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Degradation phenomena due to humidity in low voltage ZnO varistors

Mao-hua Wang [a,*], Ke-ao Hu [a], Bin-yuan Zhao [a], Nan-fa Zhang [b]

[a] *State Key Laboratory of MMCs, Shanghai Jiaotong University, Shanghai 200030, PR China*
[b] *Changzhou Chuangjie Lightning Protection Co., Ltd., Changzhou Jiangsu 213016, PR China*

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Abstract

Humidity-induced degradation in low voltage ZnO varistors was investigated. An experiment was conducted in which some varistors were put in humid condition with fixed relative humidity of 100% at 25 °C for a certain period of time. After the treatment, the samples showed serious degradation as their breakdown voltage decreased and their leakage current increased significantly. It was proposed that the diffusion and reaction of H^+ generated by dissociation of water at the surface of ceramics induced the degradation due to humidity. When the degraded low voltage ZnO varistors were subject to 110% of maximum continuous operating voltage for 120 h, thermal runaway did not occur in service, and the voltage–current characteristics of these degraded samples could also be mostly restored by polishing process at the side surface of varistors. The experimental results indicated that the diffusion and reaction of H^+ is confined to a surface layer of ceramic varistors.

Keywords: E. Varistors; Zinc oxide; Degradation; Humidity

1. Introduction

ZnO-based varistors are characterised by highly nonlinear voltage–current characteristics and a high energy-absorption capability, the nonlinear characteristics are attributed to the formation of double Schottky barriers at zinc oxide grain boundaries. As a result they are widely used as surge absorbers in electronic circuits, devices and electrical power systems to protect against dangerous over-voltage surges [1]. Nowadays with the development of micro-electronic technology and large-scale integrated circuit, ever-increasing number of varistors is being used for low voltage applications, such as in automobile electronics and semiconductor electronics.

In operation, varistor materials are often subject to various stress (high electric fields, high temperature, and aggressive ambients) that can affect their performance and useful life; the continuous leakage current and resultant Joule heat may degrade the electrical properties of the devices. Therefore, in addition to nonlinearity, the electrical stability is a technologically important characteristics of ZnO varistors. One of the major challenges in the continuing development of varistor has been to reduce their degradation. This degradation usually refers to the steady increase of leakage current. Sudden degradation during operation may increase energy loss by the varistors and causes faults to the circuits in some cases [2].

It is reported [3] that environmental moisture can lead to a substantial increase of leakage current in ZnO varistors. Even if the varistor ceramics have polymer coating, which is helpful for preventing condensation of aqueous vapor, the internal components of varistor which has sealing defects may absorb moisture in a humid environment resulting in an excessive internal leakage current. The knowledge of the degradation of low voltage ZnO varistors due to humidity exists only to a limited extent, the present work investigate how humidity induces degradation in low voltage ZnO varistors, possible mechanism and measures to prevent the degradation were put forward.

2. Experimental procedure

Reagent-grade raw materials were prepared for low voltage ZnO varistors, the composition was: 95.95%ZnO + 0.75%Bi_2O_3 + 0.8%TiO_2 + 0.5%NiO + 1.0%Co_2O_3 + 0.5%$MnCO_3$ + 0.5%SnO_2 (all in mol%). The powder mixtures were wet ball-milled in a polyethylene bottle with ZrO_2 balls for 24 h in deionized water. After dried and granulated, the powder was

* Corresponding author. Tel.: +86 519 6970660/13024173714.
E-mail address: wmh2000@sjtu.edu.cn (M.-h. Wang).

