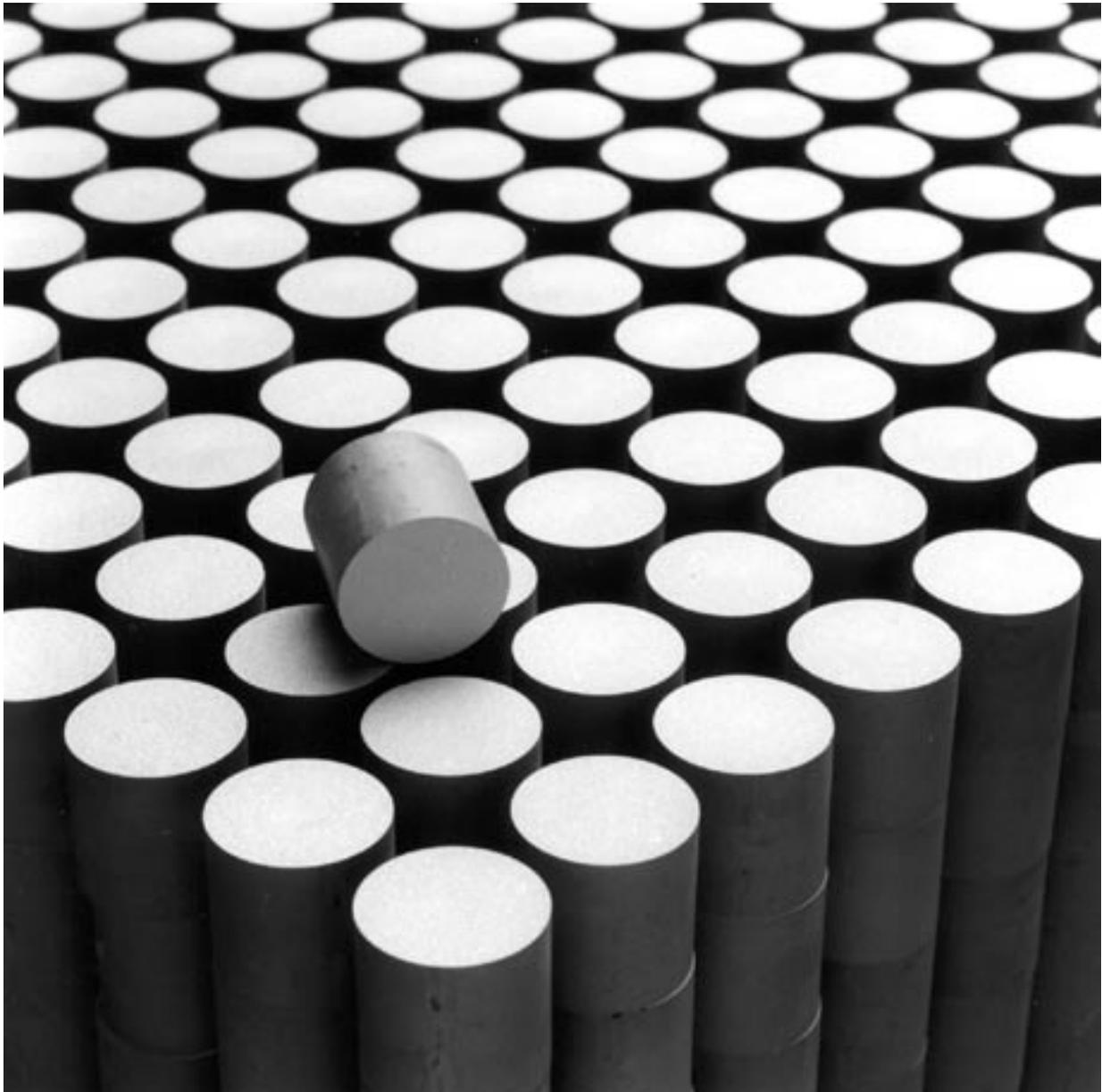# Technical information

Physical properties of zinc oxide varistors

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Manufacturing of zinc oxide varistors

Zinc oxide varistors are ceramic semiconductor devices with highly non-linear curent-voltage characteristics and with an extremely good energy capability.

These physical properties combined with a cost effective production have made the gapless surge arrester with zinc oxide varistors become the standard for overvoltage protection at all power system voltages.

