Morphological investigation of ceramics for capacitors

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Morphological investigation of ceramics for capacitors

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ABSTRACT - To control and to improve the homogeneity of a dielectric based on baryum titanate, we have investigated the different stages of the process - ceramic powder, slurry and sintered materials - by automatic image analysis methods. The influence of many parameters has been considered : formulation parameters; grinding conditions ; particle size and shape ; binder, dispersant and plastification agents; temperature and time of sintering; ...

I INTRODUCTION

The control of the microstructure of a part which depends on the raw materials and on the process route, is one of the predominant factor on its properties, and more specifically for ceramic materials as they are very sensitive to small defect or inhomogeneities [1].

For that purpose we have investigated the different stages of the process of baryum titanate ceramic capacitors by automatic image analysis and looked for the influence of many process parameters on the physical properties. We focussed our attention on the characteristics and on the dispersion state of the $BaTiO_3$ powder, on the possible characterization of the green films and of the sintered parts. In this paper a brief outlook on this larger investigation [2] will be presented.

II EXPERIMENTAL

The investigated baryum titanate powder belongs to the X7R group with a dielectric constant close to 3300. It is based on $BaTiO_3$ with additions of Nb_2O_5, CoO and MnO_2. The slurry consists of the powder suspended in a blend of solvents (azeotropic mixture of trichlorethylene - ethanol), binders (based on polyvynylbutyral, PVB), dispersant (phosphoric ester) and plastification (benzyl butyl phthalate and tetraethylene glycol diethylhexoate) agents, which is laid out on a stainless steel ribbon to obtain a film of 50 µm thickness, according to the tape casting process [3,4,5]. These films, after the serigraphy process, are stacking and then sintered to obtain blocks of capacitors of 10 * 10 cm^2 size.

Powders and green films (Fig. 1 a et b) were investigated directly from a scanning electron microscope (Jeol T330, Japan) connected to an image analyzer system, made of a host computer (SUN 3.140) and an Imaging Technology image processor Series 151, in the VISILOG (Noésis, France) environment. The size of the memory image is 256 x 256 pixels, set in a square grid. Each pixel has a depth of 256 grey levels.

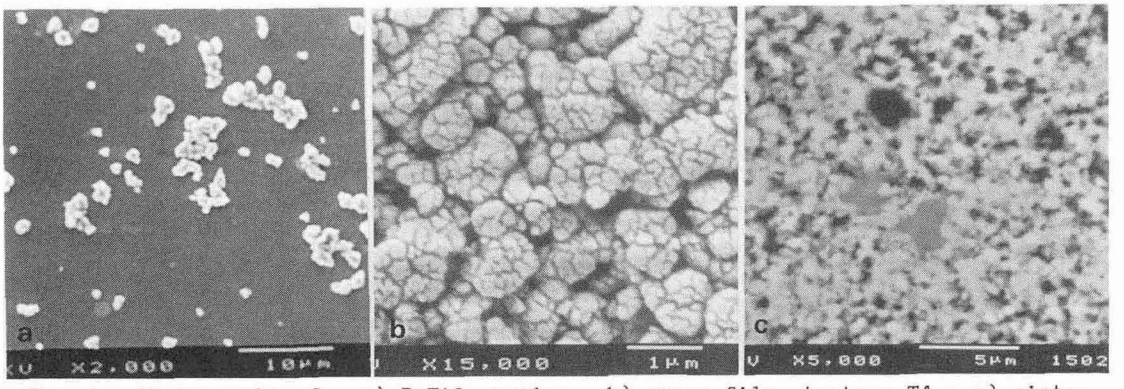

Fig. 1 : Micrographs of : a) $BaTiO_3$ powder ; b) green film, texture T4 ; c) sintered parts, S_2, at 1150°C.

Secondary electron SEM images of polished sintered parts (Fig. 1c) were investigated from an automatic image analyzer Nachet NS 1500 (Nachet-Microcontrôle, France) in the morpho-basis environment, with an hexagonal grid.

For powders the methods used are based on classical granulometry [6,7], granulomorphy [8] and shape parameters [7,9]. The granulomorphic methods are based on both a shape and a size criteria while the granulometric methods are only based on a size criterion. For the green films we have mainly used the granulometry in grey tone levels which are performed directly on the SEM images without using a threshold [10,11]. On the sintered materials the classical and derived stereological parameters were measured : volumic fraction of pores, $V_v(P)$, specific surface area of pores, $S_v(P)$, integral of mean curvature, $M_v(P/S)$, mean free path of pores, $\bar{L}_1(P)$, and the star function of the pores, $St_3(P)$, [7]. All these parameters describe globally the morphology of any material.

III. RESULTS AND DISCUSSION

Only some morphological results related to the powder, the green films and the sintered capacitors will be presented. For more details, see reference [2].

