Positron Trapping Effects in Water-filled Nanopores of Spinel Ceramics

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The water-sensitive positron trapping modes in nanoporous $MgAl_2O_4$ ceramics with a spinel structure are studied. It is shown that water-sorption processes in these ceramics leads to increase in positron trapping rates of extended defects located near intergranual boundaries. The fixation of direct positron lifetime components allows refining the most significant changes in positron trapping rate.

Keywords: Water-sorption process, Intergranual boundaries, Positron trapping.

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1. INTRODUCTION

The spinel-structured $MgAl_2O_4$ 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]. Recently, it was shown that the amount of adsorbed water in these ceramics affects not only their electrical conductivity, but also positron trapping modes of extended defects tested with positron annihilation lifetime (PAL) spectroscopy [1,2]. The positrons injected in the studied $MgAl_2O_4$ ceramics underwent two positron trapping with two components in positron lifetimes and ortho-positronium o-Ps decaying, these parameters being obtained with a so-called three-component mathematical fitting procedure. Within this approach, the shortest component of the deconvoluted PAL spectra with positron lifetime τ_1 reflects mainly microstructure specificity of the spinel ceramics and the middle component with positron lifetime τ_2 corresponds to extended defects located near intergranual boundaries. The third component with lifetime τ_3 is due to "pick-off" annihilation of o-Ps in the nanopores. It is established that the adsorbed water molecules act catalytically on positron trapping in $MgAl_2O_4$ ceramics, do not changing significantly o-Ps decaying modes [2].

To refine the most significant changes in positron trapping in $MgAl_2O_4$ ceramics caused by water sorption, a new mathematical 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-type $MgAl_2O_4$ ceramics were sintered from fine-dispersive Al_2O_3 and MgO powders using a special regime with maximal temperatures of 1200 °C, the total duration being 2 h [2].

The PAL measurements were performed with an ORTEC spectrometer with ^{22}Na source placed between two ceramic samples (see Fig. 1) at 20 °C within row of relative humidity (RH) of 25-60-98-60-25 % using humidistat PID+ (see Fig. 2).
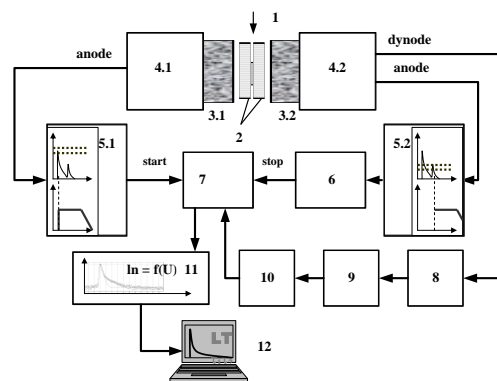

Fig. 1 – Block-scheme of conventional sample-source "sandwich" arrangement for PAL measurements using the ORTEC apparatus [1]: 1 – foil-covered ^{22}Na source, 2 – two identical samples, 3.1 and 3.2 – scintillators of γ-quanta, 4.1 and 4.2 – photomultipliers, 5.1 and 5.2 – constant fraction discriminators, 6 – delay line, 7 – time-pulse height converter, 8 – preamplifier, 9 – amplifier, 10 – single channel analyzer, 11 – multichannel analyzer, 12 – personal computer.

The selection of corresponding values for measuring chamber permit to investigation of samples at constant values of RH in the range of 25-60 % with an accuracy of ± 0,5 % and 60-98 % ₃ with an accuracy of ± 1 %. The obtained PAL data were mathematically treated within three-component fitting procedure with fixed first and second positron lifetimes using LT computer program. Using formalism for two-state positron trapping model [1], the following parameters can be calculated:

$$\kappa_d = \frac{I_2}{I_1}\left(\frac{1}{\tau_b} - \frac{1}{\tau_2}\right), \quad \tau_b = \frac{I_1 + I_2}{\dfrac{I_1}{\tau_1} + \dfrac{I_2}{\tau_2}}, \quad \tau_{av} = \frac{\tau_1 I_1 + \tau_2 I_2}{I_1 + I_2}, \quad (1)$$

where κ_d is positron trapping rate in defect, τ_b – positron lifetime in defect-free bulk and τ_{av} – average positron lifetime. The difference ($\tau_2 - \tau_b$) can be accepted as a size measure of extended defects, as well as the τ_2/τ_b ratio represents the nature of these defects [2].

