Inhibition of Positronium Formation in Yttria Stabilized Zirconia Nanopowders Modified by Addition of Chromia

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Abstract. The effect of chromia additive on defects in yttria stabilized zirconia (YSZ) nanopowders was investigated in this work. It was found that positrons are trapped at vacancy-like misfit defects at grain boundaries and at larger defects situated at triple points. Moreover, a long-lived ortho-positronium contribution was found in YSZ nanopowder without chromia. Addition of chromia prolongs the lifetime of positrons trapped at vacancy-like misfit defects which indicates segregation of Cr ions at grain interfaces and interaction of Cr with vacancy-like misfit defects. Furthermore, addition of chromia completely suppresses formation of positronium.

Introduction

Addition of 3 mol.% of yttria (Y_2O_3) to zirconium dioxide (ZrO_2, zirconia) enables to stabilize the high temperature tetragonal zirconia phase down to room temperature. Resulting material called yttria stabilized zirconia (YSZ) exhibits excellent properties for high temperature applications, thermal shielding, machining tools, etc. [1]. Deviation from stoichiometry caused by addition of trivalent yttrium ions Y^{3+} is compensated by introduction of oxygen vacancies which permit oxygen ion conductivity. Addition of a ternary stabilizer enables further modification of YSZ properties. Chromia (Cr_2O_3) has beneficial effect because it prevents particle coalescence during calcination and enables to achieve smaller particle sizes. In this work we employed positron annihilation spectroscopy (PAS) for investigation of the effect of chromia addition on YSZ nanopowders. Preliminary results have been presented in Ref. [2].

Experimental details

YSZ nanopowders doped with chromia were prepared by co-precipitation technique using water solutions of $ZrO(NO_3)_2$, $Y(NO_3)_3$ and $Cr(NO_3)_3$. The precipitates were dried at $120^{\circ}C$ and calcinated at $600^{\circ}C$ for 2 h on air. Calcinated nanopowders were compacted into disk shaped pellets (diameter $\approx$ 10 mm, thickness $\approx$ 5 mm) by uniaxial pressure of 500 MPa. Compacted nanopowders of the following compositions were investigated: ZrO_2 + 3%mol. Y_2O_3 + x mol. % Cr_2O_3, where $x =$ 0, 0.3, 0.7, 1.5, 2.9, 5.0. As a reference samples we studied also monoclinic pure ZrO_2 compacted nanopowder and well annealed pure metals Y (99.9%), Zr (99.9%) and Cr (99.99%).

A carrier-free $^{22}Na_2CO_3$ positron source ($\approx$ 1.3 MBq) sealed between 2 μm thick mylar foils was used for PAS measurements. Positron lifetime (LT) measurements were performed on a digital spectrometer with an excellent time resolution of 145 ps (FWHM ^{22}Na) [3]. LT spectra, which always contained at least 10^7 positron annihilation events, were decomposed using a maximum likelihood based procedure [4]. The source contribution consisted of two weak components with lifetimes of ~368 ps and ~1.5 ns and corresponding intensities of ~6 % and ~1 %. Coincidence Doppler broadening (CDB) measurements were carried out using a two HPGe detector apparatus

with a resolution of 1.0 keV (FWHM of the resolution function at 511 keV). At least 10^8 positron annihilation events were accumulated in each CDB spectra. Results of CDB measurements are presented as ratio curves related to a reference sample of well-annealed pure Zr.
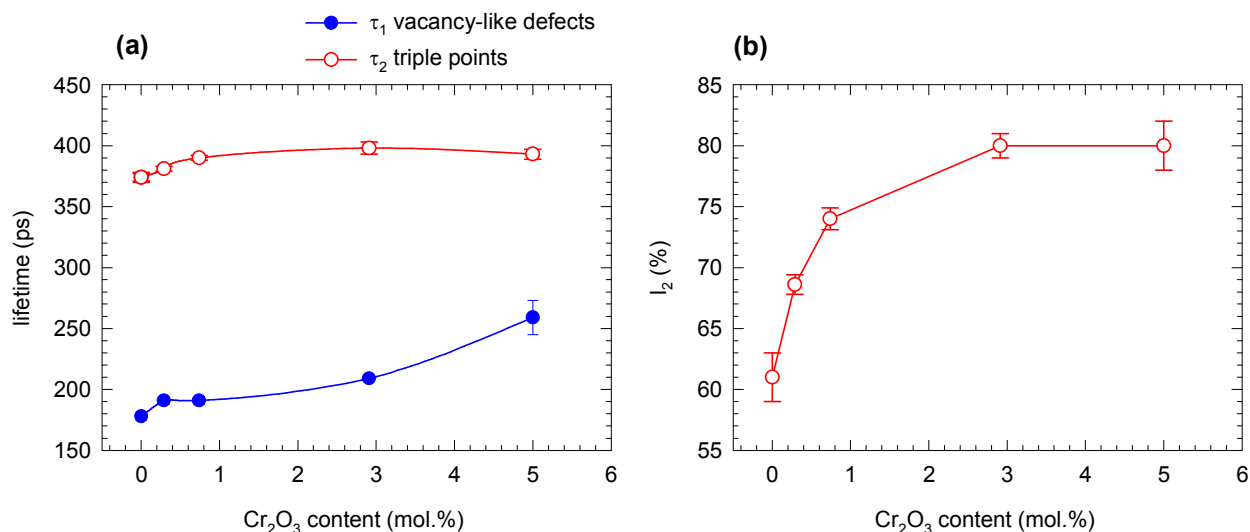