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pressed into discs of 12 mm in diameter and 2.0 mm in thickness at a pressure of 80 MPa. The discs were first pre-sintered at 900 °C and then sintered at 1250 °C in air for 1 h, with heating and cooling rates of 300 °C/h. For the studies of electrical properties, silver paste was applied to the faces of the discs (which were subsequently heated at 600 °C for 20 min) to provide electrodes. A group of low voltage ZnO varistors were used in the investigation. with a breakdown voltage of 75 V, the varistor discs were about 10 mm in diameter and 1.6 mm in thickness. To study the influence of humidity and ac voltages, the special treatment was applied to the low voltage varistors, some varistors were put in a closed chamber above the surface of water solution of a proper salt for a certain period of time before staring the measurement. The fixed value of relative humidity in air was 100% at 25 °C.

The voltage–current characteristics of low voltage ZnO varistors were measured in dc modes for lower current regions using a CJ1001 dc source/measurement unit. The breakdown voltage (varistor voltage) $V_{1\,\mathrm{mA}}$ was determined at current density of 1 mA/cm^2. The leakage current (I_L) was determined at 0.83 $V_{1\,\mathrm{mA}}$. In addition, the nonlinear coefficient α was determined from the following equation:

$$\alpha = \frac{\log I_2 - \log I_1}{\log V_2 - \log V_1} \qquad (1)$$

where I_1 = 0.1 mA, I_2 = 1.0 mA, and V_1 and V_2 are the voltages corresponding to I_1 and I_2, respectively.

The degraded varistors were subject to 110% of maximum continuous operating voltage for periods up to 120 h. After the stress, electrical characteristics were measured at room temperature. The microstructure studies were performed using a scanning electron microscopy (SEM). Sintered density (ρ) was determined by Archimedes method.

3. Results and discussion

A typical scanning electron microscope micrograph of the fractured surface of a low voltage ZnO varistor is shown in Fig. 1. The varistors were of very dense microstructure. Although some pores were present, they were very small and separated from one another. The density of ceramics was 5.29 g/cm^3, corresponding to the 96% of theoretical density (TD) of pure ZnO (TD = 5.61 g/cm^3 in ZnO), high densification could be obtained for the low voltage ZnO varistor. Such a dense microstructure could prevent permeation of humidity in ceramic varistors.

Therefore voltage–current characteristics of this ceramic varistors were studied in air with fixed relative humidity. Fig. 2 showed voltage–current characteristics of samples put in a humid condition. Sample A was a varistor with no treatment. It can be seen that serious degradation occurred in those samples treated in humid condition, the breakdown voltage decreased and leakage current increased after the treatment, the degree of degradation increased with increasing time of treatment in humid air.

The studied ceramics can be humidity sensitive material and some water can exist at the ceramic surface in air at normal conditions. Adsorbed water molecules can dissociate at the surface according to the reaction:

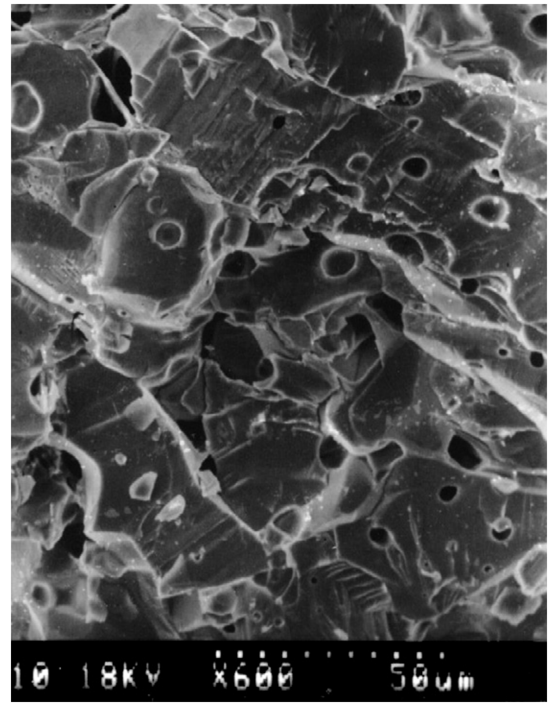

Fig. 1. SEM micrograph of fractured surface of low voltage ZnO varistor.

