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Water-sorption effects in nanoporous $MgAl_2O_4$ ceramics for humidity sensors

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Abstract. The water-sorption effects in spinel-structured $MgAl_2O_4$ ceramics are studied using positron annihilation lifetime spectroscopy. It is shown that the most significant changes caused by absorbed water in these ceramics can be revealed in positron trapping rate by assuming constant values of reduced bulk and defect-related lifetimes. The observed water-sorption processes occur catalytic effect on positron trapping rate of extended defects located near intergranular boundaries within ceramics bulk.

Keywords: spinel-structured ceramics, water-sorption process, intergranular boundaries, positron trapping.

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1. Introduction

Humidity-sensing application of stoichiometric $MgAl_2O_4$ ceramics with a spinel structure is known to be a determinant of chemical and physical water-sorption processes occurring within inner pores in ceramics bulk [1-4]. The presence of open porosity permits greater electrical conductivity due to the enhancement in the specific surface area available for water adsorption [4-6]. The spinel-structured nanoporous magnesium aluminate $MgAl_2O_4$ ceramics are perspective materials for humidity sensors mainly due to a uniform porous structure, which promotes effective adsorption of great number of water molecules [1-4]. Recently, it was shown that the amount of adsorbed water in these ceramics affects not only their electrical conductivity, but also other physical-chemical properties, such as positron trapping modes of extended free-volume defects tested with positron annihilation lifetime (PAL) spectroscopy [7, 8].

In respect to the PAL method, it is assumed that unstable positron-electron system called positronium Ps is repelled from ionic cores of atoms and tends to be located in inner pores of ceramics [8, 9]. In the ground state, the Ps exists as singlet para-positronium p-Ps and triplet ortho-positronium o-Ps, the latter demonstrating the so-called "pick-off" annihilation owing to overlapping between wave functions of o-Ps and

surrounding atoms [8-12]. The corresponding long-lived o-Ps lifetime and component intensity serve as numerical parameters of this process, being tightly connected with ceramics nanoporous structure. However, not only geometrical, but also electrostatic requirements should be satisfied to observe experimentally the "pick-off" annihilation [8]. That is why in some kinds of ceramics having a quite stretched nanoporous structure this annihilation channel is only poorly distinguished at the general background of more intensive positron trapping process.

The studied $MgAl_2O_4$ ceramics belong just to these materials. In spite of a great variety of inner and open pores, these ceramics typically show small "pick-off" annihilation intensities, which do not exceed a view % [13, 14]. In these cases, more reliable information on pore-related PAL modes can be extracted from positron trapping having shorter lifetimes.

As it was earlier shown by us [7, 15], the positrons injected into the studied $MgAl_2O_4$ ceramics underwent two positron trapping with two components in positron lifetimes and o-Ps decaying with one long-lived lifetime component, these parameters being obtained with the so-called three-component fitting procedure. Within this approach, the shortest component of the deconvoluted PAL spectra with the positron lifetime τ_1 reflects mainly microstructure specificity of the ceramics and the middle component with positron lifetime τ_2 corresponds to

extended defects located near intergranular boundaries. The third component with the lifetime τ_3 and relative intensity no more than 2% is due to "pick-off" annihilation of o-Ps in the intergranular nanopores. It is established the adsorbed water molecules act catalytically on positron trapping in $MgAl_2O_4$ ceramics, do not changing significantly o-Ps decaying modes [7].

To refine the most significant changes in positron trapping in $MgAl_2O_4$ ceramics caused by water sorption, a new methodological approach to the treatment of experimental PAL data should be developed in such a way to accumulate the catalytic effect in some non-direct trapping parameters, while other direct components (the reduced bulk and defect-related lifetimes, in the first hand) being left nearly constant.

2. Experimental

The studied spinel-structured $MgAl_2O_4$ ceramics were sintered from fine-dispersive Al_2O_3 and MgO powders using a special regime with maximum temperatures of 1200 and 1300 °C, the total duration being 2 h [7, 16]. The phase composition of ceramics obtained with X-ray diffraction established that ceramics sintered at 1200 °C contained the main spinel and large amount of additional MgO and $\alpha-Al_2O_3$ phases (6.0 and 5.8 %, respectively) and small quantity of MgO phase (1.54 %) [7, 16].

The PAL measurements were performed with an ORTEC spectrometer (^{22}Na source placed between two ceramic samples) at 20 °C within row of relative humidity (RH) of 25-60-98-60-25 % using humidistat PID+ (see Fig. 1).

