

A method for the measurement of powder distribution in green ceramic bodies

J. E. ZORZI^{*}, C. A. PEROTTONI^{†*}, J. A. H. da JORNADA^{§*}

^{}Universidade Federal do Rio Grande do Sul, Instituto de Física, 91501-970, Porto Alegre, RS, Brazil*

[†]Universidade de Caxias do Sul, CCET/DEFQ, R. Francisco Getúlio Vargas, 1130, Cidade Universitária, 95070-560, Caxias do Sul, RS, Brazil.

[§]Inmetro- Instituto Nacional de Metrologia, Normalização e Qualidade Industrial, Campus de Xerém, Rodovia Washington Luiz, Km 120.5, BR 040, Duque de Caxias, RJ, Brazil

Many defects in ceramic parts are generated in the forming process, before firing. However, in several cases, it is not clear exactly in which stage of the process of ceramics production the defects arise. Indeed, cracks and other heterogeneities are very hard to identify in green ceramic bodies using conventional techniques, mainly due to difficulties in preparing samples suitable for observation. In the case of low pressure injection molding (LPIM), this problem is often critical, because of the high binder fraction (about 50% in volume) present in the green ceramic parts.

Very fine ceramic powders can form agglomerates during the mixing of powder and binder for LPIM. In these cases, even the best debinding process will not lead to the production of good ceramic parts. Moreover, the very injection process may lead to further inhomogeneities due to the large shears and turbulence involved in the process. The non-uniform distribution of ceramic powder in the injected parts may also lead to cracking during sintering. Accordingly, in order to optimize the process of making of ceramic parts, it is imperative to verify whether the defects observed in some pieces after debinding or sintering could be tracked back to the forming process.

With this objective in mind, in this letter we describe a quantitative method for ceramic powder distribution measurement in green ceramic bodies, based in the analysis of the absorption of γ and x-ray radiation of different energies. The method described in this letter constitutes a low cost alternative to other procedures already in use for the characterization of green ceramics, including x-ray tomography [1] and NMR/MRI [2-4], among others.

The powder distribution in green ceramics bodies was obtained by the measurement of the relative absorption of photons emitted by an ^{241}Am source as they cross a thin section of a green body. This measurement, carried out at distinct positions, permits to obtain a relative density profile along different axis of the sample [5].

A narrow beam of monoenergetic photons, with an incident intensity I_0 , penetrating a layer of material with thickness x and density ρ , emerges with intensity I given by [6]

$$\frac{I}{I_0} = e^{\left[-\left(\frac{\mu}{\rho}\right)\rho x\right]} \quad (1)$$

where μ/ρ is the mass attenuation coefficient of the material. The μ/ρ coefficient depends on the incident photon energy and on the target material. The mass attenuation coefficient μ/ρ for mixtures and compounds (assumed homogeneous) are obtained according to a simple additive relationship

$$\frac{\mu}{\rho} = \sum_i w_i \left(\frac{\mu}{\rho}\right)_i \quad (2)$$

where w_i is the mass fraction of the i^{th} constituent of the mixture. In our case, the green bodies are supposed to be constituted by only two components, namely alumina (1) and binder (2). Accordingly, from the above two expressions we obtain

$$\frac{I}{I_0} = e^{\left[-\left[w_1\left(\frac{\mu}{\rho}\right)_1 + w_2\left(\frac{\mu}{\rho}\right)_2\right] \frac{\rho_1\rho_2 x}{w_1\rho_2 + w_2\rho_1}\right]} \quad (3)$$

In terms of the volume fraction (v_i) of each component, the above expression can be written as

$$\frac{I}{I_0} = e^{-[v_1\mu_1 + v_2\mu_2]x} \quad (4)$$

Moreover, as the radiation beam's cross section is almost constant along its pathway through the sample, the volume fraction of each component can be expressed in terms of an "equivalent thickness" x_i , whose summation amounts to the overall thickness of the sample. The equivalent thickness x_i corresponds to the length comprised by the i^{th} component through which the radiation beam cross before it emerges from the sample. Taking $v_i = x_i/x$, eq. (4) thus becomes

$$\frac{I}{I_0} = e^{-[\mu_1 x_1 + \mu_2 x_2]} \quad (5)$$

Considering now the absorption of radiation by a sample of overall thickness x , for distinct energies E_A , E_B and E_C , we obtain the following equations

