Water-Vapor Sorption Processes in Nanoporous MgO-Al₂O₃ Ceramics: the PAL Spectroscopy Study

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Abstract

The water-vapor sorption processes in nanoporous MgO-Al₂O₃ ceramics are studied with positron annihilation lifetime (PAL) spectroscopy employing positron trapping and positronium (Ps)-decaying modes. It is demonstrated that the longest-lived components in the four-term reconstructed PAL spectra with characteristic lifetimes near 2 and 60–70 ns can be, respectively, attributed to ortho-positronium (o-Ps) traps in nanopores with 0.3- and 1.5–1.8-nm radii. The first o-Ps decaying process includes "pick-off" annihilation in the "bubbles" of liquid water, while the second is based on o-Ps interaction with physisorbed water molecules at the walls of the pores. In addition, the water vapor modifies structural defects located at the grain boundaries in a vicinity of pores, this process being accompanied by void fragmentation during water adsorption and agglomeration during water desorption after drying.

Keywords: Positron annihilation, Trapping, Positronium, Ceramics, Nanopores, Water sorption

Background

Functional MgAl₂O₄ ceramics (MgO-Al₂O₃) with a spinel structure are known as excellent porous materials for humidity sensors [1–3]. These ceramics are thermally and chemically stable in comparison with other types of porous media possessing fast response to humidity changes [4]. An actual challenge is related to porous materials with a controllable microstructure, large specific surface area, high open porosity, optimal pore size, and distribution of free-volume entities [5, 6].

The effect of initial surface area of powdered binary oxide ingredients (MgO and Al₂O₃) on the structure of MgO-Al₂O₃ ceramics sintered at 1100–1400 °C was studied extensively in [7–10]. It was shown that the formation of this spinel-structured ceramics is substantially intensified with increase in sintering temperature and duration. In addition, the sintering temperature possessed an essential effect on the pore structure and exploitation properties of MgAl₂O₄ ceramics [7].

Traditionally, the microstructures of porous ceramics are studied using X-ray (electron, neutron) diffraction, electron microscopy, and different direct porosimetric methods [11–13]. However, the techniques of mercury and/or nitrogen intrusion porosimetry provide reliable information on open pores with radii over 2 nm [14], whereas physical processes in such ceramics depend on not only large open pores but closed nanopores too [15].

To gain knowledge about such fine free-volume entities and their effect on MgAl₂O₄ ceramics, it is reasonable to use the method of positron annihilation lifetime (PAL) spectroscopy, which is an alternative probe of structural characterization allowing the study of both closed and open pores at a nanoscale [16]. Two channels of positron annihilation were shown to be important in case of ceramics: positron trapping and ortho-positronium (o-Ps) decaying [17–19]. The latter process ("pick-off" annihilation) resulting from positronium (Ps) interaction with electron from environment (including annihilation in liquid water) is ended by emission of two γ-quanta [17]. In general, these two channels of positron annihilation are independent. However, if trapping sites will appear in a vicinity of grain boundaries neighboring with free-volume pores, these positron-Ps traps become mutually interconnected resulting in a significant complication of PAL data.

In this work, we use the PAL method developed in positron trapping and o-Ps-decaying modes to characterize...
MgO-Al₂O₃ ceramics sintered at 1100–1400 °C in different stages of water-vapor sorption and drying treatment.

Methods
The MgO-Al₂O₃ ceramics were sintered at maximal temperatures \(T_s\) of 1100, 1200, 1300, and 1400 °C for 2 h, as it was described elsewhere [7, 9, 20, 21]. In respect to X-ray diffraction measurements [7], the ceramics prepared at lower \(T_s = 1100–1200°\)C are composed of the main spinel phase and a large amount of additional MgO and Al₂O₃ phases (up to 12%), while the ceramics sintered at high \(T_s\) of 1300 and 1400 °C contain additionally only the MgO phase in the amount of 3.5 and 1.5 %, respectively.