Fig. 1. Results of LT measurements on YSZ compacted nanopowders with various chromia content: (a) lifetimes τ_1 and τ_2 attributed to positrons trapped at vacancy-like misfit defects at grain boundaries and in larger point defects at triple points, respectively (b) relative intensity I_2 of positrons trapped in the defects at triple points. Note that YSZ with zero chromia content contains also a Ps contribution.

Results and Discussion

X-ray diffraction studies revealed that compacted nanopowders exhibit nanocrystalline grains with size 12-23 nm [5,6] which is roughly one order of magnitude smaller than positron diffusion length in defect-free oxides [7]. Hence, virtually all positrons thermalized inside grains diffuse to grain interfaces and are trapped at open volume defects there. LT spectra of YSZ compacted nanopowders exhibit two components originating from positrons that did not formed positronium (Ps). Fig. 1(a) shows the lifetimes τ_1 and τ_2 of these components in YSZ compacted nanopowders with various content of chromia. Since both lifetimes τ_1, τ_2 are significantly longer than the bulk positron lifetime in zirconia $\tau_B \approx 150$ ps [6] both components represent a contribution of positrons trapped at defects. Theoretical calculations revealed that O-vacancies and also their possible complexes with Y cations are too shallow traps incapable of positron localization, while Zr-vacancies are deep traps [6]. Hence, the shorter component with lifetime τ_1 can be attributed to positrons trapped at Zr-vacancy-like misfit defects at grain boundaries. The longer component with lifetime τ_2 represents a contribution of positrons trapped at larger point defects (size comparable with small vacancy clusters) situated at triple points, i.e. junctions of three grain boundaries.

One can see in Fig. 1(a) that both positron lifetimes τ_1, τ_2 increase with increasing chromium content. Because of smaller size of Cr atoms, the lifetime of trapped positron increases with increasing number of Cr neighbors surrounding the trap. Hence, a strong dependence of positron lifetimes τ_1, τ_2 on chromia content testifies a segregation of Cr cations at grain boundaries. It was demonstrated in Ref. [6] that the ratio I_2/I_1 increases with decreasing grain size due to increasing contribution of positrons trapped in defects at triple points. The intensity I_2 of positrons trapped at triple points shown in Fig. 1(b) increases with chromia content testifying that chromia addition leads to a reduction of grain size which was confirmed also by X-ray diffraction [5].
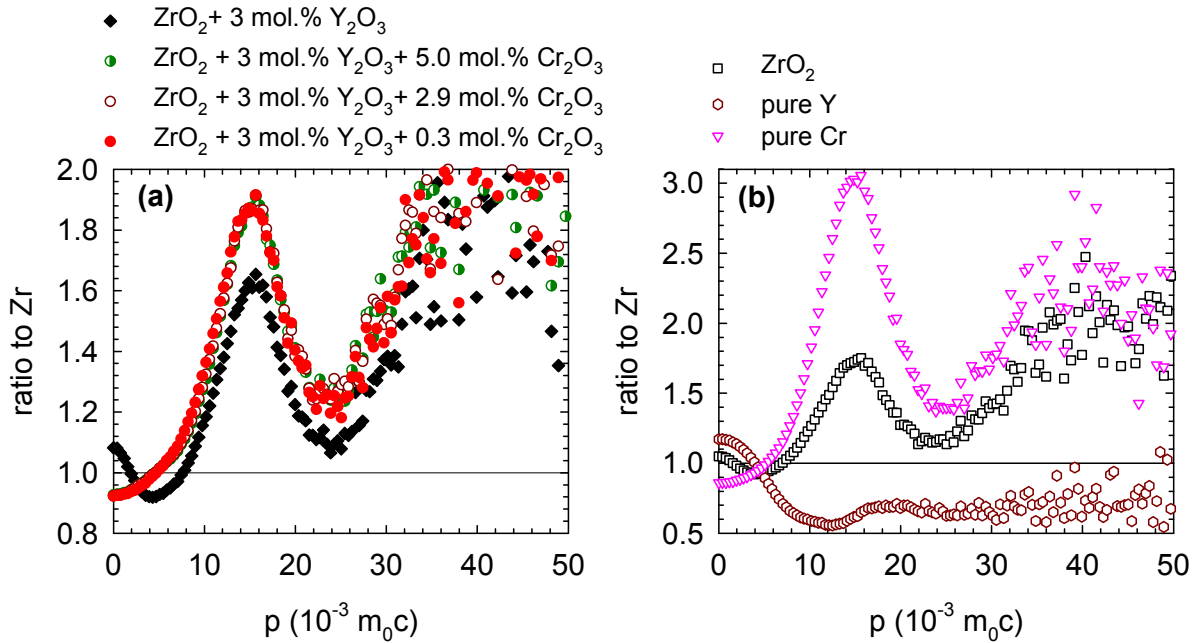
Fig. 2. CDB ratio curves (related to well annealed pure Zr): (a) compacted nanopowders, (b) reference curves for ZrO_2 compacted nanopowder and well annealed pure Y and Cr.

