

A Few Aspects about the Manufacturing Process of Five and Two Additives Metal Oxides Varistors

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Abstract: ZnO based varistors are today used for making state of the art surge arresters for all voltage levels. Essentially they are "n" semi-conductor ceramics made of ZnO (more than 90% molar percents) and many other oxides having different structural roles. This paper presents a new manufacturing technology based on 2 additional oxides Cr_2O_3 and MnO_2 , compared with the old one, having five oxides (Cr_2O_3 , MnO_2 , Co_3O_4 , Bi_2O_3 , NiO). This varistor material has a smaller electrical capacity, suitable for telecommunication applications. The chemical compositions of this new material as well as all the phases of the manufacturing process are presented too [1]. Table 1 shows the initial chemical composition of the varistor. The last four additives will be lost by evaporation after finishing the manufacturing process [2].

Keywords: manufacturing process, five and two additives, metal oxides varistors

1. Introduction

Metal Oxide Varistors (also named ZnO varistors, due to their most important component) are today used for making state of the art surge arresters for all voltage levels, from domestic low voltage to high voltage transport lines. Their main goal is to protect any piece of electrical equipment against any type of over voltage which occurs on the power supplying network (technical incident, induced voltages or lightning stroke) [1]. They are applied in modern technologies due to some important advantages such as: a high level of non-linearity for the current-voltage characteristic, a high energy absorption capacity and an excellent response time. They are essentially ceramic polycrystalline n – semiconductors. They are made from a mixture of metal oxides such ZnO (more than 90 %), Sb_2O_3 , MnO_2 , Bi_2O_3 , Cr_2O_3 , Co_3O_4 and many others [2]. But, for different purposes, not all the ingredients are necessary. This paper intends to demonstrate this.

ZnO in his natural state is an excellent semiconductor. Generally it is more likely to find more Zn^{2+} ions inside his structure. By introducing other metal oxides, Zn^{2+} ions are substituted inside the crystal structure only by bivalent metal ones. The others will be placed between the ZnO fragments and work like a supplementary potential barrier.

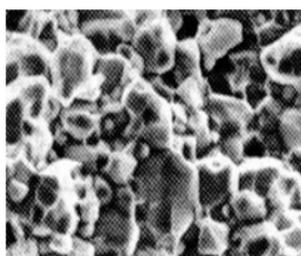


Figure 1. Micro-structure of a ZnO varistor

Figure 1 shows us the microstructure of a metal oxide varistor, as observed on the electronic microscope. We notice the large ZnO crystal grains and the inter-granular layer of other oxides, which, in fact, gives the varistance effect by introducing a supplementary potential barrier.

This micro-structure looks like a stone-wall having ZnO grains as stones and other oxides acting as cement [2].

The varistance effect consists in a non-linear (non-ohmic) relation between the crossing current (the crossing current density. In fact, at low voltage, the varistor acts as an insulator and at higher voltages, it acts like a conductor. So, it is ideal for any protective devices made for voltage suppression. Cr_2O_3 and MnO_2 are used in order to obtain different structure phases during the elaboration process. It's obviously that the amount of Cr_2O_3 and MnO_2 used during manufacturing has a highly influence over all electrical proprieties of that varistor [2]. The main purpose of this paper is to determine the influence of Cr_2O_3 and MnO_2 concentration over the electrical capacity of that varistor. The opening voltage of a certain varistor V_N is the DC voltage measured between the faces of the varistor, conventionally, when a 1 mA DC current is established through that varistor. All phases of the varistor manufacturing process are shortly described bellow:

First, all metal oxide powders are carefully weighed. After weighing, all components are mixed and grinded by using pure water and organic solvents for a few hours. Water and organic solvents are removed by slowly heating that mixture. Another grinding operation is necessary after removing those solvents. The resulting powder mixture is sifted to avoid formation of large pieces. The resulting powder is put into moulds and carefully exposed to higher pressure (hundred of bars). After pressing, the resulting piece is gradually submitted to extreme heating (at temperatures higher than 1000 °C) for a few hours. Next, the varistor is naturally cooled down. When the varistor is cooled at the environmental temperature, a small layer of

Ag is applied to both ends, as electrodes. The Ag based compound is a semi liquid paste which has to be dried before any other action could be performed (by slowly heating again). Then, the final phase of the technological process consists in submerging the heated piece into an epoxy resin powder in order to obtain the rapid polymerization of that organic insulator [1].

