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Original Article

Space-resolved study of binder burnout process in dry pressed ZnO ceramics by neutron imaging

Lise Donzel[a,*], David Mannes[b], Michael Hagemeister[c], Eberhard Lehmann[b], Jan Hovind[b], Nikolay Kardjilov[d], Christian Grünzweig[b]

[a] ABB Corporate Research, Dättwil, Switzerland
[b] Paul Scherrer Institut, Laboratory for Neutron Scattering and Imaging, Villigen, Switzerland
[c] ABB High Voltage Technology, Wettingen, Switzerland
[d] Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin, Germany

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ABSTRACT

A novel non-destructive space-resolved method for studying binder burnout is presented. Debinding of dry pressed zinc oxide green bodies was analyzed by neutron imaging. Neutrons in contrast to X-rays allow penetrating samples with large dimensions up to 80 mm and at the same time detecting variations in the organics content as small as 0.1 wt%. We used neutron radiography (2D) and tomography (3D) to investigate with a spatial resolution in the order of 100 µm the distribution of binder during burnout under three different conditions. First a reference case with green bodies placed on a plate in a lab furnace. Second, a configuration with a reduced volume of air with green bodies enclosed in a sagger and third a green body placed on an improved supporting structure. The method is extendable to other particulate materials and green bodies shaped by processes involving organic binder such as casting, extrusion and injection.

1. Introduction

Dry powder pressing is a common way to shape ceramic parts [1]. The free flowing powder is compacted to green body by means of axial or isostatic pressing. To ensure that the strength of the green bodies is sufficient to maintain its shape during handling, a small amount (i.e. < 5 wt%) of binder is added to the powder. Polyvinyl alcohol (PVA) and poly ethylene glycol (PEG) are often used as binder [2]. The binder (s) must be removed from the green body before sintering. Most of the time this occurs by thermal treatment with carefully selected heating rates, dwell temperatures and atmospheres [3]. Binder burnout is a critical step during which defects such as large pores, cracks or char traces can be generated if the process parameters are not appropriate [4]. Such defects do not disappear during the sintering phase and lead to defective final parts. Especially for green bodies of large dimensions the transport of volatile binder decomposition products from the center of the green body to the surface may be insufficient.

Standard methods to study the kinetics of binder burnout are thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) where weight loss respectively the heat flux is recorded during a temperature ramp. These methods can be combined with chemical analysis of the decomposition gases by mass or infrared spectroscopy. TGA and DSG give insight on the progress of the decomposition of the organics but do not allow resolving spatially the evolution of the binder burnout process unless the part is cut in small pieces as by Das [5].

Neutron imaging is a method for non-destructive testing with similarities to the conventional X-ray techniques. A collimated beam is sent to the sample and the transmitted component is registered by means of a two-dimensional imaging detector. Neutron imaging is a complementary technique to X-rays. While the latter are attenuated by electrons, neutrons interact with the nuclei. Therefore, the attenuation coefficient for X-rays increases in a monotonic manner with the atomic number, while for neutron no such relation exists [6]. Thermal neutrons can transmit most metals more efficiently than X-rays and have at the same time a high sensitivity for light elements such as Hydrogen, Boron or Lithium. This allows, for example, visualizing the transport of water in operating fuel cells [7] or the flow of fuel in engines with spatial and temporal resolution in 2D and even 3D [8].

In this work, radiography (2D) and tomography (3D) imaging techniques were used to study the binder burnout of zinc oxide (ZnO) ceramic green bodies. ZnO is an electro-ceramic used for overvoltage protection. Fig. 1 shows the comparison of the theoretical values of the attenuation coefficients Σ for ZnO and binder material for thermal neutrons and for 120 keV X-rays. The attenuation coefficient describes

* Corresponding author.
E-mail address: lise.donzel@ch.abb.com (L. Donzel).

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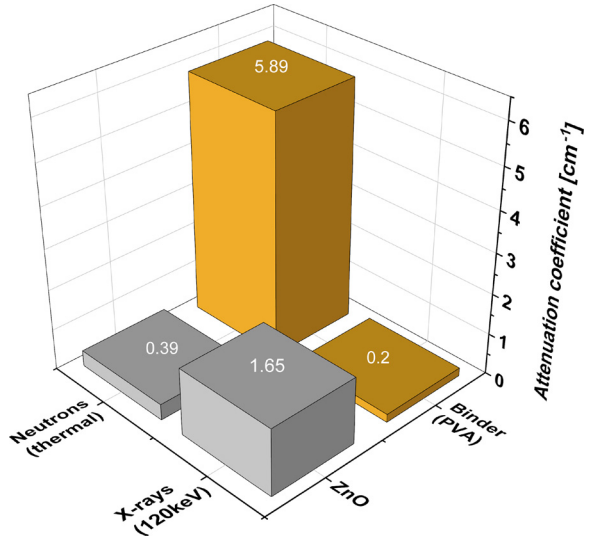

Fig. 1. Comparison of theoretical attenuation coefficients for zinc oxide (ZnO) and binder (PVA) for thermal neutrons and X-rays (120 keV).

to which extent an element or material will attenuate radiation of a certain kind and energy (more details in section 2.2).

The neutron attenuation coefficient for ZnO is about 4 times lower than the X-ray attenuation coefficient, hence much thicker samples can be transmitted by neutrons. In comparison, the Σ value for the binder is about 30 times higher for neutrons as for X-rays. The high sensitivity of thermal neutrons for the hydrogen atoms present in the binder molecules in combination with the high transparency of the ZnO bulk material allows resolving even small variations in the amount of binder.

