

POSITRON ANNIHILATION STUDY OF ZIRCONIA-BASED NANOMATERIALS

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STUDIUM NANOMATERIÁLŮ NA BÁZI DIOXIDU ZIRKONU POZITRONOVOU ANIHILAČNÍ SPEKTROSKOPIÍ

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Abstrakt

Byla provedena srovnávací studie několika materiálů na bázi dioxidu zirkonu: (i) nanoprášky tří polymorfních forem dioxidu zirkonu kompakťovaných pod vysokým tlakem – čistý ZrO_2 (monoklinický), ZrO_2 stabilizovaný 3 mol.% Y_2O_3 (tetragonální) a ZrO_2 stabilizovaný 8 mol.% Y_2O_3 (kubický), (ii) keramické materiály získané spékáním dvou výše uvedených nanoprášků ZrO_2 stabilizovaného Y_2O_3 a (iii) monokrystaly tetragonální a kubické formy $\text{ZrO}_2+\text{Y}_2\text{O}_3$. Jako základní experimentální technika byla použita spektrometrie dob života pozitronů s vysokým rozlišením. Pozitronové doby života změřené pro nanoprášky ukázaly, že dvě nejkratší komponenty spektra, ≈ 180 and ≈ 370 ps, náležejí anihilacím pozitronů v defektech asociovaných s hranicemi zrn, nejpravděpodobněji po řadě defektům vakančního typu a průsečíkům hranic zrn. Na druhé straně pozitronová spektra změřená pro keramické vzorky jsou spíše podobná spektrům získaným pro monokrystaly, čímž je dán další argument pro uvedenou interpretaci výsledků na nanopráškových vzorcích. Obecně však dominuje záchyt pozitronů i pro keramické a monokrystalické vzorky na bázi dioxidu zirkonu. S cílem osvětlit povahu možných center záchytu pozitronů byly provedeny i teoretické výpočty dob života se zahrnutím relaxací atomů v okolí defektu. Ty ukázaly, že vhodným kandidátem může být komplex kyslíková vakance–yttrium. Získané výsledky rovněž naznačují, že údaje o dvou nejkratších komponentách spektra dob života pozitronů mohou být užitečné i pro charakterizaci procesu spékání a přinést novou informaci o evoluci hranic zrn během spékání.

Abstract

A comparative study of several zirconia-based materials is reported: (i) the pressure-compacted nanopowders of the three zirconia polymorphs – pure ZrO_2 (monoclinic), yttria-stabilized ZrO_2+3 mol.% Y_2O_3 (tetragonal) and yttria-stabilized ZrO_2+8 mol.% Y_2O_3 (cubic), (ii) the ceramic materials obtained by sintering of the above two yttria-stabilized zirconia (YSZ)

nanopowders and (iii) the tetragonal and cubic YSZ monocrystals. The high-resolution positron lifetime spectroscopy is employed as a principal experimental technique. Positron lifetime data observed on the nanopowders suggest that the two shortest components, exhibiting lifetimes of ≈ 180 and ≈ 370 ps, arise from the annihilation of positrons trapped in defects associated with grain boundaries, presumably the vacancy-like defects and tripple points, respectively. On the other hand, the positron lifetime spectra observed on the ceramic materials resemble those found for the corresponding monocrystals, giving thus an additional support to the above interpretation of the nanopowders results. Generally, it is argued that positron trapping dominates also in the sintered and monocrystalline zirconia-based specimens. Theoretical calculations of positron lifetimes including atomic relaxation were performed with the aim to elucidate which defect configuration may be responsible for trapping of positrons. The oxygen vacancy–yttrium complex seems to be a likely candidate. Present results also suggests that the positron lifetime data on the two shortest components can be useful in characterization of the sintering process and bring a new information about grain boundary evolution during sintering.