2. The chemical composition of a varistor

Generally, all physical and electrical proprieties are depending of the chemical composition. Weighing all ingredients (after establishing a correct composition) is an important operation. This operation is made by using a standard METTLER electronic balance for weights more than 0.1 mg. This operation is relatively simple, because all the ingredients are delivered as powders, having a very uniform and well determined granulation.

The initial chemical composition of a standard varistor having 5 additional oxides is shown in Table 1 [2], according to a technology developed by the Génie Electrique Laboratory in Toulouse, France. All masses are reported to 500 g of mixture. The role of each component is different. There are many oxides inside this material, but the role of the last 4 oxides is not very important, because they are used only for grain growth.

TABLE 1. Initial chemical composition of a standard varistor

Substance	Percentage [%]	Mass [g] for 500 g mixture
ZnO	87.45	411.28
MnO ₂	1.843	3.75
Co ₃ O ₄	2.09	10.457
NiO	0.648	3.244
Bi ₂ O ₃	4.047	20.235
Cr ₂ O ₃	1.515	7.575
Sb ₂ O ₃	9.0466	44.345
B ₂ O ₃	0.0756	0.378
MgO	0.0438	0.219
Al(NO ₃) ₃	0.0260	0.130

The first author developed, during her stages at the Génie Electrique Laboratory from the PAUL SABATIER University of Toulouse, France, another varistor material which could be used for telecommunication applications, due to its reduced electrical capacity. It is based only to no more than 2 additive oxides (having a reduced electrical capacity).

This initial chemical composition is shown in Table 2 (all masses are reported to 500 g of mixture).

By comparing to the initial composition, we notice that only the Sb₂O₃ amount has been modified.

TABLE 2. Initial chemical composition of a new varistor

Substance	Percentage [%]	Mass [g] for 500 g mixture
ZnO	87.45	437.25
MnO ₂	1.843	9.215
Cr ₂ O ₃	1.515	7.575
Sb ₂ O ₃	9.0466	45.233
B ₂ O ₃	0.0756	0.378
MgO	0.0438	0.219
Al(NO ₃) ₃	0.0260	0.130

We insist that this is only the initial chemical composition. It will be changed after passing all the phases of the manufacturing process, due to the vaporization and decomposition of many supplementary oxides. Practically, only the first two useful oxides will remain inside the electrical material.

For the two remaining oxides we can say that their roles are:

- Cr₂O₃ is used mostly for grain growth limitation;
- MnO₂ is used as a doping element.

After weighing, all ingredients have to be carefully mixed by using the mixing ball machine. The mixing procedure can last for more than 30 hours, in order to obtain a homogeneous powder, which could be pressed after. As we mentioned before, the rest of the oxides will be decomposed after passing through all the phases of the manufacturing process.

After passing all the other phases of the manufacturing process, the most important remaining one is the heating process.

The typical thermal cycle for a ZnO based varistor is shown in Figure 2.

