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Positron annihilation studies of zirconia doped with metal cations of different valence

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Abstract. New results obtained by applying positron annihilation spectroscopy to the investigation of zirconia-based nanomaterials doped with metal cations of different valence are reported. The slow-positron implantation spectroscopy combined with Doppler broadening measurements was employed to study the sintering of pressure-compacted nanopowders of tetragonal yttria-stabilised zirconia (*t*-YSZ) and *t*-YSZ with chromia additive. Positronium (Ps) formation in *t*-YSZ was proven by detecting 3γ-annihilations of ortho-Ps and was found to gradually decrease with increasing sintering temperature. A subsurface layer with enhanced 3γ-annihilations, compared to the deeper regions, could be identified. Addition of chromia was found to inhibit Ps formation. In addition, first results of positron lifetime measurements on nanopowders of zirconia phase-stabilised with MgO and CeO_2 are presented.

1. Introduction

Zirconium dioxide (zirconia) is the basic constituent of a variety of industrial materials suited, particularly, as ceramics for operation at high temperatures. Stabilisation of high-temperature zirconia phases is, however, needed in order to avoid material failure when passing phase transformation temperatures. This is achieved by adding a proper amount of a suitable phase-stabiliser agent. Trivalent yttrium oxide (yttria) is traditionally used as stabilizer of ZrO_2 lattice referred to as yttria-stabilised zirconia (YSZ). If the yttria addition amounts 2÷3 mol.% the lattice becomes tetragonal (*t*-YSZ). Current trends in prospecting zirconia-based materials with improved properties are focused on the following directions: (i) Nanopowders are utilised as starting substances for the preparation of materials by pressure-compaction and sintering. (ii) Unlike traditional, but relatively expensive yttria (Y_2O_3), other metal oxides are examined as phase-stabilisers, e.g. magnesia (MgO) or ceria (CeO_2). (iii) Another metal oxide admixture, like e.g. chromia (Cr_2O_3) [1], is introduced together with the phase stabiliser into the ZrO_2 lattice, giving rise to ternary oxide systems.

Over the past few years, we have employed positron annihilation spectroscopy in systematic investigations of YSZ nanomaterials [2]. The present contribution communicates our latest results obtained by means of slow-positron implantation spectroscopy (SPIS) on sintering of *t*-YSZ nanopowders as well as the first conventional positron lifetime measurements on zirconia nanopowders with various stabilising agents.

2. Experimental

2.1. Samples

Pure ZrO_2 (with monoclinic structure) and *t*-YSZ nanopowders (with 3 mol.% Y_2O_3), prepared using co-precipitation technique described in [3], were investigated. The nanopowders were compacted under a uniaxial pressure of 500 MPa into disks of 15 mm diameter and 5 mm thickness. Beside the binary *t*-YSZ, the ternary nanopowders (*t*-YSZC) containing 0.3 and 0.7 mol.% Cr_2O_3 were studied, too. The specimens underwent a sequence of 1 hour annealing at temperatures $T_S = 600$, 700, 800 and 900 °C in air followed by a slow cooling to room temperature. Magnesia-, ceria- and chromia-stabilised zirconia compacted nanopowders (MgSZ, CeSZ and CrSZ, respectively, with 10, 12 and 3 mol.% of stabiliser), were prepared by a similar co-precipitation procedure.

2.2. Measurements and data analysis

SPIS experiments were conducted using a monoenergetic positron beam [4] at positron energies E_+ covering a region from 27 eV to 35 keV. Annihilation of implanted positrons was observed by a single HPGe γ-spectrometer. The shape of the Doppler broadened (DB) 2γ annihilation peak was characterised with ordinary S and W parameters. In addition, the relative fractions, F, of implanted positrons annihilated as positronium (Ps) were deduced from counts in a valley left to the annihilation peak in a way closely similar to that of paper [5]. The measurement on *t*-YSZC at E_+=35 keV (the mean positron penetration depth $\bar{z} \approx 2$ µm) could serve as the reference case with no Ps formation [2].

Conventional positron lifetime measurements were carried out at ambient temperature in air using the apparatus and data processing methods described in [2] and references cited therein.

