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Nanoporous characterization of modified humidity-sensitive $MgO-Al_2O_3$ ceramics by positron annihilation lifetime spectroscopy method

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Abstract. Investigation of nanopores in the humidity-sensitive $MgO-Al_2O_3$ ceramics modified at 1100 °C for 2 hours was performed using positron annihilation lifetime spectroscopy method. Lifetimes of the third and fourth components of positron annihilation lifetime spectra obtained by four-component fitting procedure were used for calculation of nanopores radii. Transformation in free volumes was studied in ceramics after drying and exposure to water vapor. It is established that the lifetime of the third component decreases and the intensity of this component increases in ceramics exposed to water vapor reflecting ortho-positronium decay in nanopores simultaneously with annihilation in water bubbles. The characteristics of the fourth component (lifetime and intensity) decrease in ceramics exposed to water vapor reflecting ortho-positronium trapping in free-water volume of nanopores. Final drying of the $MgO-Al_2O_3$ ceramics results in returning of ortho-positronium lifetimes and intensities to the initial values confirming good desorption of water from nanopores of ceramics.

1. Introduction

Functional spinel $MgO-Al_2O_3$ ceramics are prospective nanoporous materials for humidity sensors [1-3]. It is known to have good chemical and thermal stability in comparison with other types of porous materials and short response time to humidity changes. As shown earlier [4,5], the functionality of humidity-sensitive ceramics is dependent on microstructure of grains, grain boundaries and open pores with different sizes. The latter significantly affect the functionality of humidity-sensitive ceramics.

Typically, microstructural properties of ceramic materials are studied using X-ray diffraction, electron microscopy, porosimetry methods etc. [6-11]. However, the methods of mercury and nitrogen porosimetry provide information on open pores with radius of >5 and > 2 nm, respectively [12,13]. Physical processes in ceramics depend not only on the number and nature of large open pores, but also on nanopores. Therefore, for more information on these structural components and their influence on the exploitation properties of technologically-modified $MgO-Al_2O_3$ ceramics, additional methods of structural characterization, which would allow to study free-volume entities on the nanoscale level are needed. In this case we used positron annihilation lifetime (PAL) spectroscopy technique to study free-volume transformation in spinel ceramics as an alternative to porosimetry methods [5]. As was shown earlier in [4,14], two channels of positron annihilation can be important in case of ceramics: positron trapping and ortho-positronium (o-Ps) decaying. The latter process (so called "pick-off" annihilation) resulting from Ps interaction with electron from environment (including annihilation in liquid water) is ended by emission of two γ-quanta. In general, these two channels of positron annihilation are independent. However, if trapping sites appear in a vicinity of grain boundaries neighboring with free-volume pores, these positron-Ps traps will become mutually interconnected resulting in a significant complication of PAL data [14].

In this work, characterization of nanopores in the MgO-Al_2O_3 ceramics obtained by annealing at 1100 °C for 2 hours are presented. O-Ps decay components extracted by four-component decomposition of positron annihilation lifetime spectra in ceramics are analyzed for different conditions such as drying and exposure to water vapor.

2. Experimental details

The studied MgO-Al_2O_3 ceramics was sintered at 1100 °C for 2 hours using traditional ceramic technology [15]. The PAL studies were performed using ORTEC spectrometer with ^{22}Na source at 22 °C and relative humidity of 35 %. Investigations were performed in several stages. The initial measurements were performed on ceramic samples dried in vacuum at 120 °C for 4 hours (after initial drying). To study the interaction of inner structure of nanoporous ceramic structures with water, the same samples were placed in a distiller at 100 % relative humidity for 7 days. Than ceramics were removed from distiller and placed in the ambient atmosphere at 22 °C and relative humidity of 35 %. PAL measurements were repeated on the 1st, 2nd, 3rd and 7th days after this procedure (after exposure to water vapor). Ultimately, the MgO-Al_2O_3 ceramic was dried in vacuum at 120 °C for 4 hours (after final drying) and measurements were repeated to determine PAL reversibility in the conditions of chemical and physical desorption of water molecules. In previous works [14,15], we used three-component fitting procedures with normal statistical treatment of PAL spectra that accumulate near one million of elementary positron annihilation events. At high-statistical measurements (more than ten millions of counts), the best results were obtained with four-term decomposition procedure. Such approach allows us to study nanopores of different sizes, responsible for o-Ps decaying. Each PAL spectrum was processed multiply owing to slight changes in the number of final channels, annihilation background and time shift of the 0-th channel. In such a manner, we obtained fitting parameters (positron lifetimes τ_1, τ_2, τ_3 and τ_4 and intensities I_1, I_2, I_3 and I_4), which correspond to annihilation of positrons in the samples of interest within a quite reliable error-bar using LT software [16]. The errors in the determination of lifetimes τ_i and intensities I_i are ±0.02÷0.2 ns (increasing with τ_i) and ±0.001÷0.01 a.u., respectively.

