Effect of Sintering on Defects in Yttria Stabilised Zirconia

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Abstract. A variable energy slow positron beam was utilised to investigate depth dependent effects of sintering on the tetragonal yttria stabilised zirconia nanopowders. Positron implantation was combined with the determination of Doppler broadened profiles of annihilation radiation. The results are consistent with recent positron lifetime data showing that sintering at elevated temperatures leads to a disappearance of pores and a significant grain growth, which is demonstrated by a strong suppression of positronium formation and a substantial decrease in concentration of open volume defects at triple points, respectively, with increasing sintering temperature. An existence of a subsurface layer of a relatively high content of defects was shown in sintered samples and tentatively attributed to arise from a diffusion of open volume defects from the sample interior toward the surface or from a sintering-induced surface modification.

Introduction

Sintering is widely used for manufacturing of ceramic materials from fine particle powders. The sintering procedure is always connected with mass transfer leading to a grain growth and a disappearance of pores. Key parameters controlling the sintering process are the sintering temperature, T_S, and the mean particle size of initial powder, d_0. Indeed, knowledge of how these parameters can influence the microstructure of a sintered material is of a crucial importance.

Zirconia (ZrO_2) is the base constituent of a variety of materials purposed for high-temperature applications (refractory ceramics, abrasive tools, etc.). A stabilisation of the high-temperature zirconia phases is, however, necessary. This is accomplished by an addition of a small amount of trivalent yttrium oxide (yttria) to form a solid solution of yttria in the ZrO_2 lattice – yttria stabilised zirconia (YSZ). When ≈ 3 mol. % of Y_2O_3 is introduced into zirconia, the system possesses the tetragonal structure (*t*-YSZ).

A large amount of open volume defects is expected in YSZ. It results from (i) stoichiometry violation (oxygen vacancies and vacancy – impurity agglomerates) and (ii) a substantial volume fraction of grain boundary (GB) phase in case of YSZ powders of nanoscale particle size (GB related vacancy-like defects, triple junctions of GB's and nanometer pores). This makes positron annihilation spectroscopy (PAS) an efficient tool for microstructure investigation of YSZ nanopowders. A detailed characterisation of defects in the pressure compacted YSZ nanopowders of different yttria content prepared by the co-precipitation technique was recently carried out by means of PAS [1]. Sintering of the *t*-YSZ nanopowder was investigated using conventional positron lifetime (PLT) and Doppler broadening (DB) techniques in Ref. [2]. As a continuation of these

works, slow positron implantation spectroscopy (SPIS) was applied to study depth dependent effects of sintering on the *t*-YSZ nanopowder and the first results of this research are reported in the present contribution.

Experimental

Specimens. The *t*-YSZ nanopowders were prepared by the co-precipitation technique from salt-in-water solutions taken at stoichiometric compositions [3]. The initial nanopowder underwent calcination at 700 °C/2 h in air and then uniaxial compression under 0.5 GPa to form tablets of ≈ 10 mm diameter and ≈ 5 mm thickness. Tetragonal phase was verified by X-ray diffraction for the initial powder as well as for the sintered specimens. Transmission electron microscopy revealed a mean particle size of the initial powder to be $d_0 \approx 17$ nm. Sintering of the compacted nanopowders was performed at three temperatures, $T_S = 1000, 1200$ and 1350 °C for 2 hours in air.

   SPIS. SPIS measurements were conducted using a magnetically guided variable energy positron beam at the SPONSOR facility at Dresden-Rossendorf [4]. Doppler broadened γ-ray energy spectra at annihilation line region were recorded by means of a HPGe spectrometer (energy resolution of 1.03keV FWHM at 511keV) as a function of positron implantation energy, E_+, varied from 0.03 to 25 keV. At least 0.5×10^6 counts were accumulated in each spectra in the annihilation peak area. Ordinary sharpness S parameter was evaluated to characterise annihilation line shape. All S parameters presented in this work were normalized to the bulk S parameter value $S_0 = 0.509 \pm 0.001$ measured on cubic YSZ (*c*-YSZ) single crystal containing 9 mol. % of Y_2O_3 .