The PAL measurements were performed with the ORTEC instrument (using \(^{22}\)Na source placed between two identical sandwiched samples) [7, 22] at 22 °C and relative humidity RH = 35 % after drying, 7 days of water exposure (water vapor in a desiccator at RH = 100 %), and further final drying in a vacuum at 120 °C for 4 h. Each PAL spectrum was collected within a 6.15-ps channel width to analyze short and intermediate PAL components. To obtain data on longest-lived PAL components, the same ceramics were studied within a channel width of 61.5 ps [15]. The collected spectra were analyzed with LT software [23]. In previous works [8–10], we used three-component fitting procedures under normal statistical treatment of PAL spectra accumulated near one million of elementary positron annihilation events. At high-statistical measurements (more than ten million counts), the best results were obtained with a 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 0th channel. In such a manner, we obtained fitting parameters (positron lifetimes \(\tau_1, \tau_2, \tau_3, \tau_4\) and corresponding unity-normalized intensities \(I_1, I_2, I_3, I_4\)), which correspond to annihilation of positrons in the samples of interest within a quite reliable error bar.

Results and Discussion
Typical PAL spectra of MgO-Al₂O₃ ceramics sintered at 1400 °C detected within 6.15- and 61.5-ps channel widths are shown in Fig. 1. Four discrete exponentially decaying components were reconstructed from these spectra using the known LT program [23]. Fitting curves for all components in the region of PAL spectra’s peaks are depicted in more detail in the inserts of Fig. 1.

As it was shown earlier [7–10], the positron annihilation in humidity-sensitive MgO-Al₂O₃ ceramics is revealed through two different channels related to “free” positron trapping (the intermediate component with lifetime \(\tau_2\)) and o-Ps decaying (two long-lived components with \(\tau_3\) and \(\tau_4\) lifetimes). The first component with parameters \(\tau_1\) and \(I_1\) reflects mainly microstructure specificity of spinel ceramics with character octahedral and tetrahedral vacant cation sites along with input from annihilation of para-Ps atoms. The intermediate lifetime \(\tau_2\) is related to the size of free-volume defects near grain boundaries, and \(I_2\) intensity reflects their amount [10]. The third and fourth components (\(\tau_3, I_3\) and \(\tau_4, I_4\), respectively, originate from annihilation of o-Ps atoms in intrinsic nanopores of MgO-Al₂O₃ ceramics [7, 24].

Fitting parameters obtained within the four-component treatment of the reconstructed PAL spectra of initially dried, water-vapored, and finally dried MgO-Al₂O₃ ceramics sintered at 1100–1400 °C are gathered in Table 1. It is established that \(\tau_1\) lifetime in the dried ceramics decreases with \(T_s\), while \(I_1\) intensity increases in respect to the amount of main spinel phase like in [7, 10]. Positrons are trapped more strongly in ceramics prepared at lower \(T_s\), as reflected in the values of the second component of the reconstructed PAL spectra. As it follows from Table 1, the numerical values of this component (\(\tau_2\) and \(I_2\)) decrease with \(T_s\) (so positron-trapping parameters calculated within a two-state trapping model [16] will be also changed).

As it follows from Table 2, the calculated values of positron trapping modes in MgO-Al₂O₃ ceramics (average positron lifetime \(\tau_{av}\), bulk positron lifetimes in defect-free samples \(\tau_b\), and positron trapping rates in defects \(k_d\)) are decreased with sintering temperature \(T_s\). These parameters are in good agreement with the amount of additional MgO and Al₂O₃ phases in the ceramics [7].

At the same time, the principal water-vapor sorption processes in the studied MgO-Al₂O₃ ceramics sintered at 1100–1400 °C occur to be mostly determined by o-Ps-related components in the PAL spectra reconstructed through the four-term fitting procedure (Fig. 1). Some details of PAL spectra of the ceramics sintered at different \(T_s\) are shown in the region of the main peak and long fluent decaying of coincidence counts at a certain time in Fig. 2. As it was shown earlier [7, 15], the corresponding long-lived lifetimes \(\tau_3\) and \(\tau_4\) reflect sizes of nanopores, and their intensities \(I_3\) and \(I_4\) are directly related to the number of these nanopores [7, 15].

