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Modeling of the green body drying step to obtain large size transparent magnesium-aluminate spinel samples

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Abstract

Laboratory-scaled transparent samples have already been obtained, but upsizing the samples remains a technological challenge. Indeed, every step of the process can lead to defects that hinder optical properties. Among all of the processing steps, drying is one of the most critical, especially for large samples with complicated shapes. It can induce micro-cracks that enlarge during sintering. Optimizing this step has thus become a necessity to obtain valid samples for industrial applications. We developed a finite element method (FEM) simulation model from a simple drying profile performed on laboratory-scaled cylindrical samples. Then, we applied this model to larger industrial-scaled samples, to optimize their drying process. Finally, we obtained crack-free 75 mm diameter sintered samples, which become highly transparent after the appropriate hot isostatic pressing thermal treatment.

Keywords: Drying; Finite-element method (FEM); Optical transmission; $MgAl_2O_4$

1. Introduction

Transparent polycrystalline ceramics are generally recognized as an alternative to polymers, glasses or single crystals in extreme optical applications such as aerospace windows, armors, discharge lamp envelopes, or even jewellery.[1–3] The growing interest for this type of materials is mainly due to their strong thermo-mechanical properties up to very high temperatures (>1000 °C), to their intrinsic transparency over the visible-IR range and to the low costs of the raw materials. Nevertheless, obtaining high light transmission requires a careful control of chemical composition and microstructure during the entire process, to avoid light scattering sources such as inclusions or porosities.[4–8] First, high purity starting powders are required: impurities could induce absorption losses. Then, the green body processing should lead to a dense and homogeneous particle packing without agglomerates. Finally, the sintering process must be optimized to remove porosity. An annealing process could also be necessary to remove oxygen vacancies.

Green body processing is probably the most critical step, since it strongly influences the following sintering steps.[9,10] Among the known techniques, wet shaping processes are particularly interesting because, when processed carefully, they lead to homogeneous particle packing within the whole green body. Moreover, large agglomerates are avoided.[9,10] Nevertheless, the presence of water molecules can lead to drying issues. During their removal, the water concentration gradient induces internal stresses and even cracks, which are prejudicial for transparency. Laboratory samples are generally less damaged because of their small size (around 20–30 mm in diameter) and simple shape (generally cylindrical). However, upsizing the samples, or creating more complicated shapes for industrial applications, lead to an increase of cracking probability.[11–14] Optimizing the drying step is thus necessary to obtain large crack-free samples. Parametric experiments in an oven-dryer could be directly performed but the method is rather inaccurate. Moreover, it requires a considerable amount of ceramic slurry and drying cycles that which become rapidly expensive. Finite element method (FEM)

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simulation seems therefore an appropriate alternative for the optimization of the drying process. Several different drying profiles can be rapidly tested without using much slurry. It also gives access to phenomena which are impossible to detect experimentally (water distribution map at each time of the process). Then, an FEM simulation, if it is well parameterized, is much more quick, cheap and accurate than an empirical study. So, the aim of this work is to develop a simple and reliable method to quickly optimize the drying of large-size samples through FEM simulation.

2. Materials and methods

The starting material was a high purity magnesium-aluminate spinel ($MgAl_2O_4$) aqueous slurry (solid content 54 wt%) specifically developed by the Baïkowski company. The median particle size D_V^{50} was 110 nm (measured by laser diffraction, Horiba LA950) and the total impurity amount was around 0.01 wt% (28 ppm Na, 68 ppm K, 3 ppm Fe, 9 ppm Si, 5 ppm Ca), as reported by the manufacturer. The slurry was Büchner-casted across a polypropylene filter (pore diameter = 0.45 μm) using vacuum. After ~20 h of filtration, green bodies were easily handled. The drying step was performed in an oven-dryer with controlled hygrometry (SB, Weiss Technik) at different dwell temperatures (T_d from 50 to 100 °C) and relative humidity (*Rh* from 50 to 80%), in order to prevent crack formation. During this drying process, only the weakly bounded water molecules were removed and the sample mass reached a plateau (m_p). Thus, a thermal treatment was performed on the samples at 600 °C in air for half an hour, before considering them to be completely dried. They were weighed to define their completely dried mass (m_{dry}). Then, they were sintered at 1550 °C for 2 h in a vacuum (~10^{-6} mbar) in a VI 200/20/W oven (Pyrox). At least, a post hot isostatic pressing (HIP) treatment (1500 °C – 3 h – 200 MPa) was finally applied on the samples under argon, to obtain transparency. The light Transmission (T_λ) was measured by a Varian Cary 6000 spectrophotometer (Agilent Technologies) from the visible to the mid IR ranges.