$$\begin{aligned} \mu_1(E_A)x_1 + \mu_2(E_A)x_2 &= -\ln\left[\frac{I(E_A)}{I_0(E_A)}\right] \\ \mu_1(E_B)x_1 + \mu_2(E_B)x_2 &= -\ln\left[\frac{I(E_B)}{I_0(E_B)}\right] \\ \mu_1(E_C)x_1 + \mu_2(E_C)x_2 &= -\ln\left[\frac{I(E_C)}{I_0(E_C)}\right] \end{aligned} \quad (6)$$

where μ_i is the linear coefficient of attenuation for the i^{th} component of the mixture, and $x_1 + x_2 = x$. It is the measurement of the relative absorption of photons with different energies that will permit us to quantify separately each component present in the green body. The use of an overdetermined system of equations yields a more robust estimate for the unknowns x_i and, consequently, for the mass fraction w_i of each component of the green body.

Fig. 1 illustrate the attenuation of the radiation emitted by an ^{241}Am source, when the beam cross a typical green ceramic sample. The sets mark the peaks whose integrated intensities were determined as input parameters for (6).

Insert Fig. 1

Table I shows the dependence with the photon energy of the mass attenuation coefficient of the green ceramic components, as experimentally determined using the same equipment employed for the measurement of the radiation absorption by the green ceramic samples. The mass attenuation coefficient of the binder mixture was obtained by measuring the relative intensity decrease of three selected peaks from the emission spectrum of ^{241}Am , as they cross a cylinder made of binder, with known thickness. The mass attenuation coefficient for sintered alumina was determined in the same way.

TABLE I Dependence with photon energy of the mass attenuation coefficient of the binder mixture and sintered alumina.

Photon energy (keV)	13.93	17.75	26.35
μ/ρ of binder (cm ² /g)	0.885	0.545	0.263
μ/ρ of alumina (cm ² /g)	6.168	3.055	1.102

The ceramic powder used in this work was submicrometer-sized alumina (Al₂O₃) A-1000SG (Alcoa), with specific surface area of 9 m²/g, 99.9% purity and particle size of about 0.4 μ m. The machine used for LPIM was a Peltsman MIGL-33. The mixture was prepared directly in the LPIM machine, and consisted of 86 wt% of alumina and 14 wt% of binder. The major binder component was paraffin wax, which represent 75 wt% of the binder. Others components were added in minor proportion to the binder mixture, including polyethylene wax, carnauba wax, stearic and oleic acids [5,7].

The ceramic pieces molded with this mixture were bricks with dimensions of 34 x 63 x 10mm. These bricks were cut into several slices with 3 mm of thickness.

A schematic drawing of the equipment used in this work is show in Fig. 2. The ²⁴¹Am source employed in this work was a low-activity source used for calibration of energy dispersive solid state detectors. For the measurement of the sample absorbance, each spectrum was taken with an acquisition time of 15 min. The spatial resolution of our experimental setup is of about 1 mm. The resolution could be improved using smaller slits, at the expenses of greater acquisition times.

Insert Fig. 2

Fig. 3 shows the mass fraction of alumina *versus* position of measurement along the transversal axis of a typical sample of a LPIM green ceramics. The variation of alumina content along the transversal axis of the sample is of the same order of the experimental uncertainty of our measurements. Accordingly, within the experimental uncertainty level, this green ceramics do not show any appreciable inhomogeneity in powder distribution.

Insert Fig. 3

Fig. 4 shows the result obtained for a green ceramic piece with a non-homogeneous powder distribution. The local variation of the alumina content is quite visible in the form of a pronounced decrease in the radiation absorbed by the sample.

Insert Fig. 4

The analysis of a large set of measurements show that the alumina concentration in different points of the great majority of the ceramic samples prepared by LPIM do not vary by more than about 1 wt%, i.e, within the actual uncertainty of our measurements. Accordingly, our results rule out the possibility that the cracks that appears during the debinding or sintering steps could have its origin in the forming stage.

The method described in this letter constitute a low cost alternative the now available computadorized x-ray tomographs that has been used for green ceramics analysis. The multi-wavelength characteristic of our approach permits to get information about the mass fraction distribution of binder and ceramics in the green body. The application of the present technique to the mapping of the spatial distribution of different ceramic powders in green bodies (for instance, in ceramic parts made of $\text{Al}_2\text{O}_3 + \text{ZrO}_2$) should be straightforward. The method presented in this work permitted us to conclude that the defects observed in ceramic parts after debinding and sintering were not due to powder segregation during ceramic powder injection. In fact, confirming our result, sintered ceramic parts free of defects were obtained after optimization of the furnace programming for debinding [5,7].

