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Positron annihilation study of defect distribution in 8YSZ nanostructure

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ABSTRACT

The impact of the interfacial contribution on overall properties increases with decreasing grain size of polycrystalline materials. It is well known that distribution and size of cluster defects are rather different in bulk than grain boundaries. In light of "bottom-up" approaches, a study at the atomic level determining the distribution of crystallographic defects could clarify their contribution to the macroscopic properties, and then differentiate materials for outstanding or precise applications. In this work, Positron Annihilation Spectroscopy (PAS) is used to characterize the distribution of defects within 8 mol% Y_2O_3-stabilized zirconia (8YSZ) structures prepared by sintering through three different thermal treatments, i.e. a conventional thermal cycle in air and N_2/H_2 atmosphere, and a fast firing cycle in air, which lead to average grain sizes <260 nm.

1. Introduction

The description of size effects and associated conduction mechanisms is a main objective of research within nano-ionics [1,2]. Although the morphological characteristics of powders and materials prepared need further optimization, the discovery of electronic conductivity and large oxygen diffusivity at low temperatures, when the grain size is within the nanometric range in traditional ionic conductors [3,4], opened up a very exciting prospect of study inside the field [5].

In materials with fine grain size the density of grain boundaries is extremely high and transport along the grain boundaries might become dominant. Furthermore, in such materials the space charge regions adjacent to the grain boundaries might play a significant role. In fact, when grain size approaches width of space charge region (Debye screening length, λ), defects distribution significantly differs from the one characteristic of regular bulk materials. For small grains, local charge neutrality is not satisfied anywhere [4].

Otherwise, the concept of grain boundary regions supporting a fast ionic transport mechanism is still poorly understood [4–8]. The explanation for enhanced conduction at boundaries is also related to the formation of the space charge regions adjacent to the core in the grain boundaries. Bulk ionic defects with charge like to that of the boundary core will be depleted while those with opposite charge will be accumulated in the space charge region. If the bulk defect with high mobility is accumulated in the space charge region, the overall conductivity of the solid should increase. So, results reported in the literature suggest that grain boundaries can play a significant role in changing from ionic to electronic conductivity [9]. For example, oxygen vacancy distribution in a nano-structured zirconia based material determines phenomena such as ionic conductivity, electronic conductivity and, moisture-induced degradation [10,11] or protonic conduction, due to water incorporation in the zirconia lattice [12,13]. Efficient method and material strategies of directing or enhancing the space-charge effects, such as the introduction of interfaces or doped grain boundaries with surface active second-phase particles, have been successfully proposed [1].

However, description of macro-sized effects of the atomic architecture design is still challenging. It is evident that control of dimensions on the nanoscale has a profound influence on performance. Preparation of nanostructured materials has been made possible through the development of synthesis, processing and sintering routes, but direct characterization of prepared structures has still to be explored. Positron Annihilation Spectroscopy (PAS) was used to investigate the effects of sintering conditions on the microstructural features of the Y_2O_3-stabilized zirconia samples (YSZ). PAS is a non-destructive successful technique used to study the occurrence, nature and evolution of defects in solids [14,15], particularly lattice point defects, which cannot be detected by other techniques. PAS takes advantage of the fact that positrons are attracted to atomic-size open-volumes, where positively charged atomic nuclei are missing [16], that act as trapping centers for positrons that subsequently annihilate with electrons in that area. As a result of trapping, measurable changes in the positron annihilation

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characteristics are seen that make the identification of vacancy-type defects straightforward [17]. When an energetic positron from a radioactive isotope source enters a solid, it loses most of its energy by collisions with electrons and ions within a few ps, to reach a level of energy of the order of $k_B T$ (k_B is the Boltzmann factor and T is the temperature of the solid). Then it diffuses into the material for a length L_+ of the order of 100 nm [16] (≈150 nm according to Ref. [18]) until annihilates by interaction with an electron, after its specific lifetime in the crystal, giving off information about the annihilation site. The whole diffusion distance is of the order of magnitude of 100 μm and the information is in the form of gamma rays, giving the positron–electron annihilation primarily two 511 keV gamma rays travelling in opposite directions (in the center of mass frame) [19]. Positron lifetime (PL) and coincidence Doppler broadening (CDB) modes of PAS were used in the present work. PL reflects the local electron density at the annihilation site and gives information about the size of the positron traps and their concentration. The CDB measurements of the annihilation radiation provide data about the momentum distribution of electrons taking part in the positron–electron annihilation. The energies of the two emitted 511 keV photons present a blueshift and a redshift (Doppler broadening) in the laboratory frame related to the momentum of the electron–positron pair prior to positron annihilation. The energy shift of each of the two photons is given by:

$$\Delta E = p_L c / 2 \tag{1}$$

where p_L is the longitudinal momentum shift and c is the speed of light. The shifts of the two photons are measured simultaneously in CDB. Since the thermalized positron has an almost zero momentum, and each element has its own characteristic orbital electron momentum spectrum [19], then a measure of Doppler effect of the annihilation radiation supplies information on the electronic structure of materials and the chemical surroundings of the annihilation sites [18].

The PAS technique has been used previously for characterizing ceramics [20–23] including zirconia [18,19,24,25]. It turned out to be an important tool of investigation of nanostructed YSZ materials [18], being the study of the interaction of positrons with point defects and grain boundaries in zirconia useful to get a deeper insight into the microstructure of such complicated systems.

