Performance evaluation of zinc oxide varistor produced from powder under different spray drying conditions

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Abstract

I-V characteristics, wattloss behavior and energy absorption capability etc. are the critical characteristics for performance evaluation of ZnO varistors. In the long processing steps of this electro-ceramic with a considerable number of contributing variables, the preparation of pressing grade electro-ceramic materials is very important. It demands powders with high degree of compositional and microstructural homogeneity, high purity and reliability, proper shape and proper size and distribution. This kind of ceramic powder can be generated by spray drying. Apart from affecting the physical properties of varistor discs, the powder characteristics influence the grain growth and microstructure which are anticipated to affect the electrical behavior of the discs. To investigate this, varistor powder was produced from standard slurry under different spray drying conditions in pilot scale. Feed flow rate, atomizing air pressure and outlet drying air temperature were considered as input variables and nominal voltage, wattloss, clamp ratio, non-linear co-efficient and energy absorption capability were considered as response. It was found that nominal voltage, wattloss and energy absorption capability was highly influenced by spray drying variables but no significant influence was observed on clamp ratio and non-linear co-efficient for both the pre-breakdown and breakdown region. Not only high but consistent energy absorption capability was achieved by optimizing spray drying conditions. Thus optimization of spray drying variables could help securing desirable varistor characteristics and enhanced reliability of the electrical system.

KEY WORDS: ZnO varistor, wattloss, energy absorption capability, non-linear co-efficient, clamp ratio

1.0 INTRODUCTION

A ZnO varistor is a semi-conducting device possessing a non-linear current (I) - voltage (V) characteristic with a symmetrical sharp breakdown similar to that of a zener diode[1,2]. But unlike a diode, a varistor can limit over-voltages equally in both the polarities, thus giving rise to I-V characteristics which is analogous to the two back to back diodes. This has enabled it to provide an excellent transient suppression performance. It is a preferred approach to protect the electrical, electronic and power distribution and transmission circuits from destructive voltage levels induced by lightning impulse or switching surges over the past thirty years[3]. There are wide ranges of varistor products which are used for electrical, electronic and power distribution and transmission circuits from destructive voltage levels induced by lightning impulses or switching surges[4].

The critical application parameters for varistor discs are associated with the various region of I-V curve. These parameters are crucial in design and operation of the surge protector. The product should have a high value of non-linear co-efficient, a low value of leakage current, high energy absorption capability leading to a longer varistor life.

ZnO varistor is processed by conventional powder processing route where spray drying plays an important role. The preparation of pressing grade electronic ceramic material demands powders with a high degree of compositional and microstructural homogeneity, high purity and reliability. Spray drying is recognized as an excellent method to generate this type of powder. Relatively uniform spheres are formed by this method[5-7]. The feed slurry is in the form of solution, suspension or paste and the dried product conforms to powders, granules or agglomerates.

Apart from affecting the powder characteristics, the grain growth during the sintering process and subsequent microstructure of the varistor are also affected by spray drying. The green and the fired body, homogeneity, grain size, porosity, varistor chemistry are identified to affect the energy absorption capability remarkably[8,9].

In the present study the effect of atomizing air pressure, feed flow rate and drying air out let temperature was investigated on electrical performance like wattloss, nominal voltage, clamp ratio, non-linear co-efficient, energy absorption capability and degradation with the application of long pulse. It was found that particle and particle size distribution affected remarkably the nominal voltage, degradation and energy absorption capability. The influence indicates that by optimizing spray drying variables, it would be possible to generate arrestor with enhanced performance and thus ensuring more demanding applications with a higher system functional reliability.

2.0 EXPERIMENTAL PROCEDURE

The slurry of standard calcined varistor powder was prepared by ball milling. A fixed amount of slurry was taken for each experiment in which binder PVA was added at a concentration of 0.5% of the dry weight of the powder. A 10% solution of the binder was prepared and shear mixed for 15 minutes. The solid content and viscosity of the slurry were measured before spraying. The spray dryer was made ready for start up by cleaning and connecting the product receptacles. The exhaust fan was started and the gas burner was ignited. The atomizing air pressure was set and deionized water was fed slowly through the pumping system. As steady state operating conditions were reached, the flow was switched from water to feed slurry. After completion of spraying slurry for a particular set condition, only one parameter was changed to conduct the next experiment. The experimental conditions are given in Table 1.

