Experimental Study about the Sintering Temperature of a New Metal Oxide Varistor Material

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Abstract

Protection of any sensitive electric equipment against any type of overvoltage (including lightning applied on power networks) is a big challenge for power electronics. The most advanced and reliable devices used in order to perform this operation are metal oxide varistor based surge-arresters. These varistors are made of a mixture of different metal oxide, where the main ingredient (more than 80-90% as mass concentration) is ZnO. The real improvements of these devices could be performed only in reference with their manufacturing process, by introducing different additives, with particular influences on the electrical behavior of the semi-conductor material, especially on their non-linear relation between voltage applied and current response and on their heat absorption capability. There is no physical or analytical model in order to assess the influence of dopants (additives) on the main electrical characteristics as well as the importance of each parameter belonging to the manufacturing process. This article presents the influence of the sintering temperature on the main electrical parameters (opening voltage, non-linearity coefficient and electrical response characteristics) of two new varistor materials (with 2 and 5 additives).

1. Introduction

Varistors based on Metal Oxide Mixtures are the main component of modern surge-arresters used for protecting any sensitive piece of electric or electronic equipment against all types of overvoltages which can occur on power supplying networks. The manufacturing technology of these power electronic devices is very complex and could be improved by modifying some of the main parameters, like the sintering temperature of these powder mixtures.

This is an empirical process which will lead to the development of new semiconductor materials Metal Oxide Varistors ready to be embedded in all type of surge arresters. The varistor material is basically a polycrystalline ceramic n-type semiconductor acting as insulator at low voltage (like the 230 V AC supplying voltage), and as conductor when the material is exposed to an overvoltage.

Lightning strokes applied to power lines are the most frequent and dangerous overvoltage with devastating consequences on final consumers connected to the line (destroyed instantaneously by dielectric breakdown).

In order to perform those operations described below, two new materials were taken in consideration.

Most of the time we speak about the impact of electrical engineering on the environment, but here we have the reverse, the destroying impact of the environment on the sensitive electric circuits.

2. Manufacturing Technology of Metal Oxide Varistors

Metal Oxide Varistors are prepared from a mixture of many metal oxides such ZnO (in all compositions is more than 80 %), Sb_2O_3, MnO_2, and Co_3O_4, Bi_2O_3, Cr_2O_3, as well as other additives [2].

The two most important additives, Sb_2O_3 and MnO_2, are used in order to obtain different crystal structures during the whole technical process and they are used in all chemical composition, so the basic varistor material is made ZnO and those two additives [3]. A more sophisticated composition is based on five additives, with the other 3 taken in consideration. We will not insist on the chemical composition of these materials, only on their sintering temperature influence on the electrical behavior of that piece of equipment.

In their commercial state, having a certain granulation, each oxide is weighed with precision. After the weighing, powders are mixed and grinded with distillated water and solvents, for 20-40 hours. All the water and the solvents are evaporated by heating. A new grinding procedure is mandatory after the removal of all those solvents. The high granulation powder mixture is slightly sifted for obtaining a smaller granulation. This fine powder is posed in molds and higher pressure is applied (hundreds of barrs). After the pressing process, the newly formed varistor is gradually heated at different temperatures around 1100 °C for 20-40 hours. The varistor will be left for cooling until the environmental temperature is reached. On the cooled varistor, a thick film of Ag, inside an organic compound, is applied on its faces, as some electrodes. The Ag compound will be fully dried before finishing. The heated varistor will be coated in epoxy resin, after metal leads are applied (only when necessary) [5].

The sintering temperatures taken in consideration for both series of varistors (2 and 5 additives) were 1100, 1150, 1200, 1250, 1300, 1350 and 1400 degrees Celsius. By consequent, 7 pairs of varistors, one with 2 and other with 5 additives, obtain at one of these sintering temperature (14 in total) were produced for measurements.

They have 30 mm in diameter and a height of 3 mm, coated on the lateral side. The 7 varistors obtained for 2 additives are presented in Figure 1. The other 7 varistors obtained for the 5 additives look similar.

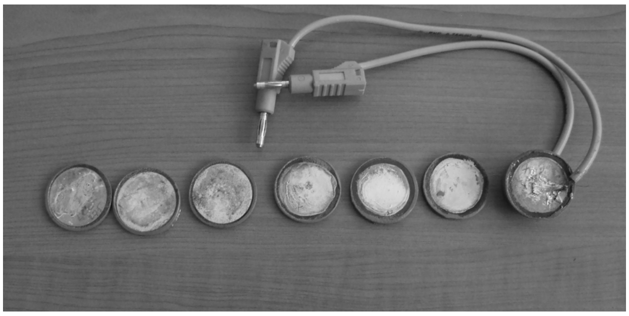

Fig. 1. The 7 varistors with 2 additives, obtained at different temperatures

All these varistors will be used for the measurements performed in order to assess their parameters.

3. Experimental Procedure

All the measurements were performed according to existing standards for low voltage varistors [6].

The measurements carried out were:

- Voltage current characteristics, function of sintering temperature for 2 additives and 5 additives;
- Non-linearity coefficient, function of sintering temperature for 2 additives and 5 additives.

