Sintering of zirconia-based nanomaterials studied by variable-energy slow-positron beam

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Abstract. A variable-energy slow-positron beam was applied to the investigations of the tetragonal yttria-stabilised zirconia (YSZ), the YSZ co-doped with small amount of Cr₂O₃. The initial nanopowders exhibiting the mean particle size of ≈ 20 nm were prepared by co-precipitation technique. Prior the sintering, the nanopowders were calcined and compacted using a pressure of 500 MPa. The ordinary shape parameters of the Doppler-broadened annihilation peak and the relative positronium 3γ-fractions were determined as functions of positron energy. The results are consistent with a remarkable sintering-induced grain growth and disappearance of porosity which is driven out from the sample interior toward a thin subsurface layer.

1. Introduction
Zirconium dioxide (zirconia) is a substance widely used in practice, e.g. in ceramic industry, due to its advantageous thermal, electronic, mechanical and chemical properties [1]: a high melting point (2750 °C), a low thermal conductivity, a good high-κ dielectricity, a low electronic conductivity, a good oxygen ionic conductivity at increased temperatures, a high hardness combined with a reasonable fracture toughness and a good resistance to corrosion and wear.

Pure zirconia is monoclinic (m) at room temperature, but it exhibits transitions to the denser tetragonal (t) and cubic (c) phases at temperatures of ≈ 1100 and ≈ 2350 °C, respectively. In order to avoid a potential mechanical deterioration of zirconia in high-temperature applications, therefore, it is necessary to stabilize the t- and c-phases down to room temperature. Required phase stability is fulfilled e.g. by the yttria-stabilized zirconia (YSZ) which is a binary oxide system with a small amount of Y₂O₃ (yttria) immersed as a solid solution in zirconia lattice (≈ 3 mol. % of yttria is sufficient for a stabilization of the t-phase). Due to the different valences of Zr (4⁺) and Y (3⁺) cations, a large amount of oxygen vacancy-like defects is brought into the lattice.

Ceramic materials are commonly manufactured from fine particle powders by sintering [2]. The sintering process activates a mass transfer resulting in a grain growth and a disappearance of pores.
Important driving parameters of sintering are the sintering temperature, the mean particle size of the initial powder and the diffusivity of the constituents.

The ternary solid solution, YSZ plus Cr$_2$O$_3$ (YSZC), is also an interesting material [3]. A smaller ionic radius of Cr$^{3+}$ compared to Zr$^{4+}$ and a possible multiple Cr valence may influence e.g. the diffusivity of Cr ions and/or grain size of YSZC.

In the present work, the tetragonal (i) binary YSZ and ternary YSZC nanopowders were prepared and subjected to a sequential sintering at various temperatures. The potentially depth-dependent sintering-induced diffusion processes were studied using variable-energy slow positron annihilation spectroscopy which is a non-destructive technique with high sensitivity to open-volume defects.

2. Experimental

The binary ZrO$_2$:3 mol. % Y$_2$O$_3$ (Z3Y) and the ternary ZrO$_2$:3 mol. % Y$_2$O$_3$:1 mol. % Cr$_2$O$_3$ (Z3Y1C) nanopowders and sintered ceramics were studied in the present work. The initial nanopowders were prepared by the co-precipitation technique similar to that of Ref. [3] from the water solutions of respective salts taken in stoichiometric proportions. The nanopowders were then calcined at 500 °C/2 h in air. The calcined nanopowders were uniaxially pressed under 500 MPa into disk-shaped pellets of ≈ 10 mm diameter and ≈ 3 mm thickness. The pressure-compacted specimens were then sintered at selected temperatures in an increasing order from 600 toward 1500 °C in air. Each sintering step lasted for 1 h with a subsequent controlled slow cooling down to room temperature and positron annihilation measurement. The $t$-phases of nanopowders as well as sintered ceramics were confirmed by means of X-ray diffraction (XRD). A mean crystallite size was estimated by XRD as 17.0±0.9 and 13±1 nm for the Z3Y and Z3Y1C, respectively. The bulk densities of specimens were also measured after each sintering step.

A magnetically guided variable-energy slow-positron beam SPONSOR [4] was utilized in the present work. The energies of incident monoenergetic positrons covered the range from 0.03 to 35 keV. The Doppler broadening (DB) of the annihilation peak was measured with a HPGe $\gamma$-spectrometer exhibiting a resolution of 1.03 keV (fwhm) at 511 keV $\gamma$-ray energy. About $5 \times 10^5$ counts were typically accumulated in the peak area. The ordinary peak-shape parameters, $S$ and $W$, were evaluated to characterise the DB effects. In case of Z3Y when positronium (Ps) formation was observed in our recent lifetime measurements [5], the relative ortho-Ps 3$\gamma$-fractions, $F$, were also deduced from measured spectra of annihilation photons following to the method described in [6]. A flat valley between the 480 and 500 keV $\gamma$-ray energy was considered for this purpose. Since no Ps formation was detected in the Z3Y1C bulk [5] the measurements on this specimen for positron energies above 10 keV have provided a reference level for the evaluation of $F$-values.