$$H_2O \rightarrow H^+ + OH^- \qquad (2)$$

The quite mobile proton H^+ are very reactive and can diffuse into the region near the grain boundary of ceramics, some of them may react with other matter encountered in their path [4]. Because ZnO-based ceramic varistors are sintered in oxidizing atmospheres, it has been reported [5] that an excess amount of oxygen exists at grain boundaries, which is very important for the nonlinearity of the voltage–current characteristics of varistors, the properties of ZnO varistors are very sensitive to

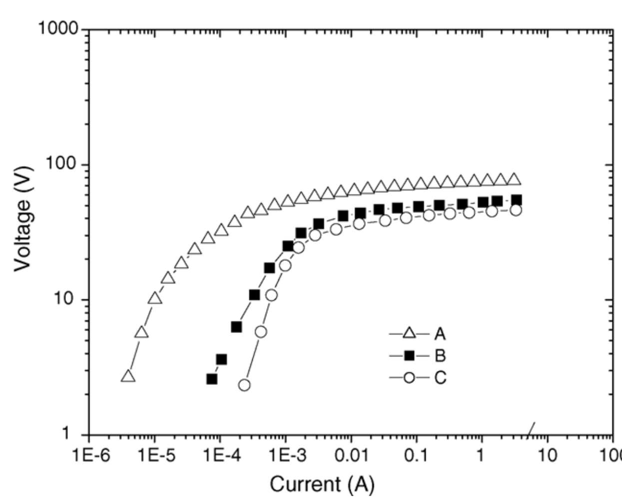

Fig. 2. Voltage–current characteristics of varistors after treatment in humid condition; sample A: untreated, samples B and C: put in humid condition (relative humidity = 100%) for 2 and 4 h, respectively.

Table 1
The variation of the electrical properties of degraded samples before and after the voltage stress

Sample	Before stress			After stress (120 h)		
	Varistor voltage, $V_{1\ mA}$ (V)	Leakage current, I_L (μA)	Nonlinear coefficient, α	Varistor voltage, $V_{1\ mA}$ (V)	Leakage current, I_L (μA)	Nonlinear coefficient, α
A	78	7.4	21.5	76	9.4	19.2
B	31	324	3.8	47	26.4	9.4
C	24	176	4.2	51	18.9	10.6

Table 2
The effect of annealing in air on electrical properties of degraded samples

Sample	Before annealing			After annealing (2 h)		
	Varistor voltage, $V_{1\ mA}$ (V)	Leakage current, I_L (μA)	Nonlinear coefficient, α	Varistor voltage, $V_{1\ mA}$ (V)	Leakage current, I_L (μA)	Nonlinear coefficient, α
A	76	6.6	21.8	79	5.7	22.1
B	34	315	4.1	64	10.2	17.7
C	28	162	5.3	71	9.9	18.6

oxidizing–reducing reactions. Due to the interaction H^+ ion to chemisorbed oxygen in the O^- state, the total negative charge at grain boundary become low (on absolute value) leading to the decrease of grain boundary potential barrier height and subsequent greatly changes the properties of the ceramics. The degradation of the low voltage ZnO varistors in this study can be explained by the diffusion and the reaction of H^+ ion, the two factors contribute to the humidity-induced degradation of the varistors provided that these varistors had excellent property to begin with.

Because varistors are usually operated under a voltage, in order to know whether the thermal runaway occurred in application, the degraded samples were subject to 110% of maximum continuous operating voltage for a period of 120 h, the experimental result were shown in Table 1.