U_B is the turn-on voltage proportional to the desired value of RH; U_c – output voltage of the humidity sensor, which is proportional to the desired value of RH in the chamber; $\varepsilon(t)$ – difference between the set and necessary values: $\varepsilon \sim U_B - U_c$; $\rho(t)$ – regulator voltage, which is proportional to the given portion of air in humidity; R – difference input in amplification regulation: k_1 ($RK1$), k_2 ($RK2$); I – integration input in the general time regulation T_i ($R6$, $C1$), D – difference input in detection loss regulation T_d ($R8$, $C2$), Σ – adder input from input voltage controlled by a voltage amplifier:

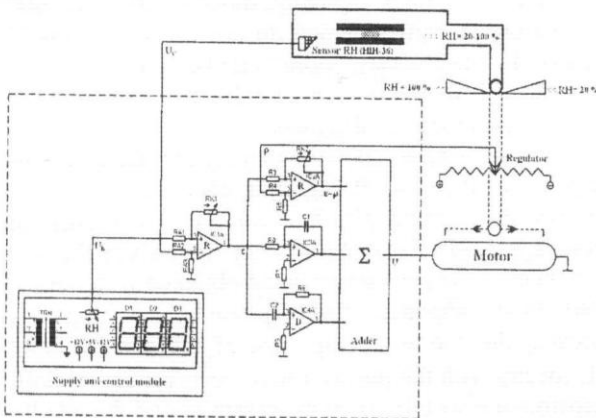


Fig. 1. Schematic of humidity control instrument PID+.

$$u(t) = k_1 \left[\left(\varepsilon(t) - \rho(t) \frac{k_2}{k_1} \right) + \frac{1}{T_i} \int_0^{T_i} \varepsilon(t) dt + T_d \frac{de(t)}{dt} \right], \quad (1)$$

where $k_1 = RK1/RA1$, $k_2 = RK2/R3$, $T_i = C1 \cdot R6$ and $T_d = C2 \cdot R8$.

These values for measuring chamber were chosen experimentally as based on previous calculations in accordance with Ziegler-Nichols criteria.

The selection of corresponding values for measuring chamber permit to investigate the samples at constant values of RH within the range 25-60 % with the accuracy ± 0.5 % and 60-98 % with the accuracy ± 1 %.

The obtained data were mathematically treated within three-component fitting procedure with the fixed first and second positron lifetimes using LT computer program by J. Kansy [17]. Only results with FIT (short abbreviation originated from fitting) values close to 1.0 [15] were left for further consideration.

Using a well-developed formalism for two-state positron trapping model [5-6, 9-11], the following parameters describing positron lifetime spectra can be calculated according to equation (1):

$$\kappa_d = \frac{I_2}{I_1} \left(\frac{1}{\tau_b} - \frac{1}{\tau_2} \right), \quad (2)$$

$$\tau_b = \frac{I_1 + I_2}{\frac{I_1}{\tau_1} + \frac{I_2}{\tau_2}}, \quad (3)$$

$$\tau_{av} = \frac{\tau_1 I_1 + \tau_2 I_2}{I_1 + I_2}, \quad (4)$$

where κ_d is the positron trapping rate in defect, τ_b – positron lifetime in defect-free bulk, and τ_{av} – average positron lifetime. In addition, the difference ($\tau_2 - \tau_b$) can be accepted as a size measure of extended defects where positrons are trapped in terms of equivalent number of monovacancies, as well as the τ_2/τ_b ratio represents the nature of these defects [14].

3. Results and discussion

Our previous PAL measurements for the studied $MgAl_2O_4$ ceramics sintered at 1200 and 1300 °C were carried out at 20 °C and RH = 35 % without special testing procedure for standard thermally-treated non-defected Ni and Al probes. In this case, the best results were obtained at the three-component fitting procedure with $\tau_1 = 0.18$ ns, $I_1 = 0.74$; $\tau_2 = 0.38$ ns, $I_2 = 0.25$ and $\tau_3 = 1.88$ ns, $I_3 = 0.02$ for ceramics obtained at 1200 °C and $\tau_1 = 0.17$ ns, $I_1 = 0.75$, $\tau_2 = 0.36$ ns, $I_2 = 0.23$ and $\tau_3 = 2.14$ ns, $I_3 = 0.02$ for ceramics obtained at 1300 °C. Despite small I_3 intensity, the third component cannot be eliminated without significant losses in the goodness of the fitting procedure. The similar component was detected by other authors in different porous substances

Table. PAL characteristics of the studied MgAl₂O₄ ceramics mathematically treated within the three-component fitting procedure.

