Some approaches for residual porosity estimating

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Abstract. Several approaches for materials residual porosity assessment are presented in this paper. Importance of development of accurate model is shown based on Al₂O₃−Ce:YAG and Al₂O₃−Ce:(Y,Gd)AG ceramic phosphors taken as model objects. The evaluated difference in the outcomes of different methods applied for estimating porosity has been shown to be as high as ~40%. The obtained results become applicable to another types of inclusions within the studied volume of a material as in the models under consideration the main role is given to a geometrical perspective of the problem.

1. Introduction

Evaluation of the material’s intrinsic porosity using data collected from the cross-section is a special case of the wide-spread problem in materials science related to determining the content of various non-uniformities. As key defects, the surfaces/slices of dense materials (single crystals, glasses, ceramics) observe pores as cross-sections and the question about their concentration and content in the material’s bulk becomes important [1, 2].

The simplest way to answer it is to inscribe pores into the found cross-sections and to evaluate their volume. However, it is very unlikely that the cross-section passes exactly through the pore centers to regard such an identification as an accurate one. It has been shown in work [3] that the size of a random cross-section is $4/\pi$ times lower than the size of a spherical pore. Authors replace all found pore cross-sections with the mean pore size $<d>$, which is additionally scaled-up by a factor of $4/\pi$. However, this consideration is quite rough approximation. Pores of diameter $D$ are shown on cross-section only in the case if the slice plane is closer or stay at $D/2$ from the pore center. As a result, finer pore fractions are represented on a cross-section in a smaller proportion to the content of this fraction in the bulk, than larger pores [4]. This aspect can be corrected using multiplier $1/D$ and renormalization of the size distribution obtained during the material study. The more significant issue, when pores of $D$ size can give different cross-sections $d$, is impossible to take into account through simple reasoning.
Therefore the estimations of pore volume fraction $\theta$ turn out to be rough in different versions of such constructions.

2. Theoretical section
In the previous work [4], we performed consistent reasoning and found an expression to connect the distribution density of pore cross-sections sizes $f(d)$ with the pore size distribution density $g(D)$ (1):

$$ f(d) = \frac{d}{L^4} \int_{-\infty}^{+\infty} \frac{g(D) dD}{\sqrt{D^2 - d^2}} $$

(1)

The following relation was obtained at the intermediate stage of expression derivation (1):

$$ nSd \left( d_{\max}^D g(D) dD \right) dD = N_S f(d) dD $$

(2)

where $S$ – area of the explored cross-section of material, $n$ – a number pore concentration in the volume $V$. The combination $nLS$ was used as $N_S$ in the work [4], where $L$ – thickness of considered layer of material. However, this is inaccurate, because expression (2) is number of slices with dimensions $[d; d + dd]$. Although in the expression (1) $L$ value has another meaning and plays the role of a normalizing factor. The exact meaning of value $N_S$ in expression (2) is the total number of pores on cross-section. It is also shown in the intermediate derivations that the combination of values $(D/L)nLSg(D)dD = nDSg(D)dD$ expresses the pores number of sizes $[D; D + dD]$, which occurred to be sliced [4]. Further integration leads to the expression $N_S = nS<\theta>$: Thus, the meaning of the normalizing factor $L$ was clarified: the mean pore size in the bulk of material $<\theta>$.

In framework of the accurate model number concentration of pores $n$ and their volume concentration $\theta$ can be calculated using data from studied slice of the material without necessity of direct calculation of function $g(D)$. The corresponding expressions (3, 4) can be obtained from (1) by inverting the integral equation and direct calculating the required values $<\theta>$ and $<\theta^3>$:

$$ n = \frac{N_V}{V} = \frac{N_S}{S(D)} = \frac{2}{\pi} \frac{1}{d} \frac{N_S}{S} $$

(3)

$$ \theta = \frac{V_p}{V} = \frac{\pi}{6} n <\theta^3> = \frac{\pi N_S}{6} \frac{<\theta^3>}{(\theta)} = \frac{N_S \pi(d^2)}{S} = \frac{S_p}{S} $$

(4)

for expressions (3-4): $V$ – volume of material; $N_V$ – the total number of pores in volume $V$; $S$ – area of the explored cross-section of material; $N_S$ – the total number of pores detected in the cross-section $S$; $V_p$ – total pore volume in the material’s bulk $V$; $S_p$ – total surface area of pore sections on the studied slice of the material; the brackets $<...>$ denote the average value of distribution.