2. Material and methods

2.1. Sample preparation

The ceramic powder used in this study was ZnO. A water-based slurry was prepared by mixing the ceramic powder and polyvinyl alcohol (PVA) as binder. The aqueous suspension containing 60 wt% zinc oxide and 0.5 wt% of binder was spray dried. Cylindrical green bodies were produced by double action axial pressing in two sizes: i) diameter of 47 mm and height of 57 mm and ii) diameter of 76 mm and height of 54 mm. The green density was 53% of the theoretical value.

To study the evolution of the binder burnout green bodies with diameter 47 mm were heated in air in a lab furnace at a rate of 30 °C/h up to various temperatures (150, 200, 300, 400 and 500 °C). The temperature was measured at the bottom of the sample. In a first burnout series the green bodies were placed in the furnace on a plate (furnace volume 0.18 m^3). In a second series they were enclosed in a sagger (volume 0.01 m^3) to simulated reduced oxygen availability. The dwell time at top temperature was one minute. The samples were quenched in air by removing them from the furnace and placing them on a ceramic plate for cooling.

In a third series, large green bodies (diameter 76 mm) were placed on two different supporting structures (Fig. 2) and heated in air at a rate of 30 °C/h. These samples were quenched after reaching 300 °C. The arrangement with three circular plates is meant to allow gaseous exchanges at the green body bottom part and thus facilitate the burnout at this location. Indeed, for samples with large dimensions, the length of the path to the sample surface is known to be critical.

2.2. Neutron transmission process

The attenuation of the neutron beam intensity follows, in a first order approximation, the Beer-Lamberts law:

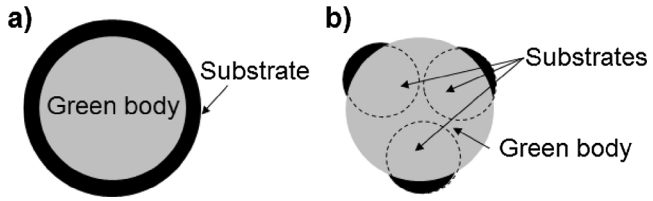

Fig. 2. Schematic representations of the two arrangements used for the third burnout experiment. (a) Green body resting on one substrate. (b) Green body placed on three substrates.

$$I = I_0 \times e^{-\Sigma \bullet t} \tag{1}$$

where I is the intensity measured behind the sample, I_0 the initial intensity of the neutron beam, t the material thickness in beam direction and Σ the attenuation coefficient, which can be defined as:

$$\Sigma = \sigma * N. \tag{2}$$

Here, σ is the interaction probability or microscopic cross-section of an element (cross-section can be found in NDS data base [9]), and N the nuclear density. The nuclear density N is given by:

$$N = \frac{\varrho \bullet L}{M} \tag{3}$$

with ρ the macroscopic density, L the Avogadro's number and M the molecular weight. If more than one element is present in the sample material (e.g. Zn and O, or C, H and O), an effective attenuation coefficient Σ_{eff} is used:

$$\Sigma_{eff} = \sum_{i=1}^{n} \sigma_i \bullet N_i \tag{4}$$

In tomography mode, Equation 1 is used by the reconstruction algorithm to eliminate the thickness effect. The resulting parameter is the three-dimensional distribution of Σ_{eff} (x,y,z). For a sample with a homogenous material composition (constant σ) the density distribution $\rho(x, y, z)$ can be extracted. Equation 1 is valid in average (over the full neutron spectrum) and does not take into account spectral shifts caused by the sample itself neither multiple scattering.

Fig. 3 shows the calculated normalized transmission behavior versus thickness for pure ZnO green body (compacted to 53% of the theoretical density) and mixtures of ZnO with 0.1–2.0 wt% of binder (PVA). For comparison, we also included the transmission behavior of ZnO for X-

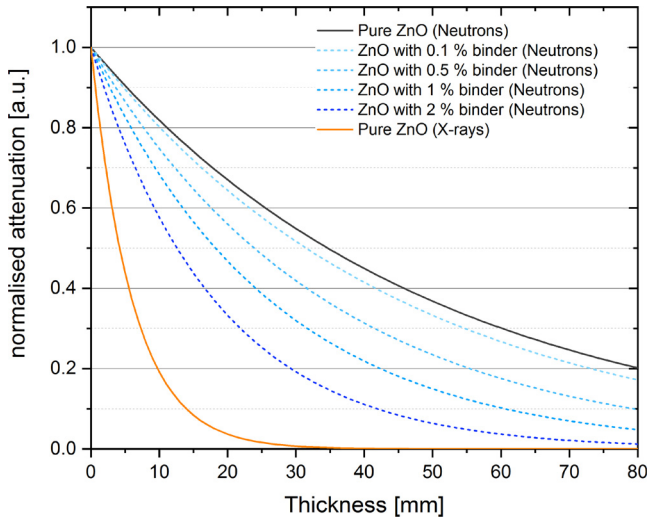

Fig. 3. Normalized neutron intensity values as function of the thickness calculated for green bodies with 53% of theoretical density and various amount of binder from 0.1 to 2%. For comparison the intensity curve of 120 keV X-rays for ZnO is shown.