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Positron Annihilation in Zirconia-Based Nanomaterials

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Abstract. High-resolution positron lifetime and coincidence Doppler-broadening measurements were performed on the yttria-stabilised zirconia compacted nanopowders differing in phase, stabiliser content and preparation conditions. On the basis of available experimental data and their comparison with theoretical calculations, it is concluded that positrons annihilate mainly in vacancy-like defects at grain boundaries and in larger open-volume defects associated probably with triple points. A fraction of positrons forming positronium and annihilating in mesopores of ≈ 3 nm diameter was also detected.

Introduction

Recent prospects for new ceramic materials have revealed that zirconia-based materials made of nanometer grain size powders offer an exceptional combination of advantageous thermal and mechanical properties. These materials thus become attractive for various industrial applications like, for example, heat-resistance structural and functional ceramics, oxygen sensors as well as solid oxide fuel cells. When the high-temperature applications of zirconia are required, however, an addition of trivalent yttrium oxide is needed so as to keep the tetragonal and cubic phases of zirconia stable. Such an addition leads to a formation of a certain amount of vacancy-like defects in the ZrO_2 lattice. Indeed, these defects influence properties of yttria-stabilised zirconia (YSZ) and the nature as well as the role of defects introduced by stabilisation is to be elucidated in details. Moreover, grain boundaries (GBs) constitute a large volume fraction in the compacted nanopowders and the role of GBs thus should be taken into consideration, too. Porosity is another important property relevant to the applications of YSZ and should be addressed in the investigations of these materials. We shall present below in details that positron annihilation spectroscopy (PAS) is a promising tool for microstructure studies of zirconia-based nanomaterials. Several PAS investigations on YSZ were published earlier, see e.g. [1-4]. Despite of this, however, there is still a rather poor understanding and ambiguous explanations of the observed PAS data and their links to microstructure of these materials.

In the present paper, high-resolution positron lifetime measurements on a series of the YSZ compacted nanopowder materials are reported. The materials studied differ in phase, stabiliser content and preparation conditions. The positron lifetime measurements were supplemented by coincidence Doppler broadening investigation of selected specimens using two HPGe detectors. The influence of defects and GBs on positron behaviour in these materials is discussed on the basis of available experimental data and their comparison with the theoretical calculations of positron

lifetimes and high-momentum parts of Doppler profiles, performed [5] within the framework of the atomic superposition method considering appropriate vacancy-type defect configurations. Preliminary results of the present investigation have been presented recently [6].

Potential of PAS for nanostructure investigations

PAS is nowadays recognised as an efficient non-destructive tool for investigations of materials structure up to the atomic scale details [7,8]. In the *conventional* PAS, energetic positrons emitted from a radionuclide, like e.g. ^{22}Na, are directly implanted into the material studied. They get quickly thermalised there and then move by quantum-mechanical diffusion through the medium. Eventually, the thermalised positron annihilates with an electron of the medium and the annihilation event is accompanied by the emission of the two energetic photons (≈ 0.511 MeV) in opposite directions. These annihilation photons convey useful information on the state of the particles participating in the annihilation event – the electron (local electronic structure is examined in this way) and the positron (positron history in the medium prior the annihilation is involved).

There are two basic PAS observables: (i) the positron lifetime (PL) which is sensitive to the local electron density probed by the positron and (ii) the Doppler broadening (DB) of annihilation radiation which reflects the local electron-momentum density at the positron site. In its coincidence mode (abbreviated as CDB), the latter technique becomes capable to disclose the contributions of the high-momentum iner-shell electrons to the DB profiles and thus provides an unique method for the investigation of the chemical environment of the annihilation sites and related phenomena.