3. RESULTS AND DISCUSSION

It is established that the adsorbed water molecules act catalytically on positron trapping modes in $MgAl_2O_4$ ceramics, do not changing significantly o-Ps decaying
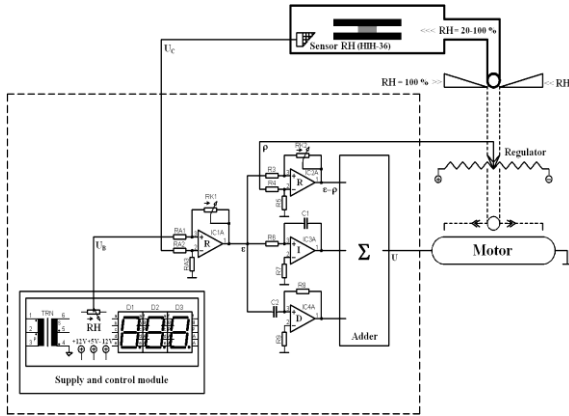
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Fig. 2 – Schematic of humidity control instrument PID+:
UB – turn-on voltage, which proportional to desired value of RH; Uc – output voltage of humidity sensor, which proportional to desired value of RH in the chamber; $\varepsilon(t)$ – difference between the set and necessary values: $\varepsilon \sim UB - Uc$; $\rho(t)$ – regulator voltage, which 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 Ti (R6, C1), D –difference input in detection loss regulation Td (R8, C2), Σ –adder input from input voltage controlling by voltage amplifier:

$$u(t) = k_1 \left[\left(\varepsilon(t) - \rho(t) \frac{k_2}{k_1} \right) + \frac{1}{T_i} \int_0^{T_i} \varepsilon(t)dt + T_d \frac{de(t)}{dt} \right], \quad (2)$$

where k_1 = RK1/RA1, k_2 = RK2/R3, T_i = C1·R6 and T_d = C2·R8. These values for measuring chamber were experimental selected based on previous calculations in accordance with Zieglera-Nicholsa criteria.

modes [2]. 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 at treatment of PAL spectra. This task can be permitted due to the treatment of experimental PAL data at the fixed values of lifetimes τ_1 and τ_2. It is established that lifetime τ_1 reflects mainly microstructure specificity of MgAl$_2$O$_4$ ceramics [2]. The adsorption processes are not change the structure of these ceramics. The lifetime τ_2 corresponds to extended defects near intergranual boundaries where ceramics are more defective. It is shown that the positrons are trapped in the same extended defects in MgAl$_2$O$_4$ independently of the content of absorbed water in their nanoporous [2].

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 mathematical 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. The treatment of experimental data was carried out at fixed lifetime values of τ_1=0.18 ns and τ_2=0.38 ns. Within this approach I_1 and I_2 intensities of the direct PAL components are

changes dependently from amount of adsorbed water in the studied ceramics. So increasing of RH from 25 to 98 % result in decreasing of I_1 intensity and increasing of I_2 intensity. The changing of RH from 98 to 25 % reflects inverse to the previous direction in I_1 and I_2 intensities (see table 1). The positron trapping in water-filled defects reflecting the second component with I_2 intensity occurs more intensive.

Table 1 – PAL characteristics of MgAl$_2$O$_4$ ceramics

RH, %	Fitting parameters					
	τ_1, ns	I_1, a.u.	τ_2, ns	I_2, a.u.	τ_3, ns	I_3, a.u.
25	0.18	0.79	0.38	0.20	2.37	0.01
60	0.18	0.78	0.38	0.21	2.55	0.01
98	0.18	0.76	0.38	0.23	2.27	0.01
60	0.18	0.77	0.38	0.22	2.26	0.01
25	0.18	0.78	0.38	0.21	2.21	0.01
RH, %	Positron trapping modes					
	τ_{av}, ns	τ_b, ns	κ_d, ns^{-1}		$\tau_2 - \tau_b$, ns	τ_2/τ_b
25	0.22	0.20	**0.59**		0.18	1.89
60	0.22	0.20	**0.62**		0.18	1.87
98	0.22	0.20	**0.67**		0.18	1.86
60	0.22	0.20	**0.64**		0.18	1.87
25	0.22	0.20	**0.61**		0.18	1.88

The lifetimes τ_3 are closed to ~2.2-2.5 ns (see Table 1). The input of this third component is not change and intensity closed to 0.01. Thus, this channel is non-significant to water sorption-desorption processes. The positron trapping modes such as the average τ_{av}, defect-free bulk τ_b and 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 MgAl$_2$O$_4$ ceramics level of ~1.9 [2], which testify to the same nature of trapping sites whichever the content of absorbed water. In contrast, most significant changes in positron trapping in MgAl$_2$O$_4$ 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 non-direct trapping κ_d parameter.

4. CONCLUSION

The fixation of all water-dependent positron trapping inputs allow to refine the most significant changes in positron trapping rate of extended defects and nanopores located near intergranual boundaries. The water sorption processes in nanoporous humidity-sensitive spinel-type MgAl$_2$O$_4$ ceramics leads to corresponding increase in positron trapping rates of extended defects located near intergranual boundaries. This catalytic affect has reversible nature, being strongly dependent on sorption water fluxes in ceramics.

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