3. Results and Discussion

Typical PAL spectra of MgO-Al_2O_3 ceramics sintered at 1100 °C for 2 hours after initial drying and after exposure to water vapor are shown in Figure 1. As demonstrated earlier [15,17], in the case of humidity-sensitive MgO-Al_2O_3 ceramics, there are two channels of positron annihilation: positron trapping with τ_1 and τ_2 lifetimes and ortho-positronium o-Ps decaying within "pick-off" annihilation (τ_3 and τ_4 lifetimes). The first component describes microstructure of spinel, the second one corresponds to positron trapping in free-volume defects near grain boundaries. The third and the fourth components are due to "pick-off" annihilation of o-Ps in nanopores and in water molecules [17].

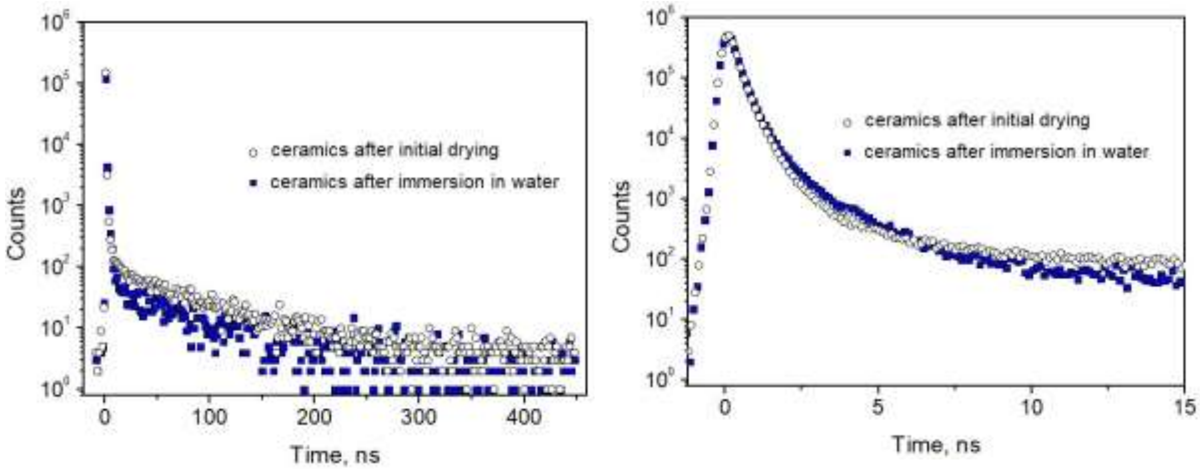

Figure 1. PAL spectra for MgO-Al_2O_3 ceramics sintered at 1100 °C after initial drying and exposure to water vapor.

As shown in Table 1, PAL parameters of the first component (τ_1,I_1) is practically unchanged since water adsorption processes do not affect structural features of spinels. The lifetime of the second defect-related component τ_2 varies around 0.46÷0.48 ns and the intensity I_2 is near 28 %. As a result, the positron trapping parameters calculated within two-state positron trapping model [15], such as average positron lifetime $\tau_{av.}$ and positron lifetime in defect-free bulk $\tau_{b.}$ remain unchanged, while positron trapping rate of defect κ_d slightly increases in ceramics after exposure to water vapor. Major changes caused by adsorption of water are observed in the third and fourth o-Ps-related components.

