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ON THE IMPORTANCE OF MORPHOLOGICAL INVESTIGATIONS FOR THE DEVELOPMENT OF CERAMIC CAPACITORS

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ABSTRACT

Automatic image analysis has been used to follow the ceramic process of dielectric capacitors in baryum titanate, from the powder to the sintered blocks, in going through the ceramic films. The influence of process parameters - formulation ; grinding conditions ; particle size and shape ; binder, dispersant, plastification agents ; temperature and time of sintering ; ... - have been investigated in relation with many physical properties of these dielectric materials.

Keywords : ceramic capacitors, baryum titanate, powder, ceramic films, sintered parts, granulometry, granulomorphy, $P(\ell)$.

INTRODUCTION

Baryum titanate powders are used to fabricate ceramic capacitors. The main problem to obtain parts of good quality is to avoid agglomerates and to have the best homogeneity in the final product. It will depend not only on the initial powder and additive characteristics, but also on the processing conditions.

In the case of baryum titanate capacitors the different stages of the process - powders, green films and sintering parts - have been investigated by mean of automatic image analysis. Although the role of the morphology is the predominant parameter on the quality of a ceramic capacitor, very few works concern that objective (see for example Karas & al., 1988). In the frame of her thesis (Prod'homme, 1992), many relationships between morphology and physical properties of $BaTiO_3$ capacitors have been established : it allows to precise the exact role of the morphology on their characteristics.

MATERIALS AND METHODS

Baryum titanate capacitors are fabricated according to a classical ceramic route: tape casting and sintering. A slurry of the powder ($BaTiO_3$, + Nb_2O_5

+ CoO + MnO_2 additives) suspended in a blend of solvents (azeotropic mixture of trichlorethylene - ethanol), binders (based a polyvynylbutyral, PVB), dispersant (phosphoric ester) and plastification (benzyl butyl phthalate and tetraethylene glycol diethylhexoate) agents is laid out on a stainless stell ribbon to obtain a film of 50 µm thickness, according to the tape casting process (Mistler & al, 1978 ; Chartier & Jorge, 1991). After serigraphy process, these films are stacking and sintered to obtain blocks of capacitors of 10 * 10 cm^2 in size.

An image analyzer system made of a host computer (SUN 3.140) and an Imaging Technology image processor Series 151 in the VISILOG environment (Noésis, France) was used to analyze powders and green films, via a scanning electron microscope. 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. Moreover an automatic image analyzer Nachet NS 1500 (Nachet - Microcontrôle, France) in the morpho-basis environment, with an hexagonal grid, was used to investigate the sintered parts. Figure 1 illustrates the microstructures of the different materials.

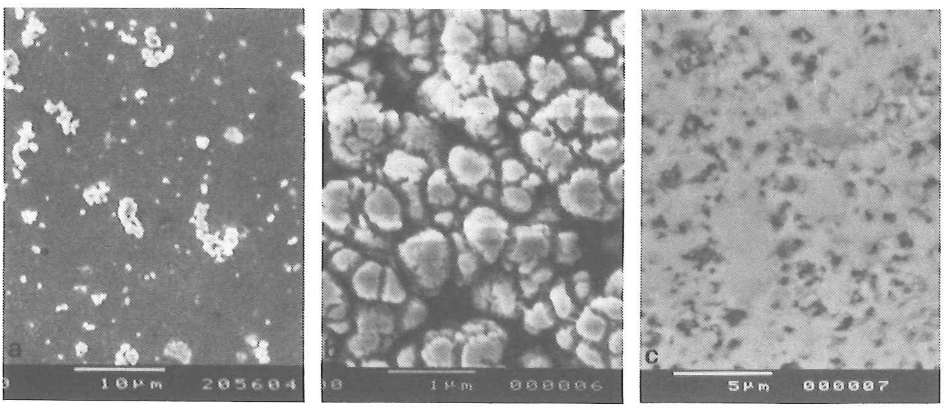

Figure 1 : Micrographs of : a) $BaTiO_3$ powder ; b) green film, texture T4 ; c) sintered parts, S_1, at 1150°C.

Powders were investigated by granulometric methods (Serra, 1982 ; Coster & Chermant, 1985;1989) - surface area, A(X), geodesic length, $L_g(X)$, maximum Feret diameter, $F_{max}(X)$, ... - by granulomorphy (Chermant & Coster, 1991) and from shape parameters (Coster & Chermant, 1985;1989 ; Chermant & Coster, 1992). Let us recall that granulometric methods are based only on a size criterion, while granulomorphic ones are based on a shape and a size criterion.