For each category of powder twelve cylindrical green bodies were produced by dry pressing in the production line machine (Hydramet Model HC-75EC Compacting press). A target weight of 159.0 gm powder was taken to produce green compacts of 38 mm in diameter. A standard pressing cycle was used and uniaxial double action compaction technique was adopted. The peak load applied for pressing three discs at a time was about 25 ton leading to a pressure about 74 MPa. They were sintered in the pot kiln with standard firing profile with the peak temperature of 1120°C and firing time 70.0 hrs. The fired bodies were passivated; their flat surfaces were ground and after ultrasonic cleaning and visual inspection for defects such as pinholes and damaged edges, the selected discs were electroded for performance evaluation.

Table 1: Setting condition for spray dryer

No. of run	Atomizing air pressure	Feed flow rate (ml/min)	Outlet drying air flow rate (°C)
1	10	71	130
2	10	258	115
3	40	258	130
4	40	71	115
5	10	172	127
Control	20	215	126

3.0 PERFORMANCE EVALUATION

Electrical performance was determined by evaluating wattloss, nominal voltage, clamping efficiency, non-linear co-efficient, energy absorption capability and degradation with the application of low amplitude long duration impulse (LA-LD). The calculation procedure is described below.

3.1 Wattloss

The degradation of varistor is a complex phenomenon which is considered to be function of barrier height, donor density, and breakdown voltage of the grains and grain boundary[10-12]. The gradual weakening of the barrier height due to the field assisted ion migration and/or current channeling through the high conductivity paths are responsible for degradation. Varistors are required to sustain constant bias voltage in normal operation without significant degradation. Wattloss is a measure of degradation and it is measured at 80% of voltages at 5 mA in the Wattloss High Temperature Tester. This corresponds to $0.8E_{0.6}$ where the figure in the subscript indicates the current density in mA/cm^2. After application of high amplitude short duration pulse of peak current 65 KA, the wattloss was again measured at $0.8E_{0.6}$ for both polarity to estimate the degradation trend.

3.2 Nominal Voltage

Varistors are rated by a voltage at which the flow of current from linear to non-linear mode starts. The rated voltage is known as “threshold”, “turn on”, non-linear” or “nominal voltage”. The nominal voltage E is evaluated as the voltage per unit thickness for the specified current density. In industrial practice it is taken at 5 mA for big discs. This figure is very close to the recommended value of 0.5 mA/cm^2. It is evaluated from the following relationship:

$$E_{0.6} = \frac{V}{t} \qquad (1)$$

Where V is the voltage and t is the thickness of the device. The value of $E_{0.6}$ is controlled by the grain size and thus by the number of the grains. The parameter can be increased by the reduction of grain

… of grains. … n this regard. … rature lead to bigger grain size and consequently reduce the nominal voltage. It was determined by High Voltage Test System.

3.3 Non-Linear Co-efficient

The most critical parameter to characterize the zinc oxide varistor is non-linear co-efficient. The co-efficient, a , is defined by the following formula:

$$\alpha = \frac{d \ln I}{d \ln V} \qquad (2)$$

The magnitude, therefore, varies with current density. It increases in the pre-breakdown region, attains a maximum value in the non-linear region and diminishes sharply in the upturn region[10]. Temperature and pressure of the test environment also significantly affect the a value. The value decreases with the increase of both the temperature[1] and pressure[13]. In non-linear region the higher value of a corresponds to the lower clamp ratio, thereby, providing better protection due to the lower increase of voltage at higher current level. The values of the voltage and current were considered the same as the clamping efficiency to calculate a .

3.4 Clamping Efficiency

The clamping efficiency is defined as the ratio of voltages in the non-linear region. This is very important parameter which affirms the ability of varistor to limit the transient voltage and the level of protection. The clamping voltage is calculated as follows:

$$\text{clampingratio} = \frac{V_2}{V_1} \qquad (3)$$

Where V_2 is the voltage per unit length at a current density I_2 in the upturn region and V_1 is the voltage per unit length at current density I_1 at the onset of non-linear region. Basically the lower the clamp ratio, the better the device.

3.5 Energy Absorption Capability

Energy absorption capability can be calculated from the measured peak current and clamp voltage, and the time duration by using the following relationship:

$$E = \int_0^t vidt = CVIt \qquad (4)$$

where C is a constant and it depends on the wave shape of testing. The value of V is taken in volt/cm, I in amp/cm^2, and t in seconds to calculate energy in J.cm^{-3}. The energy absorption capability of varistors was measured by selecting a charging voltage for a fixed charging time. Three repeated shots of 2 ms square wave was applied for each cycle.

