ZINC OXIDE BASED VARISTORS and PARALLEL CIRCUIT PROTECTION: THE STATE OF THE ART

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Key words: ZnO varistors, parallel circuit protection, historical survey, state-of-the-art, applications, main world manufacturers, R&D, Research & Development, technology trends

Abstract: In this conference the Author gives the historical of the research and the technology of Zinc Oxide based varistors since 1960 to this day with the following points:

- Discovery of the varistor effect in 1960 by Russians,
- Industrial development by Japanese,
- Current manufacture technique,
- Curreni performances: threshold voltage, residual voltage, Capacity of energy absorption, Aging.
- Main applications,
- Main manufacturers in the world.

The author described the main orientations of research and development:

- Increase of the threshold voltage (of 200 V/mm to 400 V/mm),
- Increase of the absortion capacity of energy (of 200 J/cm^3 to 600 J/cm^3),

The future technology will be:

- Chemical mixed powder method,
- Direct Oxydation of an alloy.

Varistorji na osnovi cinkovega oksida in zaščita vezij: trenutno stanje

Ključne besede: ZnO varistorji, zaščita vezja paralelna, pregled zgodovinski, stanje razvoja, aplikacije, proizvajalci glavni svetovni, R&D raziskave in razvoji, trendi tehnologije

Povzetek: V prispevku avtor podaja zgodovinski pregled razvoja in tehnologije izdelave cink oksidnih varistorjev od leta 1960 pa vse do danes in sicer:

- odkritje varistorskega efekta leta 1960 s strani Rusov
- industrijski razvoj, ki so ga opravili Japonci
- trenutne tehnike proizvodnje
- trenutne lastnosti: pragovna napetost, rezidualna napetost, kapaciteta absorpcije energije, staranje
- glavne veje uporabe
- glavni svetovni proizvajalci

Avtor opiše glavne smeri razvoja in raziskav:

- povečanje pragovne napetosti (od 200 V/mm na 400 V/mm)
- povečanje kapacitete absorpcije energije (od 200 J/cm^3 na 600 J/cm^3)

Tehnologija bodočnosti bo:

- izdelava iz kemično mešanega prahu
- direktna oksidacija zlitine

1. INTRODUCTION

Electrical circuit protection against overvoltage of atmospheric origin or coming from internal defects of the grid, needs non-linear resistive elements (i.e. elements whose current becomes very important when the voltage applied on its ends exceeds certain threshold value), such as park gaps, Silicon junction devices or varistors. The word "varistor" comes from the association two words: "Variable resistors". Before the coming of Zinc Oxide based varistors on the market of circuit protection, elements above-mentioned are used, for lack of something better, with their own disadvantages. Spark gaps represent two major disadvantages that are the variation of the protection voltage with the rise time of the overvoltage and the existence of the follow current. Silicon junction devices such as Diodes, Thyristors are used only for low voltage circuits and for small energies (in the range of 1 Joule). Varistors are represented by two types of materials, Silicon Carbide based varistors and Zinc Oxide based varistors. The first type of varistor (SiC) presents a very high leakage current (more than 10 mA) and a low nonlinearity (10 times lower than Zinc Oxide based varistors) Figure 1. One was therefore constraint to use Silicon Carbide based varistors in series with a spark gap. The threshold voltage of this association becomes very sensitive to the over-voltage rise time.

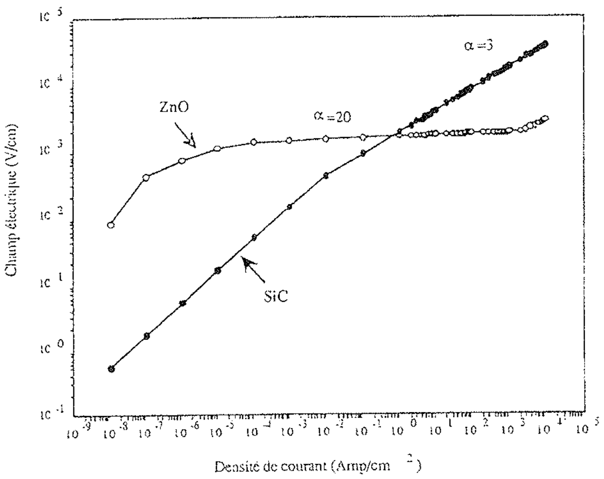

Figure 1

Zinc Oxide based varistors, recently arrived in the market, are not exempted of defects, but they represent an acceptable compromise in the field of energy, leakage current, response time and cost to be used in most of applications. In this communication, we give an overview on the history of varistors, its actual development and research undertaken in Laboratories with the aim to improve its electrical properties.