Table 1. Fitting parameters (for two components) and positron trapping modes of MgO-Al_2O_3 ceramics calculated within two-state positron trapping modes

Pre-history	Fitting parameters				Positron trapping modes		
	τ_1, ns	I_1, %	τ_2, ns	I_2, %	$\tau_{av.}$, ns	τ_b, ns	κ_d, ns^{-1}
After initial drying (ID)	0.169	68	0.462	28	0.254	0.21	1.10
1 day after exposure to water vapor (EW)	0.170	66	0.483	28	0.263	0.21	1.15
2 days after exposure to water vapor (EW)	0.170	65	0.457	29	0.258	0.21	1.14
3 days after exposure to water vapor (EW)	0.171	67	0.484	28	0.264	0.21	1.13
7 days after exposure to water vapor (EW)	0.167	67	0.462	29	0.257	0.21	1.16
After final drying (FD)	0.172	68	0.459	29	0.257	0.21	1.08

It is established that lifetimes of the third and the fourth components (τ_3 and τ_4) corresponds to the size of free volumes (nanopores), while intensities I_3 and I_4 – to the number of nanopores. As shown in Figure 2a, the lifetime τ_3 decreases in ceramics upon drying after exposure to water vapor. The intensity I_3 grows in ceramics after 1 day, indicating annihilation of o-Ps in water-filled nanopores. The presence of water in the nanopores is manifested by increase of intensity I_3 and a slight decrease of lifetime τ_3. It has to be noted that o-Ps lifetime of ~1,8 ns reflects the annihilation in the water bubbles [12,8].

The lifetime τ_4 and the intensity I_4 significantly decrease in ceramics after 1 day (Figure 2b). It relates to the penetration of nanopores by water molecules (full or partial filling) changing characteristics of o-Ps-related component. Obviously, such nanopores should have access to environmental and internal communications at the nanoscale. The intensity I_4 does not fall to zero and is near 0.9 %, it should be assumed that part of the nanopores where the disintegration of o-Ps atoms occurs, is closed. Naturally, the grains growth and the formation of closed porosity begins at the nanoscale. PAL method also provides information on the phase separation during the early stages, which contributes to a closed porosity. The third and fourth components (τ_3, I_3) and (τ_4, I_4) originate from annihilation of o-Ps atoms in intrinsic nanopores (closed and open) of MgO-Al$_2$O$_3$ ceramics. But only open nanopores can contain adsorbed water [14].

Additional investigation of the MgO-Al$_2$O$_3$ ceramics on the 2nd, 3rd and 7th day shows the increase of the lifetime τ_4 and the intensity I_4, indicating release of water from the inner voids of ceramics. After final drying in vacuum at 120 °C for 4 hours, the initial distribution of nanopores in MgO-Al$_2$O$_3$ ceramics tends to recover (Figure 2b). However, the parameters of the fourth component are not fully recovered, proving that some water molecules remain adsorbed.

The intensity I_3 decreases after 2, 3 and 7 days and after final drying confirms good desorption ability of studied MgO-Al$_2$O$_3$ ceramics (Figure 2a). Reducing the value of the lifetime τ_4 after final drying of ceramics sintered at 1100 °C with poorly developed porosity [4] can be due to the formation of thin layers of water molecules surrounding larger nanopores.

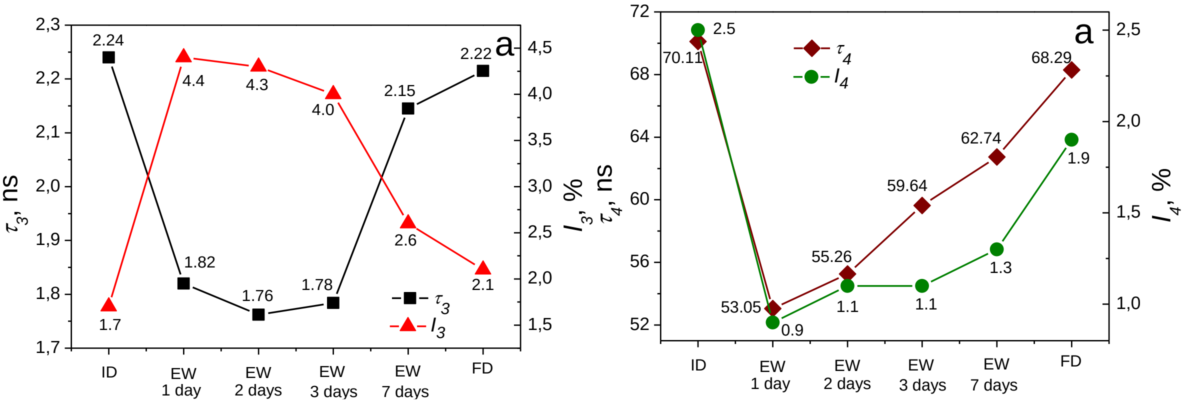

Figure 2. Dependences of the lifetime τ_3 and the intensity I_3 (a) as well as the lifetime τ_4 and the intensity I_4 (b) on the conditions of watering and drying: ID – after initial drying, EW – after exposure to water vapor, FD – after final drying.