The active part of the surge arresters are the zinc oxide varistors.

Ingredients

Zinc oxide varistors consist mainly of zinc oxide (about 90 % by weight) and small amounts of other metal oxides (additives) such as bismuth-, cobalt-, antimony- and manganese-oxide.

Metal-oxide varistors are manufactured with traditional ceramic process technology. The main operations are shown at right.

Quality in all steps

Quality in all manufacturing steps is a prerequisite for the resulting physical properties of the varistors. The most critical processes are powder preparation and sintering.

- Raw materials of highest quality are used in order to obtain a low leakage current through the varistor during the continuously applied operating voltage.

- The different metal oxides are carefully mixed in several steps in a highly automated process. Only perfectly homogenious powder guarantees a uniform current distribution throughout the whole varistor. The uniform current sharing in the varistors is one of the main reasons for their excellent energy capability.

During the heat treatment the pressed discs transform into solid ceramic bodies. At the high sintering temperature the bismuth oxide melts to form a liquid phase in which the other metal-oxides dissolve. In this process the powder particles are united by diffusion and subsequently grow into large grains.

1. Preparing of powder by weighing, milling, mixing different metal oxide materials.

2. Spray drying the milled metal oxide materials.

3. Pressing of the powder into cylindrical discs

4. Sintering of the discs for several hours at a temperature of 1100-1200 ℃.

5. Applying an insulating and passivating layer on the cylindrical surface and of metal electrodes on the flat surfaces.

6. Electrical testing and classification

Electrical characteristics

The voltage-current characteristics of zinc oxide varistors can be divided into three different regions:

- At low currents in the *pre-breakdown region* the resistivity of the material depends on temperature, with a negative temperature coefficient. Equation 1 shows the current I at a constant voltage, where E_a is an activation energy (about 0,8 eV at room temperature), k and T are Bolzmann constant and the absolute temperature, respectively.

- In the *breakdown region* the temperature dependence is very small. Equation 2 describes the performance of the varistor empirically, where α = 30-50 for $I=10^{-5}$ A/mm^2 and V is the voltage across the varistor. If $\alpha=1$ the behaviour is ohmic,

i.e. the current is proportional to the applied voltage. When $\alpha \rightarrow \infty$ the current varies infinitely for small changes in the applied field.

- In the *high current region* the curve turns upwards, which determines the impulse behaviour of the surge arresters (>1 kA). Here, the characteristics are no longer strongly non-linear as in the breakdown region. This region is determined by the bulk of the doped ZnO grains. The doping level is controlled by small additions of aluminium.

Figure 1 also shows the capacitive leakage current, which is much larger than the resistive current in the pre-breakdown region. The capacitance of a varistor with diameter 75 and height 23 mm is about 1 nF.
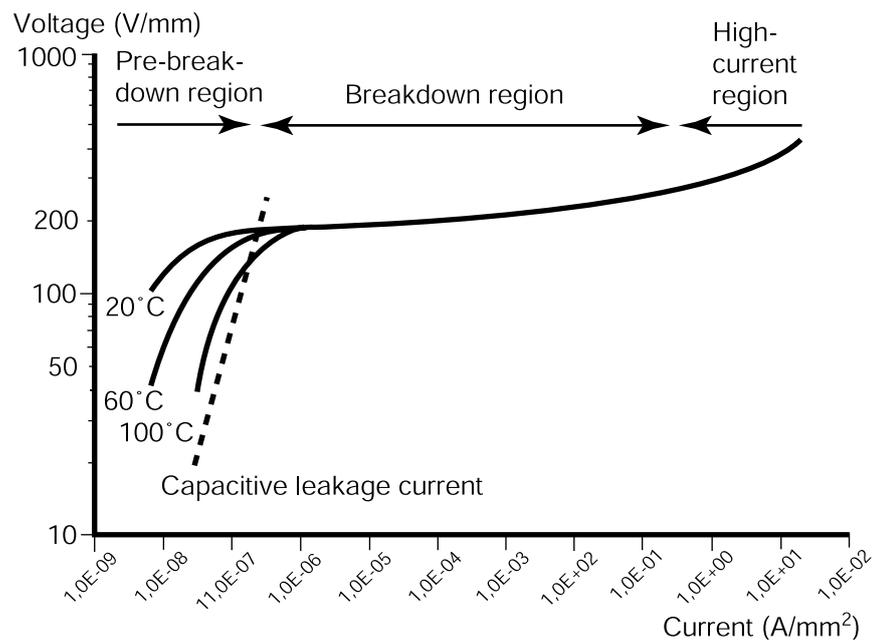
Equation 1:

