Journal of Electroceramics, 13, 739–744, 2004

Microvaristors: Functional Fillers for Novel Electroceramic Composites

F. GREUTER,[1] M. SIEGRIST,[1] P. KLUGE-WEISS,[1] R. KESSLER,[1] L. DONZEL,[1] R. LOITZL[1] & H.J. GRAMESPACHER[2]

[1]*ABB Switzerland Ltd., Corporate Research, CH-5405 Baden-Dättwil, Switzerland*
[2]*ABB Switzerland Ltd., High Voltage Products, CH-5430 Wettingen, Switzerland*

Submitted March 3, 2003; Revised March 10, 2004; Accepted March 11, 2004

Abstract. Microvaristors are tiny electroceramic particles, which have highly nonlinear, voltage controlled electrical transport properties and can be used as active fillers in a variety of insulating matrix materials for functional composites. Due to the internal grain boundary structure, each individual microvaristor particle shows an IV-characteristics similar to the one known from bulk ceramics, except for the scaled down switching voltage. By controlling the material formulation, the particle morphology and the sintering conditions the switching characteristics of microvaristors can be tailored for specific applications.

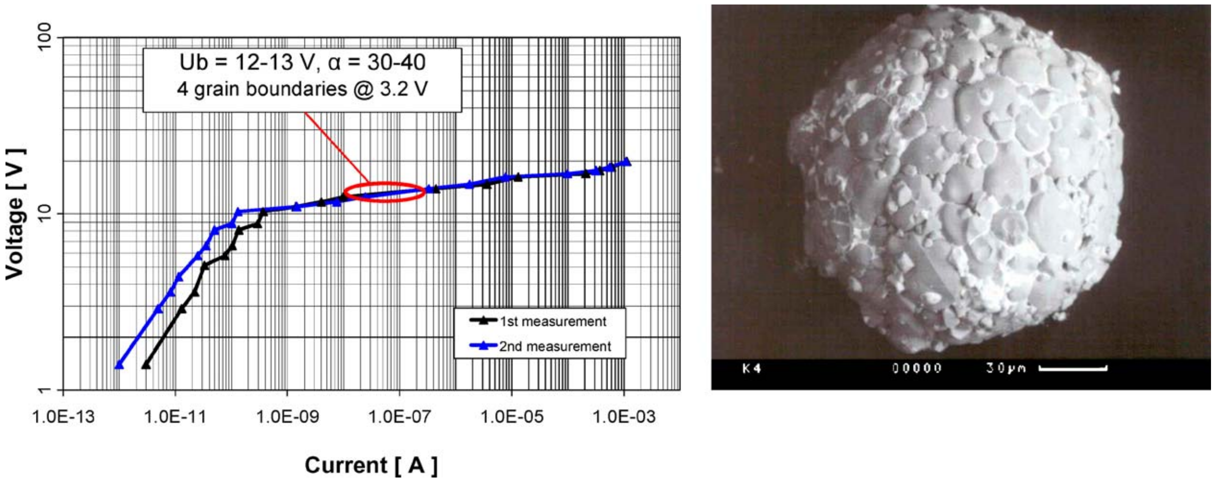
In the present paper the basic properties of ZnO microvaristors are described and it is shown how they impart their nonlinearity to the composite. A single microvaristor can withstand surprisingly high current loadings, without major changes in their electrical properties. Combined with the high manufacturing flexibility known from polymer processing, the varistor composites can be used for new solutions in overvoltage protection or control of electrical fields.

Keywords: microvaristor, nonlinear resistor, functional composite, overvoltage protection

Introduction

Electrically nonlinear materials play an important role in different applications in electronics and electrical power technology, in particular for controlling electrical fields and limiting dangerous overvoltages. Varistors based on doped ZnO ceramics are today's material of choice for protection against lightning impulses or other forms of electrical discharges [1]. For field control, e.g. at the terminations of high voltage cables or rotating machines, and for electrostatic discharge protection (ESD) of electronics, on the other hand a variety of empirically developed polymer composites is used, which show a moderate nonlinearity in their electrical transport characteristics due to a magic blend of different fillers (SiC, carbon black, TiO_2...) and their interaction with the polymer matrix [2, 3]. As a spin-off from the metal-oxide varistor technology, microvaristors [4, 5] have been developed and are being introduced in new products [6, 7]. When used as a functional filler in an insulating or semiconducting matrix the microvaristors can impart their strong electrical nonlinearity directly to the composite. This allows to combine the nonlinear electrical behavior needed for controlling overvoltages or high electrical fields with the high flexibility of polymer processing.