2. ZINC OXIDE VARISTOR STORY

In 1958, MS. Kosman and IA. Gesse in the former USSR, put forward, for the first time, nonlinear properties of Zinc Oxide based materials without a great echo in the industrial world /1/. It was only in 1968 that Matsuoka of the Matsushita Electronic Components company announces the discovery of the varistor effect after researches made on rectifier contacts between a semiconducting ceramic (Zinc Oxide) and a metal (Silver) /2, 3/. Since this date this company throws, in 15 years, in very diversified applications going from the low voltage to the high voltage protection.

Some years after publication of Matsushita in 1970, the main companies producing equipments for electricity, embarked in the same adventure. It concerns General Electric Company, Meidensha and ABB. The Meidensha Company benefits from the cooperation with Matsushita /4/.

The case of General Electric Company is very typical and merits to be related /5/. After the announcement by Matsushita in 1970 of the realization of Zinc Oxide based varistors, GE Co started in 1971 in the research and the development of the material by solving successively the problems concerning the sintering of the large pieces of varistors, the improvement of the nonlinear coefficient, the stability of the varistor under AC and DC voltage, the choice of electrodes and the coating of the varistor to avoid the flashover. These works have lasted 5 years. At the end of 1976 this Company began the production of the arrests for AC grids going from 10 KV to 600 KV. Firsts DC arresters of 588 KV, without spark gaps, are installed for the first time on the Brazilian system of ITAIPU.

Similarly to this effort of development, the researches developed strongly with as results the understanding of the conduction mechanism in this type of material, the correlation between some doping elements and electrical properties of the material. During years of 1980 one can count approximately 80 publications per year appeared in scientific reviews. Then this rate decreased to stabilize currently around 40 publications/year.

It is difficult to estimate exactly the economic weight of Zinc Oxide based varistors in the world. But one can have a precise idea of the Japanese production /6/. This country produces 1.2 Billion units per year with about $250 Millions.

In Europe producers of varistors are the following: Harris, ABB, LCC-Thomson, Soulé, Siemens, Iskra, Power development....

3. ZINC OXIDE VARISTORS: THE SATE OF THE ART

3.1 Manufacturing method

The composition

Most ZnO varistor materials contain more than 90 mol % ZnO and the composition is balanced by the addition of other oxides. A number of different additive oxides can be used to form varistor properties of a material, examples are oxides of Bi, Pr, Ba, Sr, La, Co, Mn, Ni, Co, Cr, Sb, Si, B, Ti. A typical ZnO varistor contains additions of Sb_2O_3, Bi_2O_3, CoO, MnO and Cr_2O_3. Powders of the oxides are mixed, spray dried, and they are subsequently pressed into green bodies which are sintered at temperatures around 1200°C.

Manufacturing process

Zinc Oxide based varistors are made, in general, by conventional process used for the manufacturing of ceramics. The main steps are described schematically in the figure 2. Doping additives in the form oxides powder with dimension about few microns, are weighed and mixed with ZnO by means of balls grinding. The duration of this operation takes some hours in wet medium with addition of organic products such that binders and lubricants that will facilitate following operations. The drying of the composition is accompanied by a granulation. This last operation gives a powder of spheroides of 100 μm in diameter.This powder is then pressed in mold with an appropriate form. These samples are then sintered at 1100 -1300°C. This operation is very important because it insures the crystalline growth of Zinc Oxide grains and the formation of the microstructure from which depend electrical properties of the varistor.