Keywords: Ytria-stabilized zirconia, nanopowders, sintered ceramics, positron lifetime

1. Introduction

Tetravalent zirconium oxide (ZrO_2 , zirconia) is the base ingredient of a variety of materials designated for industrial applications: refractory ceramics, solid oxide fuel cells, oxygen sensors, abrasive and grinding media, etc. Zirconia may crystallize in the three different forms: monoclinic, tetragonal and cubic [1]. Pure ZrO_2 (melting point of $\approx 2700^\circ\text{C}$) is monoclinic at room temperature. However it undergoes phase transition to the more dense tetragonal structure at $\approx 1100^\circ\text{C}$. Such a transition limits high-temperature applications of pure zirconia because of volume shrinkage and cracks are introduced. This is why a phase-stabilization of zirconia-based materials intended for use at higher temperatures is strongly desired. A formation of a solid solution of zirconia with a certain amount of trivalent yttrium oxide (Y_2O_3 , yttria) is a way how to improve phase stability of these materials. Such a process gives rise to yttria-stabilized zirconia (YSZ) materials. When ≈ 8 mol.% of yttria is added to ZrO_2 , the cubic structure of the resulting solid solution is obtained which exhibits no phase change up to $\approx 2500^\circ\text{C}$. Such an YSZ system exhibits, moreover, some improved features: a high oxygen ion conductivity, an increased hardness and a high thermal shock resistivity. In case of ≈ 3 mol.% yttria admixture, the tetragonal phase of the solid solution is formed which is metastable below $\approx 1100^\circ\text{C}$ and a coexistence of a mixture the zirconia polymorphs may occur.

The stabilization of zirconia by the yttria addition results in a non-stoichiometry of the YSZ systems. As a consequence, a substantial amount of defects is introduced into the lattice (mainly oxygen vacancies, vacancy–impurity complexes). These defects may in turn influence properties of YSZ's. It is not surprising, therefore, that non-stoichiometry-induced defects are addressed in many experimental and theoretical investigations of YSZ's.

The zirconia-based materials made of nanoparticle composites represents a modern trend of development, since exhibit improved features compared to the materials of ordinary coarse-grained origin. In this case, further small-sized open-volume structures (of 1 to 100 nm size) can be introduced into the material and deserve detailed investigations, too: (i) defects associated with grain boundaries (GB's) – the GB-related vacancy-like defects, the larger open volumes at GB intersections, and (ii) intra- and/or intergranular pores.

Thus YSZ nanomaterials represent systems of rather complicated microstructure with a variety of open-volume structures of sizes ranging from 1 to hundreds of nanometers. Many of

these features are not satisfactorily understood yet although they apparently influence potentialities of their industrial use. Such a situation is a challenge for positron annihilation spectroscopy (PAS).

PAS is an efficient non-destructive tool of microstructure studies [2]. PAS relies upon the observation of annihilation of positron probes with electrons condensed matter. When energetic positrons are implanted into the material studied, they quickly reach thermal equilibrium (typically within 10^{-11} s in metals), then continue to move through the medium via quantum mechanical diffusion and, eventually, annihilate an environmental electron. The annihilation event is accompanied by the emission of hard γ -quanta which convey useful information. During the diffusion stage, positrons may get trapped in defects, i.e., the initially non-localized positron wave obtains a strongly localized pattern concentrated in the defect. The two wide-spread PAS techniques are positron lifetime (PL) measurements and Doppler broadening of annihilation radiation. The measured PL (the inverse of annihilation rate) reflects the local electron density at the positron annihilation site. Hence, annihilations from different positron states (delocalized/trapped positrons, different defect sites) lead to a multicomponent PL spectrum. According to the lifetime spectrum measured, occurrence of positron trapping can be detected and the defects type and concentrations can be deduced. The PL technique is primarily capable to detect small-sized open-volume defects with a high sensitivity, e.g., monovacancies of a concentration as low as 10^{-6} at. $^{-1}$ in metals what is difficult or even impossible to be done by other observations.

Apart from several PAS investigations on YSZ nanomaterials performed so far [3–6], there is still a lack of a reliable knowledge and unambiguous interpretation of PAS data. The reason is in the above stated complexity of the microstructure of YSZ nanomaterials probed by positrons as well as in an insufficient quality of experimental data.

