficient α as a function of current I.

static barriers located in regions of direct ZnO grain-to-grain contact. It is widely accepted that this barrier results from the interfacial trapping of free charge within the narrow physical boundary (few Å).

2.4 Zone IV: Upturn Region

The high current density in the upturn region is mainly limited by grain resistivity in ZnO crystals and not by the effect of potential barriers localized at the grain boundaries.

The relationship between current and voltage is given by:

$$V = R_g I$$

where R_g is the equivalent resistance of grains with a value generally below 1 cm at room temperature. In other words the lower the grain resistance, the lower the voltage and, hence, the better the protection against transient surges.

3. MANUFACTURE AND STRUCTURE OF THE ZINC OXIDE VARISTOR

ZnO varistors contain ZnO as the main ingredient with several kinds of additives. A typical formulation is shown in Table 1. Each additive controls one or several parameters, such as voltage breakdown, non-linear coefficent, surge current withstanding, etc., and can be divided into three groups[2] as shown in Table 2.

Zinc oxide varistors are produced by a conventional ceramic process as shown in Fig. 3. The ZnO and other oxides with purity and particle size carefully controlled are mixed by a ball milling method using zirconia

TABLE 1
Typical Composition of a ZnO Varistor

	Mol.%
ZnO	98
Bi_2O_3	0·5
CoO	0·5
MnO	0·5
Sb_2O_3	0·5

TABLE 2
Effect of Additives of Properties of ZnO Varistors

Basic structure	Bi_2O_3
Non-ohmic properties	MnO, Al_2O_3, In_2O_3, ...
Stability	Sb_2O_3, Cr_2O_3, NiO, Glass frit, ...

balls with deionized water. A slurry is then constituted with the powder and an organic binder (PVA) which is spray dried. The resulting granulated powder is pressed to the desired shape (generally discs) with a diameter range from 4 to 100 mm and thickness in the range from 1 to about 40 mm. This is a description of the simplest process used to obtain the granulated powder.

ZnO + additives
↓
Mixing – milling
↓
Granulating
↓
Pressing
↓
Sintering
↓
Electroding
↓
Lead soldering
↓
Resin coating

Fig. 3. Flow chart for the preparation of ZnO varistors.

However other variants are possible such as:

— Heat treatment of the mixed powder (700°–900°C) before spray drying.
— Heat treatment of the ZnO alone.
— Heat treatment of ZnO and some oxides.

After pressing the pellets are sintered in electrical furnaces at high temperature (1100–1300°C) in air atmosphere. The ceramic is then electroded by metallization processes according to the application:

Silver ink screen printing for medium and low voltage applications. This technology is an economical industrial process but has the disadvantage of requiring heat treatment (600–800°C).

Aluminium flame spraying for high voltage applications which avoids heat treatment and oxide diffusion. Unfortunately the equipment is expensive.

Leads are generally attached by solder, except in the case of high voltage applications, and the material is finally mechanically protected by an organic coating. Examples of common varistor shapes are shown in Fig. 4.

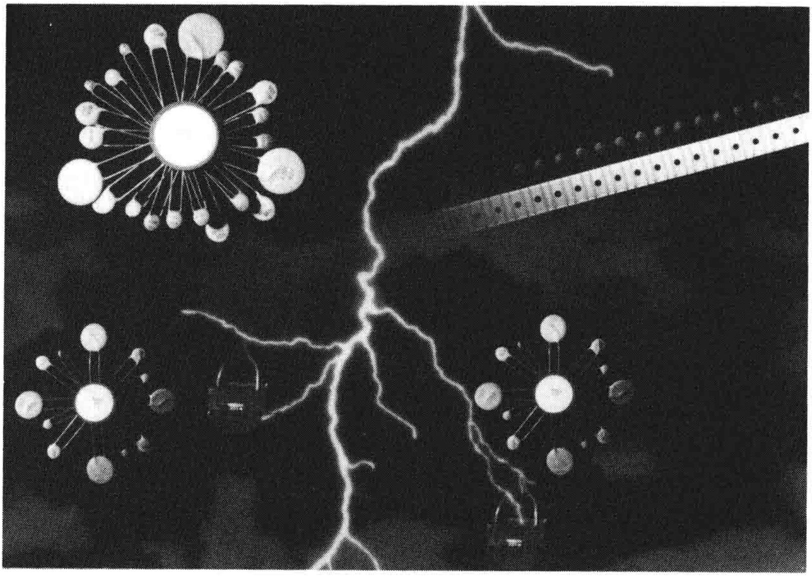

Fig. 4. Common varistor shapes.