Unlike today's varistor-type composites, the nonlinear behaviour of the new materials is dominated by the intrinsic bulk properties of the microvaristor particles and is not originating from difficult to control and stabilize particle-particle or particle-polymer-particle contacts [2–10]. The response of the filler particles is dictated by their grain boundaries and is transferred directly to the behavior of the composite, as will be shown below. Figure 1 shows a typical microvaristor particle and its highly nonlinear IV-characteristics with a nonlinearity $\alpha = d \log I / d \log U \approx 36$ and a "switching voltage" $U_b \approx$ 12–13 V. Due to the known procedures how to adjust the electrical properties of



(left) (right)

Fig. 1. Microvaristor particle (diameter 145 μm) and corresponding DC-characteristics measured by microcontacting at diagonally opposite positions (repetitive measurements shown). The breakdown voltage $U_b \sim 12$ V corresponds to 4 active grain boundaries.

ZnO-varistors by doping and sintering, the behavior of the microvaristors can be readily engineered to specific needs. In the present paper we describe some of the surprising behavior of ZnO-microvaristors and how they impart their electrical behavior to a composite material.

Experimental Procedures

The first steps of producing microvaristors are similar to the processing of metal oxide (MO) powders for varistors. ZnO particles and several metal oxide dopants are spray-dried from a water based slurry. This initial step defines the size distribution and the spherical shape of the microvaristors in their green state. Next the spray-dried granules are sintered between 1000–1200°C as loose powders, either in a batch process or in a rotary kiln. During sintering the reaction, densification and grain growth processes proceed similarly to bulk ceramics, however limited to the volume of each microvaristor. Depending on the processing route the powders may be slightly sintered together and a soft mechanical disgglomeration may be required. This is followed by classification to a given size cut, e.g. in the range of 30–120 μm, depending on the application.

The electrical characteristics of a single microvaristor or a series connection of two sintered granules was measured in air by careful microcontacting (tip radius 7 μm) and lining the particles up in a capillary tube. The measurements are tricky and we cannot exclude possible contributions from surface leakage currents or noise pick-up at the lowest current levels. Composites were prepared by mixing appropriate amounts of microvaristors with insulating matrix materials such as oils, gels, epoxies, thermoplastics, elastomers or glass, followed by molding and curing [4, 5]. Electrodes were either directly molded into the material or applied after grinding.

Properties of Microvaristors

A typical IV-characteristics measured on a single microvaristor is shown in Fig. 1. Unlike in macroscopic, disk shaped MO varistors, here the contact configuration is not well defined and may correspond to only 1-3 grains. Hence the current flow through the microvaristor is expected to be inhomogeneous and will be prone to statistical effects, as described by Bartkowiak et al. for thin samples [11]. The latter can lead to switching among different current paths, resulting in voltage steps of multiples of $\sim$3.2 V as the voltage is ramped up (switching voltage/grain boundary is $\sim$3.2 V for a good varistor [12]). Together with the experimental difficulties mentioned above, this explains the "noisy" DC characteristics for the large grain size microvaristors. The switching voltages U_b, normally defined at $\sim$1 mA/cm^2 (corresponding to $\sim 10^{-8}$–10^{-7} A/granule) are in the range of $\sim$9–24 V for the different granule sizes (100–160 μm), indicating that typically

3–8 grain boundaries are active here. This is roughly consistent with the observed grain size. Depending on the orientation of the granule, different grain configurations will be contacted and we have to expect some variations in the DC-characteristics. By contacting the same microvaristor randomly in different orientations, we indeed find some variation in U_b, however this is only $\leq$1–3 multiples of ~3.2 V.

