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INFLUENCE OF THE DIFFUSION OF OXYGEN ON THE AGING OF ZINC OXIDE-BASED VARISTORS

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Résumé - L'étude de la cinétique de réduction de varistances à base d'oxyde de zinc à 650°C et sous atmosphère CO-CO₂ a permis de relier la dégradation des caractéristiques électriques, observée lors du vieillissement sous champ électrique, à un transfert d'oxygène des grains d'oxyde de zinc vers les phases intergranulaires.

Abstract - The kinetics of reduction of zinc oxide-based varistors has been studied at 650°C in CO-CO₂ mixtures in order to correlate ageing under electrical stress to diffusion phenomena. The experimental results indicate that the main cause of the ageing is a migration of oxygen from the outer core of the ZnO grains toward the intergranular phases.

I - INTRODUCTION

The zinc oxide-based varistors exhibit a marked non-linearity in their current vs voltage characteristic, $J=f(F)$. They are in consequence widely used in the manufacturing of devices for the protection of electrical or electronic circuitry against transient overvoltages. For such a purpose, a good stability in time of the $J=f(F)$ characteristic is required /1/.

The non-linear behavior of the material is currently considered as being related to the appearance of Schottky barriers between adjacent ZnO grains, as a result of the trapping of electrons in acceptor levels at the boundary /2/. The $J=f(F)$ characteristics are subjected to evolution under an applied electric field /3/ or again by heating in a low partial pressure of oxygen /4/. In either case, the diffusion of species in the vicinity of the grain boundaries would be at the origin of the evolution /5/. If such chemical modifications actually occur they are likely to affect the rates of diffusion.

The purpose of the present work is to investigate the diffusion phenomena through comparison of the reduction rates of new and artificially aged materials.

II - EXPERIMENTAL

The ceramics investigated are of the same origin and were designed for surge protection on electric power lines, but :

- ceramic A is new
- ceramic A' has been previously aged for 410 h at 115°C under 76 % of the threshold voltage (A.C.).

Their composition, microstructure and J-F characteristic are reported in Table I, figure 1 and figure 2 respectively.

Co	Sb	Bi	Ni	Mn	Cr
0.8	3.2	3.1	0.9	0.4	0.6

TABLE I

Concentrations of additives (weight %) in ZnO based varistors A and A'.

Fig. 1 - Microstructure of varistance A, left, and A', right (back scattered electron images).

Fig. 2 - J-F characteristics of ceramics A and A'.

For each ceramic two parallelepipedic samples ($2 \times 1 \times 1 \text{ cm}^3$) were studied :

- c originating from the central region
- p originating from the outer core.

The reduction was carried out at 650°C in a gaseous mixture such as $P_{\text{CO}}/P_{\text{CO}_2} = 7.10^{-2}$ at $1.013 \times 10^5 \text{ Pa}$ overall pressure, which corresponds to $P_{\text{O}_2} \approx 10^{-20} \text{ atm}$. The changes in weight vs time were measured using a SETARAM B70 type thermobalance with a 10^{-6} relative sensitivity.

III - RESULTS AND DISCUSSION

The curves, $\Delta m/m_0 = f(t)$, of the relative mass changes with time are presented on figure 3. They clearly show that, for the new ceramic, the relative decrease in mass occurs with a faster rate when the sample originates from the central region than from the outer core, whereas the opposite behavior is observed for the artificially aged ceramic. Furthermore, the mass losses are more important for the latter.

Fig. 3 - Relative mass losses vs time $\Delta m/m_0 = f(t)$

----- new material (A)   c : sample from the central region
 ————— artificially aged material (A')   p : sample from the outer core

The extension of Fick's second law to a polycrystalline material leads to the definition of the parameter $\tilde{D}$ called apparent chemical diffusion coefficient. Its experimental determination requires that one single reduction mechanism is predominant throughout the reduction time. It can then be achieved through the use of the following equation established by NEWMAN /6/ for a parallelepipedic sample of dimensions a, b, c :

$$1 - \frac{\Delta m}{\Delta m_{\infty}} = \sum_{n=0}^{\infty} \frac{2}{\beta_n^2} \exp\left(-\frac{\beta_n^2 \tilde{D} t}{a^2}\right) \times \sum_{n=0}^{\infty} \frac{2}{\beta_n^2} \exp\left(-\frac{\beta_n^2 \tilde{D} t}{b^2}\right) \times \sum_{n=0}^{\infty} \frac{2}{\beta_n^2} \exp\left(-\frac{\beta_n^2 \tilde{D} t}{c^2}\right)$$

where Δm and Δm_{∞} are respectively the decreases in mass at time t and $t = \infty$ and $\beta_n = \pi/2 + n\pi$.