In the present work, the pressure-compacted YSZ nanopowders, differing in phase, have been investigated by means of high-resolution positron lifetime (PL) spectroscopy. Preliminary results obtained on YSZ nanopowders have recently been reported as a Conference Contribution [7]. The goal this investigation consists in making use from a comparison of nanopowder data with those obtained for similar systems of less complex structure. Therefore, PL measurements on sintered powders as well as on respective monocrystalline YSZ were performed. The PL data observed in these materials are discussed from the point of defects involved. For this purpose, PL measurements were also supplemented with the theoretical calculations on the respective systems.

2. Experimental

2.1 Specimens

The three zirconia-based nanosize powders were used in the present investigation: (i) the pure ZrO_2 (monoclinic phase, further referred to as Z0Y), (ii) the ZrO_2+3 mol.% Y_2O_3 (tetragonal, Z3Y) and (iii) the ZrO_2+8 mol.% Y_2O_3 (cubic, Z8Y). XRD and TEM characterizations revealed the mean grain size of the starting powders as 23.2, 17.6 and 15.6 nm, respectively. The powder preparation procedure has been described in details elsewhere [8]. After calcination at 700 °C, powders were pressure-compacted under 250 MPa at room temperature into tablets of 15 mm diameter and ≈ 5 mm thickness. The Z3Y and Z8Y ceramic specimens, were obtained by sintering the compacted nanopowders at 1200 °C/1 h and 1350 °C/1 h, respectively. The YSZ monocrystals of tetragonal (3 mol.% Y_2O_3) and cubic (8 mol.% Y_2O_3) phase were involved in the present PL study, too.

2.2 Measurements

The fast-fast version of a PL spectrometer described in Ref. [9] was employed in the present investigation. A positron source contained a 1.3 MBq of a carrier-free $^{22}\text{Na}_2\text{CO}_3$ water solution (iThemba Labs), dried and sealed between two 4 μm MylarC foils (Dupont). The source was sandwiched with two pieces of the material studied. Using this source, the PL spectrometer exhibited the time resolution of 163÷168 ps (FWHM) for the 1274 – 511 keV ^{22}Na coincidences. At least 10^7 counts were accumulated in each PL spectrum at a rate of typically ≈ 80 coincidence events per second. All the PL measurements were performed in air at room temperature. The accumulated PL spectra were decomposed into the discrete components by means of the maximum likelihood method described in [9]. The contribution from positron annihilations in the source salt and covering foils was subtracted on the basis of reference PL measurements with a well-annealed α -iron specimen.

3. Results and discussion

Resulting PL's and relative intensities of the individual components (τ_i , I_i , $i=1,\dots,4$) were summarized in Table 1. Not shown in the Table are the source+foils and para-positronium (pPs) components. Besides pPs, up to four components belonging to positron annihilations in the studied samples could be resolved in the measured PL spectra. The pPs component (τ_{pPs} fixed at 0.125 ns) was assumed to contribute by one third of the total ortho-positronium (oPs) intensity observed.

Table 1 Positron lifetime results on zirconia-based materials studied in the present work (positron lifetimes τ_i , intensities I_i , $\sum I_i=100\% - I_{\text{pPs}}$). The errors (standard deviations) are shown in parentheses in the units of the last significant digit. Samples are abbreviated in the 1st column in the same manner as in the text.

Sample	τ_1 [ns]	I_1 [%]	τ_2 [ns]	I_2 [%]	τ_3 [ns]	I_3 [%]	τ_4 [ns]	I_4 [%]
powd. Z0Y	0.189(2)	45(1)	0.373(4)	44(1)	2.0(1)	1.54(5)	34(2)	7.4(3)
powd. Z3Y	0.184(3)	35(1)	0.383(3)	55(1)	2.1(2)	0.96(5)	34(2)	6.4(3)
powd. Z8Y	0.184(4)	29(1)	0.371(3)	61(1)	2.0(2)	0.99(6)	32(2)	6.4(3)
sint. Z3Y	0.157(5)	47(9)	0.219(5)	53(9)				
sint Z8Y	0.180(1)	100						
mono. Z3Y	0.168(1)	85(2)	0.26(1)	15(3)				
mono. Z9Y	0.175(1)	100						