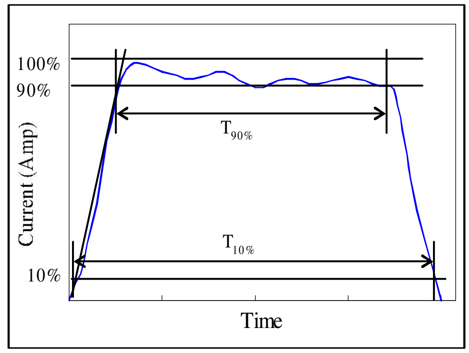

Fig. 1: Square-wave current applied to evaluate the energy absorption capability

The charging voltage was selected at a low level so that no failure occurs in the first cycle. The cycle of shot continued until all of the discs of the sample failed. The value of clamp voltage and peak current for each shot was recorded. The cumulative curve of energy absorption was plotted from the calculated energy and the number of discs failed at that energy level.

3.6 Degradation with Long Pulse Application

Conventionally the varistors are tested at a rated energy. The rated energy can be determined by subjecting the varistors to screen test, thereby, weeding out the weak devices. To verify the degradation rate with the application of long wave, some of the varistor were tested to record the wattloss. Measurement was performed on each of the samples in the Wattloss High Temperature Tester at $0.8E_{0.6}$ for both polarities after every cycle of shots. The testing was continued until all of the discs failed. The calculated energy and the measured wattloss were plotted for each cycle to correlate energy absorption and degradation.

4.0 RESULTS AND DISCUSSIONS

Varistors were fabricated using powder from all the six run conditions of the dryer to estimate the effect on electrical performance. The investigation includes I-V characterization and energy absorption capability. The degradation behavior of varistor with the application of short and long pulse waves was also evaluated.

4.1 Nominal Voltage

The nominal voltage of varistors fabricated from the powder under different run conditions of the spray dryer is shown in Fig. 2. The lowest value was obtained with powder from run 2 and the highest with run 4 which was even higher than that of the standard condition. In general spray dryer produces powder with a wide distribution of particles. The change of variables causes the percentage of fine and coarse particles to vary. As observed in run 2, a broad distribution with a higher percentage of coarse results in higher packing efficiency[14]. The higher packing efficiency has important role in sintering. For zinc oxide varistors liquid phase sintering occur due to the presence of bismuth oxide. The initial feature of this mechanism is associated with the formation of liquid and rearrangement of the particles due to capillary force. The rapid densification at the earlier stage is due to the capillary force exerted by the wetting liquid on the solid particles[15-17]. In the second stage, higher packing density and smaller pore size lead to a higher average curvature in the neck regions between the particles, thereby, raising the average driving force for sintering. In the final stage, the formation of solid skeleton prevents further diffusion through grain boundaries and consequently the grain grows. Higher growth in grain size ultimately reduces the nominal voltage of the varistors. The mean grain size calculated for run 2 from the micrograph was found to be higher[14].

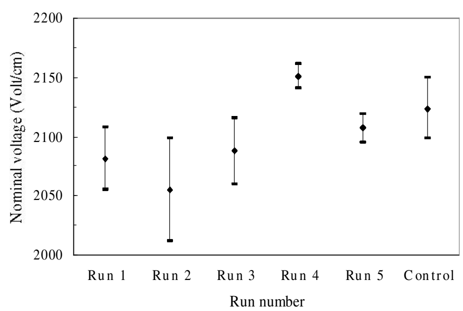

Fig. 2: Nominal voltage of varistors under different spray drying conditions

4.2 Wattloss, Clamp Ratio and Non-linear Co-efficient

The wattloss for varistor under different run conditions is plotted in Fig. 3.