So, in the initially dried MgO-Al₂O₃ ceramics sintered at 1100–1400 °C, the lifetime \(\tau_3\) increases with \(T_s\), while intensity \(I_3\) decreases (Table 1). These changes are due to the increase in the size of small nanopores with radius \(R_3\), and their reduction is caused by increasing contact between grains. The lifetime \(\tau_4\) and intensity \(I_4\) naturally decrease with \(T_s\), indicating reduction in size and number of nanopores with radius \(R_4\). The radii \(R_3\) and \(R_4\) of spherical nanopores (given in Table 2) were calculated using o-Ps-related \(\tau_3\) and \(\tau_4\) lifetimes in the known Tao-Eldrup model [25, 26]:
\[ \tau_{o-Ps} = \left[ 2 \left( 1 - \frac{R}{R + \Delta R} \right) + \frac{1}{2\pi} \sin \left( \frac{2\pi R}{R + \Delta R} \right) \right]^{-1} + 0.007 \]  

where \( \Delta R \) is an empirically derived parameter (\( \Delta R = 0.1656 \) nm for polymers [18]), which describes effective thickness of the electron layer responsible for the "pick-off" annihilation of \( o-Ps \) in a hole.

It is shown that the radius of nanopores \( R_3 \) increases from 0.309 to 0.331 nm and \( R_4 \) remains nearly at the same level (~1.8 nm) in the initially dried ceramics sintered at 1100–1400 °C (Fig. 3). In addition, free-volume fraction \( f_v \) (Table 2) was evaluated using \( o-Ps \)-related components in spherical approximation using the formula:

\[ f_v = C \cdot V_f \cdot I_{o-Ps}, \]

where \( V_f = 4/3 \cdot \pi \cdot R_{o-Ps}^3 \) is the free volume of a nanopore calculated using \( o-Ps \)-related components in spherical approximation and \( C \) is an empirical parameter equal to 0.0018 [18].

Fig. 1 PAL spectra of MgO-Al\(_2\)O\(_3\) ceramics sintered at 1400 °C registered at channel widths of 61.5 ps (a) and 6.15 ps (b), reconstructed from four-term fitting at the general background of source contribution (bottom inset shows statistical scatter of variance).
trapping sites near grain boundaries, and, respectively, the water desorption processes are accompanied by agglomeration of free-volume voids.

Water-vapor sorption processes in the studied ceramics result in essential evolution of the third and fourth o-Ps-related components. The intensity $I_3$ increases in all initially dried samples after water-vapor exposure, thus confirming o-Ps annihilation in water-filled nanopores through a “bubble” mechanism (with corresponding o-Ps lifetime close to 1.8 ns) [27–29]. At the same time, the lifetime $\tau_3$ decreases in more defective ceramics sintered at 1100 and 1200 °C but increases in more perfect ceramics sintered at 1300 and 1400 °C. After final drying, the intensity $I_3$ for ceramics sintered at 1100 and 1200 °C is not returned to initial values.

