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Processing parameters for ZnO-based thick film varistors obtained by screen printing

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Thick film varistors based on the ZnO-Bi_2O_3-Sb_2O_3 system have been prepared by screen printing on dense alumina substrates. Different processing parameters like the paste viscosity, burn out and sintering cycles, green and sintered thickness, have been studied to improve the processing of ZnO-based thick film varistors. Starting powders were pre-treated in two different ways in order to control both the Bi-rich liquid phase formation and the excessive volatilization of Bi_2O_3 during sintering due to the high area/volume ratio of the thick films. Significant changes have been observed in the electrical properties related to the different firing schedule and selection of the starting powders.

Keywords:Varistors, Thick film, screen printing, processing, electrical properties.

Parámetros de procesamiento para varistores basados en ZnO preparados por serigrafía.

Se han preparado varistores basados en el sistema ZnO-Bi_2O_3-Sb_2O_3 en forma de lámina gruesa sobre sustratos de alúmina densa. Diferentes parámetros del procesamiento como la viscosidad de la pasta, los ciclos de calcinación y sinterización y el espesor en verde y sinterizado han sido estudiados para mejorar el procesamiento de los varistores basados en ZnO preparados en forma de lámina gruesa. Los polvos de partida fueron pretratados de dos formas diferentes con el objetivo de controlar la formación de la fase líquida rica en bismuto y la excesiva volatilización de Bi_2O_3 durante la sinterización debida a la alta relación área-volumen de las láminas gruesas. Se han observado cambios significativos en las propiedades eléctricas relacionadas con los diferentes ciclos de calcinado y con la selección de los polvos de partida.

Palabras clave: Varistor, lamina gruesa, serigrafía, procesamiento, propiedades electricas

1. INTRODUCTION

Zinc-oxide based ceramics are multiphase materials which exhibit highly non-linear current-voltage response. As a consequence of this non-ohmic characteristic, these ceramics are widely used for varistors manufacturing that find application as voltage surge protectors (1,2). Although many efforts have been devoted to the development of high voltage varistors, their application for low voltage protective devices is still a matter of study. Potential applications of thick film varistors for low voltage electrical circuits have recently attracted attention from the scientific community; however severe technological problems remain unsolved (1-4).

Screen printing process for thick film manufacturing has been developed in the field of microelectronics for hybrid and integrated circuits. The advantages of this technology are among others low cost, design versatility, and high reproducibility. On the other hand, one of the main problems inherent to this technology is the relatively low green density of the films. Therefore to reach a satisfactory densification level a large amount of glass-frit is usually added for the sintering step. In the case of the ZnO- based varistor material, a significant amount of glass-frit will modify the electrical performance of the thick films but also poor densification will lead to unacceptable varistor properties. Moreover, optimum viscosity for screen printing pastes is very narrow and makes necessary to use a high content of organic additives to fit their rheological behaviour. Therefore the burn out schedule becomes also a crucial step. (3).

Menil et al (4) proposed to improve the films green density by applying mechanical pressure, either uniaxial or isostatic, onto the calcined screen printed samples. With this additional pressing step, non-linear coefficient values around 17-19 were reported for thick films sintered at 1150ºC. Unpressed screen-printed varistors were mostly short-circuited.

Other relevant point to keep in mind for thick film varistors manufacturing is the high Bi_2O_3 volatilization at the sintering temperatures due to the extremely high area/volume ratio for thick films. In recent works Peiteado et al (6) have measured a Bi_2O_3 lost up to 60 w.% in bulk varistors with area/volume ratio of 4.1cm^{-1}. De la Rubia et al (6) reported that partial Bi_2O_3 volatilization limits the highest (7) area-volume ratio possible to keep useful varistor behaviour for a certain varistor composition.

