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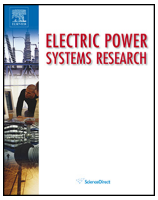

Effects of operation temperature in artificially aging of zinc oxide varistors by high current short impulses

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ABSTRACT

Nowadays surge arresters combine a complex metal oxide varistor (MOV) technology inside a polymeric housing. MOV is a sintered polycrystalline ceramic based on zinc oxide (ZnO) and small amounts of other metallic oxides (additives) usually applied to the manufacturing of surge protective devices for overvoltage protection at all power system voltage classes. The effect of operation temperature on the chemistry and microstructure of commercial zinc oxide varistor (ZOV) submitted to accelerated electrical aging by high-current short impulses were investigated by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), optical microscopy (OM), Vickers micro hardness and X-ray diffraction (XRD). The SEM analysis indicates the formation of micro voids in grain and some larger voids in grain boundary with increase of operation temperature. The EDS and XRD measurements suggests that the operation temperature in the interval of 333 K–353 K during the high-current short impulses promotes the volatilization of the Bi_2O_3 phase and formation of the pyrochlore in the ZOV body. The results of this paper suggest the necessity of getting a better knowledge of the aging process of ZnO-based varistors submitted to high operational temperatures applied to the manufacturing of gapless metal oxide surge arresters (MOSA).

1. Introduction

The use of zinc oxide varistors (ZOV–MOV) have become widespread presenting a huge range of industrial applications in the manufacturing of surge protective devices for electric power lines and electronic systems [1–3].

The ZOV are polycrystalline ceramics manufactured by sintering approximately 90 mol% ZnO powder mixed with a great variety of oxides. The most common additives – dopants are Bi_2O_3, Sb_2O_3, MnO and CoO [4–10]. A number of other additives have also been reported, including, most recently, a vast literature about the use of the rare earths [11–17].

The ZnO interaction with the dopants introduces potential barriers at the ZnO grain boundary during the sintering and improves significantly the electrical properties of the ZOV, such as voltage gradient, nonlinear coefficient, leakage current and discharge current capability [18–21]. However, although a considerable progress has been obtained in the manufacturing processes, many questions remain about the influence of the chemical nature in the electric charge transport and the interface conditions at the grain boundary of ZOV [22,23].

Aiming at finding a quantitative relationship between the microstructure and its electrical performance, a considerable amount of studies have been carried out on the effect of discharging high-current impulse amplitudes and the energy absorption capability of ZOV [24–28]. The results are in good agreement with the experimental observation that the aging of the ZOV is different for long and short duration current impulses [29,30].

Although the behavior of ZOVs under short high-current impulses (SHCI) has been extensively studied for a long time, there is no clear description about the exact mechanisms involved in their degradation [31–38]. At this sense, the most plausible explanation is based on the formation of a potential barrier in the surface layer of zinc–oxide grains, where Zn and O-vacancies act as acceptors and donors [39–42].

In spite of the large number of investigations about the influence of moisture on the ZOVs degradation, there are few studies on the chemical changes of ZOVs aged by SHCI [43–48]. However, these studies are still not completely satisfactory and the effect of the

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ambient, or better, operation, temperature on the accelerate aging of the ZOVs submitted to SHCI draws attention and some additional work. In this sense, as far as the authors are aware, no detailed physico-chemical investigations about the influence of the operation temperature in the microstructure of ZOVs during accelerate aging by SHCI were reported up to the moment.

In order to obtain a better definition of the behavior of ZOVs under operational stresses, it is very important to know the acceptable ranges for the limits of the ZOVs electrical properties. Part of this knowledge, the principal goal of this paper, can be only achieved by carrying out a set of scientific experiments. This paper aims at evaluating the influence of the limits of the operation temperature on the microstructure of ZOVs submitted to aging by SHCI.

2. Experimental

2.1. Study of the current impulse on ZnO varistor sample

This study considered detailed construction requirements for the manufacturing of metal oxide surge arresters for surge protection of medium and high voltage lines. The lightning discharge probability [49] and the operational conditions were also verified and considered. The ZOVs were manufactured according to the standard formulation for metal oxide gapless surge arresters for medium and high voltage systems (12 kV to 144 kV), therefore, applied to the design of high duty distribution and high voltage sub transmission metal oxide surge arresters.

Initially, the leakage current and power losses, at the reference voltage, of 45 ZOVs samples, from the same manufacturing batch, were determined. These samples were divided in 3 sets of 15 samples. These first recorded data were used for a subsequent electrical evaluation of the aging of the ZOVs samples [50]. Each sample was conveniently accommodated inside nylon cells, equipped with two contact electrodes.

Next, when necessary, before each SHCI application, the internal cells temperature were automatically raised from room temperature (293 K), monitored, and regulated to the final pre-defined testing temperatures (333 K and 353 K), by means of thermocouples introduced in a small drilled hole on the lateral surface of the cells, a heating rate of 5 K/min was applied.