This result revealed that the degradation due to humidity did not cause thermal runaway, on the contrary, the varistor voltage ($V_{1\ mA}$) of sample B increased from 31 to 47 V, and leakage current (I_L) decreased from 324 to 26.4 μA after application of continuous operating voltage, the electrical characteristics of these samples could be slightly improved, the reason may be that the degraded varistors were affected by Joule heat resulting from continuous operating voltage, the Joule heat cause the moisture evaporation which lead to improvement in electrical properties. This conclusion was in agreement with annealing experiment, some degraded samples due to humidity were annealed at 450 °C in air for 2 h, the leakage current began to decrease greatly, the annealing results for samples A, B and C were shown in Table 2. Moreover, a fraction of leakage current may flow through the surface of degraded varistors, which is parallel with the inside leakage current, so this degraded varistors can not give rise to thermal runaway in application.

The degradation of the low voltage ZnO varistors induced by humidity obviously has resulted from the reaction of hydrogen ion with chemisorbed oxygen. However it is not clear whether the reaction is confined to a surface layer or also affects the inner part of the varistors. When some degraded low voltage ZnO varistors were ground and polished with SiC paper at the side surface of the samples, the polishing method was shown in Fig. 3. It was found that the voltage–current characteristics of these samples could be mostly restored by the polishing process for samples B and C, the results were shown in Fig. 4. This phenomenon indicated that the H^+ did not diffuse

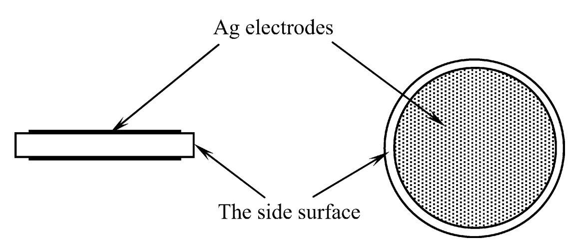

Fig. 3. Sketch of polishing with SiC paper at the side surface of degraded varistors.

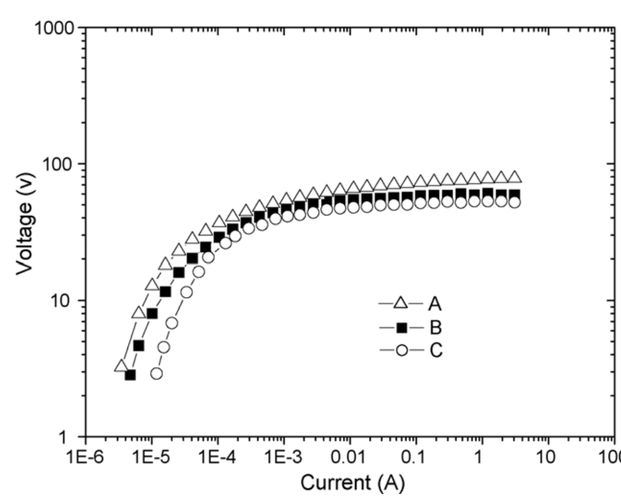

Fig. 4. Effect of polishing process at ceramic surface on voltage–current characteristics of degraded varistors sample A: untreated, samples B and C: ground and polished with SiC paper.

into the inner part of the varistors but the surface layer, and react with ceramics, which was in accordance with the dense microstructure. The conclusion is different with previous studies [6].

Most commercial ZnO ceramic varistors of disk shape have a polymer coating, which prevent the influence of environmental moisture. However, more and more ZnO varistors used in electronic circuits are being fabricated as chip varistors. To be surface-mountable these varistors have no polymer coating [7]. Thus, more attention should be paid to the humidity-induced degradation in ceramic varistors.

4. Conclusion

Environmental moisture induces serious degradation in low voltage ZnO varistors through the diffusion and reaction of H^+ ion, which lead to the breakdown voltage decreased and leakage current increased. When the degraded samples were operated under 110% of maximum continuous operating voltage for a period of 120 h, this degradation did not result in thermal runaway after electrical stress. It was found that voltage–current characteristics of these degraded samples could be mostly restored by the polishing process at the side surface of ceramics. The result indicated that the diffusion and reaction of H^+ ion is confined to a surface layer of ceramic varistors.

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