There were two different interpretations of the two shortest lifetime components, τ_1 and τ_2 , reported for the nanopowder samples in the earlier literature [4–6]. While Wang et al. [4] suggested the shorter components to arise mainly from the annihilation of positrons *inside* nanograins, authors [5,6] related these components to the GB's rather than to the grain interior. In our paper [7], the latter interpretation was given further support by the apparent correlation of $I_2 : I_1$ ratios with the mean particle size. The observed behaviour of the ratios then can be understood assuming that positrons in nanopowders annihilate predominantly either in the vacancy-like defects at grain surface (the τ_1 -component) or in larger open-volume defects associated probably with triple points at GB intersections (the τ_2 -component).

A further support of this concept for nanopowders has come in this work from the PL measurements on the sintered ceramic materials and monocrystalline specimens. The data on the sintered specimens shown in Table 1 exhibit a pattern which is significantly different from that for the nanopowder materials and resembles more the results obtained for the corresponding monocrystalline specimens, see Table 1. This is pronounced especially for the cubic polymorph

and can be regarded as another argument favouring our above interpretation of the two shortest lifetime components in the nanopowder materials. The GB's contribution is indeed suppressed after sintering and positron annihilation in the grain interior, which microstructure is naturally more similar to that of the respective monocrystals, become dominating. On the other hand, the interpretation of lifetime τ_1 , observed for the monocrystalline specimens, is far not straightforward. As shown in our recent study [10], slightly shorter bulk lifetimes are suggested by theoretical calculations for zirconia polymorphs. A more open structure of the lattice due to the non-stoichiometry-introduced oxygen vacancies in the YSZ system can hardly be taken as a possible cause of this discrepancy. Moreover, very short positron diffusion lengths observed in slow-positron beam experiments [11] suggest dominating role of positron trapping. A likely candidate for positron trapping centre may appear the oxygen vacancy-yttrium (V_O -Y) complex. Indeed, the overall picture may become much more complex due to the possible contributions of other defect configurations [10] and to trapping/detrapping of positrons from the oxygen vacancies and the other shallow defects, which cannot be fully excluded.

In order to have a more definite idea about the positron lifetime corresponding to V_O -Y complexes, we relaxed atomic positions of the V_O -Y defect in the second nearest neighbour configuration using the VASP code [12] (Vienna ab initio simulation package) considering neutral charge state of the defect. The resulting atomic configuration served as input for atomic superposition calculations [13]. The positron lifetime amounted to 166 ps when considering electron-positron correlations in the form [14]. This lifetime is not so far from the measured experimental value and indicate that V_O -Y complexes could be responsible for the component detected in experimental PL spectra in YSZ systems.

The nature of the τ_2 -components observed in the tetragonal monocrystal and sintered specimens remains also yet unclear. It seems obvious, that contrary to the cubic monocrystal, the tetragonal monocrystal contains open volume defects, which can trap positrons and are not occurring in the corresponding specimens with the cubic structure. Due to the above mentioned metastability of the tetragonal phase, however, the thermal history of the specimens is an important factor in this kind of studies. Misfit defects at phase boundaries can be tentatively considered as a cause of positron trapping. Extended investigations seem to be necessary to clarify this picture.

An appreciable amount of pores is indicated by the oPs τ_4 -component observed in the nanopowder specimens, shown Table 1. On the other hand, similar components were found to be absent in the sintered materials. Indeed, the sintering process of ceramics, in which the surface energy is to be lowered, is accompanied by a volume shrinkage connected with the disappearance of pores. Our observations are consistent with such a picture.

A behaviour of the long lifetime components during sintering process resembling the differences between the nanopowder and sintered materials shown in Table 1 was observed by Yagi et al. [5] on the system of a slightly different composition: $ZrO_2 + 2 \text{ mol.}\% Y_2O_3$. In their work, sintering is seen by PAS as a gradual transformation of the two components in the $\tau < 0.5 \text{ ns}$ region into the single-component lifetime spectrum ($\tau \approx 170 \text{ ps}$) and a vanishing of the oPs components above 1100°C .

