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2011 J. Phys.: Conf. Ser. 265 012020

(http://iopscience.iop.org/1742-6596/265/1/012020)

International Workshop on Positron Studies of Defects (PSD 08) IOP Publishing
Journal of Physics: Conference Series **265** (2011) 012020 doi:10.1088/1742-6596/265/1/012020

Positron annihilation study of yttria-stabilized zirconia nanopowders containing Cr_2O_3 additive

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Abstract. Yttria-stabilized zirconia compacted nanopowders, doped with trivalent chromium oxide, were studied by means of high-resolution positron lifetime and coincidence Doppler broadening techniques. The observed data suggest that positrons annihilate mainly in vacancy-like defects at grain boundaries or in larger open volumes most likely located at triple points. The results also show that an addition of Cr_2O_3 leads to a decrease in grain size.

1. Introduction

Zirconia (ZrO_2) has a high melting point (2700° C), a low thermal conductivity and a variety of other advantageous properties [1]. Thus, zirconia exhibits a big potential of use in a wide area of applications, especially at high temperatures. Favorable properties of ZrO_2 are still enhanced if zirconia-based materials for applications are produced starting from powders of nanoscopic size.

However, the *pure* zirconia, which is monoclinic at room temperature, undergoes a transformation to the tetragonal phase at $\approx 1100°$ C temperature. Such a transformation is connected with a considerable volume shrinkage leading even to a creation of cracks within ZrO_2 structure. Obviously, this effect inhibits any use of the pure zirconia in high-temperature applications.

Thus, a stabilization of the high-temperature ZrO_2 phase is required to make a full use of advantageous zirconia features in industry. It is well known, that the stabilization of the high-temperature phase of zirconia can be achieved by an addition of ≈ 3 mol.% (≈ 5.7 wt%) of the trivalent yttrium oxide Y_2O_3 (yttria) so as to form a solid solution of Y_2O_3 in the ZrO_2 lattice [1]. Materials, in which the stabilization of the high-temperature phase is attained by means of an yttria addition, are conventionally called yttria-stabilized zirconia (YSZ).

YSZ nanomaterials represent a complex system with a considerable amount of open-volume defects of a sub-micrometer size. First, the introduction of Y^{3+} ions into the ZrO_2 lattice leads to a violation of stoichiometry. This results in a large amount of oxygen vacancies and

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vacancy–solute complexes. Second, grain boundaries (GB's) in nanostructured YSZ materials and defects associated to GB's (vacancy-like defects, triple points at GB intersections) become of increasing importance. Third, the pores of a nanometer size are expected to occur in YSZ materials made of nanopowders. These nanosized structures undoubtedly underlay macroscopic properties of zirconia-based materials. Detailed microstructural information should thus be regarded as a factor of crucial importance for tailoring YSZ materials for practical applications.

Some other metal-oxide additives are being examined to improve properties of YSZ's, in particular to prevent grain growth during the preparation of nanopowders. Recently, Korduban et al. [2] has suggested that an addition of a small amount (≈ 1 mol.%) of Cr_2O_3 diminishes the particle size of the YSZ nanopowders prepared by the co-precipitation technique. Indeed, an effect of a Cr_2O_3 addition on defects nature and behaviour in such a 'ternary' oxide YSZ system, is to be investigated and compared to the 'binary' YSZ one, i.e. the YSZ with no Cr_2O_3 additive. It should also be mentioned that in YSZ chromium atoms predominantly exist in the form of trivalent ions though other charge states (like Cr^{5+}) cannot be fully excluded [3]. This indicates that Cr^{3+} ions will be accompanied by oxygen vacancies like in the case of Y^{3+} ions.

Positron annihilation spectroscopy (PAS) is nowadays a well-established efficient tool for defect studies [4; 5]. Several PAS investigations of zirconia-based nanomaterials were already performed before [6–9]. Despite of these studies, there is still a lack of sufficiently complete and precise experimental data on YSZ nanomaterials which would allow for an unambiguous interpretation. Recently, we have carried out extensive investigations of various pressure-compacted YSZ nanopowders by means of the positron lifetime (LT) and coincidence Doppler broadening (CDB) techniques [10; 11]. The detailed *ab-initio* theoretical calculations of positron parameters for the perfect ZrO_2 lattice and a variety of defect configurations conceivable in the YSZ have been also conducted by us [12; 13] in order to assist the interpretation of the PAS experiments. As a continuation of our preceding efforts, we report in the present Contribution on a LT and CDB study of several ternary YSZ systems with a different Cr_2O_3 content, for which there are no PAS studies available yet.