$$I = I_0\, exp\, (-E_a/kT)$$

Equation 2:

$$I_1/I_2 = (V_1/V_2)^{\alpha}$$

Figure 1: Typical zinc oxide varistor characteristics

Microstructure

During the sintering process the metal oxide powder transforms to a dense ceramic body with varistor properties. The picture fig. 2 shows the micro-structure of
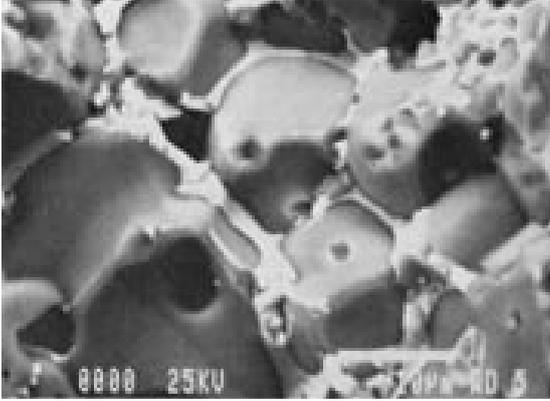

Figure 2: Fracture surface of zinc oxide varistor at 2400 times magnification.

a fracture surface of a zinc-oxide varistor observed in a scanning electron microscope at 2400 times magnification. The surfaces of the intercrystalline fracture follow the ZnO-grain boundaries. The grain size of the ZnO is about 10 µm. The light areas between the ZnO-grains are a bismuth-rich intergranular layer, which is accumulated at triple points between the grains and forms a continuous network. The small particles are a spinel phase ($Zn_7 Sb_2 O_{12}$) with a diameter of 1-4 µm.

The bulk of the ZnO grain is a n-type semi-conductor with good electrical conductivity ($\delta \leq 0,1$ Ωcm). The boundaries, on the other hand, form highly insulating layers at low voltages ($\delta = 10^{12}$ Ωcm). The thickness of the boundary-layers is about 0.2 µm. Thus, in the pre-breakdown region, the applied operating voltage is distributed on the intergranular layers only. If the voltage exceeds the breakdown voltage of the layers, the resistance of the intergranular layers abruptly decreases. The voltage at breakdown of the layers (defined at l=10^{-6} A/mm^2) is about 3 V/layer, independent of material composition. Since the voltage across the grain is about 3 V at breakdown, the breakdown voltage of the varistor is directly proportional to the number of grains between the varistor electrodes. For that reason the breakdown voltage V_B of a varistor can be controlled by controlling the grain growth during sintering. For a given sintering time, a higher temperature causes the grains to grow faster which means there will be fewer grains leading to a lower V_B.

Some of the other additives affect the grain growth, particularly the which precipitates in the form of fine particles of a spinel-type ($Zn_7 Sb_2 O_{12}$). These particles inhibit grain growth and promote a uniform distribution of the ZnO grain size.

Conduction mechanisms

Pre-breakdown region

The conduction mechanism in the pre-breakdown region is explained by means of energy barriers in the grain boundaries, similar to metal-semiconductor devices, e.g. the Schottky diode. At each boundary a potential barrier is formed by capturing of electrons by acceptor impurities, resulting in a negative surface charge. The negative interface charge is compensated by ionized, positively charged donors in a space charged region formed on each side of the grain boundary. An applied electric field has the effect of lowering these barriers, which gives rise to a small current through the barriers. This current is temperature dependant. A higher temperature increases the energy of the electrons and they will more easily pass the barriers. Figure 1 clearly shows this temperature dependance.