For most DC-measurements we have determined the characteristics twice in order to check for the reproducibility. At low currents ($<10^{-10}$ A), variations might be due to changes in the (surface) leakage currents of the granule or in the noise pick-up and have to be considered with care. Changes at higher currents are most likely due to the statistical effects described by Bartkowiak et al. [11] or some variations in the contact position. As can be seen in Figs. 1–3 the reproducibility of the IV-curves is in general quite good. This is even more surprising since each measurement point takes a few seconds and the maximum current densities are in the range of ~10–100 A/cm^2, depending on what local cross section is assumed (granule diameter or contact point). Despite such high current or energy densities there is very little degradation of the DC characteristics of an individual microvaristor. This can only be understood by a good cooling of the varistor particle by the contacts. Still higher loadings were probed with 8/20 μsec current pulses as shown in Fig. 2. Generally, up to ~100 mA no relevant degradation of the IV-characteristics was observed, whereas for impulses in the range of 1–10 A an irreversible degradation occurred, increasing the leakage currents at low voltages by 4-5 orders of magnitude.

Varistor Composites and Applications

For the transition from a single microvaristor to a macroscopic ensemble of microvaristors in a composite, there is a variety of effects to be considered which are not all well understood and may depend on the processing and the matrix material. The major aspects are the packing arrangement of the particles and the microscopic properties of the particle-particle contacts. In practice there is a given particle size distribution, as e.g. determined by sieving, which will affect the packing in the composite. Also, for processing reasons the maximum filling degree may not be realized due to the viscosity requirements in molding operations. As the filling degrees normally are well above the percolation threshold, the filler content itself has only a small influence on the overall behavior of the composite. However, for electrical composites the connectivity of the filler particles is a crucial parameter. For

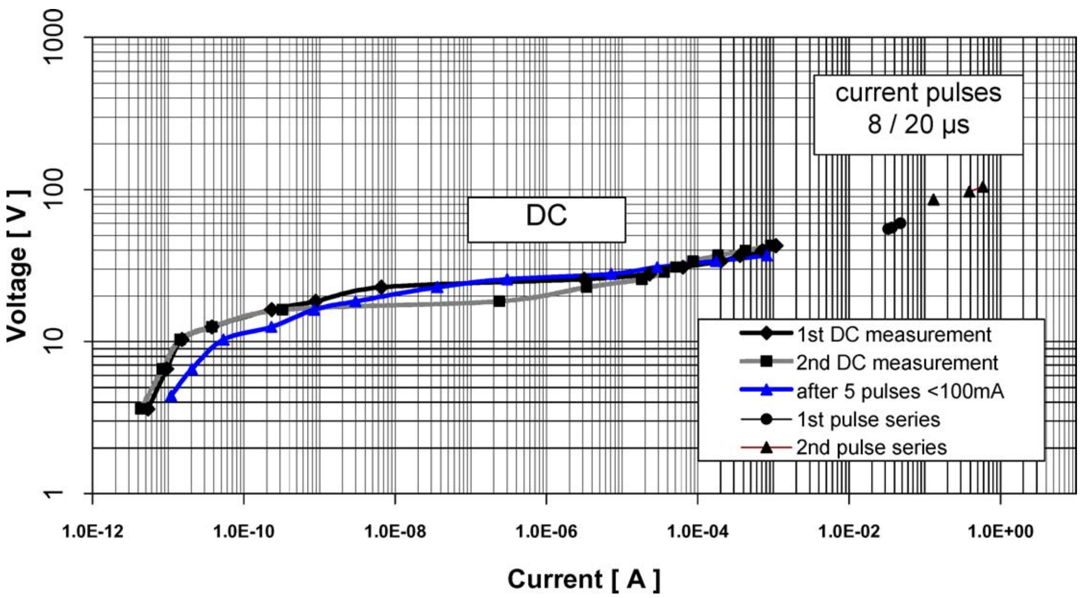


Fig. 2. 1st and 2nd DC-measurement up to 1 mA on a single microvaristor (diameter ~200 μm) followed by 5 impulses up to ~100 mA. The following DC-measurement does not show any significant degradation despite the high current loadings.