During the diffusion stage, a portion of positrons can get localised (trapped) in nano-sized defets like e.g. vacancies, vacancy clusters, vacancy – impurity atom complexes, dislocations, microvoids, GBs associated defects, etc. The capability of trapping positrons in these *open-volume* defects arises from a suppressed Coulomb repulsion between the positron and the surrounding positive ions. It can lead to the existence of a localised state at the defect site which is energetically advantageous compared to the delocalised Bloch state of a free positron. In favorite cases, the small precipitates (nanoclusters) of impurity atoms can also act as trapping centres for positrons, because of a higher affinity of impurity atoms to positrons compared to the host. Thanks to the positron trapping phenomenon, defects behaviour constitutes the principal motivation of many PAS studies. The great advantage of PAS is its exclusive sensitivity to defect concentrations. In metals, for example, concentration threshold for detection of monovacancies lies typically at $10^{-6} \div 10^{-7}$ at.$^{-1}$ and dislocations detection starts at around 10^{-16} m^{-2} [7]. Of course, the defect type can be characterised on the basis of PL measurements, too. Moreover, positrons can easily reach GBs by diffusion if grain size become comparable to positron diffusion length (typically ≈ 100 nm).

In insulators and materials containing large internal surfaces, a fraction of thermalised positrons can form positronium – a hydrogen-like bound state of an electron and the positron. Due to the exchange interaction, positronium is repelled to the empty interatomic cavities and thus becomes to be a useful probe of larger open volumes of $1 \div 10$ nm size (free-volume cells in polymers, nano- and mesopores in porous materials) [8].

It is obvious that PAS is capable to probe structural elements inherently belonging to nanostructured materials. Most positrons emitted by radionuclides, however, enter the medium with kinetic energies of several hundreds of keV and penetrate typically to depths of several hundreds of micrometers. Thus the conventional PAS probes the *volume* properties of materials. For the studies of nanostructured surfaces, thin layers and interfaces as well as for depth profiling of materials structures in the submicrometer range, the techniques based on utilizing monoenergetic slow-positron beams (≤ 50 keV) with variable energy [9] are being developed in the last two decades. Undoubtedly, positron beams represent a further enhancement of PAS power in nanostructure

investigations, extend the scale of solvable problems and have become highly required devices in this research field at present.

Experimental

Specimens. The three zirconia-based nanosize powders were used in the present investigation: pure ZrO_2 (denoted below as Z0Y, monoclinic phase), ZrO_2+3 mol.% Y_2O_3 (Z3Y, tetragonal) and ZrO_2+8 mol.% Y_2O_3 (Z8Y, cubic). The mean grain size of starting nanopowders was determined by XRD and TEM observations as 23.2, 17.6 and 15.6 nm, respectively. Powders were calcinated at 700 °C/2h and pressed at room temperature into tablets of 15 mm diameter and 5 mm thickness. The three different pressures of 250, 500 and 1000 MPa were applied. In addition, a pure ZrO_2 compacted powder (Z0Yb, monoclinic, mean grain size of 40÷50 nm, calcinated at 1100 °C and pressed under 1000 MPa) and a monocrystalline ZrO_2+3 mol.% Y_2O_3 (Z3Yx, tetragonal) were also studied in the present work. The other details of materials preparation were given elsewhere [10,11].

Measurements. A 1.3 MBq of the carrier-free $^{22}Na_2CO_3$ (iThemba Labs) sealed between MylarC foils (Dupont) of 4 μm thickness was used as a positron source. A PL spectrometer [12] in its fast-fast modification was employed in the present work. The spectrometer exhibited the time resolution of 0.163÷0.169 ns (fwhm). All the above listed materials were characterised by means of the PL method and at least 10^7 counts were accumulated in each PL spectrum. The spectra were analysed with the aid of the maximum likelihood procedure [12]. CDB measurements were performed using a spectrometer equipped with the two HPGe detectors [13] having an energy resolution of 1.05 keV at 511 keV. The Z0Y, Z3Y, Z8Y nanopowders, compacted under 1000 MPa, and the Z3Yx monocrystal were studied also by means of CDB. About 10^8 counts were accumulated in each CDB spectrum. A well-annealed iron served as a reference material for determining relative CDB profiles. All the PL and CDB measurements were performed in air at ambient temperature.

Results and discussion

Measured PL spectra were decomposed into up to four components (positron source contribution and para-positronium component were subtracted). The resulting lifetimes τ_i and intensities I_i are summarised in Table 1. The relative CDB profiles observed in the present work are shown in Fig. 1.