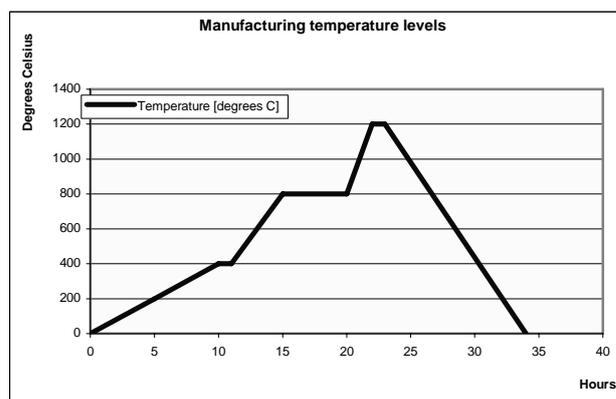


Figure 2. The thermal cycle of a ZnO based varistor manufacturing process

The resulting piece of semiconductor equipment will be carefully put to electrical measurements in order to determine all its parameters.

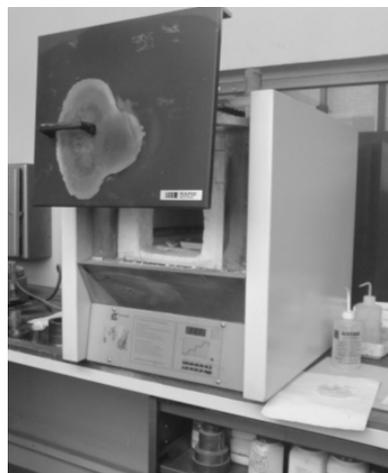


Figure 3. Ceramic programmable heater

One of the most important aspects of the manufacturing process is the baking temperature. In Figure 1, it represents the higher peak level (a small line) when the varistor is exposed to at least 1000 °C (1200 in Figure 2) starting from the 22nd hour to the 23rd hour. The heating installation is presented in Figure 3. This installation is fully programmable and all temperature levels are set automatically, according to software specifications.

The baking temperature, as well as the chemical composition, is essential for varistor behaviour.

3. Experimental procedure and results

This paper presents the influence of the baking temperature on the electrical parameters, for a small varistor group made by us. Only the leaking (defined in the first chapter current is measured. The electrical installation used for leaking current measurement is shown in Figure 4. The purpose of all measurements is to determine which is the optimal temperature level in order to obtain the best electrical results. All experiments related to this paper were made at the "Génie Electrique" Laboratory, from PAUL SABATIER University in Toulouse, France by using equipment located there.

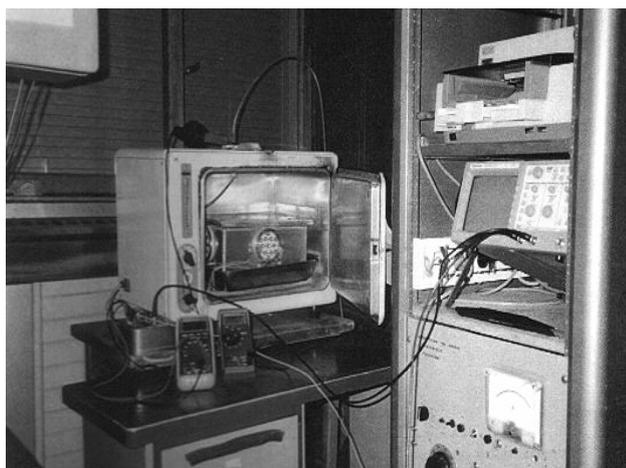


Fig.4. The experimental equipment

All measuring processes were made inside a thermal insulated chamber.

The experimental series of varistors were disks having 30 mm in diameter, with open metallic faces on both sides and an epoxy coating on the lateral side.

They were placed inside the insulating box and exposed to different voltages in order to obtain the opening one. All data are automatically recorded by the acquisition system located on the PC.

The varistor was placed inside. Only the leaking current was measured. All measurements were carried out for a nominal voltage of 300 V DC. This voltage is the DC nominal voltage of an AC 230 V varistor, the most common low voltage varistor used mainly, of course, for domestic surge arrester appliances inside single phase indoor circuits (sockets, outlets, etc.).