varistor composites this is particularly important, since in the nonlinear part of the IV-characteristics the current flow is filamentary, even in bulk varistor ceramics [12]. The particle size distribution then also becomes important, with large particles being dominant for the connectivity. The particle arrangement together with the quality of the particle-particle contacts strongly affect the connectivity of the composite. Little information is available on microscopic particle contacts in composites [2–5, 8–10], in particular about the possible presence of very thin polymeric layers penetrating the contact areas [8, 9]. If such interfacial layers are present with a thickness large enough to suppress tunnelling [8, 9], they add a high contact resistance and strongly affect the connectivity of the composite. Other factors affecting the contact resistance are the contact areas (constriction resistance), possible insulating surface layers (depletion or contamination layers), contact pressure (curing stresses, capillary forces [2, 10]) etc. For the present varistor composites good interparticle contacts are aimed at, since the nonlinear behavior is a property of the filler itself. Ideally the contact resistance has to be much smaller than the resistance of a microvaristor.

In Fig. 3 an attempt was made to characterize the contact between two microvaristors A and B in air, which were measured individually before and after being connected in series. Granules with large grain sizes were used to better detect any contact properties. The measured switching voltages were $U_b(A) \sim 13$ V, $U_b(B) \sim 17$ V and $U_b(A+B) \sim 35$ V, showing that there might be a voltage drop of $\Delta U_G \sim 5$ V at the particle-particle contact. Given the difficulty in measuring and positioning the small particles we can only take this as an indication for an extra voltage drop of a few volts ($\Delta U_G \sim 3$–10 V) at the particle contacts. Surface band bending and adsorbed layers are possible origins of such small extra barriers, which may contribute to the overall IV-properties, in particular for low field composites.

Figure 4 compares the IV-characteristics of the most simple composite (oil as matrix) to the IV-curves of a few microvaristors measured as individual particles, showing that the varistor behavior is transferred from the microvaristor to the composite. Due to the particle size distribution, there is a spread in the switching voltage $U_b \approx 40$–70 V of the measured microvaristors (A, B, C, E; all from same powder batch). Here the particles were sintered such as to produce composites with a field strength of ~800 V/mm in oil. The filler for the composite was in the range of 32–125 μm, whereas for the individual measurements the larger particles around 125 μm were selected. Considering a sample of 1 mm height and a cross section of 1 cm^2, the

