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PALS study on the defect structure of yttria-stabilized zirconia

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Abstract

Powders of stabilized ZrO_2–8 mol% Y_2O_3 (YSZ) have been obtained by mechanical milling in zirconia vials. The samples were characterized by X-ray diffraction (XRD). Positron annihilation lifetime (PALS) measurements were performed to investigate the lattice defects originated by the incorporation of yttria and those mechanically induced. The XRD results indicate the formation of tetragonal YSZ solid solution. PALS results indicate that positron trapping occurs at different kinds of defects such as vacancy-like defects, grain boundary and associated defects.
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1. Introduction

The strategic functional zirconia material has found extensive application in electrochemical devices, such as gas sensors, solid oxide fuel cells and water hydrolysis cells (Wang et al., 2000; Guo and Zhang, 2003). When a trivalent oxide, e.g. Y_2O_3, is added to ZrO_2 as stabilizer, lattice defects like oxygen vacancies V_O^{2+} and negatively charged substitutional solutes Y_{Zr}^- are created in the ZrO_2 lattice. The conductivity of stabilized ZrO_2 is determined by the defect structure, including V_O^{2+}, Y_{Zr}^- and negatively charged or neutral defect associates. The reactions of the defect production can be summarized as follows (Wang and Nowick, 1981):

$$Y_2O_3 \rightarrow 2Y_{Zr}^- + V_O^{2+} + 3O_O,$$
$$Y_{Zr}^- + V_O^{2+} \rightarrow (Y_{Zr}^- V_O^{2+})^+,$$
$$(Y_{Zr}^- V_O^{2+})^+ + Y_{Zr}^- \rightarrow (Y_{Zr}^- V_O^{2+} Y_{Zr}^-)^0.$$

Mechanical milling has proved to be an effective processing technique to produce nanocrystalline materials. Under milling, the powders are subjected to severe plastic deformation giving rise to particle and grain refinement, creating, simultaneously, different kinds of defects (Koch, 1989, Weeber and Bakker, 1988).

The positron annihilation lifetime (PALS) technique is based on the measurement of the positron lifetime inside the studied material (Brandt and Dupasquier, 1983; Hautojarvi, 1979). After the positron reaches the thermal equilibrium with the host material, it eventually annihilates an electron leading to the emission of gamma rays, which gives the experimental information. The annihilation can take place in interstitial regions characterized by an extended Bloch state (free state) or as trapped positrons in a bound state. Different kind of defects (such as monovacancies, larger vacancy clusters, dislocations) can act as trapping centres but only neutral or negatively charged ones can be effective positron traps (Puska and Nieminen, 1994).

Preliminary results on positron lifetime parameters in the ZrO_2–8 mol% Y_2O_3 stabilized system prepared by mechanical milling are presented. X-ray diffraction (XRD) was employed to identify the phases. The starting powder oxides and the single crystal were also studied.

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2. Experiments

The ZrO_2–8 mol% Y_2O_3 single crystal was commercially obtained from Swaroswski. Accurate amounts of ZrO_2 (99%) and Y_2O_3 (99.99%) commercial powders from Aldrich were mechanically milled to obtain 8 mol% yttria-stabilized zirconia (YSZ). The milling, in air atmosphere, was performed in a Retsch MM2 horizontal vibratory mill for 70 h at a frequency of 30 Hz. In order to avoid contamination during milling, zyrconia vials and balls were used with a ball-to-powder mass ratio of 10:1. The powder samples were uniaxially pressed at 20 kN in 8 mm diameter pellets. The YSZ pellets were also annealed at 1200 °C for a 1 h.

XRD patterns were recorded with a Philips PW1710 diffractometer using CuK_α radiation ($\lambda = 1.5418$ Å) in the $10^\circ \leqslant 2\theta \leqslant 100^\circ$ range at 0.02°/s.

PALS measurements were done at room temperature in a conventional fast–fast coincidence system with two plastic detectors. The time resolution (FWHM) was 260 ps and 3×10^6 counts were accumulated for each spectrum. The radioactive source, $^{22}NaCl$ (10 μCi), was deposited onto a kapton foil (1.42 g/cm^3) and sandwiched between two sample specimens. The source contribution (17% of 386 ps for the annihilation in kapton foil and 1% of 2.0 ns) and the response function were evaluated from a reference sample (Ni metal) using the RESOLUTION code (Kirkegaard and Eldrup, 1972, 1974).

3. Results and discussion

Fig. 1 shows the XRD patterns obtained after 10 and 70 h of milling. A mixture of phases are present at low milling times: a cubic phase and or tetragonal phases corresponding to Fm3m and P42/nmc space groups, respectively, and also the monoclinic phase. Only the tetragonal phase is observed after 70 h of milling indicating the incorporation of yttrium into the crystal structure of ZrO_2. A reduction of the crystallite size is noticed from the wide width of the diffraction peaks.

The PALS lifetime spectra were decomposed into three exponential decays, $n(t) = \sum_i I_i \exp(-t/\tau_i)$, each being positron state characterized by a positron lifetime, τ_i, with a certain intensity, I_i ($\sum_i I_i = 1$). In all cases, the long lifetime component ($1.6 < \tau_3 < 2.0$ ns with intensity less than 1%) is assigned to positron annihilation in the source itself.