The lifetimes τ_3 and τ_4 are used for calculation of radii (R_3 and R_4) of nanopores within Tao-Eldrup model [19-21]:

$$\tau_{o-Ps} = \left[2\left(1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R+\Delta R} \right) \right) + 0.007 \right]^{-1}, \tag{1}$$

where ΔR is the empirically determined parameter (in the classical case $\Delta R \approx 0.1656$ nm), describing effective thickness of the electron layer responsible for the “pick-off” annihilation of *o-Ps* in the hole.

The contribution corresponding to nanopores with radii R_3 and R_4 was calculated by semiempirical equation:

$$f_v = C \cdot V_f \cdot I_{o-Ps}, \tag{2}$$

where $V_f = 4/3 \cdot \pi \cdot R_{o-Ps}$ – free volume calculated from o-Ps-related components; I_{o-Ps} – intensities of o-Ps-related components, C – empirical parameter (0,0018).

Changes of radius of free volumes (or size of nanopores where o-Ps decayed) caused by water sorption processes in the MgO-Al$_2$O$_3$ ceramics, sintered at 1100 °C for 2 hours are shown in Figure 3a. The most significant changes in ceramics caused by immersion of water are observed in largest nanopores with radius of ~18 Å. The intensity of this component (as well as intensity I_3) does not return to initial value after final drying of ceramics (Figure 3a and Figure 3b), because not all water is eventually released from nanopores. As was shown in [14,15], the o-Ps “pick-off” annihilation in nanopores with radius R_3 occurs in dry pores and in the “bubbles” of liquid water adsorbed by these pores. The o-Ps “pick-off” annihilation in nanopores with radius R_4 occurs in free volume of pores, because physisorbed water molecules are formed at the pore walls in the form of thin layer.

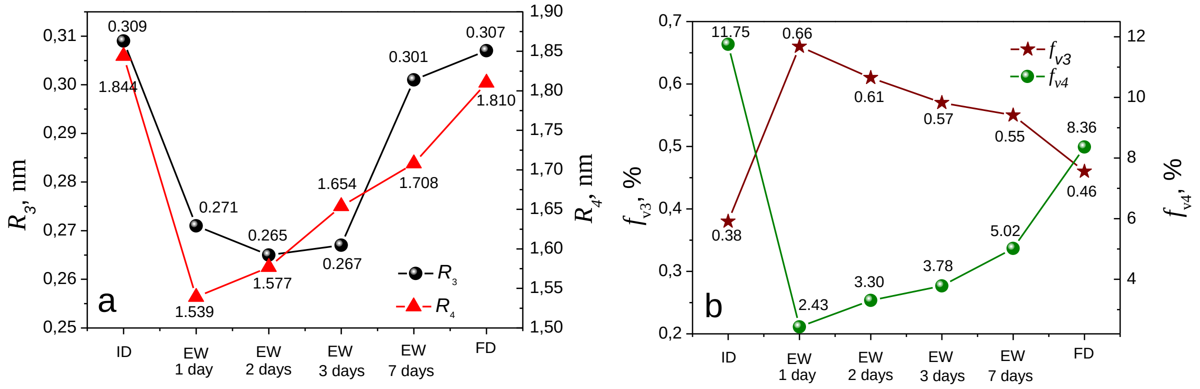

Figure 3. Dependences of radius R_3 and R_4 (a) as well as f_3 and f_4 (b) on the conditions of watering and drying: ID – after initial drying, EW – after exposure to water vapor, FD – after final drying.

4. Conclusions

It is established that the lifetimes of the third and the fourth o-Ps-related components of PAL spectra decrease in MgO-Al_2O_3 ceramics after exposure to water vapor. The free volume of the largest nanopores decreases, while o-Ps decay in smaller nanopores occurs simultaneously with "pick-off" annihilation in water bubbles. The Ps annihilation in nanopores with adsorbed water vapor is shown to occur via two mechanisms: o-Ps decaying in nanopores with radius of 0.3 nm including "pick-off" annihilation in liquid water and o-Ps trapping in free volume of nanopores with physisorbed water molecules at the pore walls.

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