Let’s consider another two models for estimating porosity. The first of them, the simplest model, assumes inscribing pores of the same size into the found cross-sections. The derivation of expression (1) contains a multiplier $(D/L)$. It appears because only fraction of pores in the considered layer of thickness $L$ occurs to be sliced – pores in the layer of less thickness $D$. Thus, reverse multiplier should be applied to determine pore size distribution in the materials bulk. In the language of distribution function, this means that $g(D) = (L/D)f(D)$, where $L$ simply plays the role of the normalizing coefficient and equal to the harmonic mean $<1/d>^{-1}$. For such model we obtain expressions (5, 6):

$$ n = \frac{N_S}{SL} = \frac{N_S}{S} \left( \frac{1}{d} \right) $$

(5)

$$ \theta = \frac{V_p}{V} = \frac{\pi}{6} n \int \frac{(1/d)^{-1}}{d} f(d)d^3 dd = \frac{N_S \pi}{S} \int f(d)d^2 dd = \frac{N_S \pi(d^2)}{S} = \frac{2 S_p}{3 S} $$

(6)
The second model, modified, is based on work [3]. It was shown that the cross-section size of a spherical pore is $4/\pi$ times lower than its size. Therefore, we use the same approach as for the simplest model, but increase pore sizes by this coefficient. In the language of distribution function, we obtain the expression $g(D) = (L/D)\phi(\pi D/4)$, that adds $4/\pi$ multiplier of appropriate power in the expressions for calculating the average values of $n$ and $\theta$ (7, 8):

$$n = \frac{N_s}{S_0} = \frac{\pi N_s}{4} \left(\frac{1}{\alpha}\right)$$

(7)

$$\theta = \frac{V_p}{V} = \frac{N_p}{S} \cdot \frac{4}{\pi} \left(\frac{1}{\alpha}\right)^2 \frac{\pi (d^2)}{6} = \frac{32}{3\pi^2} \frac{S_p}{S} \approx 1.08 \frac{S_p}{S}$$

(8)

3. Experimental section

Validation and comparative analysis of presented approaches for assessing the residual porosity of materials was conducted using model – Al$_2$O$_3$–Ce:YAG and Al$_2$O$_3$–Ce:(Y,Gd)AG composite ceramic phosphors. A series of composite ceramics were prepared by solid-state reactive sintering in vacuum using high purity commercial oxides. In brief, the molar ratio of Al$_2$O$_3$/YAG was controlled to be 0.75; the Ce$^{3+}$ and Gd$^{3+}$ concentrations were set to be 0.1 at% and 25 at%, respectively, according to the stoichiometric ratio of (Ce$^{3+}$Y$^{3+}$Gd$^{3+}$):Al$^{3+}$=3:5 for YAG phase. 0.8 wt% tetraethyl orthosilicate (TEOS) and 0.08 wt% MgO were used as sintering aids. Powder mixtures were ball milled, dried, sieved, and air-annealed. The green bodies were cold isostatic pressed, and sintered at 1765°C under vacuum of $5.0\times10^{-4}$ Pa for 4, 8 and 12 hours. Finally, composite ceramics were air-annealed to recover oxygen stoichiometry and mirror polished for further measurements.

The porosity of ceramic samples was characterized by confocal laser scanning microscopy (CLSM, LSM 800, Zeiss, Germany) using a laser with wavelength of 642 nm and 63x zoom. After acquiring elementary sample sections (“slices”) of about $100\times100$ µm$^2$, which were separated to each other by 250 nm in depth, the 3D volume ($100\times100\times15$ µm$^3$) was rebuilt by using appropriate software (Arivis AG). To calculate the section pore size and to quantify the number of the pores from the cross-section, all slices were merged along z axis and were represented in the xy plane. The residual porosity was calculated by simplest, accurate, and modified (using Ref. [3]) models.