Bi_2O_3 volatilization takes place from the Bi_2O_3-rich liquid phase that forms during sintering. Varistor functional microstructure is achieved through the following reactions (8):

$$2ZnO + 3/2Sb_2O_3 + 3/2Bi_2O_3 + 3/2O_2 < 900^{\circ}C \quad Zn_2Sb_3Bi_3O_{14} \text{ (pyrochlore)} \qquad [1]$$

$$2Zn_2Sb_3Bi_3O_{14} + 17ZnO \; 900\text{-}1050^{\circ}C \; 3Zn_7Sb_2O_{12} + 3Bi_2O_3 \text{ (liquid)} \qquad [2]$$

Proper densification of the varistor material is obtained when Bi_2O_3 liquid phase appears leading to liquid phase sintering. However, if temperature is increased bismuth volatilization is also increased and becomes significant for the final electrical properties. Such an effect is even more marked for the thick film geometry, with a very high area/volume ratio (two orders of magnitude higher than for bulk ceramics). Within this framework, a reasonable approach to overcome such difficulties might be based on the formation of the Bi_2O_3 rich liquid phase at low temperatures, so that Bi volatilization kinetic is hindered and Bi loss avoided. For this purpose, different processing strategies leading to the formation of Bi_2O_3 rich liquid phase at low temperatures have been studied (9).

The aim of this work is to study the process of manufacturing ZnO-based varistor thick films by screen printing and control the Bi_2O_3 volatilization while improving the densification.

2. EXPERIMENTAL PROCEDURE

2.1 Powder preparation

The nominal composition of the varistor powder used in this work is 95.5 mol% ZnO, 1.5 mol% Sb_2O_3, 0.5 mol% Bi_2O_3, 0.5 mol% Co_3O_4, 1.25 mol% NiO and 0.75mol% MnO. Two different processing strategies have been designed:

-Batch SCM: prepared by a classical mixed-oxide route followed by a calcination treatment at 950ºC-1h and mill to break the agglomerates formed during the calcination.

-Batch SP: classical mixed-oxide route but replacing the Sb_2O_3 by the equivalent amount of a previously synthesized $Zn_7Sb_2O_{12}$ ortorrombic spinel phase.

Average grain size of the starting powders is 0.7-0.8μm measured by Laser-Coulter and crystalline phases were characterized by X-ray diffraction (XRD) in a D5000 Siemens Diffractometer using $CuK\alpha_1$ radiation. Fig.1. shows powder XRD of the two starting materials; the main components ZnO, $Zn_2Bi_3Sb_3O_{14}$ and $Zn_7Sb_2O_{12}$ spinel phase for batch SCM and ZnO, Bi_2O_3 and $Zn_7Sb_2O_{12}$ for batch SP can be observed according to the processing strategies designed.

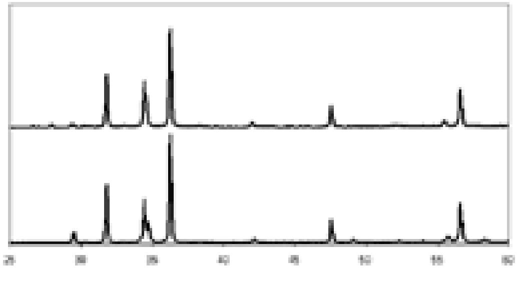

Fig. 1- XRD patterns of the three starting powders previous to sintering Zn=ZnO (JCPDS 36-1451), Bi=Bi_2O_3 (JCPDS 71-0465, Sp=$Zn_7Sb_2O_{12}$ (JCPDS 36-1445) and Py=$Zn_2Bi_3Sb_3O_{14}$

2.2 Thick films preparation

The pastes for screen printing were prepared as follow: 60% in weight of active powder were homogenized and milled in a planetary mill for 8h with 40% in weight of organic vehicle composes of α-terpineol as solvent, ethylcellulose like binder and [2-(2-butoxi-etoxi-ethyl)] acetate as plastificant. Dolapix was used like dispersant.