A contribution of Ps annihilation was found in LT spectra of YSZ compacted nanopowder without chromia. The formation of Ps in YSZ nanopowder is clearly demonstrated by two long-lived components with lifetimes $\tau_{o-Ps,1} = (1.8 \pm 0.1)$ ns, $\tau_{o-Ps,2} = (30 \pm 2)$ ns and corresponding relative intensities $I_{o-Ps,1} = (1.5 \pm 0.1)$ %, $I_{o-Ps,2} = (6.1 \pm 0.3)$ %. These components come from the pick-off annihilation of ortho-positronium (o-Ps). The principal o-Ps component $\tau_{o-Ps,2} \approx 30$ ns corresponds to nanoscopic pores with diameter of ≈ 3 nm estimated using the semi-empirical correlation between the o-Ps pick-off lifetime and the cavity size [8]. This component can be attributed to o-Ps localized in big cavities between crystallites. The shorter and weaker o-Ps component with lifetime $\tau_{o-Ps,1} \approx 1.8$ ns can be attributed to sub-nanometer voids with diameter of ≈ 0.6 nm situated at intersections of crystallite interfaces. Note that the para-positronium (p-Ps) component with lifetime $\tau_{p-Ps} = 125$ ps and relative intensity $I_{p-Ps} = 1/3 (I_{o-Ps,1} + I_{o-Ps,2})$ was considered in fitting.

Interestingly, no Ps contribution was detected in the compacted nanopowders containing chromia. Even an addition of only $x = 0.3$ mol. % of Cr_2O_3 is sufficient to suppress Ps contribution in compacted nanopowders below the detection limit of LT spectroscopy ($I_{o-Ps} < 0.5$ %). X-ray photoelectron spectroscopy (XPS) performed on ternary $ZrO_2 + 3$%mol. $Y_2O_3 + x$ mol. % Cr_2O_3 nanopowders revealed that yttrium ions are present in the main oxidation state Y^{3+} only. On the other hand, chromium ions are present not only in the main oxidation state of chromia Cr^{3+}, but also in Cr^{2+} and Cr^{5+} oxidation states [5]. Possible explanation of the observed Ps inhibition is that the paramagnetic Cr^{5+} ions act as donors [5] and introduce thus electrons at grain boundary regions. As a consequence any bound state between positron and electron localized at grain boundary is immediately broken in collisions with these quasi-free electrons introduced by Cr^{5+} ions. Since Ps can be localized only at open volumes among particles, the suppression of Ps component by chromia doping further confirms a strong segregation of Cr ions at grain boundaries.

In a recent positron annihilation study [9] carried out on a mixture of Cr_2O_3 and Al_2O_3 nanopowders o-Ps formation inhibition was observed with increasing concentration of Cr_2O_3 and attributed to Cr^{3+} cations which may capture free electrons in the spur created by slowing down positron. This may happen also in our case of YSZ nanopowders doped with chromia since Cr has higher redox potential than Zr and Y. However, it has to be mentioned that in regular YSZ lattice reduction of Cr^{3+} ions to Cr^{2+} requires formation of additional oxygen vacancy in order to retain electrical neutrality. Hence, Cr cations scavenging electrons should be located at grain boundaries.