Results and discussion

The measured S parameters for the pristine *t*-YSZ compacted nanopowder prior to sintering and the *t*-YSZ specimens sintered at the three differnt temperatures T_S are displayed as functions of positron energy E_+ in Fig. 1. For a reference purpose, S parameters obtained in Ref. [1] for *c*-YSZ single crystal are included in the Figure, too. Except for the three lowest positron energies, the S parameters acquired for the pristine nanopowder lie well above all the other S values displayed at Fig. 1. Two trends of S parameters obtained for the sintered *t*-YSZ samples can be seen in Fig. 1:
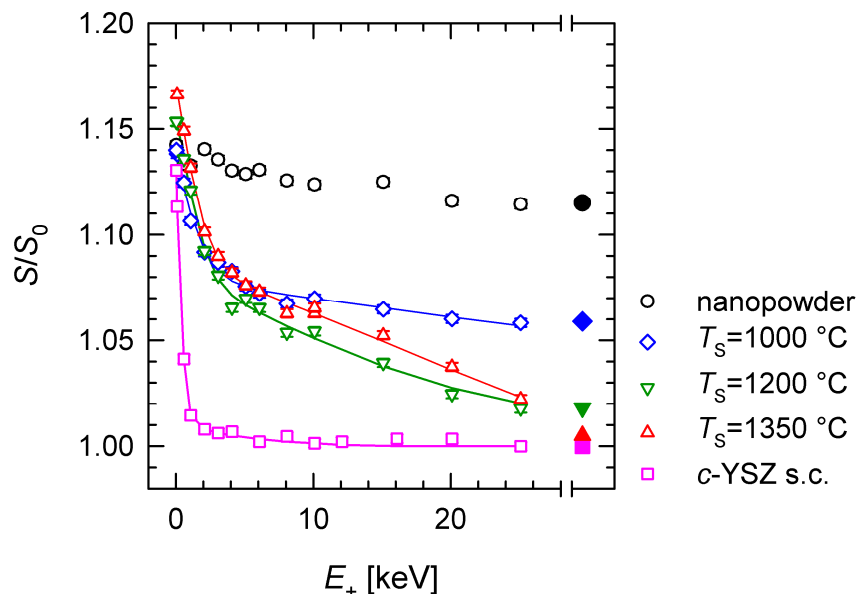

Fig. 1. The measured S parameters (open symbols) as functions of positron implantation energy E_+ . Solid lines represent results of analysis using the VEPFIT software [5]. Enlarged full symbols on the right-hand side show bulk S parameters (at depth ~ 50 μm) measured by the conventional DB technique.

(a) a monotonic growth of the near-surface S parameters (i.e. S values measured for the lowest E_+), when T_S is increased, and (b) a decrease of S parameters for positrons annihilating in larger depths of the sample (i.e. positrons of higher E_+). Note that the S parameters measured for the higher E_+ (i.e. the larger depths – the mean penetration depth of positrons with incident energy $E_+ = 30$ keV is 1.6 μm) at $T_S = 1000$ °C are substantially lower than those for the pristine compacted nanopowder. A further decrease of S parameters in this region of implantation energies was found for $T_S = 1200$ and 1350 °C, but in this case the measured data became already rather close to each other. It can be also noticed that none of the S values measured for the t-YSZ drops below that for the c-YSZ single crystal taken at the same E_+. However contrary to c-YSZ single crystal where S parameter quickly converges to a bulk value and exhibits plateau-like behaviour at $E_+ > 6$ keV, in sintered t-YSZ samples S parameter exhibits a pronounced decrease in the whole energy range covered by SPIS measurements. This testifies that the near-surface region in sintered t-YSZ samples differs from the bulk. To obtain S parameters characterizing bulk of sintered t-YSZ samples we employed conventional DB spectroscopy and the obtained S parameters are inserted in Fig. 1. From conventional DB measurement we obtained bulk S parameters which are not influenced by the near-surface region since the mean penetration depth of fast positrons from ^{22}Na source into zirconia is ≈ 47 μm. One can see in Fig. 1 that in the sintered t-YSZ samples the bulk S parameter is lower than S parameters in the near-surface region while for the pristine compacted nanopowder and c-YSZ single crystal the S parameters converged to the bulk value already in the near-surface region.