When the trivalent oxide Y_2O_3, is added to ZrO_2 as stabilizer, lattice defects like oxygen vacancies and negatively charged substitutional solutes are created in the ZrO_2 lattice. The defect reaction can be written, using the Kröger–Vink notation for point defects [26], as:

$$Y_2O_3 \xrightarrow{ZrO_2} 2Y'_{Zr} + 3O_O^X + V_O^{\bullet\bullet} \tag{2}$$

$V_O^{\bullet\bullet}$ and Y'_{Zr} having, respectively, +2 and −1 charge respect to the lattice, represent the main defects in bulk zirconia. However, because of coulombic interaction between charged defects, a large amount of negative oxygen vacancies and vacancy-solute atom complexes result in the lattice. At low temperatures only a relatively small fraction of free oxygen vacancies are present as unassociated [19]. The majority tends to be present as associated with substitutional yttrium, forming $Y'_{Zr}V_O^{\bullet\bullet}$ [27,28] complexes at low yttrium concentration and more complex associates, such as $Y'_{Zr}V_O^{\bullet\bullet}Y'_{Zr}$, with a higher yttrium concentration [19]. Due to their strong positive charge, $V_O^{\bullet\bullet}$ are not likely to attract positrons, but the associated defects $Y'_{Zr}V_O^{\bullet\bullet}$ and $Y'_{Zr}V_O^{\bullet\bullet}Y'_{Zr}$ have a low or no positive charge and so can interact with positrons. Other possible defects with a negative charge, such as V''''_{Zr} occur in low concentrations [19].

In nanocrystalline materials grain boundaries and defects associated with them have a significant role in Positron Annihilation Spectroscopy. In fact, being the positron diffusion length L_+ comparable to the mean grain size, positrons thermalized inside the grains can easily reach grain boundaries during their lifetime by their diffusion motion, thus probing those regions and becoming trapped there. It is known that grain boundaries in compacted nanocrystalline powders have a highly defective structure with a high density of open-volume defects [29]. Hence, one can expect that positrons become trapped and annihilate in these open-volume sites [18]. In ionic materials the grain boundary core is characterized by a fairly strong positive charge with a concomitant negatively charged space-charge region that compensates the positive potential. In YSZ the latter region is proved to be characterized by low oxygen vacancy concentration and a correspondingly high yttrium-ion concentration [19], thus being a likely trapping region for positrons. The positive grain boundary core repels positron, but the size of the potential barrier (a few tenths of eV) does not prevent positrons from getting trapped in much deeper positron potential wells at the space charge zone of the grain boundaries [10,18,30].

2. Experimental

2.1. Preparation and crystallographic/morphologic characterization of YSZ powders and compacts

The following commercially available cubic ZrO_2 stabilized with 8 mol% Y_2O_3 nanocrystalline powders (8YSZ, Nanostructured & Amorphous Materials, Inc., USA) was used as starting material, with a mean particle size of 60 nm and the following chemical analysis (wt.%): Y_2O_3 (13.3), HfO_2 (2–3), Al_2O_3 (0.01), Fe_2O_3 (0.01), SiO_2 (0.02) and Na_2O (0.01).

The specific surface area of the powders and density were measured by one point N_2 adsorption (monosorb, Quantachrome, USA) and He-multipicnometer (Quantachrome, USA), respectively. The errors of those techniques are ±5% and ±10%, respectively. The particle size distribution and the zeta potential of nanoparticles were determined by dynamic light scattering and laser Doppler velocimetry, respectively (Zetasizer Nano ZS, Malvern S, UK). In order to carry out particle size distribution and zeta potential measurements, basic aqueous suspensions ($pH = 9$) of 8YSZ powders with solid contents of 10^{-3} g l^{-1} were prepared.

The green compacts were obtained by cold isostatic pressing (CIP) of powders at 200 MPa. In order to select the optimum temperature range to obtain sintered 8YSZ samples with high porosity, dynamic sintering experiments were performed on prismatic samples (6 mm × 4 mm × 4 mm) using a push-rod dilatometer (Netzsch, Germany) in air or under flowing atmosphere of N_2/10 vol.% H_2. Tests were recorded at temperatures up to 1450 °C at heating and cooling rates of 5 °C min^{-1}. Two hours dwell thermal treatment at 1250 °C, using 5 °C min^{-1} as heating and cooling rates, was performed in N_2/H_2 (8YSZ-N_2/H_2) and air (8YSZ-Air) atmospheres. A fast firing cycle (FF) [31] in air was also considered (8YSZ-FF). The FF cycle was composed of a fast heating ramp of 20 °C min^{-1} up to a temperature of 1250 °C followed by a 20 hour dwell at 1150 °C after a cooling ramp of 15 °C min^{-1}. FF was performed in a tubular furnace with flowing atmosphere (Severn Furnaces Limited, UK) which uses a Eurotherm programmer. When it was necessary the sintering atmosphere was purged prior to heating by applying vacuum to the sealed tube and filling it with the desired gas. During the thermal cycle the gas flow was maintained. All the gases were of high purity standards.

Phase identification of the as-received powders and sintered samples was carried out by XRD with a diffractometer (D5000, Siemens, Germany) using a Cu Kα radiation collected at room temperature over a range of $20° \leq 2\theta \leq 80°$ at a step scan rate of 2°s^{-1}. The results were processed using the ASTM-Files 37–1484, 48–0224 and 82–1246 for monoclinic, tetragonal and cubic phases, respectively. Furthermore, phase identification was also performed by Raman Spectroscopy using the 514.5 nm excitation line from an Ar ion laser (Spectra Physics 163-M42-010) in backscattering geometry on a