Acknowledgments

This work was partially supported by PRONEX/CNPq, PADCT, and FAPERGS (Brazil). The authors would like to thank Alcoa S.A. (Brazil) for the sample of alumina powder employed in this work.

References

1. T. RABE and A. KUNZMANN, *Ber. Dtsch. Keram. Ges.*, **75** (1998) 19.
2. A. S. WALLNER and W. M. RITCHEY, *J. Mat. Res.*, **8** (1993) 655.
3. P. S. WANG, D. B. MINOR and S. G. MALGHAN, *J. Mat. Sci.*, **28** (1993) 4940.
4. L. GARRIDO and J. L. ACKERMAN, *J. Mag. Res.*, **88** (1990) 340.
5. J. E. ZORZI, PhD Thesis. Universidade Federal do Rio Grande do Sul, Porto Alegre - RS, Brazil, 2001.
6. B. D. CULLITY, in "Elements of X-Ray Diffraction" (Addison-Wesley Pub., USA, 1978).
7. J. E. ZORZI, C.A. PEROTTONI and J.A.H. da JORNADA, *J. Mat. Sci.*, **37** (2002) 1801.

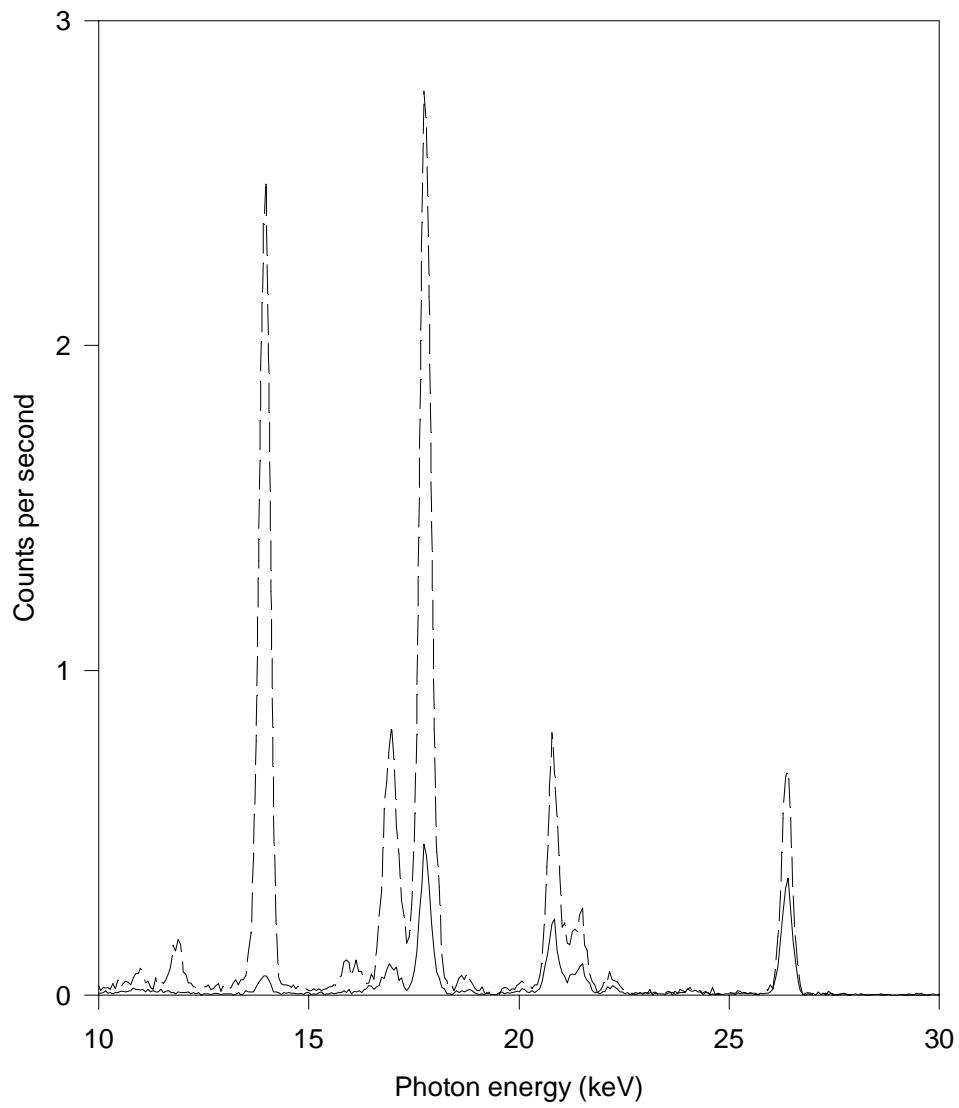
Figure Captions

Fig. 1 Attenuation of the radiation emitted by an ^{241}Am source as the beam cross a green ceramic body. The dashed line represents the peaks from an ^{241}Am source. The continuous line show the spectrum attenuated by absorption as the radiation cross a thin sheet of a green body.

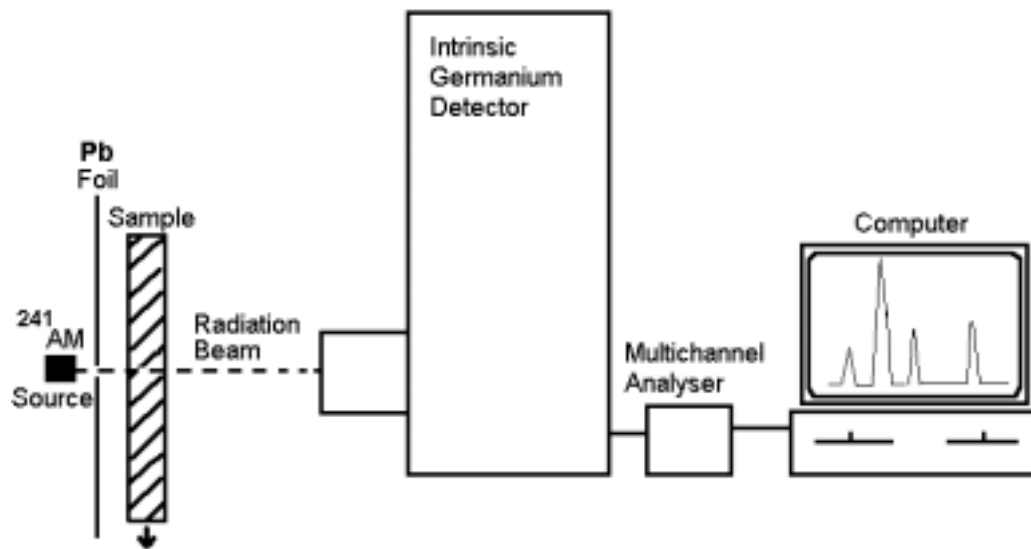
Fig. 2 Schematic drawing of the equipment used for the evaluation of the ceramic powder distribution in green bodies.

Fig. 3 Mass fraction of alumina along the transversal axis of a typical green ceramic piece.

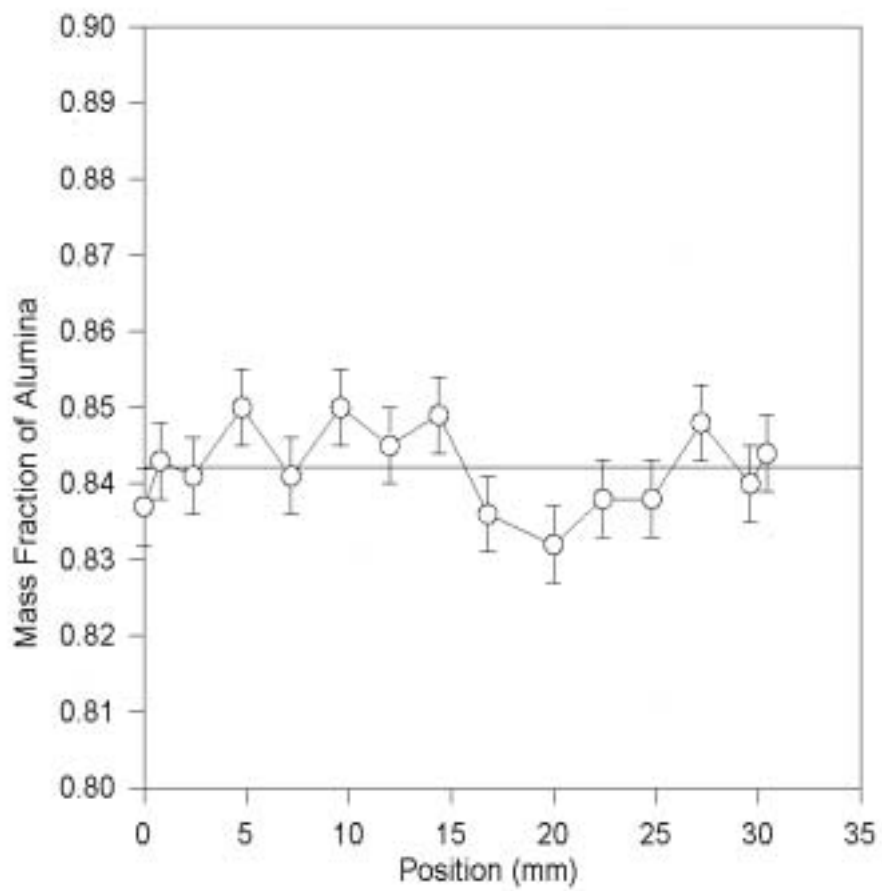
Fig. 4 Mass fraction of alumina in a non-homogeneous green ceramic piece.