The texture and superficial porosity of the green films have been investigated by texture analysis using granulometry in grey tone levels. That was undertaken by openings directly on grey tone images from the SEM, without a threshold process (Michelland & al., 1989; Prod'homme & al., 1991).

The sintered parts have been analyzed from stereological parameters - specific surface area, $S_V(P)$, mean length of pores, $L_1(P)$, integer of mean curvature, $M_V(P/S)$, and star function in $\mathbb{R}^3$, $St_3(P)$ - determined from the $P(\ell)$ function (Coster & Chermant, 1985;1989), with the NS 1500 on SEM images.

RESULTS AND DISCUSSION

From the very large number of results obtained by Prod'homme in her thesis (1992), in the following we shall present only some specific morphological results on the powder, the green films and the sintered capacitors, insisting mainly on the consequence on the quality of the materials obtained.

Powders

Figure 2 illustrates the fact that granulometric and granulomorphic distributions on projected particles can permit to control its state of dispersion, while the optimum ratio of the dispersant agent was determined from rheological measurements. It has been precised that this dispersant agent reduces the ratio of agglomerates, the mean and the variance of the particle size (Figure 2a) and the presence of branching in the grains. The consequence is then a better homogeneity in the shape of the $BaTiO_3$ grains. Moreover a specific dispersant can lead to a decrease in the grain size and to a better homogeneity in the shapes : a greater homogeneity is linked to the absence of very concave shapes.

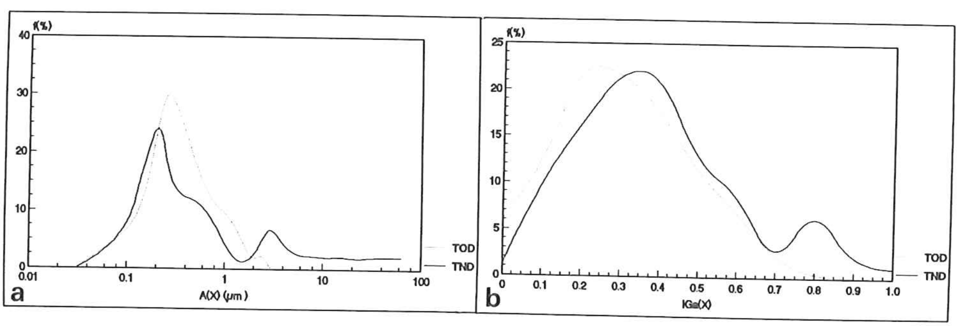

Figure 2 : Effect of the presence (TOD) or not (TND) of the phosphoric ester dispersant agent on the dispersion of $BaTiO_3$ powder : a) granulometric distributions of projected surfaces, A(X); b) granulomorphic distributions of the geodesic lengthening according to the surface area, $IG_a(X)$.

Green films

Aggregates lead systematically to inhomogeneities in these materials and, by consequence, to a decrease in the dielectric properties. These inhomogeneities can be either agglomeration of $BaTiO_3$ grains and/or a network of superficial microcracks. So the aggregate ratio is a crucial parameter to access to the green films. The physical properties increase with the homogeneity which depends on the ratio of the binder (polyvynylbutyral, PVB) and of the plastification (a mixture of phthalate + glycol) agents. Different conditions of milling (CB) and of formulation have been explored and it has been observed that whatever are the textures, T, there is a synergy between these parameters. That is the case for many characteristics: density, mechanical strength, plasticity of the film, strain to rupture,... (Prod'homme, 1992), (Figure 3). For the different milling conditions it implies therefore to define an optimum formulation. Close to the optimum conditions, there is a great sensitivity of the material characteristics with regard to the optimum process conditions.