In the following, we will insist on the drying step. It was optimized by FEM simulations on the COMSOL Multiphysics software.

3. Theory/calculation

As already said in the introduction, we will insist on the drying step which is a key issue to obtain large crack free samples. It was optimized by FEM simulations on the COMSOL Multiphysics software. In this section, we will explain how we have proceeded and what hypothesis we have done to develop our model.

Common drying processing induces cracks inside samples. It means that there are strong internal stresses occurring during this step most likely due to an inhomogeneous shrinkage. Indeed, by measuring the diameter of samples before and after the drying step, one can notice that it decreases of about 2%. As large agglomerates were not observed in the slurry by laser diffraction, the inhomogeneous shrinkage is rather due to water concentration gradients.[13–16] In the following, optimizing the drying step will consist in reducing these water concentration gradients.

It is important to notice that shrinkage gradients also depend on the geometry of the sample.[11,12,14] In this paper, we develop the drying optimization of small cylindrical-shaped samples (diameter = 37 mm – height = 12 mm). As all the parameters used in our model are not-geometry dependent (see the following), it can be applied to more complicated shaped or larger samples. The new geometry is taken into account by the meshing of the FEM program.

The drying step consists in a thermal treatment aimed at evaporating the water within the ceramic sample. Consequently, both matter and heat transfers by diffusion within the green body must be considered (Fig. 1).

Thus, the Fick (Eq. (1)) and Fourier (Eq. (2)) laws were applied, respectively, for matter and heat transfers.

$$\frac{dC}{dt} = D_w * \nabla^2 C \tag{1}$$

$$\frac{dT}{dt} = D_t * \nabla^2 T \tag{2}$$

where C (mol m^{-3}) is the water concentration; D_w (m^2 s^{-1}) is the water diffusion coefficient; t (s) is the time; T (K) is the absolute temperature and D_t (m^2 s^{-1}) is the thermal diffusivity of the sample. In this model, we consider no vapor diffusion inside the green body. Moreover, D_w is derived from literature data on brick samples[17,18] and fixed at 10^{-6} m^2 s^{-1}.

At the sample sides, we consider a very thin equivalent limit layer through which the matter and heat transfers with the air can occur.[15] We assume that this layer is in temperature and humidity equilibrium with the surface of the sample. Thus, within this layer, the relative humidity is assimilated to the water activity a_w (Fig. 1) defined by Eq. (3).

$$a_w = \left[\frac{P_v}{P_0}\right]_{T_s,\text{layer}} \tag{3}$$

where P_v (Pa) is the vapor pressure within the equivalent limit layer in equilibrium with the wet sample surface; P_0 (Pa) is the saturation water vapor pressure of totally free water molecules at the temperature T_s (K) of the sample surface.

Indeed, water molecules can be more or less linked to the ceramic grain surface. When the link is weak, the water molecules can be easily evaporated and $P_v \sim P_0$ ($a_w \sim 1$). For strongly bonded water molecules, the evaporation can be modeled by decreasing the water activity (and thus P_v is also decreasing). The water activity can be estimated from sorption isotherms, which represent a_w as a function of the water content X (water mass per 1 kg of dry sample) for different T_s.[15] As previously explained, the purpose of this study was to develop the simplest model to optimize the drying step. That is why, in a first approximation, we considered the effect of T_s on the water activity to be negligible. Moreover, we decided to model a_w with