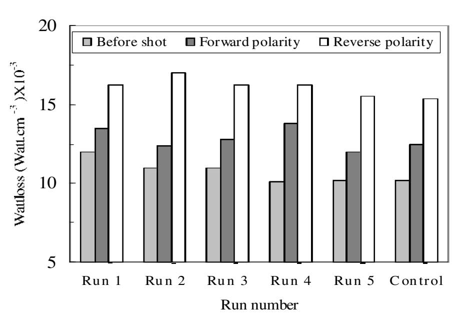

Fig. 3: Degradation of varistors after application of HASD pulse of 65 KA

This was higher for run 1, 2 and 3 before the application of high amplitude short duration pulses. But the degradation was more for run 1 and 4 for forward polarity and for run 2 for reverse polarity after the application of high amplitude short duration pulses of current 65 KA. Wattloss is dependent on leakage current, which is the function of barrier height, donor density and average voltage drop in each grain. So the higher wattloss may be attributable to the higher donor density and lower barrier height[18-20]. It is also suggested by Bowen and Avella[21] that larger grain size may lead to an increased density of leakage current. The clamp ratio and non-linear co-efficient for the varistor discs are summarized in Table 2. There were no significant differences for both the pre-breakdown and breakdown region.

Table 2: Clamp ratio and non-linear co-efficient of the varistors

No. of run	Clamp ratio		Non-linear co-efficient	
	0.3-5 mA	5 mA-5 KA	0.3-5 mA	5 mA-5 KA
1	1.32	1.73	7.64	13.86
2	1.34	1.74	7.00	13.77
3	1.35	1.74	6.66	13.98
4	1.32	1.73	7.35	14.48
5	1.34	1.73	6.72	14.10
Control	1.33	1.73	7.04	14.51

4.3 Energy Absorption Capability

The energy absorption capability of the varistors made with powders processed under various spray drying conditions is illustrated in Fig. 4.

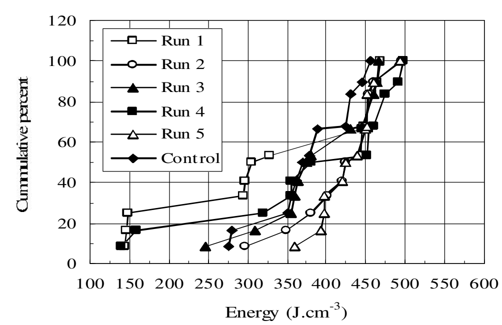

Fig. 4: Energy absorption capability of varistors under different spray condition

Significant influence of the variables was observed on the energy absorption capability. On the basis of initial failure the performance can be said to be lower for both runs 1 and 4, and higher for run 5. The failure commenced at about 150 $J.cm^{-3}$ for both runs 1 and 4. However, in statistics, neither the lowest nor the highest value is well accepted parameter for comparing the distribution. The mean or the median can be considered to evaluate the performance. The mean standard deviation value of the varistors is presented in Fig. 5. The values were higher for both runs 2 and 5 but more consistent with run 5. The higher energy absorption capability for the runs 2 and 5 cannot be readily explained. Perhaps, the increased amount of moisture and higher mean size[13] had some form of positive influence during sintering which ultimately led to the enhanced performance. The lower value of standard error for energy absorption refers to the significance of the difference from one run to another.

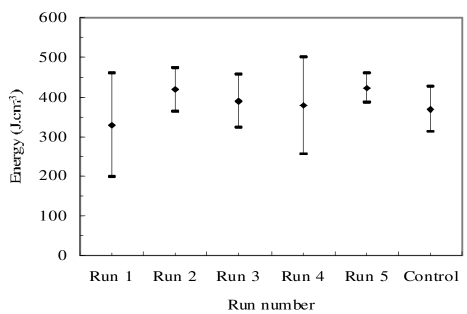

Fig. 5: Mean energy standard deviation of varistors under different spray condition

4.4 Degradation under Low amplitude Long Duration Impulse (la-ld) test

Degradation under low amplitude long duration impulse (LA-LD) test was estimated by measuring the wattloss after each cycle of the destruction test. The varistor was cooled down before measuring the wattloss after the classification of energy in each cycle. The wattloss value obtained by the Wattloss High Temperature Tester after each cycle is presented in Fig. 6. No significant degradation, that is, the rise in wattloss was observed up to the energy level of 259 J.cm^{-3}. The difference in wattloss within this level is due to the variation of the ambient temperature.