Breakdown region

Several different models, have been proposed to explain the grain-grain conduction at breakdown. The model of Greuter et al. and Mahan et al. both associate the highly non-linear conduction with a triggered tunnelling mechanism involving hole creation. When the voltage exceeds a critical value of about 3 V per grain boundary, it is possible for some electrons, which have overcome the potential barrier, to absorb so much energy in the high potential field ($F > 10^{-6}$ V/cm), that holes are created by means of impact ionization. The positively charged holes drift to the negatively charged grain boundary, where they reduce the overall charge. The hole-current therefore reduces the height of the barrier. This sudden reduction of the barrier height explains the dramatic increase in current. The breakdown voltage per barrier does not depend on varistor composition or processing. Tunnelling is so far the only mechanism proposed, capable of qualitatively describing grain-to-grain conduction at breakdown.

High current region

In the high current region the voltage drop across the ZnO grains is dominating. The behaviour in this region can be controlled by means of doping the ZnO grains in order to change the grain resistively, e.g. with aluminium. However, doping also effects the properties in the pre-breakdown region, because some of the aluminium will be located in the intergranular layers, thereby reducing the barrier height. In order to avoid a high leakage current, doping additives have to be used carefully. Appropriate doping levels have been identified by intensive research work, which has also led to a deeper understanding of the electronic phenomena occurring at the grain boundaries.

Long term stability

Under extreme electrical stresses the non-linear characteristics of a varistor can degrade. This degrading phenomena is due to diffusion of the doping elements and of oxygen. Extremely high electrical fields in the vicinity of the grain boundaries cause the elements to migrate from the grain boundaries. By addition of certain elements this effect can be eliminated. Furthermore, environmental influences can deteriorate the electrical properties of the varistor surface. Under oil or in SF6 gas with low oxygen content the potential barriers can be reduced at the surface. This can be effectively inhibited by coating the surface with mum allowable operating voltage and at an elevated temperature of 115°C, see Figure 3.

The varistor characteristics improve during the stabilizing. For ABB varistors this improvement is obtained especially in the low current region - which is the region determining the behaviour under normal service conditions.
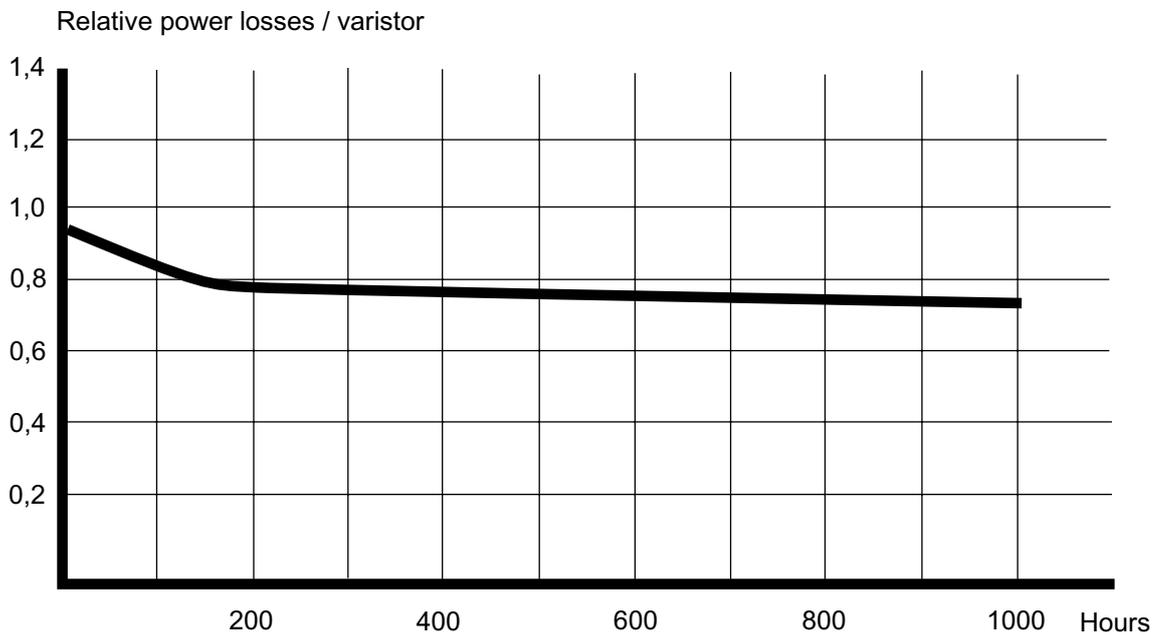
Relative power losses / varistor

Figure 3: Power losses P/P_0 of an ABB zinc oxide varistor as a function of time

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