2. Experimental

2.1. Samples

The binary and ternary YSZ nanopowders were prepared by the co-precipitation technique starting from water solutions of $ZrO(NO_3)_2$, $Y(NO_3)_3$ and $CrCl_3 \cdot 6H_2O$ taken at stoichiometric compositions. Further details of the preparation procedure are given in Refs. [2; 14; 15]. The final oxide nanopowders were obtained by calcination at 600° C/1 h in air. All the nanopowders contained 3 mol.% of Y_2O_3. The resulting binary and ternary YSZ nanopowders were uniaxially pressed under 500 MPa into tablets of 10÷12 mm in diameter and ≈5 mm thickness. Specimens of the four different content x_{Cr} of Cr_2O_3 were investigated: $x_{\mathrm{Cr}} = 0, 0.3, 2.9, 5.0$ mol.% of Cr_2O_3. These specimens are below abbreviated as Z3Y, Z3Y-$C_{0.3}$, Z3Y-$C_{2.9}$ and Z3Y-$C_{5.0}$, respectively. Their tetragonal structure was examined by X-ray diffraction and the mean grain size of the binary YSZ nanopowder (≈ 20 nm) was estimated by this technique as well.

A monocrystal of the cubic ZrO_2+9 mol.% Y_2O_3 (denoted hereafter as Z9Y, purchased from Crystec, GmbH) was also investigated to facilitate data interpretation. In addition, pure Zr, Y and Cr well-annealed metals were used as reference samples in CDB measurements. Testing LT measurements verified these specimens as virtually defect-free materials in which practically all positrons annihilate from the delocalised state.

2.2. Apparatus and data acquirement

The positron sources were fabricated using the carrier-free $^{22}Na_2CO_3$ activity supplied by iThemba Labs. A drop of about 1.3 MBq of the activity in water solution was dried and sealed between the 4 μm thick mylarC foils (DuPont). The source was sandwiched with two identical tablets of the material studied.

LT measurements were conducted using the fast-fast configuration of a BaF_2 spectrometer [16]. Using the above positron source–specimen sandwich, the spectrometer exhibited a time resolution of 165 ps (FWHM for ^{22}Na), $\approx 80 \div 100\,s^{-1}$ coincidence count rate and a peak-to-background ratio better than $\approx 10^3$. More than 10^7 coincidence events were accumulated in each LT spectrum. A maximum-likelihood procedure [16] was utilized to decompose the LT spectra into discrete components. The fractions of positrons annihilating in the source salt and covering foils were determined from separate LT spectra measurements with a well-annealed α-iron reference specimen. The annihilations in the source were then re-calculated to the YSZ case following to the method developed by Surbeck [17].

In CDB experiments, a two-detector (HPGe–HPGe) coincidence spectrometer [18] was utilized. The spectrometer showed an energy resolution of 1.1 keV (FWHM) at the 511 keV energy, a coincidence count rate of $\approx 500\,s^{-1}$ and a peak-to-background ratio of $\approx 10^5$. At least 10^8 counts were collected in each two-dimensional CDB spectrum. The results of the CDB measurements are expressed as Doppler-broadened profiles (DBP) of the samples studied related to the DBP of a well-annealed pure Zr reference specimen.

3. Results and discussion

The results of present LT measurements on the binary Z3Y and ternary Z3Y-$C_{x_{Cr}}$ nanopowders are summarised in table 1. The four-component LT spectrum, exhibited by the Z3Y sample, illustrates a typical behaviour observed [10] on a variety of binary YSZ nanopowders: (i) the shortest lifetime $\tau_1 \approx 0.185$ ns arises due to positron trapping in vacancy-like defects, (ii) the second lifetime $\tau_2 \approx 0.375$ ns comes from larger defects of open volumes comparable to a few vacancies and (iii) the two longest lifetimes $\tau_3 \approx 2$ ns and $\tau_4 \approx 30$ ns result from positronium (Ps) formation and subsequent ortho-Ps pick-off annihilation in voids or pores.

Table 1. Positron lifetimes τ_i and relative intensities I_i obtained for compacted nanopowders in the present work. Relative intensities were normalized so that $I_1 + I_2 + 4(I_3 + I_4)/3 = 100\,\%$. Errors (1 std. deviation) are given in the units of the last significant digit of the corresponding value.