The microstructure of zinc oxide varistors is schematically shown in Fig. 5. The essential parts of varistor materials are the conducting ZnO grains and the potential barriers localized at the grain boundaries that are responsible for varistor action. As a matter of fact, the actual structure given in Fig. 6, is comprised of semiconducting grains surrounded or not by crystalline phases such as:

— spinel type $Zn_7\ Sb_2\ O_{12}$,
— pyrochlore type $Zn_2\ Bi_3\ Sb_3\ O_{14}$,
— $Bi_2\ O_3$ $(\alpha, \beta, \gamma, \delta)$.

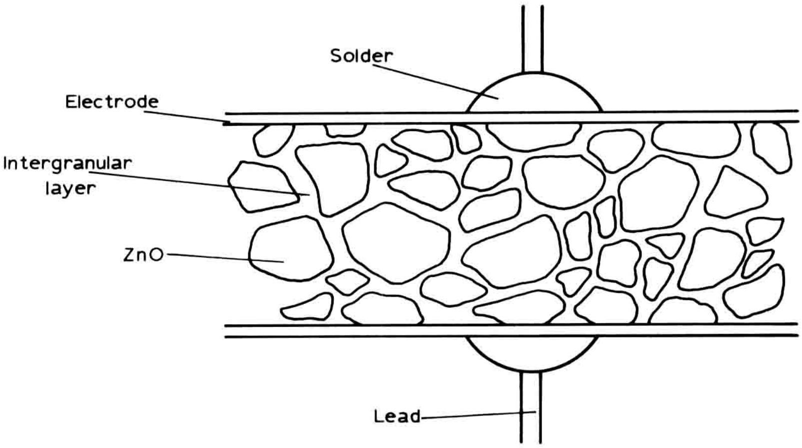

Fig. 5. Simplified structure of ZnO varistor.

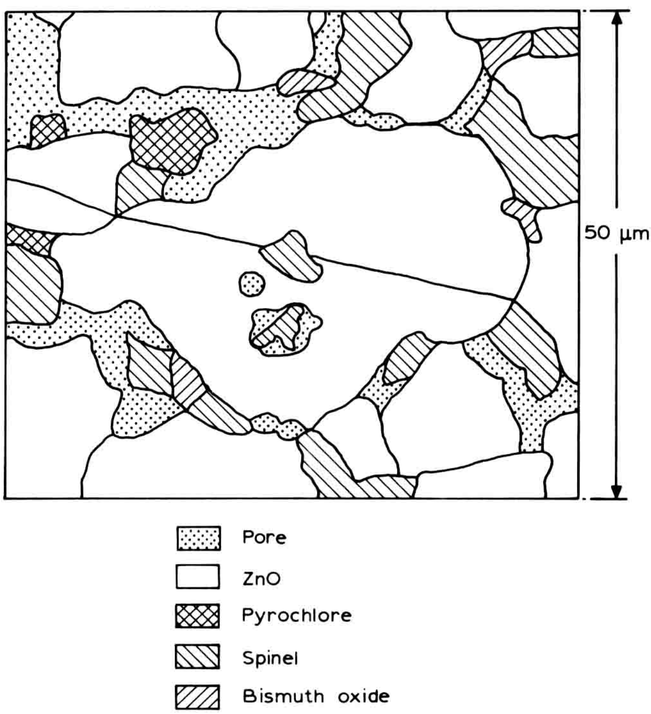

Fig. 6. Actual structure of ZnO varistor (after Graciet[12]).

