Unified model of multichannel positron annihilation in nanoporous magnesium aluminate ceramics

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Abstract. The unified multichannel positron annihilation model in humidity-sensitive nanoporous MgAl2O4 ceramics with a spinel structure was generalized. It is shown that this model unifies the channels of positron trapping and ortho-positronium decaying. Within this approach, the first component in the lifetime spectra reflects microstructure specificity of the spinel structure with character octahedral and tetrahedral cation vacancies, the second component responsible to extended defects near intergranual boundaries and the third component correspond to “pick-off” annihilation of ortho-positronium in the water-filled nanopores of ceramics.

1. Introduction

Sintered nanoporous MgAl2O4 ceramics with a spinel structure are one of the most perspective materials in view of their application as active elements for humidity sensors [1-3]. Because of significant complications in the microstructure of these ceramics revealed at the levels of individual grains, intergranual boundaries and pores, the further progress in this field is dependent on the development of new characterization techniques, which can be used in addition to traditional ones. This concerns, in part, the positron annihilation lifetime (PAL) spectroscopy, the method recently applied to ceramics because significant complications in correct interpretation of the obtained data [4].

Several attempts have been made to develop a unified phenomenological model describing positron annihilation in metallic Cu-, W-, Ni-contained powders [5], some kinds of sintered BaTiO3 [6,7] and SrTiO3 [8,9] perovskites, nanocrystalline ferrites [10] and hot-isostatic-pressed transparent magnesium aluminate MgAl2O4 ceramics [11]. It was shown that the main channels of positron annihilation in these materials could be ascribed to positron trapping and ortho-positronium o-Ps decay modes, the best fitting being achieved using at least three independent components in the resolved lifetime spectra [10-13]. In terms of this model, the second positron trapping component with lifetime $\tau_2$ is attributed to free-volume defects such as vacancy-like clusters, powder particle surfaces neutral or negatively-charged vacancies especially near intergranual boundaries. The shortest component named the reduced bulk positron lifetime $\tau_I$ is mainly due to annihilation in defect-free bulk with small mixing from other positron trapping channels. The largest component is responsible for a so-called o-Ps “pick-off” annihilation [4].

Thus, in the case of sintered functional ceramics, two channels of positron annihilation should be considered – the positron trapping and o-Ps decaying. In general, these processes are independent
ones. However, if trapping sites will appear in a vicinity of intergranual boundaries neighboring with free-volume pores, they can become mutually interconnected resulting in a significant complication of the measured PAL spectra. This occurs provided the input of one of the above annihilation channels will be significantly changed. As was shown early in [14], the PAL characteristics for MgAl2O4 spinel-type ceramics affected to water-sorption treatment enhancing o-Ps decaying over positron trapping modes. In these work we shall try to generalize the unified model of multichannel positron annihilation in humidity-sensitive spinel-type MgAl2O4 ceramics taking into account the microstructure specificity of a spinel structure and influence of water-sorption processes in nanopores on positron trapping modes.

2. Experimental
The studied MgAl2O4 ceramics were prepared in a special regime with maximal sintering temperature \( T_s = 1100-1400 \, ^\circ\text{C} \) during 2 h from initial fine-dispersive powders of MgO and Al2O3 as was described in more details elsewhere [14-16]. In respect to X-ray diffraction analysis, the ceramics sintered at 1100-1200 \, ^\circ\text{C} \) contained main spinel phase and additional MgO and \( \alpha \)-Al2O3 phases. In contrast, the ceramics sintered at 1300-1400 \, ^\circ\text{C} \) contained only small quantity of MgO phase (3.5 and 1.5 \, %, respectively) [14,16].

PAL measurements with a full width at half maximum of 270 ps were performed at 20 \, ^\circ\text{C} \) and \( \sim 35 \, \% \) relative humidity using an ORTEC spectrometer [4,17]. The \( ^{22}\text{Na} \) isotope source placed between two sandwiched samples as it was described in more details elsewhere [13-15,17]. In order to change interrelation between positron trapping and o-Ps decay modes in the deconvoluted PAS spectra, we placed the samples into distillated water for 12 h. Then, the PAL measurements were repeated once more with water-moistened ceramics at the same conditions [14].