CDB ratio curves (related to well annealed pure Zr) for YSZ compacted nanopowders with various chromia content are plotted in Fig. 2(a). The CDB ratio curve for YSZ compacted nanopowder without chromia exhibits a sharp peak at zero momentum due to a p-Ps contribution. This peak is absent in CDB curves measured in YSZ compacted nanopowders modified by addition of chromia testifying that the presence of chromia suppresses formation of both o-Ps and p-Ps and ruling out o-Ps spin conversion. The main feature of all CDB curves in Fig. 2(a) in the high momentum region is a peak located at $p \approx 15 \times 10^{-3} \ m_0 c$.

Fig. 2(b) shows CDB ratio curves (related to well annealed Zr) measured on reference samples of pure ZrO_2 compacted nanopowder and well annealed pure Y and Cr. The CDB curve measured on ZrO_2 compacted nanopowder testifies that the peak located at $p \approx 15 \times 10^{-3} \ m_0 c$ is mainly due to a contribution of positrons annihilated by 2p-oxygen electrons (see Ref. [6] for discussion). However, one can see in Fig. 2(b) that the CDB curve for pure Cr exhibits a peak which is a little sharper than that for oxygen, but is located at the same position. The CDB curve measured in pure Y differs only slightly from that for pure Zr because of similar electron structure of these two elements. The ratio curve for pure Y is almost flat and positioned below that for pure Zr. Hence, the peak located at $p \approx 15 \times 10^{-3} \ m_0 c$ detected in $ZrO_2 + 3\%mol. \ Y_2O_3$ compacted nanopowder represents a contribution of positrons annihilated by oxygen electrons. This peak is obviously more pronounced in YSZ with chromia due to additional contribution of positrons annihilated by Cr electrons. Moreover, due to normalization of CDB curves the absence of p-Ps contribution at low momenta shifts the CDB ratio curves for YSZ with chromia up in the high momentum region, which can be seen in Fig. 2(a).

Summary

YSZ compacted nanopowders doped with chromia were prepared and characterized in this work. Both LT and CDB technique indicate a strong segregation of Cr cations at grain boundaries. Positronium which is formed at inter-granular open volumes in YSZ compacted nanopowders is suppressed below the detection limit by doping with chromia. This appears due to Cr cations segregated at grain boundaries.

Acknowledgements

References

[1] A.H. Heuer and L.W. Hobbs: *Science and Technology of Zirconia. Advances in Ceramics* Vol. 3 (The American Ceramic Society, Columbus, OH 1981).

[2] I. Procházka, J. Čížek, O. Melikhova, J. Kuriplach, T.E. Konstantinova and I.A. Danilenko: Positron annihilation study of yttria-stabilized zirconia nanopowders containing Cr_2O_3 additive, J. Phys.: Conf. Series Vol. 265 (2011), p. 012020

[3] F. Bečvář, J. Čížek, I. Procházka and J. Janotová: The asset of ultra-fast digitizers for positron-lifetime spectroscopy, Nucl. Instrum. Methods Phys. Res. A Vol. 539 (2005), p. 372-385

[4] I. Procházka, I. Novotný and F. Bečvář: Application of Maximum-Likelihood Method to Decomposition of Positron-Lifetime Spectra to Finite Number of Components, Mater. Sci. Forum Vol. 255-257 (1997), p. 772-774

[5] A. Yashshchishyn, A.M. Korduban, V.V. Trachevskiy, T.E. Konstantinova, I.A. Danilenko, G.K. Volkova and I.K. Nosolev: XPS and ESR spectroscopy of ZrO_2-Y_2O_3-Cr_2O_3 nanopowders, Functional Materials Vol. 17 (2010), p. 306-310

[6] J. Čížek, O. Melikhova, I. Procházka, J. Kuriplach, R. Kužel, G. Brauer, W. Anwand, T.E. Konstantinova and I.A. Danilenko: Defect studies of nanocrystalline zirconia powders and sintered ceramics, Phys. Rev. B Vol. 81 (2010), p. 024116

[7] R. Krause-Rehberg and H.S. Leipner: *Positron Annihilation in Semiconductors – Defect Studies*, (Springer, Berlin 1999).

[8] M. Eldrup, D. Lightbody and J.N. Sherwood: The temperature dependence of positron lifetimes in solid pivalic acid, Chem. Phys. Vol. 63 (1981), p. 51-58

[9] S. Huang, Y. Dai, H. Zhang and Z. Chen: Chemical quenching and inhibition of positronium in Cr_2O_3/Al_2O_3 catalysts, Wuhan University J. Natur. Sci. Vol. 16 (2011), p. 308-312

Positron and Positronium Chemistry X

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