We made 6 varistors having 30 mm diameter (high energy absorption capacity ones). Normally, only 20 mm ones are industrially recommended. The height of them was about 2 mm. They were coated with epoxy resin.

All 6 varistors have the same chemical composition and the same manufacturing process, except the baking temperature, which is clearly shown on Table 3.

TABLE 3 Leaking current versus baking temperature

Baking temperature [degrees C]	1050	1120	1150	1200	1250	1300
Leaking current [μ A]	0.21	0.17	0.15	0.012	0.33	3

The relation between those two parameters for all 6 varistors is graphically shown in Figure 5:

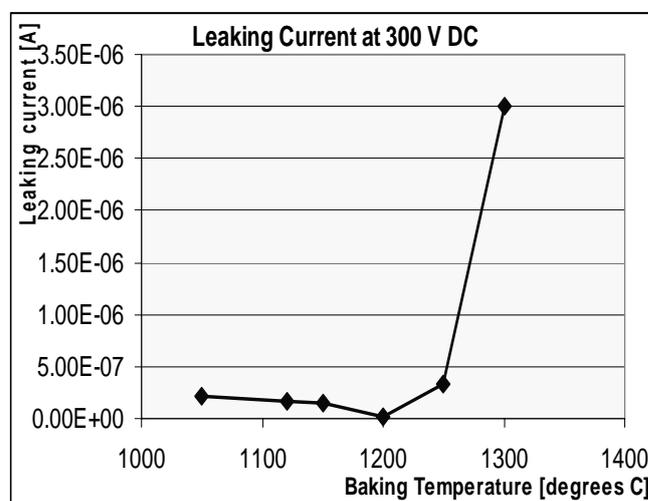


Figure 5. The relation between the leaking current and the varistor baking temperature at 300 V DC

All measurements were performed at an environmental temperature of 21 degrees Celsius. For other environmental temperatures, data could be totally different. No electric shocks were applied. The dynamical characteristics (obtained after some electrical shocks) are not presented by reasons of paper dimension. The evolution of the non-linearity coefficient is not shown too.

In order to obtain parameters able to evaluate the material itself, it is recommendable to use, as a reference, the leaking current density, obtained by dividing the measured leaking current by the surface of that varistor. But, in our case, conclusions could be given by studying the leaking current only.

The opening voltage of a certain varistor V_N is the DC voltage measured between the faces of the varistor, conventionally, when a 1 mA DC current is established through that varistor. The manufacturer of that varistor must indicate the measurement tolerance of that voltage, (less than ± 10 %, according to CECC 42000 Test 4.20) According to the same standard, the leaking current I_S is

defined (measured) as the current crossing through the varistance at the nominal V_{DC} voltage (smaller than V_N); Of course, the electrical resistance of the varistor is obtained by simply dividing that V_{DC} voltage by the I_s current measured through the varistor. All those values are highly influenced by the parameters of the manufacturing process.

4. Conclusions

By measuring the leaking current (or the leaking current density), we notice that there is not a linear relation between them. Our goal is to obtain a small leaking current in nominal service conditions, in order to reduce losses and heating during the standby period of the surge-arrester. By studying the graphic relation it is obvious that, for a baking temperature about 1200 °C, we obtain a small leaking current of 0.01 μA , hardly detected even by the micro-ampere meter. So, for a standard manufacturing process, the baking temperature of a metal-oxide varistor must remain around 1200 °C.

For smaller temperatures, there is a small increase of the leaking current, due to insufficient ZnO grains made during the heating process.

For higher temperatures, the effect is even dramatic. At 1300 °C, the leaking current is about 3 μA with a higher growth tendency. Those baking temperatures must be avoided. This phenomenon is caused by Sb_2O_3 's evaporation on higher temperatures.

In order to obtain a high quality varistor, only 1-2 hours are enough for the baking process.

The baking temperature is well influenced by the chemical structure and composition of that varistor.

Future studies will be carried out on this direction in the future.

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