The positron lifetime parameters determined for all the samples are displayed in Fig. 2. In order to analyse the YSZ samples, the average positron lifetime defined by $\tau_{av} = \sum_i I_i \tau_i$ was evaluated since it is a useful parameter, almost independent of data treatment. From this statistical parameter, one can extract

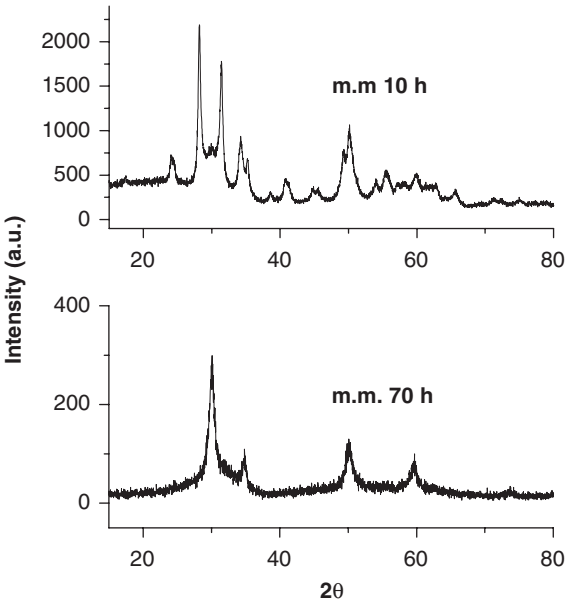

Fig. 1. X-ray diffraction patterns for ZrO_2–8 mol% Y_2O_3 after 10 and 70 h of milling.

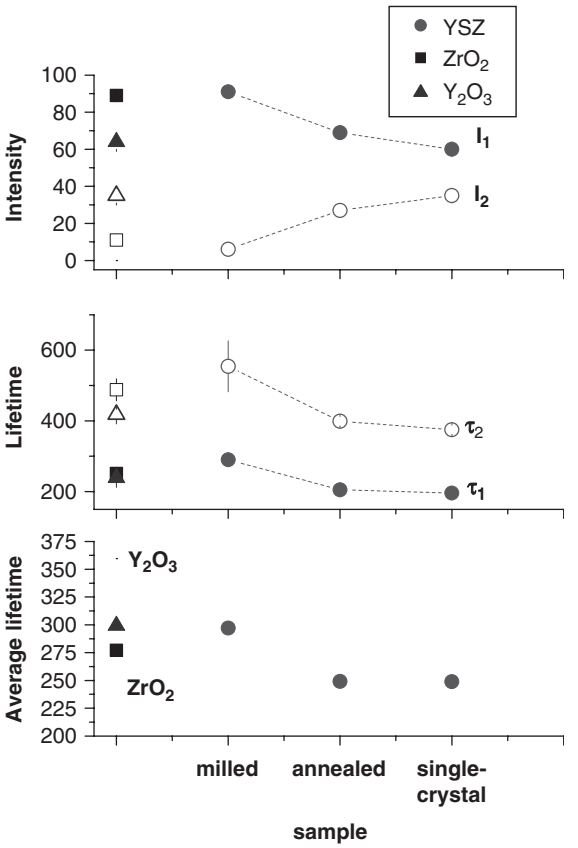

Fig. 2. Positron annihilation parameters for the different analysed samples. Full (open) symbols indicate first (second) lifetime component.

information about positron trapping when a separation in different component with similar positron lifetime is not possible.

Fig. 2 also shows the average lifetime of all samples, decreasing its value from ~300 ps for milled and starting powders samples to 250 ps corresponding to the single crystal.

Two main components are found for the single-crystal specimen, the first being lifetime ($\tau_1 = 196$ ps) assigned to bulk annihilation, although its value is higher than recent theoretical calculations for similar oxides (~140 ps as reported by Kuriplach et al., 2005). Meanwhile, the second annihilation component ($\tau_2 = 370$ ps) takes into account some intrinsic defects due to sample preparation and usually present in this kind of material.

The obtained values, $\tau_1 = 239_6$ ps for Y_2O_3 and $\tau_1 = 251_2$ ps for ZrO_2 starting powders, are rather high for bulk positron lifetime even for an oxide material. Unfortunately, no references data are available in the literature for these oxides unless a value of 170 ps attributed to positron lifetime in zirconia grains obtained after annealings at 1200 °C of partially stabilized zirconia by Yagi et al. (1999). Moreover, experimental and calculated values for positron lifetime between 200 and 300 ps are usually ascribed to cation vacancies in different metal oxides (Puska and Nieminen, 1994; Tuomisto et al., 2003; Macchi et al., 2001). Fuertes et al. (2004) found a similar value for τ_1 on studying the La_2O_3–ZrO_2 system prepared by mechanical milling. In consequence, this first lifetime component may be considered as a mean value of bulk annihilation and a vacancy-like trapping centre.