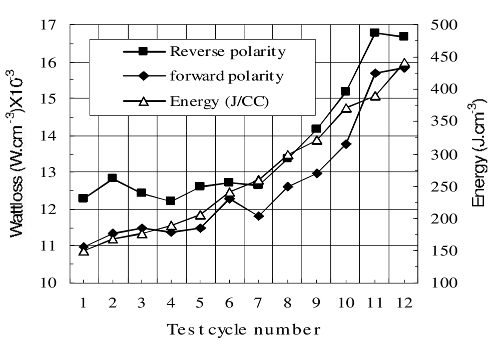

Fig. 6: Degradation of varistors with the injection of low amplitude long duration (LA-LD) impulse

5.0 CONCLUSION

The influence of spray drying variables on the varistor performance was quite significant. Varistor fabricated with higher fraction of fine particles increased the nominal voltage due to the smaller grain size in the sintered ceramic body. Degradation behavior of varistor was also influenced depending upon the powder used. Power containing higher fraction of coarse degraded remarkably after application of high amplitude short duration pulse. Energy absorption capability of the varistor was found to be significantly influenced by the powder used. There is certain level of combination in fine and coarse particles in the powder which was helpful for energy absorption capability. Hence, optimization of spray drying condition could help to achieve varistor with enhanced energy and better reliability.

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Gas nitriding of En40B steel with highest growth rate of the case and reduced white layer formation.

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Abstract

Nitriding is now a well established process for producing very hard (approximately 1000 VHN) and wear resisting surfaces on low alloy steels without any distortion and dimensional changes. In gas nitriding the thickness of the case depth is reported to increase with the increase of ammonia in the conventional NH_3/H_2 gas mixture which consequently increases the thickness of undesirable surface iron-nitride (white layer). In this investigation the growth kinetics of a nitrided layer have been investigated by nitriding En40B steel at 470^o, 520^o and 570^{o}C for 6 to 96 h in gaseous environments containing 10% to 80% ammonia. The conditions were selected in such a way to produce nitrided specimens with and without white layer. A metallographic technique was used to reveal different zones of the nitrided surface and thicknesses of these zones were recorded using microscope. The nitrided layer thickness is found to increase parabolically with increasing the processing time. The growth kinetics of this hardened layer produced a linear relationship with nitriding potential at all temperatures up to a certain point where a white layer formed. At 470^{o}C the growth rate is constant where presumably g'-Fe_4N only is present while at 520^{o}C this constancy appears in the presence e-Fe_3N. At 570^{o}C the growth rate continues to increase, but not linearly, even when g'-Fe_4N is present and constancy appears well ahead of the presence of e-Fe_3N phase. The findings conclusively suggest that the growth rate of the nitrided layer reached to a maximum with the increase of ammonia content in the gas mixture up to an optimum level where the thickness of the white layer is a minimum.

KEYWORDS: Gas nitriding, Diffusion layer, Nitriding potential, Growth rate, Compound zone, Microhardness.

1. INTRODUCTION

Nitriding is a thermochemical process of surface hardening of ferritic iron to a range of alloy steels containing aluminium chromium, vanadium, titanium, molybdenum and tungsten. The basic mechanism of this process is that when nitrogen comes in contact with a heated steel surface the latter absorbs the former and nitrogen atoms take up interstitial positions in the atomic structure. In the presence of suitable alloying elements these atoms can precipitate in the metal to form a fine dispersion of alloy nitrides in an iron matrix and thus nitride particles form an extremely hard (1000 VHN) and wear resistant surface for tribological applications. Nitriding treatment improves the fatigue properties of engineering components [1]. It is employed as a pretreatment of tool steel substrates for PVD hard coatings which provides hardening and increases load support effect on the substrate [2, 3, 4, 5]. This pretreatment reduces the plastic deformation of the tool substrate which results in eventual coating failure. Sun and Bell [6], Van Stappen et al. [7] and Zeghni et al. [8] found reduced wear on TiN after prenitriding treatment of tool substrates. Prenitriding is reported to increase adhesion [9, 10] and nitrided subsurface improves wear of PVD coatings by >1.5 times [11].

In gas nitriding a far greater surface hardness is achieved which is less susceptible to softening at elevated temperature of around 650^{0}C. Because of relatively low reaction temperature (about 500^{0}C) and the process does not involve any phase change, distortion and dimensional changes are reduced to a minimum and surface hardening is achieved without loss of strength within the previously tempered core.

In commercial process, gaseous nitriding is used particularly dissociated NH_3 as the nitriding medium. In contact with iron, NH_3 is catalytically dissociated, and the nitrogen atom diffuses into the steel to form the alloy nitrides.

The nitrogen solubility at the surface of the iron is determined by the equilibrium:

$$K = pNH_3 /(pH_2)^{3/2}$$

where, K is the equilibrium constant at a given temperature, pNH_3 and pH_2 are partial pressures of NH_3 and H_2 respectively in the gas. K values from literatures