Table 1. Positron lifetimes and intensities measured in the present work (standard deviations are given in parentheses in units of the last significant digit).

Material	Pressure [MPa]	τ_1 [ns]	I_1 [%]	τ_2 [ns]	I_2 [%]	τ_3 [ns]	I_3 [%]	τ_4 [ns]	I_4 [%]
Z0Y	250	0.189(2)	39(1)	0.372(4)	38(1)	2.0(1)	1.35(4)	34(2)	6.5(2)
	500	0.184(3)	36(1)	0.372(3)	42(1)	1.7(1)	1.17(6)	33(2)	5.8(1)
	1000	0.187(3)	37(1)	0.363(4)	41(1)	1.82(7)	1.89(5)	28(1)	5.6(1)
Z3Y	250	0.184(3)	30.6(8)	0.383(3)	48.8(8)	2.1(2)	0.86(4)	35(2)	5.2(2)
	500	0.181(3)	25.3(8)	0.377(3)	53.2(8)	1.8(1)	0.95(5)	34(2)	6.3(2)
	1000	0.179(4)	22(1)	0.368(3)	55(1)	1.8(1)	1.55(7)	30(1)	7.0(1)
Z8Y	250	0.184(4)	26(1)	0.371(3)	53(1)	2.0(2)	0.86(5)	32(2)	5.6(2)
	500	0.185(3)	27(1)	0.364(3)	52(1)	2.3(1)	1.67(3)	30(2)	5.3(2)
	1000	0.196(3)	28(1)	0.377(3)	50(1)	2.3(2)	1.24(3)	35(3)	6.1(2)
Z0Ym	1000	0.179(1)	71.5(5)	0.369(4)	15.6(5)			26(3)	0.78(5)

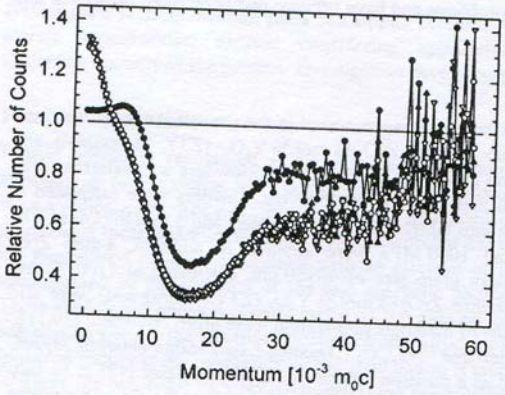

Fig. 1. Observed ratios of DB profiles to that of well annealed iron: ● – Z3Yx (tetragonal, monocrystal), ▲ – Z0Y (monoclinic, nanopowder), ∇ – Z3Y (tetragonal, nanopowder), ○ – Z8Y (cubic, nanopowder). The nanopowders were compacted under 1000 MPa.

Positron lifetimes calculated for the Zr-vacancy or Zr-vacancy+O-vacancy complexes in Ref. [5] seem to resemble observed τ_1-values for Z0Y, Z3Y and Z8Y samples, see Table 1. However, the τ_1-component can hardly be fully explained by positron trapping in vacancy-like defects *inside* grains. First, a low equilibrium concentrations of Zr vacancies occur in these materials at room temperature. Second, the nanocrystalline grain size of compacted powders results in a significant volume fraction of GBs. Positrons thermalised inside grains can thus easily reach GBs since only a weak role of positron trapping is expected due to a low positron binding to defects suggested by theoretical calculations [5]. Hence positrons are supposed to annihilate mainly in vacancy-like defects at GBs (τ_1-component) and in larger open-volume defects associated probably with triple points at GBs (τ_2-component). Present interpretation is different from that of Ref. [2] in which positron trapping mainly inside grains is assumed. On the other hand, a similar point of view as our one is shared by authors [3,4]. We can give further supporting arguments here. First, compared to the pure zirconia, observed intensity ratios I_2:I_1 are significantly dropped in the Z8Y for all pressures applied and in Z3Y under 250 MPa. It is demonstrated in Fig. 2 that the ratios I_2:I_1 correlate roughly linearly with the reciprocal values of the mean grain size d. Indeed, the smaller the grains, the better the chance for a positron to reach GB by diffusion motion and get trapped there. Such behaviour of I_2:I_1 can be understood as resulting from the expected concentration proportionality to $\sim d^{-3}$ and $\sim d^{-2}$ for triple points and vacancy-like defects at GBs, respectively. An increased role of positron trapping in defects at GBs in the compacted *nanopowders*, compared to the Z3Yx *monocrystal*, is indicated also by an enhanced low-momentum region of the observed CDB profiles in Fig. 1. In the high-momentum part, there is virtually no difference in the CDB-ratio curves observed for various specimens (Fig. 1). Such behaviour demonstrates a shape similarity of the