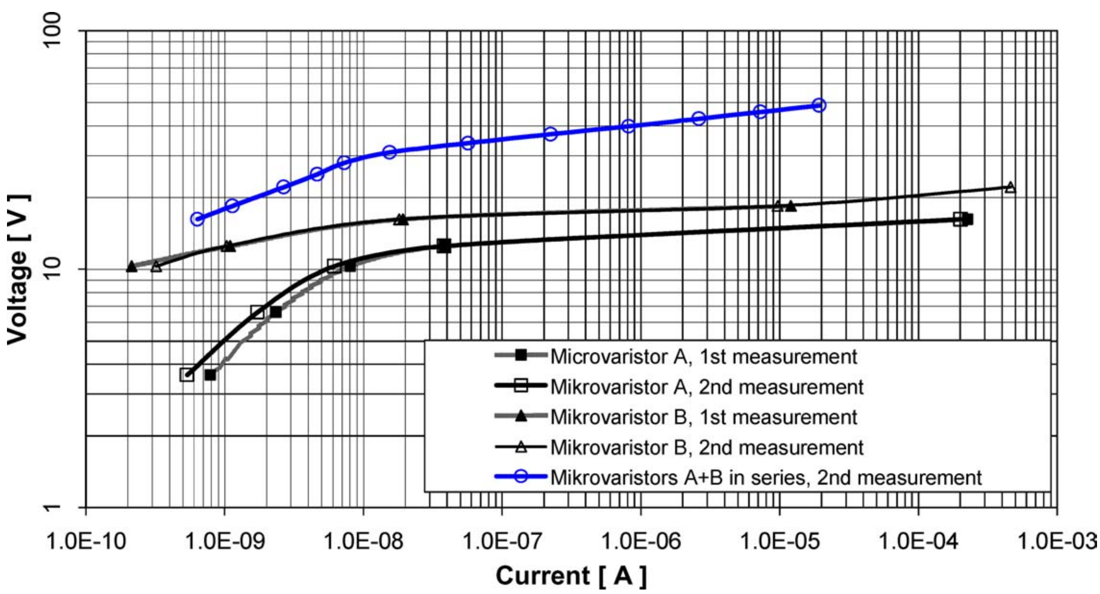


Fig. 3. IV-characteristics of two individual microvaristors A and B, randomly picked from the same powder batch, and their series connection A + B.

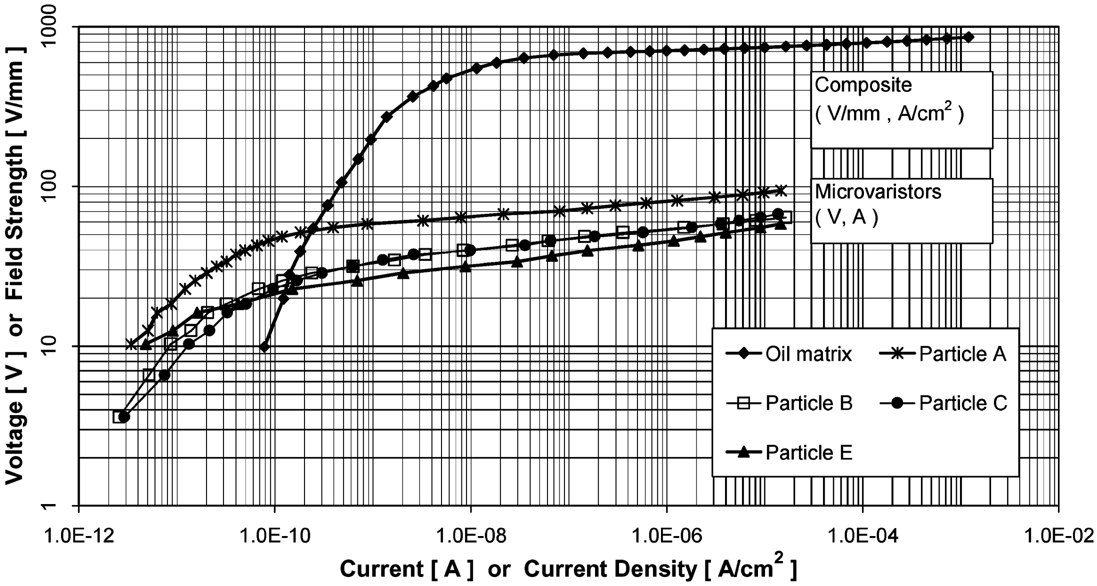


Fig. 4. Comparison of the DC-characteristics of a few randomly selected microvaristors (A, B, C, E) and of the corresponding varistor composite with Midel-oil as the matrix (filling degree ~60v-%). Note that for the microvaristors the data are given in absolute values, whereas for the composite normalized values are used.

IV-curves of the microvaristors can be made to roughly overlap the composite by shifting them up by a factor of 18 ± 5 along the voltage axis and by ~100 along the current axis. Assuming an average effective particle diameter of ~80 μm and a voltage drop $\Delta U_G \sim$ 10 V at the contacts, the vertical shift can be understood, if the current path in the composite is extended by a factor ~1.7, which is not unrealistic for a loosely compacted composite. For higher compaction, as e.g. in a thermoset with a high internal curing stress, this factor may go down to ~1.3. The shift of two decades along the horizontal axis in Fig. 4, on the other hand, provides a lower limit for the number of active current paths per cm^2. If the measured leakage currents of the microvaristors were correct, it would mean that only one percent of the contacted granules carries current in the composite. Due to the measuring limitations and possible surface leakage currents from the microvaristor and sampler holder (humidity, contaminations) the true leakage current/granule must be lower and hence the number of paths per area will be somewhat larger than from the above worst case estimate. However the small contact area between two microvaristors is a major constriction, which reduces the total current density.