Regarding the second lifetime, τ_2, higher than 400 ps, and that the kapton source correction has a similar lifetime value (386 ps) but with a corresponding intensity higher than in the reference sample, the defect assignment to this lifetime could not be unambiguously done. However, it is known that large open volumes defects like microvoids give place to positron lifetimes of about 500 ps (Kajcsos et al., 2001). The presence of this kind of defects is expected in porous ceramics, like the starting oxides and milled pellets. The above discussion is also valid for the milled sample since similar positron annihilation parameters were observed.

For the sample annealed 1 h at 1200 °C, a gradual recovery of the single-crystal annihilation parameters is observed.

In consequence, for all the studied powder samples, it is tempting to associate τ_1 with a mean value of bulk annihilation and a vacancy-like trapping centre and τ_2 with a higher size defect site. Moreover, the formation of $(Y_{\bar{Z}r}V_O^{2+}Y_{\bar{Z}r})^0$ was previously reported (Subbarao and Maiti, 1984; Butler et al., 1981; Mackrodt and Woodrow, 1986; Yashima et al., 1992) in agreement with our results.

4. Conclusion

Powders of ZrO_2–8 mol% Y_2O_3 have been obtained by mechanical milling with the tetragonal structure. The PALS results on milled samples indicate that positron annihilation occurs in vacancies and in large open volume defects like vacancy-clusters and microvoids.

The comparison of the results obtained for the single-crystal and the annealed YSZ sample indicates a recovering of the defects produced by milling on heating. New studies are in progress to perform a better identification of the τ_2 sites.

References

Brandt, W., Dupasquier, A. (Eds.), 1983. In: Positron Solid State Physics. North-Holland Publishing Co., Amsterdam.

Butler, V., Catlow, C.R.A., Fender, B.E.F., 1981. The defect structure of anion deficient ZrO_2. Solid State Ionics 5, 539–542.

Fuertes, M.C., Salgueiro, W., Somoza, A., Porto López, J.M., 2004. Thermal evolution of La^{3+}/ZrO_2 solid solutions obtained by mechanochemical activation. Scripta Mater. 50, 301–305.

Guo, X., Zhang, Z., 2003. Grain size dependent grain defect structure: case of doped zirconia. Acta Mater. 51, 2539–2547.

Hautojarvi, P., 1979. In: Positrons in Solids. Spring, Berlín.

Kajcsos, Zs., Duplâtre, G., Liszkay, L., Lázar, K., Lohonyai, L., Pál-Bobeley, G., 2001. Positron and positronium in zeolitas. Mater. Sci. Forum 363–365, 238.

Kirkegaard, P., Eldrup, M., 1972. POSITRONFIT: a versatile program for analysing positron lifetime spectra. Comput. Phys. Commun. 3, 240.

Kirkegaard, P., Eldrup, M., 1974. Positronfit extended: a new version of a program for analysing position lifetime spectra. Comput. Phys. Commun. 7, 401.

Koch, C.C., 1989. Materials synthesis by mechanical alloying. Annu. Rev. Mater. Sci. 19, 121.

Kuriplach, J., Melikhova, O., Brauer, G., 2005. Basic positron properties of oxides: a computational study. In: Eighth International Workshop on Positron and Positronium Chemistry, Coimbra, Portugal.

Macchi, C., Somoza, A., Dupasquier, A., López García, A., Castro, M., 2001. Positron trapping in $BaTiO_3$ perovskite. J. Phys.: Condens. Matter 13, 5717–5722.

Mackrodt, W.C., Woodrow, P.M., 1986. Theoretical estimates of point defect energies in cubic zirconia. J. Am. Ceram. Soc. 69, 277–280.

Puska, M.J., Nieminen, R.M., 1994. Theory of positrons in solids and on solid surfaces. Rev. Mod. Phys. 66, 841.

Subbarao, E.C., Maiti, H.S., 1984. Solid electrolytes with oxygen ion conduction. Solid State Ionics 11, 317–338.

Tuomisto, F., Ranki, V.K., Saarinen, Look, D.C., 2003. Evidence of the Zn vacancy acting as the dominant acceptor in n-type ZnO. Phys. Rev. Lett. 91, 205502.

Wang, D.Y., Nowick, A.S., 1981. Dielectric relaxation from a network of charge defects in dilute CeO_2: Y_2O_3 solid solutions. Solid State Ionics 5, 551–554.

Wang, Z., Chen, Z.Q., Zhu, J., Wang, S.J., Guo, X., 2000. Evidence of defect associates in yttrium-stabilized zirconia. Radiat. Phys. Chem. 58, 697–701.

Weeber, W.A., Bakker, H., 1988. Amorphization by ball milling. A review. Physica B 153, 93.

Yagi, Y., Hirano, S., Ujihira, Y., Miyayama, M., 1999. Analysis of the sintering process of 2 mol% yttria-doped zirconia by positron annihilation lifetime measurements. J. Mater. Sci. Lett. 18, 205–207.

Yashima, M., Ishizawa, N., Yoshimura, M., 1992. Application of an ion-packing model based on defect clusters to zirconia solid solutions: I, modeling and local structure of solid solutions. J. Am. Ceram. Soc. 75, 1541–1549.