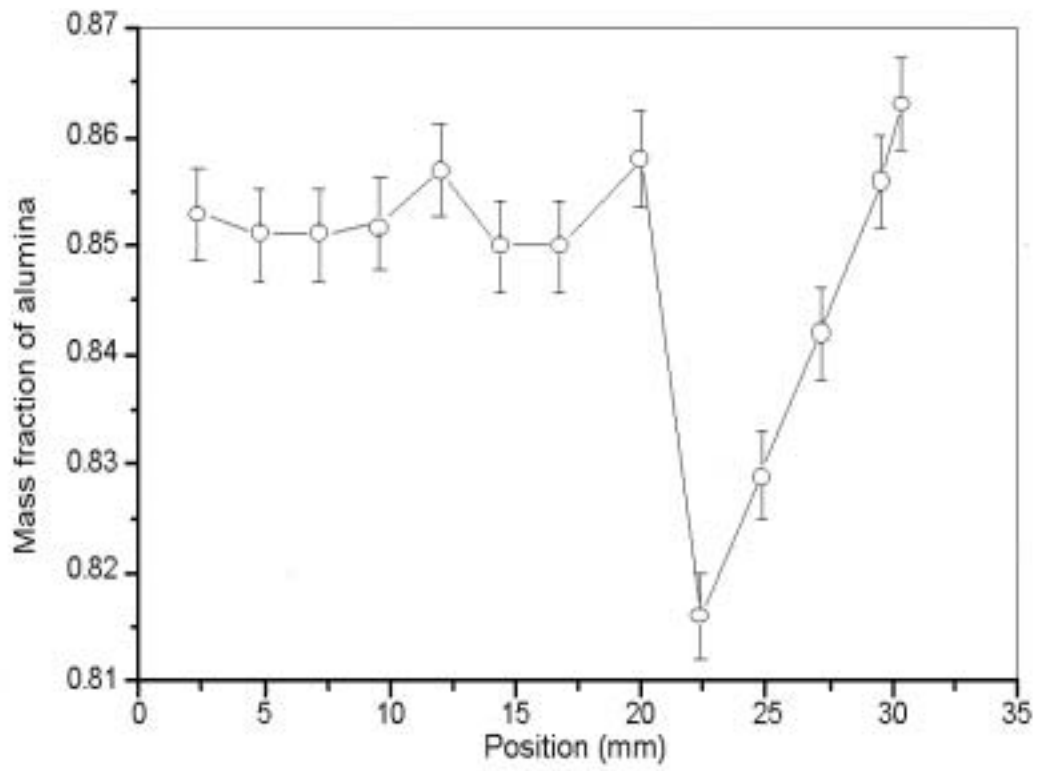
J. E. ZORZI, C.A. PEROTTONI and J.A.H. da JORNADA, Fig. 1.



J. E. ZORZI, C.A. PEROTTONI and J.A.H. da JORNADA, Fig. 2.



J. E. ZORZI, C.A. PEROTTONI and J.A.H. da JORNADA, Fig. 3.



J. E. ZORZI, C.A. PEROTTONI and J.A.H. da JORNADA, Fig. 4.