Fig.2 shows that pastes SP and SCM have pseudoplastic behaviour, with viscosities of 4000 and 5000mPa·s at 200s^{-1} respectively. This rheological behaviour is optimum for screen printing. Previously to the deposition of ZnO-based varistor pastes onto dense alumina substrates, platinum electrode is screen-printed onto the substrates and fired at 850ºC-1h. After that, layers of varistor ink are deposited by screen printing by a DEK 65 screen printing machine with a polyester mesh. Each layer is dried in oven at 150ºC-15min. Each green layer produces a thickness around 10μm. When more than ten layers are deposited appears structural defects after drying, therefore the highest green thickness that can be obtained for this pastes is around 100μm. To avoid the appearance of cracks, six layers of varistor paste were deposited. For all the films, green thickness was in the range of 60-70μm according with the mesh opening and the number of deposited layers. Two different burn out cycles have been used; calcination at 600ºC without dwells, with heating-cooling rate of 1ºC/min and calcination at 425ºC with dwells at 195, 270 and 385ºC during 30, 20 and 20min respectively, with heating-cooling rate of 0.5ºC/min. Calcined samples were sintered at temperatures between 900 and 1150ºC with 1h soaking time. Thickness of sintered samples ranged between 30-40μm. Green and sintered surfaces were characterized by optical microscopy. Sintered thick films were characterized by FESEM (Hitachi S-4700) equipped with EDS. Finally for electrical characterization, gold top electrode is deposited by sputtering. V-I measurements were carried out using a multimeter (Keitley 2410).

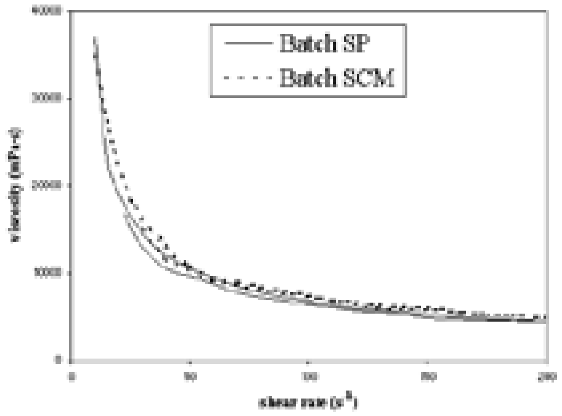

Fig. 2- Viscosity against shear rate for batches SP and SCM

3. RESULTS AND DISCUSSION

Samples calcined at 600ºC without intermediate dwells show black carbon rich spots originated by a non-adequate