### Table 1

| Sample               | $\tau_1$ (±0.002), ns | $I_1$ (±1), % | $\tau_2$ (±0.005), ns | $I_2$ (±1), % | $\tau_3$ (±0.002), ns | $I_3$ (±0.2), % | $\tau_4$ (±0.02), ns | $I_4$ (±0.1), % |
|----------------------|------------------------|---------------|------------------------|---------------|------------------------|-----------------|------------------------|-----------------|
| $T_s = 1100 \degree$ |                        |               |                        |               |                        |                 |                        |                 |
| Initial drying       | 0.169                  | 68            | 0.462                  | 28            | 2.240                  | 1.7             | 70.14                  | 2.5             |
| Water vapor          | 0.170                  | 66            | 0.483                  | 28            | 1.820                  | 4.4             | 53.05                  | 0.9             |
| Final drying         | 0.172                  | 68            | 0.459                  | 29            | 2.215                  | 2.1             | 68.29                  | 1.9             |
| $T_s = 1200 \degree$ |                        |               |                        |               |                        |                 |                        |                 |
| Initial drying       | 0.164                  | 73            | 0.443                  | 24            | 2.347                  | 1.1             | 70.51                  | 2.0             |
| Water vapor          | 0.160                  | 64            | 0.426                  | 31            | 2.047                  | 3.8             | 58.67                  | 0.4             |
| Final drying         | 0.163                  | 72            | 0.429                  | 23            | 2.290                  | 3.1             | 68.87                  | 1.7             |
| $T_s = 1300 \degree$ |                        |               |                        |               |                        |                 |                        |                 |
| Initial drying       | 0.155                  | 82            | 0.414                  | 16            | 2.426                  | 0.8             | 68.74                  | 1.4             |
| Water vapor          | 0.161                  | 76            | 0.400                  | 21            | 2.619                  | 1.8             | 58.33                  | 0.7             |
| Final drying         | 0.156                  | 82            | 0.421                  | 15            | 2.448                  | 0.7             | 68.17                  | 1.4             |
| $T_s = 1400 \degree$ |                        |               |                        |               |                        |                 |                        |                 |
| Initial drying       | 0.152                  | 88            | 0.388                  | 11            | 2.504                  | 0.7             | 62.32                  | 0.8             |
| Water vapor          | 0.160                  | 77            | 0.409                  | 20            | 2.562                  | 2.2             | 57.35                  | 0.6             |
| Final drying         | 0.154                  | 89            | 0.402                  | 10            | 2.539                  | 0.7             | 61.85                  | 0.8             |

### Table 2

| Sample               | Positron trapping modes | Free-volume parameters |
|----------------------|-------------------------|------------------------|
|                      | $\tau_{av}$ ns | $\tau_{up}$ ns | $\kappa_0$ ns$^{-1}$ | $R_{nm}$ nm | $\sim f_0$ % | $R_{fs}$ nm | $\sim f_{fs}$ % |
| $T_s = 1100 \degree$ |                        |                        |                        |             |               |             |               |
| Initial drying       | 0.254                  | 0.21                  | 1.10                  | 0.309       | 0.38         | 1.844       | 11.75         |
| Water vapor          | 0.263                  | 0.21                  | 1.15                  | 0.271       | 0.66         | 1.539       | 2.43          |
| Final drying         | 0.257                  | 0.21                  | 1.08                  | 0.307       | 0.46         | 1.810       | 8.36          |
| $T_s = 1200 \degree$ |                        |                        |                        |             |               |             |               |
| Initial drying       | 0.232                  | 0.19                  | 0.94                  | 0.319       | 0.26         | 1.852       | 9.62          |
| Water vapor          | 0.252                  | 0.21                  | 1.19                  | 0.293       | 0.72         | 1.636       | 1.16          |
| Final drying         | 0.229                  | 0.19                  | 0.93                  | 0.296       | 0.61         | 1.821       | 7.77          |
| $T_s = 1300 \degree$ |                        |                        |                        |             |               |             |               |
| Initial drying       | 0.197                  | 0.17                  | 0.66                  | 0.325       | 0.20         | 1.818       | 6.18          |
| Water vapor          | 0.213                  | 0.19                  | 0.80                  | 0.340       | 0.52         | 1.630       | 2.40          |
| Final drying         | 0.198                  | 0.17                  | 0.63                  | 0.327       | 0.20         | 1.807       | 6.06          |
| $T_s = 1400 \degree$ |                        |                        |                        |             |               |             |               |
| Initial drying       | 0.178                  | 0.16                  | 0.44                  | 0.331       | 0.19         | 1.701       | 3.07          |
| Water vapor          | 0.211                  | 0.18                  | 0.78                  | 0.335       | 0.63         | 1.613       | 1.74          |
| Final drying         | 0.179                  | 0.16                  | 0.40                  | 0.334       | 0.19         | 1.692       | 3.02          |
This confirms the remainder of sorbed water in the nanopores with size near 0.3 nm and slight desorption ability of these MgO-Al₂O₃ ceramics samples (Fig. 3). In MgO-Al₂O₃ ceramics sintered at 1300 and 1400 °C, the intensity of the third component returns to initial value, confirming high efficiency of water adsorption-desorption processes.