Sample	τ_1 [ns]	I_1 [%]	τ_2 [ns]	I_2 [%]	τ_3 [ns]	I_3 [%]	τ_4 [ns]	I_4 [%]
Z3Y	0.182 (1)	27 (2)	0.379 (1)	63 (2)	1.5 (2)	0.7 (1)	30 (1)	7.1 (3)
Z3Y-$C_{0.3}$	0.191 (3)	31 (1)	0.381 (2)	69 (1)				
Z3Y-$C_{2.9}$	0.224 (1)	24 (1)	0.406 (2)	76 (1)				
Z3Y-$C_{5.0}$	0.259 (8)	20 (2)	0.393 (4)	80 (2)				

It can be expected that a substantial portion of positrons thermalised inside grains of ≈ 20 nm size can diffuse to GB's during the lifetime of positrons. It has been discussed by Guo [19; 20] that yttrium segregates at the GB interfaces in YSZ. For this reason, GB's are surrounded by negatively charged compensating layers characterized by a depletion of oxygen vacancies $V_O^{\bullet\bullet}$ (the Kröger notation [21] is used in the following). At the same time the GB cores in YSZ are positively charged [20]. It should also be noted that the potential 'barier' for positrons at GB's in YSZ due to the mutual repulsive interaction of positrons and GB's is about 0.2 eV, as deduced from [22], which does not prevent positrons from trapping at the GB core. The structure of grain boundaries in sintered cubic and tetragonal YSZ materials has recently been studied in detail by Matsui et al. [23]. Among others, it is shown that Y segregation in tetragonal YSZ materials increases with temperature (above 1100 ° C). In this respect, it is unclear to what extent the segregation of yttrium (and thereby GB charging) occurs also in our samples that were not sintered (see also [20] and references therein). There are no experimental data regarding possible Cr segregation at GB's in YSZ. We just note that the ionic radius of the Cr^{3+} ion is very similar to that of the Zr^{4+} ion, indicating a lower tendency to segregation compared to Y. The topic of cation segregation at GB's in YSZ and related oxygen vacancy depletion is rather complex and we shall not discuss it further here.

In any case, we suppose that the positrons which did not form Ps annihilate at GB's or their close vicinity from trapped states at the two kinds of defects: (i) vacancy-like defects present at GB's, and (ii) larger open-volume defects situated probably in triple GB's junctions (triple points). Simple spatial considerations and the assumption of uniformly distributed vacancy-like defects in the GB layer lead to the proportionality of the I_2/I_1 ratio to d^{-2}, where d stands for the mean grain size. The proportionality constant for YSZ's was estimated from a fit to the data of Ref. [10] for binary YSZ nanopowders and it is used below to estimate the grain size of YSZ-$C_{x_{Cr}}$ nanopowders.

Contrary to the binary YSZ system (sample Z3Y), the LT spectra of all the ternary systems Z3Y-$C_{x_{Cr}}$ exhibited only two components, see table 1. The shortest lifetime τ_1 gradually increases with the Cr_2O_3 content up to ≈ 0.26 ns. This may be attributed to an increase of the open volume of vacancy-like defects surrounded by Cr atoms in the GB vicinity, probably due to a smaller atomic radius of Cr compared to Zr or Y.

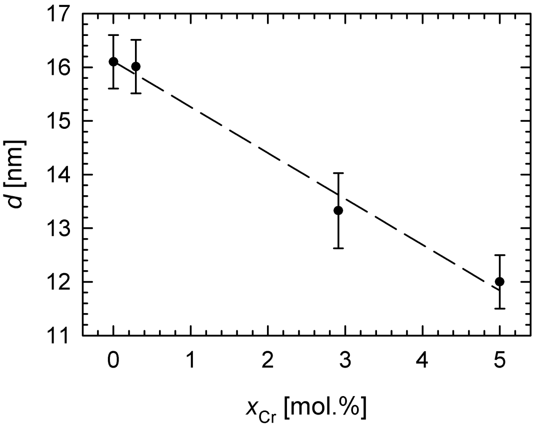

Figure 1. Estimated mean grain size d vs. Cr_2O_3 content x_{Cr}. The dashed line represents the linear regression of data points.

The longer lifetime τ_2 in the Z3Y-$C_{x_{Cr}}$ does not show any monotonic dependence on the Cr_2O_3 content suggesting thus that this component arises from positron trapping in free volumes among grains (most likely triple points), comparable to a few vacancies. The intensity ratio I_2/I_1 clearly increases with the increasing Cr_2O_3 content. We have used the above described procedure to estimate the mean grain size d of the ternary Z3Y-$C_{x_{Cr}}$ systems from the observed I_2/I_1 data. In figure 1, the estimated mean grain size d is plotted as a function of Cr_2O_3 content x_{Cr}. It is seen from the figure that an increased Cr_2O_3 content leads to a smaller grain size, which is in accordance with findings [2] that chromium dopants inhibit particle clustering during calcination and shift the onset of particle coalescence to higher temperatures.