4. Conclusions

Positron lifetime (PL) spectra exhibited by the pressure-compacted nanopowders and sintered ceramics of yttria-stabilized zirconia polymorphs were measured with a high time resolution and a high counting statistics in the present work. PL data on corresponding monocrystalline specimens were collected for comparison, too. It is concluded that positrons

annihilate mainly as trapped in defect structures associated with grain boundaries (vacancy-like defects, triple points) in the nanopowder materials, whereas annihilation in grain interiors becomes gradually dominate in the sintered specimens. Finally, a remark can be made on utility of PAS for observation of sintering. Beside a 'traditional' approach utilizing the orthopositronium porosity components, the sintering process of zirconia-based nanoceramics may be followed also via the shorter lifetime components (< 0.5 ns) if a sufficiently high-resolution PL spectrometer is involved and a large counting statistics is acquired. Generally, the latter approach is interesting and deserves a more attention in the future because it might bring a new information about the details of grain boundary evolution during the sintering ceramic materials.

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Literature

- [1] <http://www.americanelements.com>
- [2] Hautojärvi P., Corbel C., in: Positron Spectroscopy of Solids, Proc. Int. School of Physics «Enrico Fermi», Course CXXV, Varenna (Italy) 1993, Eds. Dupasquier A., Mills A.P., Jr., IOS Press, Amsterdam 1995, p. 491.
- [3] Ito K., Yagi Y., Hirano S., Miyayama M., Kudo T., Kishimoto A., Ujihira Y., Journ. Ceram. Soc. Japan 107, 123 (1999).
- [4] Wang Z., Chen Z.W., Zhu J., Wang S.J., Guo X., Radiat. Phys. Chem. 58, 697 (2000).
- [5] Garay J.E., Glade S.C., Asoka-Kumar P., Anselmi-Tamburini U., Journ. Appl. Phys. 99, 024313 (2006).
- [6] Yagi Y., Hirano S., Ujihira Y., Miyayama M., Journ. Mater. Sci. Let. 18, 205 (1999).
- [7] Cizek J., Melikhova O., Kuriplach J., Prochazka I., Konstantinova T.E., Danilenko I.A., *phys. stat. solidi (c)* 4 (2007), DOI 10.1002/pssc.200675844.
- [8] Konstantinova T., Danilenko I., Pilipenko N., Dobrikov A., in: *9th Cimtec – World Ceramics Congress. Ceramics: Getting into the 2000's – Part A*, edited by Vicenzini P., Techna Srl. 1999, p. 305. Slipenyuk A.M., Glinchuk M.D., Bykov I.P., Ragulya A.V., Klimenko V.P., Konstantinova T.E., Danilenko I.A., *Ferroelectrics* 298, 289 (2004).
- [9] Becvar F., Cizek J., Lestak L., Novotny I., Prochazka I., Sebesta F., Nucl. Instrum. Methods A 443, 557 (2000).
- [10] Melikhova O., Kuriplach J., Cizek J., Prochazka I., Anwand W., Brauer G., Konstantinova T.E., Danilenko I.A., *phys. stat. solidi (c)* 4 (2007), DOI 10.1002/pssc.200675858.
- [11] Grynszpan R.I., Saude S., Mazerolles L., Brauer G., Anwand W., Radiation Phys. Chem. 76, 333 (2007).
- [12] Kresse G., Hafner J., Phys. Rev. B 47, 558 (1993); *ibidem* B 49, 14251 (1994); Kresse G., Furthmüller J., Comput. Mat. Sci. 6, 15 (1996); Kresse G., Furthmüller J., Phys. Rev. B 54, 11169 (1996).
- [13] Puska M.J., Nieminen R.M., Journ. Phys. F: Metal. Phys. 13, 333 (1983). Seitsonen A.P., Puska M.J., Nieminen R.M., Phys. Rev. B 51, 14057 (1995).
- [14] Boroński E., Nieminen R.M., Phys. Rev. B 34, 3820 (1986). Puska M.J., Mäkinen S., Manninen M., Nieminen R.M., Phys. Rev. B 39, 7666 (1989).