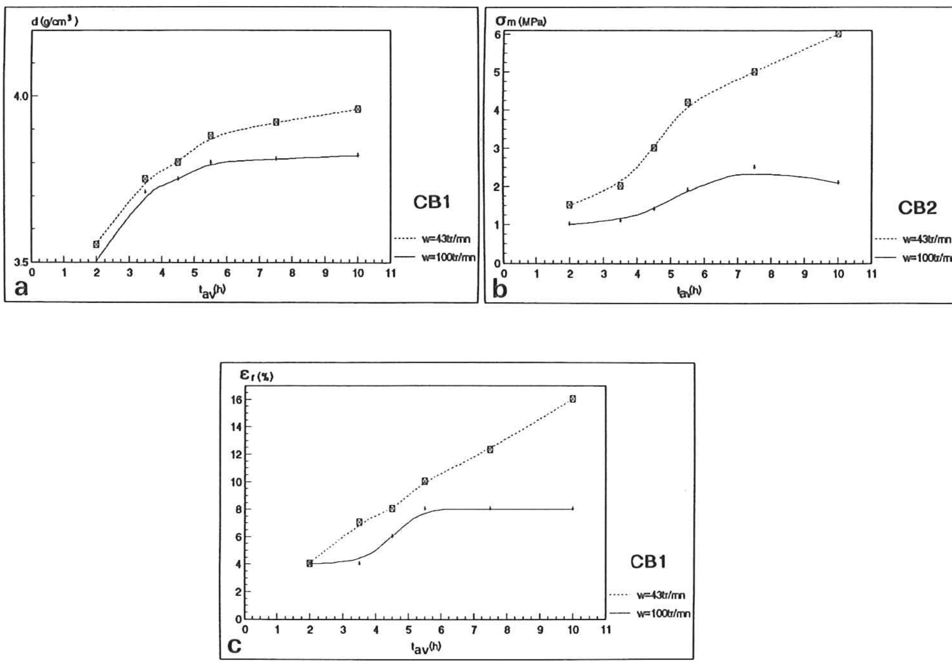

Figure 3 : Change in some characteristics of the green material with the milling conditions (rotating speed of the jar, w) as a function of the milling time, t_{av} : a) density, d, ; b) maximum tensile stress, σ_m; c) strain to rupture, ε_r. The curves correspond, for each figure, to texture T_1 and T_4 (respectively w = 43 tr/mn and 100 tr/mn).

Sintered parts

The classical stereology and derived parameters are easy to measure on the sintered parts in $BaTiO_3$. It gives precious information on the mechanisms which are involved at the microstructural scale during sintering. For different types of specimens, S, corresponding to different microstructures, although the sintering conditions are similar, the distributions in the volumic fraction of solid are different, informing on the heterogeneities of the sintered blocks. The change in the volumic fraction of pores, $V_v(P)$, informs on the densification : it is maximum between 1100 and 1150°C (Figure 4). As for the mean length of pores, $L_1(P)$, it is relatively stable, with a coarsening of pores close to 1250°C. Regarding the specific surface area, $S_v(X)$, it decreases with temperature as there is a rounding of the pores, creation and growth of the necks. Parallely there is an increase, then positive values and followed by a decrease for the integral of mean curvature.

Moreover the presence of agglomerates in the initial structure generates a significant delay during the densification.

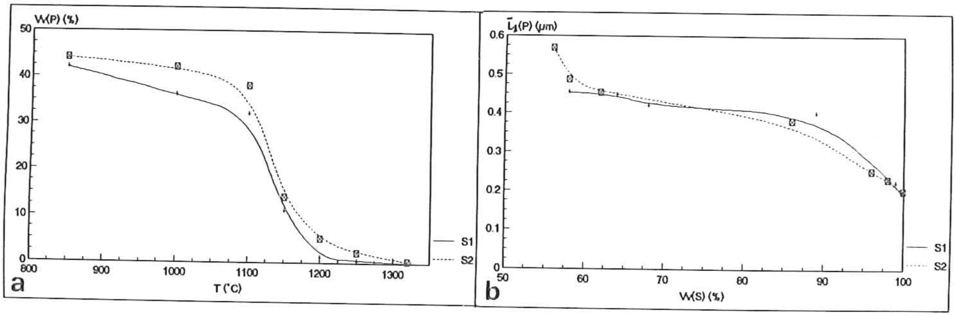

Figure 4 : Change in the volumic fraction of pores, $V_v(P)$, as a function of the sintering temperature, T, and of the mean length of pores, $L_1(P)$, as a function of the volumic fraction of solid, $V_v(S)$, for two types of texture, T_1 and T_4 (noted S_1 and S_2 respectively), of initially different homogeneity.

CONCLUSION

Automatic image analysis can also be a technique to follow the process to develop ceramic materials, to quantify their microstructure and to establish relationships between the morphology of the grains and physical properties.

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