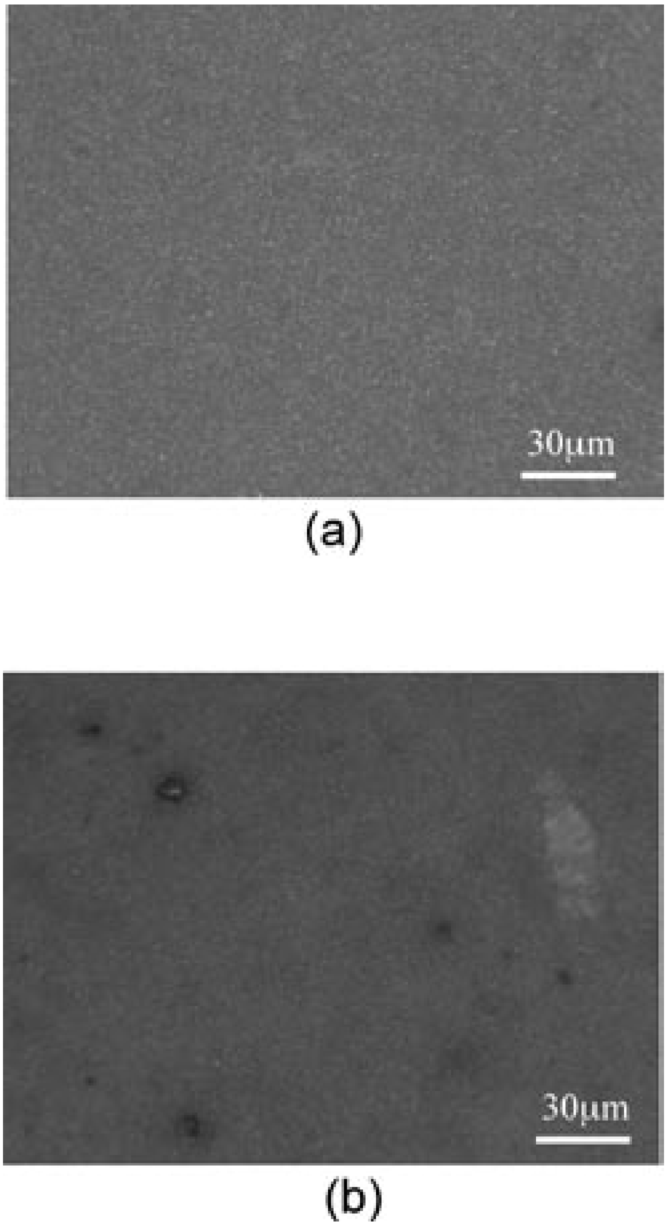

Fig. 3- Optical microscope micrographs for thick films sintered at 1050ºC-1h. (a) batch SP, calcined at 425ºC with intermediate dwells, (b) batch SP, calcined at 600ºC.

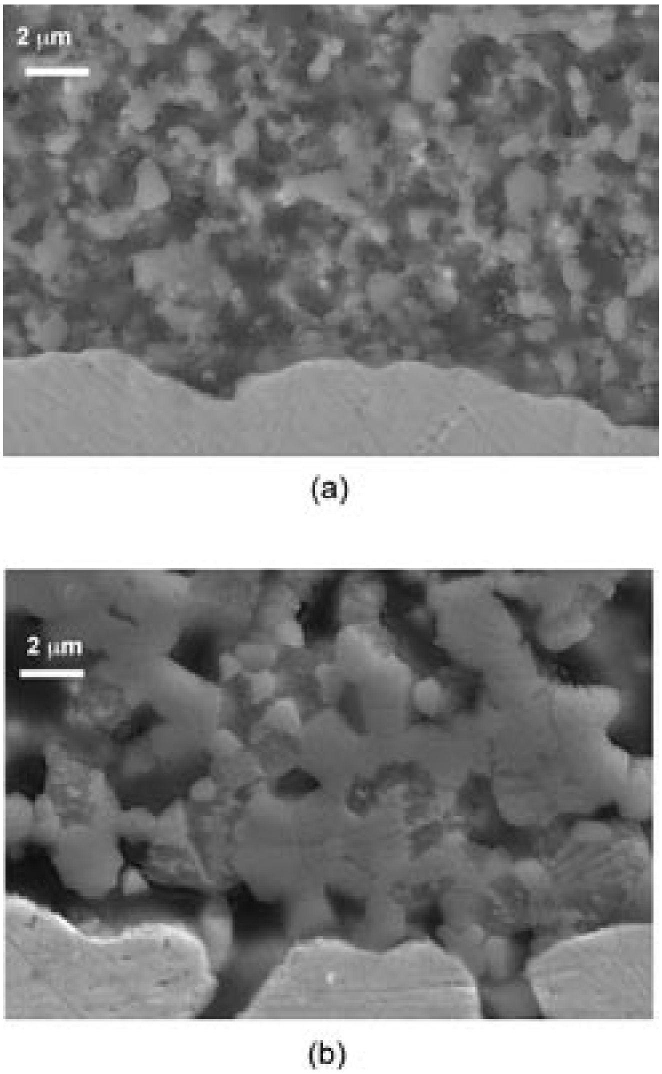

Fig. 4- SEM micrographs of thick films of. Batch SP sintered at 900ºC (a) and batch SCM sintered at 1050ºC (b)

TABLE I. EVOLUTION OF NONLINEAR COEFFICIENT α WITH SINTERING TEMPERATURE (SOAKING TIME=1 HOUR) FOR THICK FILMS PREPARED BY SCREEN PRINTING.