4. Results and Discussion

Pore section size distribution and the residual porosity of model ceramic samples synthesized at 1765°C for 4, 8 and 12 hours are presented on Figure. 1a,b. Some reduction of mean pore sizes and their size variance with the increase of sintering duration from 4 to 12 hours is caused by completion of densification at higher densities. Samples co-doped with Ce$^{3+}$ and Gd$^{3+}$ in the range of 4-8 hours sintering features lower driving forces of densification due to incomplete formation of Ce:(Y,Gd)AG solid solution. As a result, within this time interval the mean pore section size increases by 13% till 223 nm with the porosity being reduced by 19% down to 0.0076 vol.% (Figure. 1a, inset; 1b). Anyway, after 12-hour isothermal treatment, Al$_2$O$_3$–Ce:(Y,Gd)AG composite ceramics has “pore-free” structure. In turn, Al$_2$O$_3$–Ce:YAG composite ceramics possess larger pore amount per unit volume simultaneously with their lower size variance (Figure. 1a,b).

Evaluated by the accurate model (4) residual porosity values for Al$_2$O$_3$–Ce:YAG and Al$_2$O$_3$–Ce:(Y,Gd)AG samples range in 0.0167-0.0065 vol.% and 0.0093-0.0049 vol.%, respectively (Figure. 1b). Taking into account equal concentrations of the used SiO$_2$ and MgO additives, observed values prove some positive influence of Gd$^{3+}$ ions on densification of Ce:(Y,Gd)AG ceramic solid solutions on the final stage of sintering.
Figure 1. Section pore size distribution (a) and residual porosity (b) of Al$_2$O$_3$–Ce:YAG and Al$_2$O$_3$–Ce:(Y,Gd)AG composite ceramic phosphors obtained by reactive sintering in vacuum at 1765°C for 4-12 hours.

Results of the simplest model (6) are underestimated by ~33%, the ones obtained by the modified model (8) based on [3] are overestimated by ~8%. Thus, the total difference of porosity estimations reaches ~40%. As a result, the lower limit of the porosity estimation for Al$_2$O$_3$–Ce:YAG ceramics is comparable to the upper limit of the porosity estimation for Al$_2$O$_3$–Ce:(Y,Gd)AG ceramics (Figure 1b). In practice, this can lead to wrong conclusions about material properties when comparing data obtained using different porosity estimation models. It is a bright example of the necessity to clearly understand, which model for porosity assessment was used in a certain literary source, technical documentation, etc.

5. Conclusions

Based on the integral connection between pore size distribution in the bulk and pore section size distribution observed on the slice, accurate model is demonstrated to establish the “intuitive” method for porosity assessment as a fraction occupied by the pore sections on the studied slice of the material. Comparison with another two models was carried out. The evaluated difference in the outcomes of different methods applied has been shown to be as high as ~40% based on Al$_2$O$_3$–Ce:YAG and Al$_2$O$_3$–Ce:(Y,Gd)AG composite ceramics taken as model objects. Such a huge variance among the calculated values demonstrates the importance of the analysis of each certain porosity assessment approach applied when comparing the experimental data.

Acknowledgments

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References

[1] Rice R W 1995 The porosity dependence of physical properties of materials: A summary review Key Engineering Materials 115 1-20
[2] Messing G L and Stevenson A J 2008 Materials science: Toward pore-free ceramics Science 322 (5900) 383-4
[3] Zhang W, Lu T, Wei N, Wang Y, Ma B, Li F, Lu Z, Qi J 2012 Assessment of light scattering by pores in Nd:YAG transparent ceramics J. Alloys Compd. 520 36–41
[4] Kosyanov D Yu, Yavetskiy R P, Parkhomenko S V, Doroshenko A G, Vorona I O, Zavjalov A P, Zakharenko A M, Vornovskikh A A 2019 A new method for calculating the residual porosity of transparent materials J. Alloys Compd. 781 892–7