3. Results and discussion

In figure 1, shape parameters $S$ were plotted against positron energy $E_+$. For $E_+$ below 2 keV, the observed $S$-parameters fell from their surface value close to the bulk one, $S_{\text{bulk}}$. In addition, a contribution of para-Ps formation in Z3Y specimen can be seen in figure 1 as (i) enhanced $S$-parameters, compared to the Z3Y1C specimen, and (ii) a bulge with a wide maximum at $\approx 4$ keV. The contribution of Ps vanished for $T_s > 900$ °C. The $E_+$-dependences of $W$-parameters displayed a mirror patterns compared to those for $S$-parameters, as expected. Present findings are consistent with our earlier positron lifetime studies [5] in which all positrons in the compacted YSZ nanopowders and the YSZ ceramics sintered up to 1200 °C were shown either to annihilate from trapped states in defects (saturated trapping) or to form Ps. Ps formation was found, moreover, to disappear after sintering of the YSZ nanopowders at 1000 °C and Ps formation was even not observed at all in YSZC. The latter phenomenon is a consequence of an efficient suppression of Ps formation by the Cr cations segregated along grain boundaries (GBs) [5].

In the energy region $E_+ > 20$ keV, the back-diffusion of positrons toward the specimen surface becomes negligible. Hence the $S_{\text{bulk}}$-parameters can be well-approximated as the $S$-values of figure 1.
averaged over $E_+ > 20$ keV. The $S_{\text{bulk}}$-values for Z3Y and Z3Y1C were plotted against $T_S$ in figure 2. Overall decrease in $S_{\text{bulk}}$-values with increasing $T_S$ is seen from the figure. For $T_S < 900$ °C, the $S_{\text{bulk}}$-values for Z3Y exceed significantly those for Z3Y1C. Above this temperature, both specimens exhibit mutually the same values of $S_{\text{bulk}}$. In addition, the measured bulk densities, $\rho$, were plotted in figure 2, exhibiting a sharp increase between 900 and 1100 °C sintering temperatures which coincides roughly with a region of disappearance of pores in the bulk [5]. This sharp increase is then followed by a slow approaching to a $\rho$-value for the t-YSZ single crystal (6.1 g∙cm$^{-3}$).

Figure 1. Measured $S$-parameters plotted as functions of positron energies $E_+$ for different sintering temperatures $T_S$: the left panel – Z3Y, the right panel – Z3Y1C.

Sintering leads to a decrease of the $S_{\text{bulk}}$-parameters due to two processes: (1) the grain growth which causes a decrease in the concentration of defects associated to GBs and (2) the disappearance of pores leading to a diminishing of the Ps contribution. These processes were observed and treated in more details in our previous LT and CDB study of bulk zirconia [5]. In this work, both processes were obviously observed in the Z3Y sample, while only the process (1) can be seen for the Z3Y1C specimen due to an absence of the Ps contribution. Hence, the difference of the $S_{\text{bulk}}$-parameters for Z3Y and Z3Y1C can be regarded as an indicator of the porosity in Z3Y. Inspection of figure 2 clearly reveals that the porosity is essentially removed by sintering at 1000 °C. A decrease of the $S_{\text{bulk}}$-values after further sintering at higher temperatures is caused solely by the sintering-induced grain growth.

The above picture is further supported by the observed relative ortho-Ps $3\gamma$-fractions, $F$, which were plotted against $E_+$ for various sintering temperatures $T_S$ in figure 3. Note that a bulge similar to that seen in $S$-values for Z3Y nanopowder around $E_+ \approx 6$ keV corresponding to a mean penetration depth of $\approx 200$ nm is shown also by $F$-values. Moreover, $F$-fractions vanished for $T_S > 900$ °C, similarly like the para-Ps contributions to $S$-parameters did (see figure 1). In this way, an existence of a subsurface layer with enhanced porosity is independently testified.

Figure 2. $S_{\text{bulk}}$-values (averaged $S$-parameters for $E_+ > 20$ keV) and bulk densities $\rho$ plotted as functions of $T_S$: $\bullet$ – $S_{\text{bulk}}$ for Z3Y, $\circ$ – $S_{\text{bulk}}$ for Z3Y1C, $\Delta$ – $\rho$ for Z3Y. Dashed horizontal line stands for a density of the t-YSZ single crystal.

4. Concluding remarks
Zirconia-based nanograin materials exhibit
significant structure non-homogeneities on a scale of ≈ 100 nm. Behaviour of positrons and Ps in such materials is thus given a rather complicated pattern. Positrons thermalised in grain interiors with a relatively low defect concentration may easily diffuse to the nearest GB where they will get trapped in GB-associated open-volume defects (misfit defects of a mono-vacancy size or triple points [5]). Such positrons, therefore, can hardly diffuse to a distance exceeding the mean grain size (≈ 20 nm). On the other hand, GBs and nanopores may facilitate diffusion of Ps and those positrons which get thermalised there.

Experimental data obtained in the present work, illustrate that the depth profiling of sintering-induced microstructure changes by means of the variable-energy slow-positron beam reveal pronounced effects which are complementary to the bulk studies of zirconia-based nanomaterials by positron annihilation techniques. The two near-surface regions could be distinguished according to the observed depth profiles of S- and F-parameters in Z3Y and Z3Y1C specimens. Below $E_+ \approx 2$ keV, positrons and Ps may diffuse back to the surface which becomes likely a dominating process responsible for a sharp decrease in S- and F-values in this region. Then, a subsurface region of residual porosity occurs, ranging up to $E_+ \approx 6$ keV. This region is likely a result of sintering-induced mass transfer accompanied with the grain growth and disappearance of pores. The remnant gas contained in the pores is gradually diffused from the specimen interior toward its surface during sintering and may thus assist to more stable pore structures in the subsurface region. This subsurface residual porosity vanishes above $T_S \approx 1000$ °C. Taking into account large variations of densities illustrated by figure 2, the estimated depths of the two near-surface regions could be set decreasing from 80 to 20 nm and 500 to 130 nm, respectively, when $T_S$ is risen from its initial value to 1500 °C.

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