Sintering Temperature (ºC)	SCM	SP
900	No IV	20
950	2	15
1000	8	10
1050	14	9
1100	9	7
1150	8	6

burn out step. After sintering, craters and macroscopic cracks are clearly observed. On the contrary, samples calcined at a lower temperature but with specific dwells do not show these craters. These results can be observed in Fig 3. Most of the samples calcined at 600ºC without dwells are short circuited and therefore result impossible to obtain reliable thick films with varistor behaviour. Calcined samples at lower temperature are not short circuited and show reasonable reliability. Fig.4. show SEM micrographs of a SP thick film sintered at 900ºC and a SCM sintered at 1050. As a general behaviour, SP films sinter at low temperatures meanwhile SCM films need to be treated at higher temperatures to densify. This behaviour is determined by the powder processing strategy.

Table 1 shows the values of the nonlinear coefficient α for batch SP and SCM calcined at 425ºC and sintered between 900-1150ºC with soaking time of 1h. Different electrical response for both batches is clearly observed, reflecting the processing strategies. Batch SP present a good varistor behaviour at the sintering temperature of 900ºC, exhibiting nonlinear coefficient α = 20. This is a consequence of the designed strategy which improves densification at low temperatures. For batch SP, the spinel phase $Zn_7Sb_2O_{12}$ is used as Sb precursor instead of Sb_2O_3 avoiding the reactions 1 and 2 (9). The release of the Bi-rich liquid phase takes place at 740ºC due to the existence of a eutectic reaction in the binary system ZnO-Bi_2O_3 (10,11). On the other hand when sintering temperature increases above 900ºC, a substantial Bi_2O_3 volatilization occurs and therefore the non-linear coefficient decrease is very significant. Bismuth is being removed from the varistor microstructure vigorously due to the high A/V ratio (around 300 cm^{-1}).

For batch SCM, reaction 2 has taken place only partially, therefore this system initially presents $Zn_7Sb_2O_{12}$ spinel phase, $Zn_2Bi_3Sb_3O_{14}$ pyrochlore phase and ZnO. Therefore, at low sintering temperatures like 900ºC, almost all of the Bi_2O_3 is included in the $Bi_3Zn_2SbO_{14}$ pyrochlore phase (reaction 1). This phase is solid up to its decomposition which is above 900ºC and reaction 2 does not take place. Since there is not almost Bi_2O_3 free the film does not properly densify during the sintering treatment. The best electrical behaviour for batch SCM is at 1050ºC, this is because of proper densification driven by the appearance of the liquid phase. However, the electrical response never is as high as batch SP and the reason is that at these temperatures Bi_2O_3 volatilization is significant. Thick films from batch SCM sintered at 950ºC present small varistor behaviour consequence of the little releasing of Bi_2O_3 since reaction 2 only has taken place partially at this temperature and the samples do not densify properly. Nonlinear coefficients α are clearly lower than the obtained values for thick films sintered at 900ºC for the strategy SP. Therefore it is possible to prepare a thick film with good varistor behaviour avoiding an excessive volatilization of Bi_2O_3 with the processing strategies of batch SP and decreasing the sintering temperature up to 900ºC.

4. CONCLUSIONS

Processing parameters of the varistor pastes, firing schedules and powder preparation strategies have been analysed to obtain ZnO-based thick film varistors by screen printing. The optimization of these parameters have made possible to obtain thick film varistors with α values as high as 20. The incorporation of the previously synthesized $Zn_7Sb_2O_{12}$ spinel phase as source of Sb_2O_3 allows a lower sintering temperature, 900ºC, and so prevents excessive Bi_2O_3 volatilization, which due to the extremely high area-volume ratio of the films represents the major challenge in manufacturing these devices.

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