PALS study on the defect structure of yttria-stabilized zirconia

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Abstract

Powders of stabilized ZrO$_2$–8 mol% Y$_2$O$_3$ (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.

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$_2$O$_3$, is added to ZrO$_2$ as stabilizer, lattice defects like oxygen vacancies V$_{O}^{2+}$ and negatively charged substitutional solutes YZr are created in the ZrO$_2$ lattice. The conductivity of stabilized ZrO$_2$ is determined by the defect structure, including V$_{O}^{2+}$, YZr and negatively charged or neutral defect associates. The reactions of the defect production can be summarized as follows (Wang and Nowick, 1981):

\[ Y_2O_3 \rightarrow 2YZr + V_{O}^{2+} + 3O_2, \]
\[ YZr + V_{O}^{2+} \rightarrow (YZrV_{O}^{2+}), \]
\[ (YZrV_{O}^{2+})^+ + YZr \rightarrow (YZrV_{O}^{2+}YZr)_0. \]

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$_2$O$_3$ 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.
2. Experiments

The ZrO$_2$–8 mol% Y$_2$O$_3$ single crystal was commercially obtained from Swarowski. Accurate amounts of ZrO$_2$ (99%) and Y$_2$O$_3$ (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, zirconia 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$_\alpha$ radiation ($\lambda$ = 1.5418 Å) in the $2\theta = 10^\circ$–$80^\circ$ 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 $3 \times 10^6$ 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, $n(t) = \sum I_i \exp(-t/\tau_i)$, each being positron state characterized by a positron lifetime, $\tau$, with a certain intensity, $I_i (\sum I_i = 1)$. In all cases, the long lifetime component ($1.6 < \tau < 2.0$ 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 $\langle \tau \rangle = \sum I_i/\tau_i$ was evaluated since it is a useful parameter, almost independent of data treatment. From this statistical parameter, one can extract...
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 Kurilplach 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, $\tau_1 = 239_{8}$ ps for Y$_2$O$_3$ 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 $\tau_1$ on studying the La$_2$O$_3$–ZrO$_2$ system prepared by 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, $\tau_2$, higher than 400 ps, and that the kapon 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 $\tau_1$ with a mean value of bulk annihilation and a vacancy-like trapping centre and $\tau_2$ with a higher size defect site. Moreover, the formation of (Y$^2_0$Z$^0_0$) 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$_2$O$_3$ 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 $\tau_2$ sites.

References


