PROCEEDINGS OF THE INTERNATIONAL CONFERENCE NANOMATERIALS: APPLICATIONS AND PROPERTIES
Vol. **4** No 1, 01MAN04(3pp) (2015)

Positronium Characterization of Nanopores in Technologically Modified $MgO\text{-}Al_2O_3$ Ceramics

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(Received 01 March 2015; revised manuscript received 01 August 2015; published online 25 August 2015)

It is established that positron annihilation lifetime spectroscopy can be successful used as porosimetry method to study of nanopores size and transformation of free volume in humidity-sensitive $MgO\text{-}Al_2O_3$ ceramics in adsorption-desorption cycles using lifetimes of ortho-positronium-related components. It is shown that the fourth component gives information about water-free volume or nanopores size, while the third component reflects positronium trapping both in nanopores and in water "bubbles".

Keywords: Spinel, Ceramics, Positronium, Nanopores, Water-immersion, Drying.

PACS numbers: 82.45.Xy, 92.60.Jq

1. INTRODUCTION

It is known that the ceramics with spinel structure are one of the best porous materials for humidity sensors [1]. Functional $MgO\text{-}Al_2O_3$ ceramics are thermally and chemically stable in comparison with other types of porous materials with a short time to changes in humidity operation.

As was shown early [2,3], the functionality of humidity-sensitive spinel ceramics is dependent on microstructure of grains, grain boundaries and pores. These elements significantly affect on their nanostructurization. In addition, electrical properties of ceramics depend on the sorption processes in these materials.

Traditionally, microstructural characteristics of ceramic materials are studied using X-ray diffraction, electron microscopy, porosimetry methods, etc. However, the methods of mercury and nitrogen porosimetry is provide information on open pore with radius > 5 and > 2 nm, respectively [4]. Physical processes in ceramics depend not only on the number and nature of large open pores, but also on the closed nanopores [5]. So for more information on these structural components and their influence on the properties of $MgO\text{-}Al_2O_3$ ceramics, reasonable to use additional methods of structural characterization, which would allow to study the closed and open pores and other free-volume entities on the nanoscale level. In this case we used positron annihilation lifetime spectroscopy (PALS) tools to study free-volume transformation in spinel ceramics caused by different sintering temperature as porosimetry methods [3]. In this work we would like to study sorption ability of $MgO\text{-}Al_2O_3$ ceramics sintered at 1100 °C in different stage of water-immersion and drying.

2. EXPERIMANTAL

The $MgO\text{-}Al_2O_3$ ceramics were sintered at 1100 °C for 2 hours using traditional ceramic technology [2,3,5-8]. The PALS investigation were performed using ORTEC spectrometer (^{22}Na source) [6]. High-statistical investigations were held in several stages after following procedures further processing samples. The initial measurements were performed on ceramic samples dried in vacuum at 120 °C for 4 hours. To study the interaction of connectivity porous ceramic structures, the same samples were moistened by water (placed in a distiller, the relative humidity was 100 %) for 8 hours (1 day) at 22 °C. PALS measurements were repeated at 1, 2, 3 and 7 days after the procedure. At the last stage samples of $MgO\text{-}Al_2O_3$ ceramic were dried again in a vacuum at 120 °C for 4 hours and repeated measurement to determine of PALS reversibility of physical adsorption of water molecules at exactly the same temperature. To maximum assessment of free volume in ceramics and calculation of nanopores size, the PALS spectra were decomposed by LT computer program into four components with positron lifetimes τ_1, τ_2, τ_3 and τ_4 and intensities I_1, I_2, I_3 and I_4. The errors were ± 0,005 for I_3 and ± 0,0001 for I_4.

3. RESULTS AND DISCUSSION

As we shown early [5-8], in the case of humidity-sensitive $MgO\text{-}Al_2O_3$ ceramic, there are two channel of positron annihilation: positron trapping (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 is reflect microstructural specifies of spinel, the second one correspond to positron trapping defects located near grain boundaries. The third and fourth components are due to "pick-off" annihilation of o-Ps in nanopores filled by water.