1. Powders

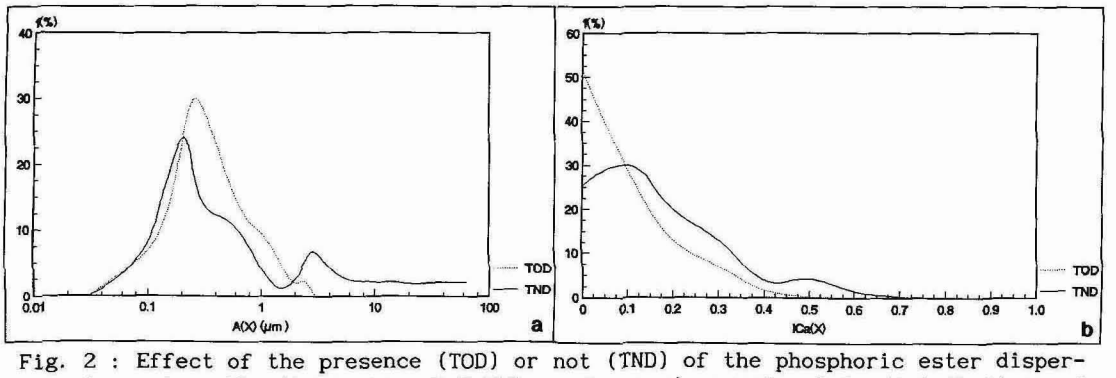

Fig. 2 : Effect of the presence (TOD) or not (TND) of the phosphoric ester dispersant agent on the dispersion of $BaTiO_3$ powder : a) granulometric distributions of projected surfaces, A(X); b) granulomorphic distributions of the concavities, ICa(X).

Granulometric and granulomorphic distributions on projected particles were established on initial powders. It allows to control its state of dispersion, while the optimum ratio of the dispersant agent was determined from rheological measurements. The role of this agent has been evidenced [12] : it reduces the ratio of agglomerates and leads to a better homogeneity in the shape of the $BaTiO_3$ grains as there are on one way a reduction in the mean and the variance of the particle size (Fig. 2a) and on the other way a greater homogeneity of the grain shape as the more concave shapes, due to the presence of branching, have disappeared (Fig.2b).

2. Green Films

One of the most important morphological parameter to accede for the green films is the aggregate ratio as after sintering it leads systematically to inhomogeneities, and so to a decrease in the dielectric properties. The inhomogeneities can be either an agglomeration of $BaTiO_3$ grains and/or a network of superficial microcracks (or anfractuosities). It has been shown that the role of an optimum ratio of binder and plastification agents, respectively polyvynylbutyral (PVB) and a mixture of phthalate + glycol, is essential [2]. Systematically if you increase the homogeneity, the physical properties are also increased, such as the density, the mechanical strength or the plasticity of the material.

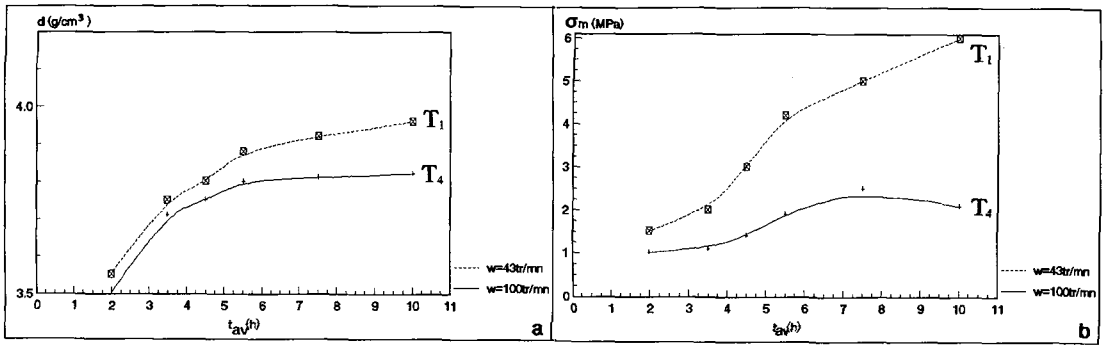

Fig. 3 : Change in the characteristics of the green material with the milling conditions (rotating speed of the jar, w) as a function of the milling time, time, t_{av} : a) density, d, ; b) maximum tensile stress, σ_m. It corresponds to texture T_1 and T_4.

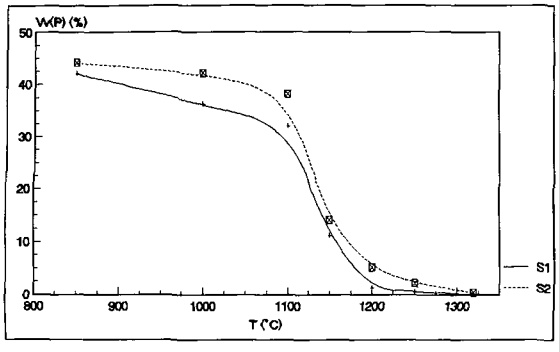

Fig. 4 : Change in the volumic fraction of pores, $V_V(P)$, as a function of the sintering temperature, T, for two types of texture, T_1 and T_4 (noted S_1 and S_2 respectively) , of initially different homogeneity.

Tests performed with different conditions of milling and of formulation have shown the existence of a synergy between these parameters, whatever are the textures, T, (Fig. 3). But close to the optimum conditions, there is a great sensitivity of the material characteristics with regard to the optimum process conditions. Then that implies to define an optimum formulation for the different milling conditions.

3. Sintered Parts

The homogeneity of the sintered materials has been investigated from the change in the stereological and derived parameters. For two different types of specimens, S_1 and S_2, corresponding to texture T_1 and T_4, one observes a large decrease of the porosity with the temperature from 1100°C (Fig. 4), due to the process of densification which is maximum between 1100 and 1150°C. Moreover the presence of agglomerates in the initial structure generates a significant delay during the densification.

IV. CONCLUSION

The knowledge of the microstructure of a dielectric ceramic is very important to reach as a morphological quality fault of the material will be passed largely on its subsequent quality.

The techniques of image analysis are irreplaceable as they allow to quantify the microstructure and to establish relationships between the grain arrangement and the microscopical properties.

ACKNOWLEDGEMENTS

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