Let us assume that all grains have the same size and potential barriers, the same electrical characteristics whatever their situation in the bulk, and that moreover secondary phases are disregarded. Thus, for a ceramic whose thickness is E, grain size d, the voltage breakdown (at 1 mA) is:

$$V_{1\,\mathrm{mA}} = 3E/d = 3n \tag{1}$$

where n is the number of barriers in the direction of the electric field and 3 V is the voltage breakdown per barrier. It is observed that this value is roughly independent of the chemical composition and fabrication process of the varistor.

As an example, a varistor with 1 mm thickness and 20 µm size grain has a voltage breakdown of 150 V corresponding to 50 barriers. A given breakdown voltage can therefore be achieved by changing the ceramic thickness or the grain size. Both methods actually used in industry. Although eqn (1) is experimentally proved, the model proposed by Einzinger[3] is quite different (Fig. 7). The potential barrier does not exist at each grain boundary. In other words, the varistor effect can be absent between two grains. Moreover, the barriers, if present, have different characteristics and can be separated into 'good' and 'bad' barriers.[4] As a result, the varistor electrical properties are closely correlated with the homogeneity of grain size and of barrier distribution and characteristics in the bulk, i.e. the homogeneous distribution of the additives.

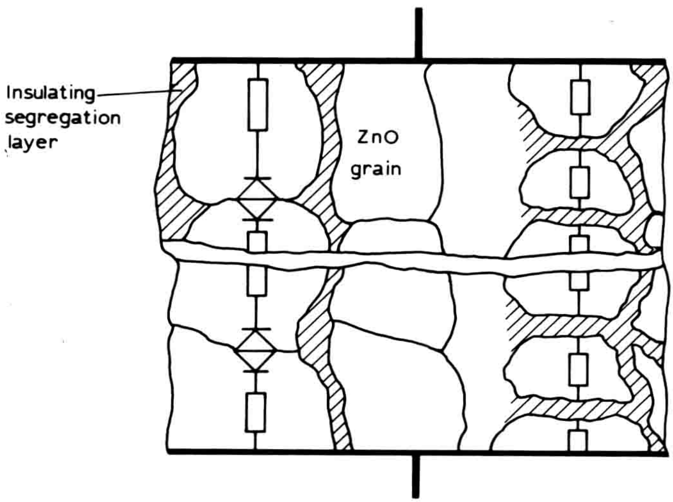

Fig. 7. Model of the actual structure of ZnO varistor (after Einzinger[3]).

4. ELECTRICAL PROPERTIES AND LIMITS OF ZnO VARISTORS

The performances of the ZnO varistors are ordinarily expressed by the following properties:

— static voltage–current relationship,
— capacitance and dielectric losses,
— response time,
— surge withstand capability,
— surge energy capability,
— reliability.

4.1 Static Current–Voltage Relationship

The current–voltage relationship is shown in Fig. 8. The voltage $V_{1\,mA}$ corresponding to 1 mA current is arbitrarily taken as a reference to define

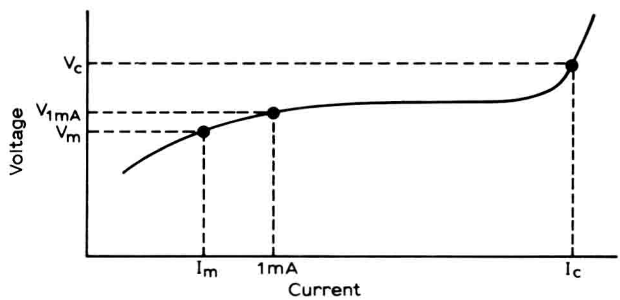

Fig. 8. Typical current–voltage characteristic.

the fabrication tolerance limit generally, ±10%. Its temperature coefficient is negative (−0·05%/°C). V_m is the voltage which the varistor can withstand in continuous operation. Generally V_m is approximately equal to 0·8 V_{1mA}. The current I_m corresponding to V_m is called leakage current and ranges from 1 to 100 μA. The lower its value, the lower the dissipated power.

The other zone of practical interest in the I–V curve is the high current region. In this region the lower the voltage, the better the surge protection.