The obtained spectra were mathematically treated with LT computer program of J. Kansy [18], the best results corresponding to three-component fitting. In general, we used 4-5 measured spectra for each pair of samples differed by a total number of elementary annihilation events in the range of 0.9-1.2 millions. Each of these spectra was multiply treated owing to slight changes in the number of final channels, annihilation background and time shift of the spectrum. Then, the variance of statistically weighted least-squares deviations between experimental points and theoretical curve was taken into account to compare the obtained results. Only results with deviations quite close to 1.0 (the optimal deviation ranges from 0.95 to \( \sim 1.1-1.2 \) [4,15]) were left for further consideration. In such a way, we obtained the numerical PAL parameters (positron lifetimes \( \tau_1, \tau_2 \) and \( \tau_3 \) and intensities \( I_1, I_2 \) and \( I_3 \)) which correspond to annihilation of positrons in the samples of interest.

The positron trapping modes in the sintered MgAl2O4 ceramics were calculated using a known formalism for two-state positron trapping model [4,17]:

\[
\tau_{av.} = \frac{\tau_1 I_1 + \tau_2 I_2}{I_1 + I_2}, \quad \tau_b = \frac{I_1 + I_2}{I_1 I_2} \quad \text{and} \quad \kappa_d = \frac{I_2}{I_1} \left( \frac{1}{\tau_b} - \frac{1}{\tau_2} \right),
\]

where \( \tau_{av.} \) is average positron lifetime,
\( \tau_b \) – positron lifetime in defect-free bulk,
\( \kappa_d \) – positron trapping rate in defect.

In addition, the \( (\tau_2 - \tau_b) \) difference was accepted as a size measure for extended free-volume defects where positrons are trapped (in terms of equivalent number of monovacancies), as well as the \( \tau_2/\tau_b \) ratio was taken in a direct correlation to the nature of these defects [4,12].

3. Results and Discussion
The normalized PAL spectra for as-prepared and water-immersed MgAl2O4 ceramics sintered at 1100, 1200, 1300 and 1400 \, ^\circ\text{C} \) are shown in figure 1. They are characterized by a narrow peak and region of long fluent decaying of coincidence counts in a time. The mathematical decay of such curve can be
represented by a sum of decreasing exponents with different values of power-like indexes inversed to positron lifetimes [14,19,20].

![Figure 1. Peak-normalized PAL spectra for as-prepared (a) and water-immersed (b) MgAl2O4 ceramics sintered at 1100-1400 °C](image)

As was shown early in [14,15], in the case of MgAl2O4 ceramics, two channels of positron annihilation should be considered – the positron trapping with shortest $\tau_1$ and middle $\tau_2$ lifetimes and o-Ps decaying with longest $\tau_3$ lifetime, these channels being independent ones (see figure 2).

Taking into account the model described in [10,12,15], the shortest lifetime component (the first channel of positron annihilation) in the studied ceramics reflects mainly the microstructure specificity of the spinels. So in the case of MgAl2O4 ceramics, the empty tetrahedral and octahedral cation vacancies proper to spinel-type structure are known to be potential positron traps, the trapping in octahedral vacancies having a larger free volume being preferential [12]. So, the average volume of these tetrahedrons $V_{\text{tetra}}$ and octants $V_{\text{octa}}$ can be chosen as main free-volume parameters for ceramics under consideration.

It is well known that radius of tetrahedral and octahedral sites in a spinel structure can be simply calculated through lattice parameter $a$ [11,15]:

$$R_{\text{tetra}} = \sqrt[3]{\frac{u - 1}{4}}a - R_0,$$

$$R_{\text{octa}} = \left(\frac{5}{8} - u\right)a - R_0,$$

where $u$ is a so-called oxygen parameter and $R_0$ is oxygen atom radius (1.32 Å).

Since the oxygen parameter $u$ in oxide spinels is close to 0.385 and only slightly depends on cation type [11], the estimated tetrahedral site radius reaches of 0.58 Å, which gives $V_{\text{tetra}}$ (in spherical approximation) reaching 0.82 Å³. At the same time, the estimated octahedral site volume $V_{\text{octa}}$ is as high as 0.95 Å³.