RH, %	Fitting parameters						Positron trapping modes				
	τ_1 , ns	I_1 , a.u.	τ_2 , ns	I_2 , a.u.	τ_3 , ns	I_3 , a.u.	τ_{av} , ns	τ_b , ns	κ_d , ns ⁻¹	$\tau_2 - \tau_b$, ns	τ_2/τ_b
$T_s = 1200\text{ }^\circ\text{C}$											
25	0.18	0.79	0.38	0.20	2.37	0.01	0.22	0.20	0.59	0.18	1.89
60	0.18	0.78	0.38	0.21	2.55	0.01	0.22	0.20	0.62	0.18	1.87
98	0.18	0.76	0.38	0.23	2.27	0.01	0.23	0.20	0.67	0.18	1.86
60	0.18	0.77	0.38	0.22	2.26	0.01	0.22	0.20	0.64	0.18	1.87
25	0.18	0.78	0.38	0.21	2.21	0.01	0.22	0.20	0.61	0.18	1.88
$T_s = 1300\text{ }^\circ\text{C}$											
25	0.17	0.85	0.37	0.14	2.37	0.01	0.20	0.18	0.44	0.18	2.01
60	0.17	0.83	0.37	0.16	2.81	0.01	0.20	0.19	0.52	0.18	1.98
98	0.17	0.81	0.37	0.17	2.42	0.01	0.21	0.19	0.56	0.18	1.97
60	0.17	0.83	0.37	0.16	2.34	0.01	0.20	0.19	0.50	0.18	1.99
25	0.17	0.84	0.37	0.15	2.38	0.01	0.20	0.19	0.49	0.18	2.00

like to spinel ceramics [14]. It can be surmised this component is owing to predominant o-Ps "pick-off" decay in the intergranular nanopores filled with adsorbed water [5]. It is established the adsorbed water molecules act catalytically on positron trapping modes in MgAl₂O₄ ceramics, do not changing significantly o-Ps decaying modes [7]. Nevertheless, refining the most considerable changes in positron trapping in the studied ceramics caused by water sorption is a difficult problem through a large quantity of arbitrary fitting parameters when treating the PAL spectra.

This task can be solved due to the treatment of experimental PAL data at the fixed values of some fitting parameters such as the reduced bulk lifetime τ_1 and defect-related lifetime τ_2 .

It is established that the lifetime τ_1 mainly reflects microstructure specificity of the studied MgAl₂O₄ ceramics [7]. The adsorption processes do not change the structure of these ceramics. In respect to our previous XRD measurements, the MgAl₂O₄ ceramics sintered at 1200-1300 °C contains the prevailing spinel-type phase [7].

The lifetime τ_2 corresponds to extended defects located near intergranular boundaries where the studied ceramics are more defective [7, 15]. It is shown that the positrons are trapped in the same extended defects in MgAl₂O₄ ceramics sintered at different temperatures independently of the content of adsorbed water in their nanoporous [7].

Thus, the lifetimes of the first and the second PAL components (τ_1 and τ_2) at the treatment of experimental PAL data can be considered nearly constant. Within this methodological approach, all changes in the fitting parameters of these components will be reflected in their intensities (I_1 and I_2). The third longest component with lifetime τ_3 is non-fixed.

In accordance to the previous PAL results for the studied MgAl₂O₄ ceramics, the lifetimes τ_1 and τ_2 are in

the levels of 0.17-0.20 ns and 0.36-0.38 ns, respectively, in dependence on sample pre-history. The treatment of experimental data was carried out at these fixed values of lifetimes. The best FIT was obtained at the constant lifetimes $\tau_1 = 0.18$ ns and $\tau_2 = 0.38$ ns for ceramics sintered at 1200 °C and $\tau_1 = 0.17$ ns and $\tau_2 = 0.37$ ns for ceramics sintered at 1300 °C. It should be noted that these results are in well agreement with the previous data obtained without non-defected Ni and Al probes in natural conditions (20 °C and RH = 35 %).

Within this approach, I_1 and I_2 intensities of the direct PAL components change dependently on the amount of adsorbed water in the studied ceramics sintered at 1200 and 1300 °C. So, increase in RH from 25 to 98 % result in decreasing I_1 intensity and increasing I_2 intensity. The change of RH from 98 to 25 % reflects inverse to the previous direction in I_1 and I_2 intensities (see Table). The positron trapping in water-filled defects located near intergranular boundaries reflecting the second component with I_3 intensity occurs more intensive.

The lifetimes τ_3 are close to ~2.2-2.8 ns (see Table). The input of this third component is not changed and is close to 0.01. Thus, this channel is non-significant to water sorption-desorption processes.

The positron trapping modes such as the average τ_{av} and defect-free bulk τ_b lifetimes as well as the difference $\tau_2 - \tau_b$ are non-changed with RH. In addition, the positron trapping centre (τ_2/τ_b) is formed on a typical for MgAl₂O₄ ceramics level of ~1.9 [7, 17], which testify to the same nature of trapping sites whatever the content of adsorbed water.

In contrast, the most significant changes in positron trapping in MgAl₂O₄ ceramics caused by water sorption reflect in positron trapping rate in defect κ_d . Thus, the catalytic water-sorption effect in the studied spinel-structured ceramics is accumulated in the non-direct trapping κ_d parameter.

4. Conclusions

The treatment of experimental PAL data at constant values of reduced bulk and defect-related lifetimes allow to refine the most significant changes caused by adsorbed water in the spinel-structured $MgAl_2O_4$ ceramics. The observed water-sorption processes cause the catalytic effect on the positron trapping rate of extended defects located near intergranular boundaries inside ceramics bulk.

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