The observed changes of the near-surface S parameters likely arise from a sintering-induced modification of the surface, e.g. the surface oxidation, which may enhance positron trapping at the sample surface layer. The behaviour of S parameters at the largest depths of the sample can be qualitatively understood in the light of recent PLT results, obtained in Refs. [1,2] for the t-YSZ samples prepared by the same technique as in the present work. In the pristine t-YSZ compacted nanopowder, saturated *positron* trapping in vacancy-like defects, associated with GB's, and in larger open volumes situated at triple points was found, the latter trapping mechanism being the dominating one [1]. Indeed, a greater role of positron trapping in larger open volume defects brings also the higher S values in the pristine compacted nanopowder. Moreover, an appreciable fraction of ≈ 10 % of *positronium* (Ps) formed in nanometer-size inter-granular pores was observed in the t-YSZ nanopowder [1]. The narrow momentum distribution of para-Ps self-annihilation contributes also to increased S parameters in the pristine compacted nanopowder. Sintering of compacted nanopowders at $T_S = 1000$ °C (or higher temperatures) leads [2] to (i) removal of residual porosity which is expressed by a suppression of Ps formation below the detection limit (< 1 %), (ii) a significant grain growth which is reflected by a strong decrease of the contribution of positrons annihilated in defects at triple points. Both these effects cause a decrease of S parameters in the sintered samples. Hence, the observed behaviour of S parameters at large depths is consistent with the inferences implied by the PLT data of Refs. [1,2], in particular with a disappearance of pores and a substantial grain growth induced by sintering of t-YSZ nanopowders.

The pattern displayed by the measured S values of Fig. 1 in the *whole* E_+ interval, however, suggests that more complex depth profiles of the microstructure are formed. It is immediately apparent from the Figure, that at least two depth regions should be distinguished in the t-YSZ materials under study. To get a better insight into the problem, a semi-quantitative analysis of the measured S parameter curves for the three temperatures T_S was performed using fitting or modelling modes of the VEPFIT software [5]. A multilayered structure (model 5 in terms of Ref. [5]) was considered here. The two regions, referred to as the 'subsurface layer' and the 'sample interior', could be clearly identified in the analysis. The subsurface layer of ≈ 100 nm thickness could be characterised with the bulk sharpness parameter and positron diffusion length, S_{subsf} and $L_{+,subsf}$, respectively. The values of $S_{subsf}/S_0 = 1.084\pm0.002$, 1.065 ± 0.002 and 1.079 ± 0.002 and $L_{+,subsf} = 7\pm1$, 16 ± 1 and 15 ± 1 nm were obtained for $T_S = 1000$, 1200 and 1350 °C, respectively. The samples sintered at 1200 and 1350 °C exhibit comparable parameters for the subsurface layer while in the sample sintered at 1000 °C the subsurface layer is characterized by higher S_{subsf} and shorter $L_{+,surf}$.

During sintering process individual grains are merged and the residual porosity is removed from the sample. The pores are pushed toward the surface and removed by diffusion to the surface which represents a sink with infinite capacity. This diffusion motion leads to a formation of a subsurface layer characterized by high values of S_{subsf} and short positron diffusion lengths $L_{+,subsf}$ due to very high density of open volume cavities. The other parameters introduced in the model describing the sample interior could not be deduced with a reasonable accuracy because the quality of fit is almost independent of them. This occurred mainly due to the fact that the measured S parameters at high E_+ are still far from a plateau corresponding to bulk value which was confirmed by comparison with conventional DB measuremets. This indicates that due to diffusion towards the surface the density of open volume pores decreases from the subsurface layer toward the sample interior which is reflected by gradually decreasing S parameters at high energies $E_+ = 5 - 30$ keV , see Fig. 1. Mass-density variations due to sintering were also examined and found to be of minor importance.

Summary

A depth profiling of the microstructure changes in the t-YSZ compacted nanopowder and ceramics obtained by sintering up to 1350 °C was performed by means of SPIS involving S parameter measurement and also by conventional DB measurements. The results were found to be consistent with the PLT data of Ref. [1] which demonstrated that sintering leads to a disappearance of pores and a significant grain growth, expressed in a strong suppression of Ps formation and a substantial decrease in concentration of open volume defects at triple points, respectively. A subsurface layer of a relatively high content of defects was identified in sintered samples and tentatively attributed to a diffusion of open volume defects from the sample interior toward the surface during sintering although a sintering induced surface modification could also contribute.

To authors' knowledge, there has yet been no attempt to employ SPIS combined with DB measurements for the depth profiling of microstructure changes induced by sintering of nanopowders. Despite of limitations discussed in the preceding Section, the present work suggests that such experiments can reveal well-pronounced trends in measured data and thus provide a useful information about microstructure evolution during sintering, which may extend findings obtained by means of more traditional PLT measurements.

Acknowledgements

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