3. Results and discussion

3.1. Compacted nanopowders

In table 1, observed positron lifetimes and intensities (τ_i , I_i , $\sum I_i$=100) for compacted nanopowders are presented. The mean crystalite sizes d estimated from X-ray diffraction are shown in the table as well. Since crystallite size is substantially smaller than the mean positron diffusion length, positrons annihilate at GBs from trapped states in two kinds of defects: (i) vacancy-like misfit defects situated along grain boundaries (GBs), lifetime τ_1, and (ii) larger defects at intersections of GBs (triple points) and comparable in size with few-vacancy clusters, lifetime τ_2. The lifetimes τ_1 and τ_2 in MgSZ and CeSZ appeared to be considerably greater than in the other samples. This may consist in different influence of Mg and Ce stabiliser cations on electronic structure of the zirconia host lattice. Since in compacted nanopowders positrons are annihilated predominantly at GBs relatively strong variations of positron lifetimes τ_1 and τ_2 for various stabilisers indicate segregation of stabiliser cations at GBs.

Table 1. Crystalite size d determined by X-ray diffraction and positron lifetime data on zirconia-based compacted nanopowders. The ortho-Positronium (oPs) lifetime and the total Ps intensity including para-Positronium contribution are shown. Amounts of additives are given in mol.%. In parentheses, standard deviations are indicated in units of the last significant digit.

Sample	d [nm]	τ_1 [ps]	I_1 [%]	τ_2 [ps]	I_2 [%]	τ_{oPs} [ns]	I_{Ps} [%]
pure ZrO_2 (monoclinic)	23	187(3)	42(2)	377(4)	48(2)	31(2)	9.6(4)
t-YSZ (ZrO_2+3%Y_2O_3)	18	174(3)	27(2)	373(3)	63(2)	30(2)	9.7(4)
MgSZ (ZrO_2+10%MgO)	11	261(3)	52(2)	441(4)	41(2)	18.1(2)	6.0(5)
CeSZ (ZrO_2+12%CeO_2)	9.1	254(4)	22(1)	408(1)	76(1)	19.7(4)	2.0(5)
CrSZ (ZrO_2+3%Cr_2O_3)		178(3)	16(1)	374(3)	84(1)		
t-YSZ + 0.3%Cr_2O_3	18	191(3)	32(1)	381(2)	69(1)		
t-YSZ + 0.7%Cr_2O_3	15	191(3)	26(1)	390(2)	74(1)		

In addition, Ps formation in pores of a few nanometer in size (nanovoids) was observed in all compacted nanopowders except of those containing chromia. Pores with radius of ≈ 1.5 nm were observed in pure ZrO_2 and binary *t*-YSZ compacted nanopowders, while MgSZ and CeSZ contain smaller nanovoids with radius of ≈ 0.9 nm. This correlates reasonably with smaller crystallite size in MgSZ and CeSZ compacted nanopowders and appears to be in accordance with expectations of an aggregate model [6] for the cavities between primary nanoparticles. Ps formation is suppressed below the detection limit as a result of Cr cations segregated along grain boundaries whenever a small amount of Cr_2O_3 is introduced into the ZrO_2 lattice [1,2].