As was shown early in [12], the positron trapping in tetrahedral vacancies dominates in the first PAL component, while the overall positron trapping in octahedral vacancies, is preferential for inverse spinel-type structures.
It is shown (see table 1) that in as-prepared sample the lifetime \( \tau_1 \) of this first component slightly decreases with \( T_s \), while the intensity \( I_1 \) increase. Obviously, these changes reflect structural perfectiveness of ceramics prepared at higher \( T_s \). It should be noted that these tendencies are maintained in water-immersed MgAl2O4 ceramics too. But the intensity \( I_1 \) substantially decrease in samples after 12 h into water, while the lifetime \( \tau_1 \) remains invariable and only slightly rises in more perfect ceramics structure prepared at higher \( T_s = 1400 \) °C (see table 1 and table 2).

Table 1. PAL characteristics of as-prepared MgAl2O4 ceramics mathematically treatment within three-component fitting procedure

| \( T_s \) °C | \( \tau_1 \) ns | \( I_1 \) a.u. | \( \tau_2 \) ns | \( I_2 \) a.u. | \( \tau_3 \) ns | \( I_3 \) a.u. | \( \tau_{av} \) ns | \( \kappa_0 \) ns\(^{-1} \) | \( \tau_2 - \tau_3 \) ns | \( \tau_3 / \tau_2 \) |
|----------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|-----------------|----------------|-----------------|
| 1100     | 0.24           | 0.68           | 0.50           | 0.30           | 2.59           | 0.02           | 0.32           | 0.28            | 0.6             | 0.21            | 1.7             |
| 1200     | 0.23           | 0.70           | 0.47           | 0.28           | 2.39           | 0.02           | 0.30           | 0.27            | 0.6             | 0.20            | 1.7             |
| 1300     | 0.22           | 0.72           | 0.44           | 0.26           | 2.19           | 0.02           | 0.27           | 0.25            | 0.6             | 0.19            | 1.7             |
| 1400     | 0.19           | 0.76           | 0.36           | 0.22           | 1.90           | 0.02           | 0.24           | 0.21            | 0.6             | 0.15            | 1.7             |

By accepting two-state positron trapping model [4,17], the longer \( \tau_2 \) lifetime can be treated as defect-related one, these positron trapping defects being located near intergranual boundaries [13,16]. In respect to initial XRD measurements [14,13], in the studied MgAl2O4 ceramics, the amount of additional phases is dependent on \( T_s \). In accordance with scanning electron microscopy data presented in [15], the observed additional phases are non-uniformly distributed within ceramics bulk, being more clearly pronounced near intergranual boundaries. So the positrons are trapped more strongly in the spinel-type ceramics obtained at lower \( T_s \), which is reflected in the middle component of lifetime spectra.

As it followed from table 1 and table 2, the fitting parameters of this lifetime component (\( \tau_2 \) and \( I_2 \)) significantly decrease with \( T_s \) and practically does not change in water-immersed ceramics sintered at lower \( T_s \) (1100 and 1200 °C). Nevertheless, these parameters increase in ceramics obtained at higher \( T_s \) (1300 and 1400 °C), especially the intensities \( I_2 \). Consequently, the corresponding positron trapping modes of extended defects near intergranual boundaries will be changed too.
Table 2. PAL characteristics of water-immersed MgAl2O4 ceramics mathematically treatment within tree-component fitting procedure