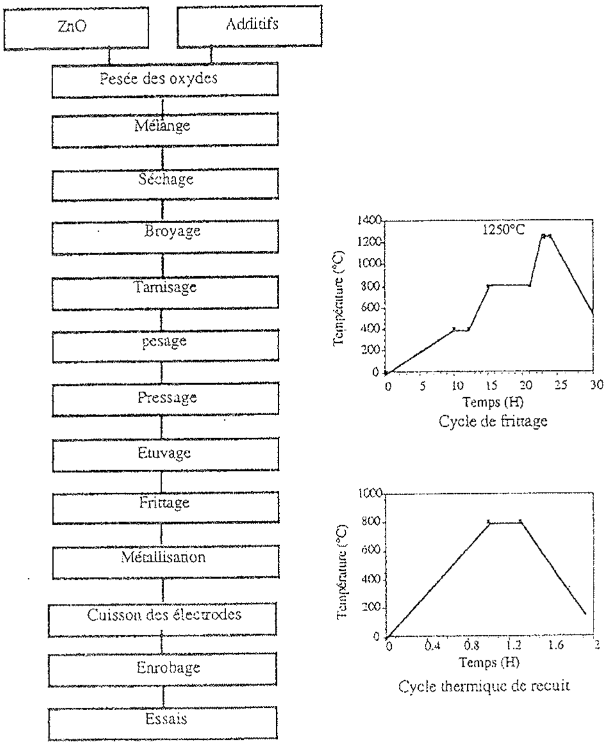

Figure 2

On sintered samples one deposits electrodes on the two parallel faces of the varistor bloc and an insulating layer of glass or of synthetic resin to avoid the flash over during shocks of great amplitude current.

3.2 The microstructure of ZnO varistor materials

The resulting microstructures consist of ZnO grains and intergranular phases. Intergranular phases are spinels of the type $Zn_7Sb_2O_{12}$, and a number of Bi-rich phases. There are other minor phases which are not readily detectable by conventional technique.

Spinel grains are usually present between the ZnO grains. The grains of spinel are considered to be electrically insulating and do not directly contribute to the non-linear current/voltage characteristics. Bi-rich phases may be present between the ZnO grains and spinel grains and these can form a three dimensional network along triple grain junctions of ZnO. The majority of the ZnO grain boundaries in the varistor material are devoid of intergranular film but they instead contain segregated Bi atoms.

The chemical formulations of the sintered products are complex and their complexity is further compounded by the nature of the doping elements that are invariably present in each phase. The major dopant in the ZnO phase is cobalt but manganese, chromium, nickel and antimony are also present in very small concentrations. The main compounds of the intergranular material are all doped by chromium, manganese, cobalt and nickel.

The breakdown voltage of a varistor is determined by the ZnO grain sizes in the varistor material. The ZnO grain size varies from few microns in the material for high voltage applications, to hundred microns in the material for very low voltages in electronics. The grain sizes are controlled by the amount and the nature of added oxides.

The basic building block of the ZnO varistor is the ZnO grain formed as a result of sintering. During this process, various chemical elements are distributed in such a way in the microstructure that the near-grain boundary region becomes highly resistive, and the grain interior becomes highly conductive.

The functional microstructure of ZnO varistor materials can be described as consisting of

- doped semiconducting ZnO grains ;
- ZnO interfaces which provide the barriers to electrical conduction and which give rise to the non-linear current - voltage characteristics ;
- a continuous network provides an alternative conduction path, that avoids the barriers that are associated with the ZnO interfaces, and can give a significant contribution to the conductivity in the prebreakdown region of the current-voltage characteristics.

3.3 Electrical characteristics

I(V) curve and energy absorption capability /7/

Generally some electrical tests (on-line or off-line) are performed on varistors. First of all, one measures the electrical characteristic current-voltage I (V). From zero to 10 mA, this measure is made by means a DC voltage and automatically. Above 10 mA, one operates with short impulse current to avoid an excessive overheating of the varistor. For varistors to be used in medium and high voltage arrests, other tests are performed to insure their good behavior to thermal and electrical stresses.

Presented in the order where these tests are made, the first test is the aging test. To do this test, one applies a polarization voltage, a fraction of threshold voltage, for example Up= 0.6 Us, and one records the leakage current. This current has to be constant or maintained at a certain value that avoids the thermal run away. To accelerate the ageing and to limit the duration of the test to 1500 h, the sample is placed in a oven at 115°C.

Then one simulates lightning strokes by applying shocks of 65 kA impulse current of 4/10μs form. The variation of the threshold voltage after these tests, must be between 8 and 10%. Finally, one submits samples to long duration impulses (2 ms) to simulate switching overvoltage. Characteristics of these impulses are such that energy applied to the sample must be in the order of 100 J/cm^3. The variation of threshold voltage must be close to 0%.

Equivalent circuit

The equivalent circuit of the varistor can be represented by the following diagram (Fig. 3), where Ri and Ci are the resistance and the capacity of the joint of grain with

Ri dependent strongly the applied voltage Rej is the resistance of the Zinc Oxide grain. One adds an inductive element L because during of tests in shocks one observes a delay between the current and the voltage. One can use the following equation to represent a varistor:

$$U = kI^{1/\alpha} + RgI + LdI/dt$$

Where:

k = a constant depending on the value of the threshold voltage,

α = the nonlinear coefficient,

Rg= the resistance of the Zinc Oxide grain,

L= the inductive part of the varistor.