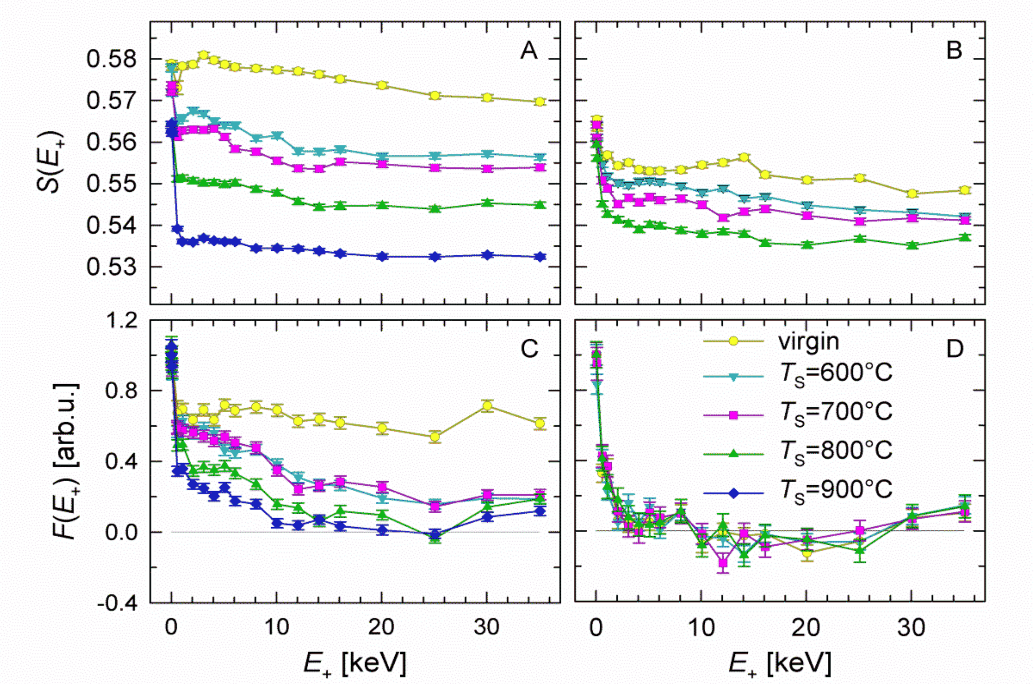

Figure 1. SPIS results (*S*- and *F*-parameters) for *t*-YSZ (left panels) and *t*-YSZC (right panels).

3.2. Sintering of t-YSZ and t-YSZC

Binary *t*-YSZ, where Ps is formed, and ternary *t*-YSZC containing 0.7 mol.% Cr_2O_3, where Ps formaton is inhibited, were selected for investigation of the influence of sintering on defect structure. In figure 1, parameters *S* and *F*, respectively, measured in *t*-YSZ and *t*-YSZC nanomaterials are plotted versus the positron energy E_+. It can be immediately seen from the figure, that for energies $E_+ < 0.3$ keV ($\bar{z} < 2$ nm) a portion of positrons or Ps diffused back to the surface and annihilated there from a surface state. At positron energies $E_+ > 20$ keV ('bulk' region with $\bar{z} > 1$ μm), plateau-like dependences of both *S*- and *F*-values as functions of E_+ are observed. In the virgin *t*-YSZ nanopowder, Ps formation takes place in the whole positron energy range, i.e. at the surface and also in the bulk. This is reflected by *S* parameter in the bulk which is increased due to a sharp contribution of para-Positronium (cf. figures 1A,B) and *F* parameter in figure 1C which is substantially enhanced compared to ternary *t*-YSZC in figure 1D, where *F*-values consistent with zero were found above $E_+ \approx 0.5$ keV. An approximate absolute calibration of the *F*-parameter scale may be deduced from ortho-Ps lifetime measurements in *t*-YSZ bulk nanopowders [2] leading to the probability of ≈ 2 % for 3γ annihilation of Ps in bulk.

The plateau values of *S* exhibit a well-pronounced decrease with increasing sintering temperature both in the binary *t*-YSZ and the ternary *t*-YSZC, see figures 1A,B. This behaviour should be regarded as a consequence of the sintering-induced grain growth and disappearance of pores. The latter process seems to be dominating for the first annealing step (T_S = 600 °C) leading to a strong decrease of the *F* parameter in *t*-YSZ (see figure 1 C). In ternary *t*-YSZC, disappearance of pores takes place as well but since formation of Ps in this sample is inhibited it is not reflected by the F parameter. Above T_S = 700 °C, the disappearance of open space defects at triple points dominates leading to a significant decrease of S-values, while changes of the F parameter are very small. The existence of an intermediate layer between the surface and the bulk region is, in addition, indicated by the data in figure 1. The layer is characterised by the S- and F- values which are remarkably lower than the respective surface parameters, but slightly enhanced compared to the bulk region. The upper boundary of the intermediate layer can be estimated to lie between ≈ 100 and 300 nm (respective positron energies of ≈ 6 to 10 keV). An origin of this layer may be tentatively assigned to sintering-induced moving of open-volume defects from the sample interior toward its surface.

4. Conclusions

Structural studies of zirconia-based nanomaterials stabilised by yttria, chromia, magnesia and ceria revealed three kinds of open volume defects: (i) vacancy-like defects along GBs, (ii) larger point defects with size comparable to a cluster of vacancies at intersections of GBs and (iii) pores between grains. Ps is formed in the pores in all samples except of those containing chromia, which inhibits Ps formation. Sintering of compacted nanopowders leads to disappearance of pores followed by grain growth.

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