By decorating the microcontacts with small metal flakes [13], the overall connectivity can be improved. This results in a reduced switching field of a composite, a higher energy absorption capability (up to 200 J/cm^3 without puncturing) and an increased dielectric constant. First experiments with microcontacting also indicate that ΔU_G is reduced to <3 V.

By careful optimization of the properties of the microvaristors, the microcontacts and the processing, highly nonlinear varistor composites can be realized, which open up new possibilities in overvoltage protection and electric field control. Figure 5 shows the example of a new type of cable termination for high voltage cables. A nonlinear material is needed at the edge of the semiconducting cable screen near the cable end, where high electrical fields have to be limited to avoid flashovers or damages to the cable. With field calculations, the optimum properties and geometric dimensions for the microvaristor composite were determined. Then silicone based varistor composites were tailored for this application. The prototypes successfully passed all the harsh tests required by high voltage engineering standards [7]. With today's known field control materials such applications can only be realized for the lower voltage levels (≤36 kV).

(left) (right)

Fig. 5. Prototype of a new high voltage cable termination for ≥84 kV (right). The inner most layer (left) provides the field grading and consists of a microvaristor composite with silicone as a flexible matrix. This field grading tube is molded into a insulating silicone housing.

Conclusions

Microvaristors are a new type of functional filler for nonlinear electrical composites. They are a spin-off from the established metal oxide varistor technology. Electrically active grain boundaries inside each individual particle provide the high nonlinearity and a switching voltage of ∼3.2 V/boundary. Such microvaristors can withstand surprisingly high local current densities. In a composite the particle packing, their connectivity and the properties of the interparticle contacts are important parameters for a homogeneous current flow and a high energy uptake. By adjusting the sintering conditions, the varistor formulation and the microcontacting, the electrical properties of the composite can be tuned to specific applications.

References

1. L.M. Levinson, *Adv. In Varistor Tech., Ceramic Transactions*, **3**, (1989).
2. E. Martensson, U. Gäfvert, U. Lindefelt, and C. Önneby, *J. Appl. Phys.*, **90**(6), 2862 and 2870 (2001).
3. F.A. Modine and H.M. Hyatt, *J. Appl. Phys.*, **64**, 4229 (1988).
4. R. Strümpler, P. Kluge-Weiss, and F. Greuter, *Adv. Sci. Technol.*, **10**, 15 (1995).
5. J. Glatz- Reichenbach, B. Meier, R. Strümpler, P. Kluge- Weiss, and F. Greuter, *J. Mater. Sci*. **31**, 5941 (1996).
6. R. Strobl, W. Haverkamp, and G. Malin, *Elekrizitätswirtschaft*, **99**(26), 68 (2000).
7. H.J. Gramespacher, T. Christen, L. Donzel, and F. Greuter, in Jicable 03, *Conf. Proc.*, (versailles), 2003.
8. G.R. Ruschau, S.Yoshikawa, and R.E. Newnham, *J. Appl. Phys.*, **72**(3), 953 (1992).
9. E.M. Cashell, J.M.D. Coey, G.E. Wardell, V.J. McBrierty, and D.C. Douglass, *J. Appl. Phys.*, **52**(3), 1542 (1981).
10. R. Strümpler and J. Glatz-Reichenbach, J. of Electroceramics, **3**(4), 329 (1999).
11. M. Bartkowiak, G.D. Mahan, F.A. Modine, and M.A. Alim, *Jpn. J. Appl. Phys.*, **35**, L414 (1996).
12. F. Greuter and G. Blatter, *Semicond. Sci. Technol.*, **5**, 111 (1990).
13. P. Kluge-Weiss, F. Greuter, and R. Strümpler, US patent 6,469,611 B1.