All the experiments were carried out at the LAPLACE Laboratory, from the Paul Sabatier University in Toulouse, France, by using a dedicated DC measuring facility, presented in Figure 2a.

The principle of this experiment is very simple. It means that for a certain imposed voltage, provided by the programmable DC source, current could be measured with a high precision, using a microampermeter.

Measurements are performed inside an insulated chamber. All of them all performed in DC regime, as required by regular procedures for overvoltage protections.

The electric schema of the measuring equipment is also presented below, in Figure 2b.

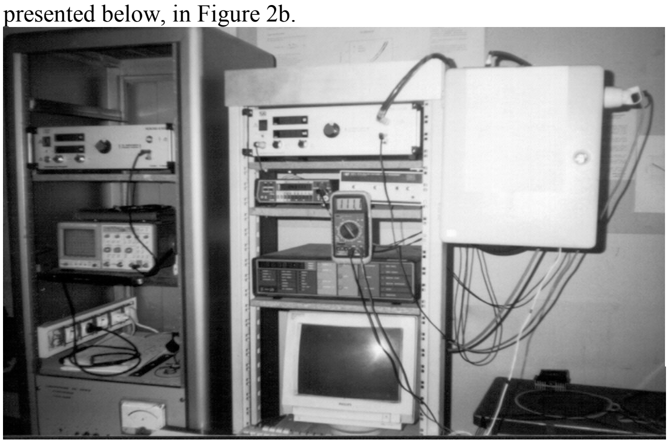

Fig. 2a. The testing facility for low voltage varistors

Temperature inside the measuring box must be kept constant, around 20 degrees Celsius.

Environmental temperature is also important, because current inside a varistor is thermal activated, so we have to maintain same conditions for all tests.

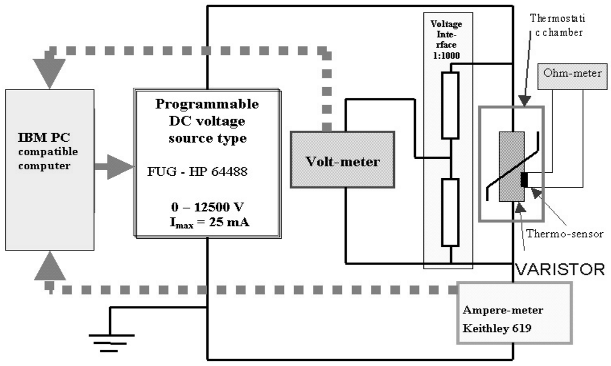

Fig. 2b. The electric shema of the testing facility for low voltage varistors

The relation between current and voltage is non-linear and the non-linearity coefficient α is given by [2]:

$$\alpha = \frac{\ln(I_2) - \ln(I_1)}{\ln(U_2) - \ln(U_1)} = \frac{\ln \frac{I_2}{I_1}}{\ln \frac{U_2}{U_1}} = \frac{d\ln(I)}{d\ln(U)} \quad (1)$$

Where I_1, I_2 are two consecutive values of the current obtained for two consecutive voltages U_1 and U_2.The principle of this experiment is very simple. It means that for a certain imposed voltage, provided by the programmable DC source, current could be measured with a high precision, using a microampermeter.

The Voltage-Current Characteristics obtained, for their lower most important section, are presented in Figure 3 and Figure 4, both for 2 and for 5 oxides.

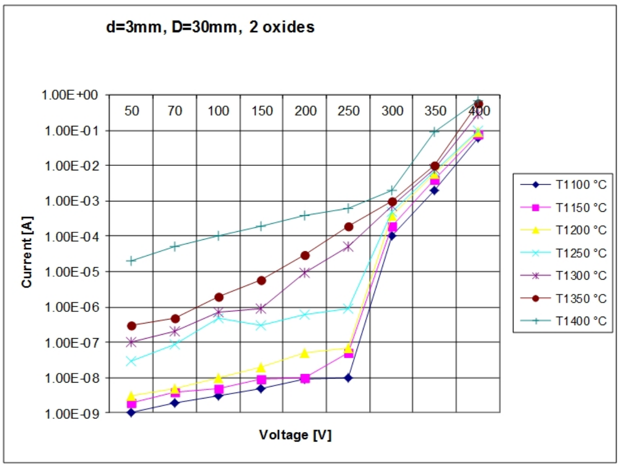

Fig. 3. Voltage-Current characteristics function of sintering temperature for 2 additives

We notice that the maximum leakage current, for voltages around 320 V DC (peak value of the standard 230 V AC power supplying voltage)is obtain for a sintering temperature of around 1400 degrees Celsius and the current is higher for higher sintering temperatures. All the current values are very closed starting from 300 V DC.

We easily notice that, using a 5 oxides based material, we obtain almost the same Voltage-Current characteristics as for the 2 oxides one, but, in this case, the resulting current is a little bit higher as value.