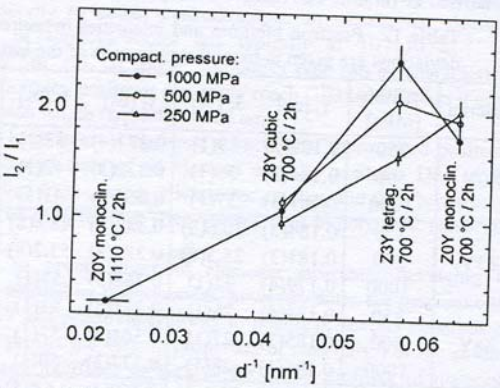

Fig. 2. Observed intensity ratios I_2/I_1 as functions of the inverse mean grain size d.

yttrium and zircon contribution in this momentum region in accordance with the theoretical findings [5]. On the other hand, a non-monotonic behaviour of observed τ_1-values in dependence of the yttria content (Table 1) suggests that the nature of the τ_1-component is complex and a minor contribution from positron trapping in vacancy-like defects inside grains may take place. From Fig. 2, it can be noted that the tetragonal YSZ may be less resistive towards pressure-induced changes under the two higher pressures applied

The ortho-positronium τ_4-components of ≈ 6 % intensity were observed in Z0Y, Z3Y and Z8Y specimens, see Table 1, indicating a certain amount of mesopores. The pore size and volume fraction in these three materials appear not to depend on applied pressure, thus suggesting that the compressibility of powders reaches already saturation in the range of pressures applied. The semi-empirical correlation between the ortho-positronium lifetime and the pore size [14] was used to estimate the pore diameter in Z0Y, Z3Y and Z8Y as $\approx 2.5 \div 3.5$ nm for $\tau_4 \approx 30$ ns. The diameter is considerably smaller then the mean grain size of starting nanopowders. Similarly as in Ref. [1], this component can be regarded as arising from mesopores among primary grains. Longer lifetime components of ≈ 100 ns (and of a weak intensity, indeed) could not be detected in the present work. The occurrence of the larger pores among secondary particles formed by aggregation of primary grains remains an open question and a matter of further investigations of the present materials. Obviously, the suppression of the porosity component, as exhibited by the lifetime spectrum of the Z0Ym specimen (Table 1), is to be related probably to a greater grain size leading to a less pore concentration. A similar effect, i.e. a diminishing of such a mesopore component when grain size is increased, was also reported in Ref. [1] for specimens compacted under considerably lower pressure of 50 MPa.

Conclusions

In the present work, positrons in the zirconia-based compacted nanopowders are assigned to annihilate mainly at GBs: (i) in vacancy-like defects at grain surface and (ii) in the larger open-volume defects, likely associated with triple points. A formation of positronium and its annihilation in mesopores was also observed. PL parameters appeared to be correlated with the composition, microstructure and preparation conditions, demonstrating the effectiveness of PAS method for microstructural investigations on YSZ nanomaterials. The method reflected the defect type (vacancy-like defects, triple points, mesopores) and mean nanograin size. For obtaining a more detailed structural information about these YSZ nanopowder materials, it appeared advantageous to combine PL data with CDB measurements.

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