| $T_\text{sw}$, °C | Fitting parameters | Positron trapping modes |
|------------------|-------------------|-------------------------|
|                  | $\tau_1$, ns | $I_1$, a.u. | $\tau_2$, ns | $I_2$, a.u. | $\tau_3$, ns | $I_3$, a.u. | $\tau_\text{av}$, ns | $\tau_b$, ns | $\kappa_d$, ns$^{-1}$ | $\tau_2 - \tau_b$, ns | $\tau_2/\tau_b$ |
| 1100             | 0.24            | 0.56          | 0.50          | 0.29          | 1.88          | 0.15          | 0.33          | 0.29          | 0.7           | 0.21          | 1.7 |
| 1200             | 0.23            | 0.59          | 0.48          | 0.28          | 1.88          | 0.13          | 0.32          | 0.28          | 0.7           | 0.20          | 1.7 |
| 1300             | 0.22            | 0.54          | 0.46          | 0.32          | 1.88          | 0.15          | 0.31          | 0.27          | 0.9           | 0.19          | 1.7 |
| 1400             | 0.21            | 0.56          | 0.43          | 0.32          | 1.94          | 0.12          | 0.29          | 0.26          | 0.9           | 0.17          | 1.7 |

Indeed, the values of such parameters as $\tau_\text{av}$, $\tau_b$ and ($\tau_2 - \tau_b$) decrease with $T_\text{sw}$ in good accordance with amount of additional phases in the intergranual boundaries. But in all cases, the same type of positron trapping centre is formed since there are no differences in $\tau_2/\tau_b$ value with $T_\text{sw}$ (see table 1 and table 2). The character size of these extended positron traps near intergranual boundaries estimated due to ($\tau_2 - \tau_b$) difference is close to single-double atomic vacancies [4]. Nevertheless, the positron trapping rate of such extended defect $\kappa_d$ decrease from 0.6 ns$^{-1}$ in as-prepared samples sintered at 1100 and 1200 °C to 0.7 ns$^{-1}$ in water-moistened ceramics ones and substantially increase to 0.9 ns$^{-1}$ in ceramics obtained at 1300 and 1400 °C. It means that water-sorption processes act catalytically on positron trapping in MgAl2O4 ceramics. Nevertheless, there were no significant changes in $\tau_2/\tau_b$ and ($\tau_2 - \tau_b$) parameters testifying in a favour of the same nature of trapping sites whichever the content of absorbed water.

The third longest component (lifetime $\tau_3$ and intensity $I_3$) in the resolved lifetime spectra is due to “pick-off” annihilation of o-Ps atoms in the intergranual pores [4,14]. In as-prepared samples, the $\tau_3$ lifetimes decrease from ~2.6 to 1.9 ns with increase in $T_\text{sw}$, but $I_3$ intensity leaves at the same level close to 2 %. These changes are connected with more branched structure of the open pores [21] of the ceramics sintered at higher $T_\text{sw}$ (1300 and 1400 °C). With $T_\text{sw}$ growing, the o-Ps “pick-off” decaying occurs preferentially in the nanopores filled by absorbed water; while the ceramic samples sintered at relatively low $T_\text{sw}$ (1100 and 1200 °C) show this process in both water-filled and water-free nanopores.

In addition, in water-moistened ceramics sintered at 1100-1300 °C, the longest $\tau_3$ lifetime decreases to ~1.88 ns (see table 2) approximating to 1.84 ns value which is character for o-Ps “pick-off” decaying in liquid water at 20 °C [22]. However, this lifetime does not change after water-immersion treatment in ceramics with more perfect structure (sintered at $T_\text{sw} = 1400$ °C). In all water-moistened samples, the intensity of this component increases from 0.02 to 0.12-0.15 indicating a large content of absorbed water present in ceramics bulk.

4. Conclusions

Thus, the unified multichannel positron annihilation model in nanoporous MgAl2O4 ceramics with a spinel structure can be generalized involving discrete positron trapping and o-Ps decaying due to “pick-off” annihilation of o-Ps atoms in the intergranual pores. The shortest component in the lifetime spectra ($\tau_1 \approx 0.19-0.24$ ns) reflects mainly microstructure specificity of the spinel structure with character octahedral and tetrahedral cation vacancies. The extended defects near intergranual boundaries with the different amount of additional phases are supposed to be responsible for middle lifetime component ($\tau_3 \approx 0.36-0.59$ ns). The third lifetime component ($\tau_3 \approx 1.88-2.6$ ns) corresponds to “pick-off” annihilation of o-Ps in the water-filled nanopores of ceramics. In addition, the water-sorption processes act catalytically on positron trapping.

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