As expected, the parameters of the first component (τ_1, I_1) practically unchanged since sorption processes do not affect on the structural features of spinels (Table 1). The lifetime of second defect-related component τ_2 is near ~0.46 ÷ 0.48 ns and the intensity I_2 is ~0.28. As a result, the positron trapping parameters calculated within two-

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Table 1. Fitting parameters for $MgO\text{-}Al_2O_3$ ceramics mathematically treatment with four-component fitting procedure

Pre-history	τ_1, ns	I_1, a.u.	τ_2, ns	I_2, a.u.	τ_3, ns	I_3, a.u.	τ_4, ns	I_4, a.u.
After drying	0.169	0.68	0.462	0.28	2.240	0.017	70.11	0.025
1 days	0.170	0.66	0.483	0.28	1.820	0.044	53.05	0.009
2 days	0.170	0.65	0.457	0.29	1.762	0.043	55.26	0.011
3 days	0.171	0.67	0.484	0.28	1.784	0.040	59.64	0.011
7 days	0.167	0.67	0.462	0.29	2.145	0.026	62.74	0.013
After drying	0.172	0.68	0.459	0.29	2.215	0.021	68.29	0.019

Table 2. Positron trapping modes and transformation of free volumes in $MgO\text{-}Al_2O_3$ ceramics sintered at 1100 °C after different duration of drying

Pre-history	τ_{av}, ns	τ_b, ns	κ_d, ns^{-1}	R_3, Å	$\sim f_{v3}$, %	R_4, Å	$\sim f_{v4}$, %
After drying	0.254	0.21	1.10	3.09	0.38	18.44	11.75
1 days	0.263	0.21	1.15	2.71	0.66	15.39	2.43
2 days	0.258	0.21	1.14	2.65	0.61	15.77	3.30
3 days	0.264	0.21	1.13	2.67	0.57	16.54	3.78
7 days	0.257	0.21	1.16	3.01	0.55	17.08	5.02
After drying	0.257	0.21	1.08	3.07	0.46	18.10	8.36

state positron trapping model [6], such as average positron lifetime $\tau_{av.}$ and positron lifetime in defect-free bulk $\tau_{b.}$ unchanged, while positron trapping rate of defect κ_d slightly increases after water-immersion (Table 2). Major changes caused by sorption of water observed in the third and fourth o-Ps-related components. It is established that the number of nanopores correspond to the intensity of third and fourth components [3, 5]. Thus, the intensity I_4, which corresponds to the number of larger nanopore radius ~ 18 Å, significantly decreases after 1 day after water-immersion. The lifetime τ_4 decreases which reflects lessening of nanopore radius calculated within Tao-Eldrup model (Table 1). It is connected with penetration of nanopores by water molecules (fully or partially filling) changing characteristics of o-Ps-related component. Obviously, such pores should have access to environmental and internal communications at the nanoscale.

As the intensity I_4 does not fall to zero and is near 0.9%, it should be assumed that part of the nanopore where the disintegration of o-Ps atoms, is closed. Closed pores in ceramics can also be seen in micrograph [3,8]. Obviously, the grains growth and the formation of closed porosity begins at the nanoscale. PALS method also provides information on the phase separation in the early stages, which contributes to a closed porosity.

Additional studies of $MgO\text{-}Al_2O_3$ ceramics after 2, 3 and 7 days after water-immersion shows a gradual increase in the lifetime τ_4 and 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 pores in $MgO\text{-}Al_2O_3$ ceramics tends to recovery. However, the parameters of the fourth component is not fully recovered, testified that some water molecules remaining adsorbed.

Transformation of free volume caused by moisture sorption processes in ceramics $MgO\text{-}Al_2O_3$, sintered at 1100 °C, given also in Table 2. Besides nanopore with radius R_3 and R_4 calculated by the model Tao-Eldrupa, defined contribution corresponding to free volume (nanopores) by semi-empirical equation [9]:

$$f_v = C \cdot V_f \cdot I_{o\text{-}Ps}, \quad (1)$$

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

The most significant changes caused by moisture sorption processes are observed for the largest nanopore radius of ~ 18 Å. The intensity of this component does not return to initial value after drying of ceramics, because not all water released into the nanopore interior. Reducing the value of the lifetime τ_4 after drying of ceramics with poorly developed porosity can be due to the formation of thin layers of water molecules surrounding the large pores that completely freed moisture at 120 °C.

The lifetime τ_3 decreases after water-immersion of ceramics with a gradual increase in drying and intensity I_3 grows, indicating annihilation of o-Ps in water-filled nanopores (Table 1). The presence of water in the nanopores of smaller radius ~3 Å after drying reflects in increasing of intensity I_3 and a slight decreasing of lifetime τ_3. It is noted that the lifetime of o-Ps ~ 1,8 nm reflects the annihilation in the water "bubbles" with radius near 3 Å. Its number increasing in accordance with intensity I_3.

4. CONCLUSION

It is shown that lifetimes of third and fourth o-Ps-related component of PALS spectra decreases in water-immersed $MgO\text{-}Al_2O_3$ ceramics reflected decreasing of free-volume after water-immersion. The amount of biggest nanopores decreases, while positronium trapping in smaller nanopores carried out simultaneously with annihilation in water "bubbles".

ACKNOWLEDGEMENT

This research was funded by Ministry of Education and Science of Ukraine (grant DB/KIBER, No 0115U000446).

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