The values of $\tilde{D}$ and $\Delta m_{\infty}/m_0$ calculated from the experimental $\Delta m/m_0 = f(t)$ curves, recorded for reduction times of 20 up to 60 hours, are presented in Table II. The weak weight losses observed during the 20 first hours of the experiments correspond to the equilibration of the surface. The apparent chemical diffusion coefficient $\tilde{D}$ appears to remain practically constant, whereas the $\Delta m_{\infty}/m_0$ ratio increases significantly when the ceramic has been artificially aged.

Sample	$10^7 \tilde{D} (\text{cm}^2 \text{s}^{-1})$	$10^6 \Delta m_{\infty}/m_0$
A c	6	340
p	6	310
A' c	10	415
p	6	460

TABLE II

Apparent diffusion coefficients $\tilde{D}$
and relative mass losses $\Delta m_{\infty}/m_0$.

The ceramics studied have been processed using liquid phase sintering at 1300°C. For such a temperature, the electrochemical potentials of most components are expected to nearly homogenize, at least in the grain boundaries region. On cooling - which is rather fast in manufacturing conditions - the electrochemical equilibrium cannot be maintained since the variation $\partial \tilde{\mu}_i / \partial T$, for any i component, is not the same in all phases. Electrochemical potential gradients are thus created once the ceramic has reached room temperature, and are expected to be the steepest in the external part, where the cooling is the fastest. In such a non-equilibrium material, any increase of intensive thermodynamic variables is likely to stimulate mass transfer in order to bring the material back to equilibrium. For example, the ageing treatment at 115°C and under an electric field shall allow oxygen to move from the regions where its electrochemical potential is high toward those where it is lower.

It is worthwhile noting that the chemical diffusion coefficients reported for monocrystalline ZnO at 650°C [7] are at least 10^6 weaker than $\tilde{D}$ obtained after our measurements at the same temperature. This means that, in the cases we studied, the ZnO bulk was not involved in the first step of the reduction. The latter could actually be controlled by intergranular phases, mainly located at the triple joints, which would pick up oxygen during the ageing treatment, as indicated by the high values of $\Delta m_{\infty}/m_0$ for the so treated materials.

Thus, it seems reasonable to consider that the deterioration of the $J=f(F)$ characteristic observed after the ageing treatment is the result of a transfer of oxygen from the external part of the ZnO grains toward the grain boundaries and then the intergranular phases, which would alter the Schottky barriers. The main driving force for this transfer would be the change in the electrical field near the grain boundaries, induced by the external electrical stress.

Such an interpretation is consistent with the restoration of the $J = f(F)$ characteristic observed after heating up the ceramic at 400-600°C in an atmosphere of pure oxygen and subsequent cooling /8/.

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REFERENCES

- /1/ Hennebique, I., Leroy G. and Vicaud A., *Epure*, 3 (1984) 2.
- /2/ Mahan, G.D., *Grain Boundaries in Semiconductors*. Published by Elsevier Science, New-York (1982) 333.
- /3/ Mizuno, M., Hayashi, M. and Mitani K., *IEEE, Trans. on Power Appar. Syst.*, PAS-100(5) (1981) 266.
- /4/ Salmon, R., Bonnet, J.P., Graciet, M., Onillon, M. and Hagemmuller, P., *Solid State Commun.*, 34, (1980) 301.
- /5/ Philipp, H.R. and Levinson, L.M., *Advances in Ceramics*, 7 (1984) 1.
- /6/ Newman, A.B., *Trans. Am. Inst. Chem. Engr.*, 27 (1931) 203.
- /7/ Kofstad, P. *Non-stoichiometry, Diffusion and Electrical Conductivity in Binary Metal Oxides*", Ed. John Wiley and Sons, New York (1972) 338.
- /8/ Philipp, H.R. and Levinson L.M., *J. Appl. Phys.*, 50(1) (1979) 383.