Another mechanism of water-vapor sorption processes similar to one reported in [30] is realized in the studied MgO-Al₂O₃ ceramics through the fourth component of the PAL spectra. Unlike the third component, the intensity \( I_4 \) decreases in water-vapor exposure ceramics samples. Since this intensity does not drop to zero being within 0.4–0.9 % domain, it should be assumed that there exists a fraction of closed nanopores where o-Ps are trapped [15]. After final drying (in a vacuum at 120 °C for 4 h) of the ceramics samples previously exposed to water vapor, the initial pore size tends to be restored (Table 2 and Fig. 3). However, it does not recover entirely, suggesting that some fraction of water molecules remain adsorbed. The intensity \( I_4 \) does not return to initial value in ceramics sintered at 1100 and 1200 °C with poorly developed open porosity (Table 1). Most probably, physically adsorbed water is not fully eliminated at 120 °C in these ceramics samples. The decreased \( \tau_4 \) value for ceramics dried after water-vapor exposure can be connected with formation of thin layers of water molecules covering the walls of pores with radii of 1.5–1.8 nm,

![Fig. 2 PAL spectra of MgO-Al₂O₃ ceramics sintered at 1100–1400 °C registered under channel widths of 61.5 ps (a) and 6.15 ps (b).](image)
which are not completely removed after vacuum annealing at 120 °C for 4 h.

Conclusions
The method of PAL spectroscopy in high-measurement statistics is employed to study water-vapor sorption processes in MgO-Al₂O₃ ceramics sintered at 1100–1400 °C temperatures for 2 h. It is shown that positrons are trapped more strongly in the ceramics obtained at lower \( T_s \), which was reflected in the second component of the four-term decomposed PAL spectra. The third and fourth longest-lived components in these spectra are due to annihilation of o-Ps atoms in the nanopores, the corresponding radii being calculated from \( \tau_3 \) and \( \tau_4 \) lifetimes using the known Tao-Eldrup model. The final drying in a vacuum at 120 °C for ceramics previously exposed to water vapor does not restore initial pore size, confirming sensitivity of PAL method to the amount of water molecules adsorbed in the nanopores. The Ps annihilation in nanopores with adsorbed water vapor is shown to occur via two mechanisms: (1) o-Ps decaying in nanopores with radius of 0.3 nm including “pick-off”

![Fig. 3 Nanopore radii \( R_3 \) and \( R_4 \) in MgO-Al₂O₃ ceramics sintered at 1100–1400 °C changed in water adsorption-desorption cycles](image)
annihilation in the “bubbles” of liquid water and (2) o-Ps trapping in free volume of nanopores (1.5–1.8 nm) with physisorbed water molecules at the pore walls. The water vapor modifies defects in ceramics located near grain boundaries, this process accompanied by void fragmentation at water adsorption with further void agglomeration at water desorption after drying.

Competing Interests
The authors declare that they have no competing interests.

Authors’ Contributions
HK performed the experiments to study the nanopore transformation caused by the water-vapor sorption process in the MgO-Al2O3 ceramics and drafted, wrote, and arranged the article. AI participated in the PAL measurements and treatment of spectra. OSH supervised the work and finalized the manuscript. IH sintered the ceramics samples. VS participated in the treatment of the PAL data. All authors read and approved the final manuscript.

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