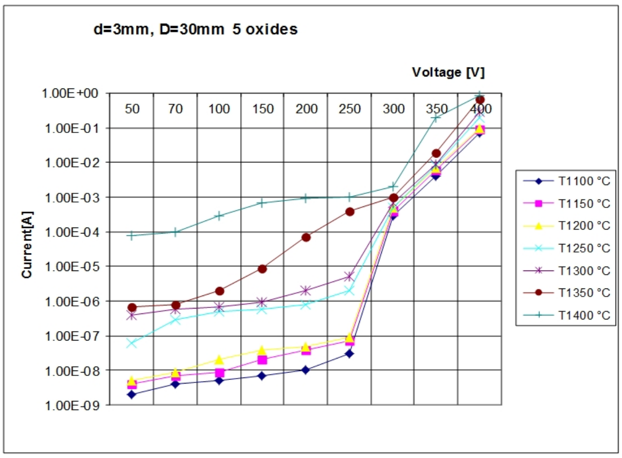

Fig. 4. Voltage-Current characteristics function of sintering temperature for 5 additives

Same observations as for 2 oxides are valid here too, with current values very closed to previous material.

The variations of the non-linearity coefficient with the voltage, for different sintering temperatures, both for 2 oxides and 5 oxides materials, are shown in Figure 5 and Figure 6.

The 5 oxides material is a little bit more sensitive, for all sintering temperatures, but differences are not so important.

Values of the non-linearity coefficient do not exceed 45, but they are in the range of required ones, which must be higher than 20, and desirable around 30-35 for a common low voltage varistor on the market.

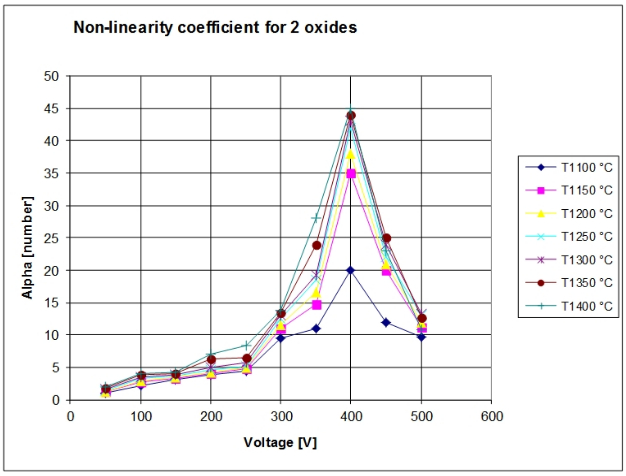

Fig. 5. Non-linearity coefficient versus voltage function of sintering temperature for 2 additives

On these graphs we can notice that the non-linearity coefficient has a peak value for around 380 – 400 Volts, increasing with the increased sintering temperature, with a maximum for the 1400 degrees Celsius temperature and closely approached values for both materials, which, in a certain way, could be predictable [4].

Excellent performance of the varistors is obtained with a simple 1150 degrees Celsius sintering temperature, both for 2 and for 5 oxides. So, no need for extra-heating the varistor during the manufacturing process, performances are almost the same, with no significant relevance.

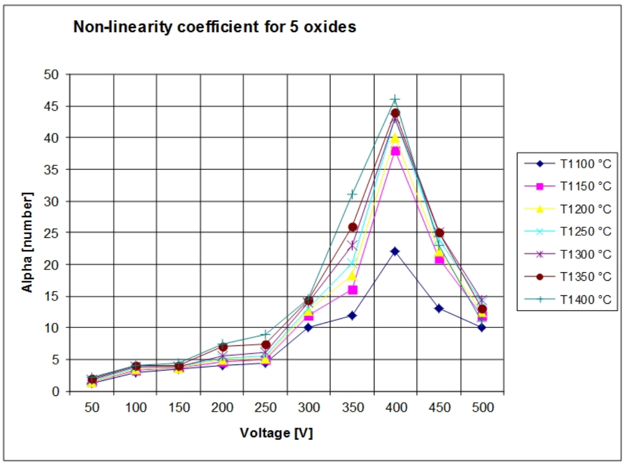

Fig. 6. Non-linearity coefficient versus voltage function of sintering temperature for 5 additives

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A more sophisticated material, with 5 oxides performs almost in the same conditions like a simple 2 oxides one.

4. Conclusions

This is an experimental procedure which could be used for the assessment of varistor materials, in order to obtain better compositions and manufacturing parameters.

The materials involved are new ones, not tested before. A first observation is that the 5 oxides material is a little bit more accurate, but the technology for making it (and the price) could increase a little bit. A simple 2 oxides material acts almost the same, with lower costs.

We noticed that by increasing the sintering temperature all characteristics are going higher, which is useful only when speaking about the non-linearity coefficient, which has to be as higher as possible, and the leakage current for normal voltages as lower as possible (a contradiction). Most of the values measured are close, which is useful.

By taking in consideration all these conclusions, we can consider that the optimal sintering temperature must be kept around 1200 – 1300 degrees Celsius, for at least 20 hours, an important conclusion which could be taken in consideration by manufacturers.

Future studies could be completed with the influence of the sintering pressure on the electrical behavior.

5. References

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