There are no lifetimes above 1 ns and, hence, no ortho-Ps annihilations were observed in Z3Y-$C_{x_{Cr}}$. This can be understood as an effect of paramagnetic centers associated with Cr'_{Zr} dopants which suppress the Ps formation below the detection limit (less than 1 %) even for $x_{Cr} = 0.3$ mol.% .

The DBP ratio curves related to the well-annealed pure Zr for the binary Z3Y and ternary Z3Y-$C_{x_{Cr}}$ compacted nanopowders are plotted in figure 2. Ratio curves exhibit a pronounced maximum at electron momentum $p \approx 15 \times 10^{-3}\, m_0c$, which represents a contribution of positrons annihilated by the oxygen $2p$ electrons [8]. Contrary to the Z3Y, indeed, no enhancement at low momentum region ($p \approx 0$) is observed in Z3Y-$C_{x_{Cr}}$ specimens due to an absence of the para-Ps contribution. DBP ratio curves for YSZ binary and ternary nanopowders are located well below that for the Z9Y monocrystal indicating thus that the fraction of positrons annihilated by the oxygen electrons is reduced in the Z3Y-C$_{x_{\mathrm{Cr}}}$ nanopowders. The CDB response of the annealed pure Cr was also included in figure 2. It exhibits a peak centered almost at the same position as that for the 2p oxygen electrons. Hence it is difficult to resolve an effect of the Cr addition (if any) on DBP ratio curves.

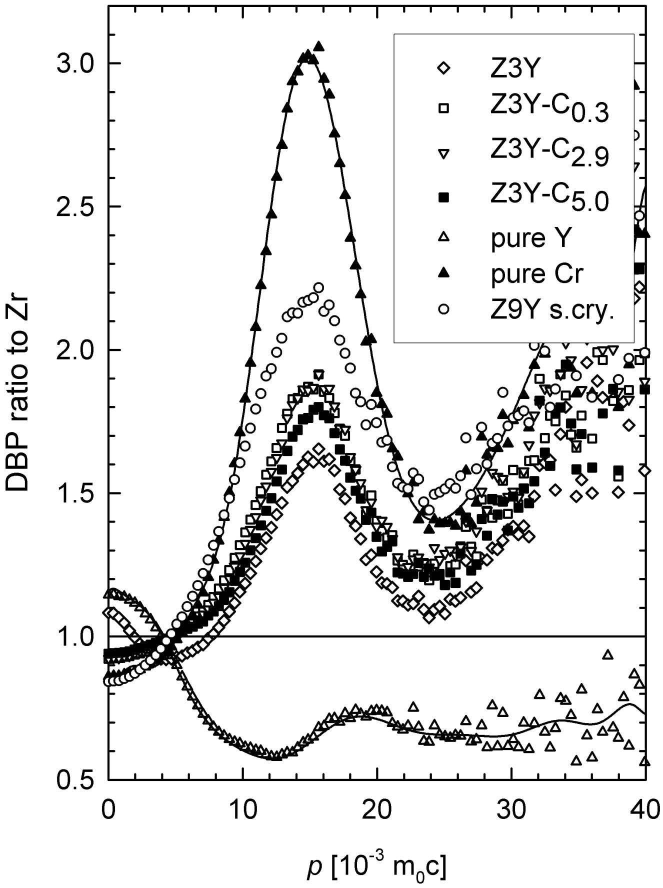

Figure 2. Measured DBP ratios as functions of the electron momentum p. The solid lines are drawn to guide eyes only.

4. Summary

The ternary yttria-stabilized zirconia pressure-compacted nanopowders with a different content of Cr_2O_3 were studied in the present work using positron annihilation spectroscopies: the positron lifetime and coincidence Doppler broadening techniques. The results of this study can be summarized in the following items:

- Positrons annihilate (i) in the vacancy-like defects situated at grain boundaries, or (ii) at GB triple points.
- The addition of the trivalent chromium oxide leads to a decrease in grain size.
- The paramagnetic centers introduced due to an addition of the Cr atoms suppress the Ps formation in voids and pores below the detection limit.

Acknowledgements

The financial support of the present work by the Ministry of Education, Youths and Sports of the Czech Republic (CR) – the scientific plan No. 0021620834, the Czech Scientific Foundation

– contract No. GA 106/06/0270, and the Grant Agency of the Academy of Sciences of the CR – projects Nos. KAN300100801 and KJB101120906 is highly acknowledged. The present work was also supported from the National Academy of Science of Ukraine (scientific plans Nos. A 116/06 H and A 106U006933).

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