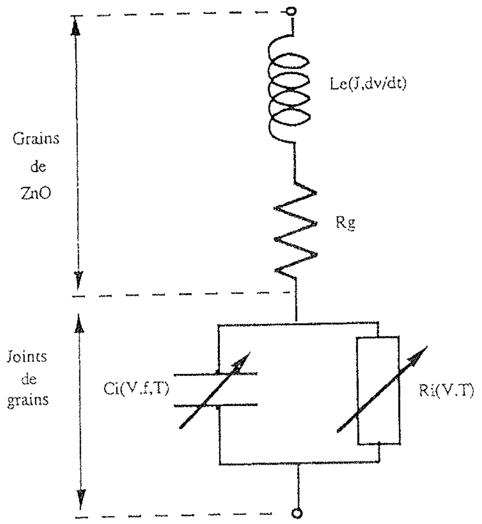

Figure 3

3.4 Conduction mechanism of Zinc Oxide Varistor /6/

Because of the granular structure of the varistor, there are in the ceramic potential barriers between Zinc Oxide grains due to a trapped electrons. These barriers of potential oppose to the passage of the current for low level voltage giving a high resistivity of the material. When the applied voltage to two adjacent grains is near 3 volts approximately, a recombinaison phenomenon is produced neutralizing the space charge and provoking a collapse of the potential barrier. The resistivity of the material decreases then strongly and it is limited only by the resistivity of Zinc Oxide grains.

3.5 Application of Zinc oxide Varistor in low voltage network

The overvoltages are always present in electrical networks (at low or high voltage). For low voltage system, the overvoltages come from the external side of the grid (lightning overvoltage, overvoltage coming from defect of the distribution system), as well as from the internal side (fusion of fuses in inductive circuit,..etc...). One estimates that the overvoltages can occur on the average 5 times per year with amplitude that can reach 4 KV. Taking into account on the other hand that the dielectric breakdown of most of domestic electrical machines do not exceed 1500 Volts (the rule 2U + 1000), one can see easily that it arrives often to observe the breakdown of these machines or in the most favorable case to observe a shortening of their duration of life. It is therefore imperative to protect them by protective devices that one puts in parallel to the entry of the power line. In a system with 3 phases, one inserts them between phases, between phases and earth and between neutral and earth.

Components used in protective system (a module) are generally Zinc oxide varistors and the gas spark gap. Useful characteristics of Zinc oxide varistors are:

- A very good non-linearity coefficient (more than 50)
- The variable threshold voltage following the thickness,
- A very good coefficient of quality: V (1mA)/V (5kA) =1.6-1.8
- A high capacity of energy absorption (200J/ cm^3)
- A weak drift of the electrical characteristic with the aging.

The spark gap is a protective device used in the past in the area of telecommunications. It is composed metallic electrodes and a ceramic envelope filled with a rare gas. On the wall of the envelope one deposits lines of graphite that serve as starter of the discharge. The energy absorption capacity of the spark gap is not great. Its interest resides in the low value of the capacity. For this reason, one uses them to protect signal lines.

Low voltage protection modules or low voltage arrests are made to be connected to the public distribution system or to electrical installations with voltage below l000V, for their protection against atmospheric or industrial overvoltages. Modules are realized with Zinc oxide varistors or in association of Zinc oxide varistors and spark gaps. Spark gaps are rarely used alone for the power line 250/ 400 V because of the extinction problem.

The multi-step protection is often used in very low voltage installation (< 50 V) to obtain a strong power dissipation and a weak residual level voltage.

4. CONCLUSIONS

Concerning research works, it is important to point out the following points:

- Research on the influence of the some doping elements on electrical properties of the ceramics,
- Research on chemically mixed oxides. These oxides are obtained by pyrolyse of nitrates or oxalates of metals dissolved in water. This method allows to obtain a homogeneous mixture,
- Research on others types of materials: SnO to replace ZnO, Praseodymium Oxide to replace the Bismuth Oxide,

– Research on the manufacturing process and the composition to increase the threshold voltage (from 200 volts to 400 volts per mm) and the energy absorption capability of the varistors (from 100 J/mm to 300 J/mm).

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