Quantitatively the ability of the varistor to limit the transient voltage can be expressed by the clamping ratio C_r:

$$C_r = V_c / V_{1\,mA}$$

where V_c is measured for a given peak current I_c. The more C_r is near 1, the better the varistor protects. For example with $V_{1\,mA} = 200$ V and $V_c = 420$ V at 1000 A the clamping ratio C_r is 2·1.

4.2 Capacitance and Dielectric Losses

As a result of the presence of insulating potential barriers on either side of each grain boundary, the varistor has a capacitance that depends on its surface area and thickness. The capacitance and dielectric losses have the characteristic frequency dependences shown in Fig. 9.

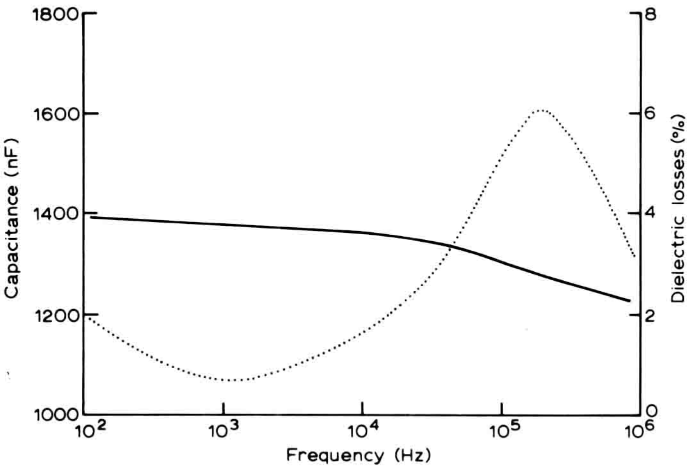

Fig. 9. Typical dielectric spectrum of a ZnO varistor. (——) Capacitance, (. . . .) dielectric losses.

These curves can be explained by the equivalent circuit shown in Fig. 10 in the case of a single grain boundary. The ZnO grain is equivalent to a resistance R_c. The depletion layer is represented by a capacitance C_{bl} (or C_{br}) and a parallel resistance R_{bl} (or R_{br}). To complete this schematic representation, contribution from a secondary crystalline phase is represented by a capacitance C_{il} and a parallel resistance R_{il}.

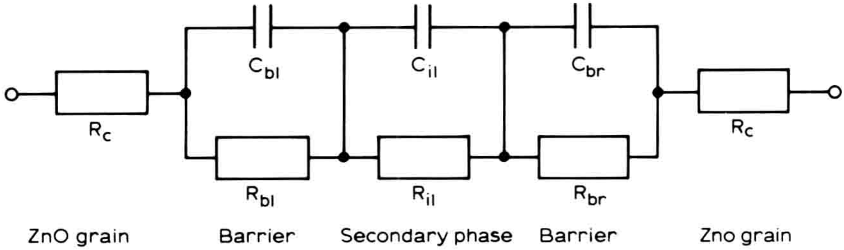

Fig. 10. Equivalent circuit for grain boundary.

The apparent capacitance of the varistor depends on its surface area, thickness and an apparent dielectric constant ε_a given by:

$$\varepsilon_a = \varepsilon v \times d/e$$

where v is the true dielectric constant of ZnO, d the average grain size and e the thickness of the depletion zone.

The capacitance range of ZnO varistors lies between approximately 50 pF and 5000 pF. These relatively high values of capacitance do not permit operation in high frequency applications.

4.3 Response Time

The response time of the varistor material itself lies in the nanosecond range. The lead inductance of the terminals increases the response time and must be as low as possible.

4.4 Surge Current Withstand Capability

Zinc oxide varistors exhibit a modified voltage–current curve when subjected to surge current as shown in Fig. 11. In particular, the leakage current increases at constant voltage. In other words, the electrical power increases and, hence, the temperature of the ceramic. As the leakage current has a positive temperature coefficient, the power increases again and such conditions can lead to a thermal runaway.

As can be observed from this curve, the high current region is not modified after the application of surges and, therefore, the protection level is not shifted. In order to quantify these modifications, the relative variation of $V_{1\,mA}$ is calculated before and after surge application as illustrated in Fig. 12.