After reaching the testing temperature, the heating process was finalized, and in less than 1 min interval, that considers the heat losses of the cells, a 20 kA 8/20 μs SHCI was applied to each cell-sample. Finally, the samples were left to cool down to room temperature (293 K) and a leakage current and power losses test was carried out again [50]. The test sequence considers 20 of such cycles of heating, SHCI application, cooling and leakage current and power losses evaluation [50].

The 20 kA level considers that microstructural aging effects at present a higher definition. This can be also verified for discharge current levels of 10 kA, 15 kA and 30 kA [50]. However, in these cases, the microstructural degradation is not well defined, once the microstructural stresses appear randomly throughout the samples. The choice also considers the possibility of evaluating deeply aged ZOVs, close to end of their technical life period.

One sample of each of the 3 SHCI tested set (293 K—25 °C, 333 K—60 °C and 353 K—80 °C) were randomly selected to be submitted to a microstructural evaluation.

2.2. Microstructural ZOV characterization

In order to evaluate the effect of the operation temperature on the microstructure of commercial ZOVs aged by SHCI, four types of samples were evaluated. A standard and non aged one; a sample degraded by SHCI at 293 K; a sample degraded by SHCI at 333 K and a sample degraded by SHCI at 353 K.

The aged and unaged ZOV samples were analyzed through X-ray diffraction with phase quantification by Rietveld method. The phase transitions were monitored by X-ray diffractometer, Shimadzu XRD 6000, by using a monochromatized Cu$K\alpha$ radiation (graphite crystal, 1.5418 Å, 40.0 kV, 30.0 mA) and divergence/reception slits of 2 mm/0.6 mm were used for collecting the XRD data at $10^\circ < 2\theta < 70^\circ$, with $\Delta 2\theta$ of 0.02° and a step time of 2 s. The X-ray diffraction data was refined by the RIETAN-2.000 Rietveld refinement program [51].

A Phillips XL30 scanning electron microscope coupled to energy dispersive X-ray spectrometer (SEM/EDS) was employed for the morphological and microstructural evaluation of the ZOVs before and after SHCI aging. Prior to investigation, the ZOVs samples were embedded into epoxy resin and then successively polished using different size of abrasives and diamond paste grits. Microstructural analysis was carried out after etching the polished surfaces with 6 M NaOH solution for about 5 min to get an enhanced topography and then washed carefully with large amount of distilled and deionized water. The specimens were sputtered with a thin film of carbon to make them conductive and improve image resolution. The grain sizes may be estimated through the linear intercept method [52].

The Vicker micro hardness (VHN) of ZOV samples before and after SHCI aging was determined using an MH-6 digital micro hardness tester (0.098–9.8 N). For the measurement of hardness, at first, the top face of the samples was ground and polished by the polishing machine. The VHN was estimated according to the following equation:

$$VHN = \left(\frac{P}{d^2}\right).C \tag{1}$$

where P is the applied load, d is the diagonal length of indenter impression and C is a constant that takes the value of 0.1891.

3. Results and comments

The general microstructure of ZOV before and after SHCI aging tests was examined by SEM as shown in Fig. 1. The samples consisted mainly of ZnO and spinel grains, the latter of which were approximately 1 μm in size. EDS coupled to SEM, in Fig. 2, indicates that ZOV samples showed significant amounts of bismuth oxide (Bi_2O_3) and antimony oxide (Sb_2O_3) dissolved in spinel phases.

The Bi_2O_3 and Sb_2O_3 combined with ZnO grains produce highly non-Ohmic properties improving the non-linear coefficient conferring a high stability of the double Schottky barriers in ZOV [53,54]. Bi_2O_3 is the most essential component for producing non-Ohmic behavior of ZOV whilst addition of Sb_2O_3 controls the ZnO grain growth [55–57]. Due to the higher atomic weight of bismuth (Bi), the intergranular Bi_2O_3 phase appears in SEM micrographs as a white phase, whereas the ZnO grains and spinel $Zn_7Sb_2O_{12}$ appear light and dark grey respectively as shown in Fig. 1.

The distribution of the elements in the ZOV samples before and after SHCI accelerated aging were measured by EDS according to the color mapping on the distribution of zinc, bismuth, antimony and oxygen as shown in Fig. 2. The micrographs of EDS colorful maps shown that three different phases could be readily identified in the microstructure of the ZOV before and after SHCI aging.

The aged ZOV clearly show different microstructures relatively to the unaged ZOV. A ZnO phase was the most abundant which agrees deeply with the fact that ZnO is the main component of ZOVs. Before SHCI aging the Bi, O and Sb elements were distributed in the vicinity of grain boundary of the ZOV as in Fig. 2a. After SHCI aging the EDS mapping analysis – in Fig. 2b and d – indicated a Bi, Sb and oxygen enrichment of ZnO grains, as consequence of current localization, and the associated joule heating of the ZOVs