Water-Sorption Effects near Grain Boundaries in Modified MgO–Al₂O₃ Ceramics Tested with Positron–Positronium Trapping Algorithm

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Water-sorption processes near grain boundaries in the MgO–Al₂O₃ ceramics prepared at different temperatures were studied using positron annihilation lifetime spectroscopy. Numerical values of three- and four-component treatment of spectra were used for study of physical- and chemical-sorption processes in the MgO–Al₂O₃ ceramics. To apply mathematical approach in the form of positron–positronium trapping algorithm into three-component treatment of positron annihilation lifetime spectra it was shown that physical-adsorbed water did not modify positron trapping sites near grain boundaries in water-immersed MgO–Al₂O₃ ceramics and localized mainly in nanopores. The chemically-adsorbed water modifies structural extended defects located near grain boundaries that accompanied them by void fragmentation at water desorption.

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1. Introduction

Humidity-sensitive MgO–Al₂O₃ ceramics are well-known materials with extended porous structure providing their wide functional applications [1–3]. These ceramics are stable in comparison with other porous functional materials possessing rapid response to humidity changes [4]. These changes provide by microstructure of grains, grain boundaries and pores (or free-volume entities) in ceramic materials [5, 6].

Influence of initial surface area of initial components (MgO and Al₂O₃) on the structural properties of MgO–Al₂O₃ ceramics prepared at 1100–1400°C was studied early in [7–10]. As was established in [11], structural properties of spinel ceramics depend on their sintering temperature and duration. Structure of humidity-sensitive MgO–Al₂O₃ ceramics is improved with the increase of sintering temperature, which mainly results in the transformation of pore size distribution and decrease of amount of MgO/Al₂O₃ phases located near grain boundaries. Evolution of pore size distribution (increases of amount and quantity of open micro-, macro- and nanopores) in humidity-sensitive spinel ceramics leads to better water-adsorption and desorption processes with minimal hysteresis of exploitation characteristics in these materials [7, 11].

Porous structure of functional materials are studied using traditional methods such as X-ray diffraction, electron microscopy and different porosimetry methods, etc. [12, 13]. However, porosimetry techniques provide information on open pores with radii over 2 nm [13], whereas processes of capillary condensation in such ceramics depend also on nanopores smaller than 2 nm [14].

To study such small nanopores and free volumes in ceramic structure we used the method of positron annihilation lifetime (PAL) spectroscopy, which is alternative tool of structural characterization of open and closed nanopores [15]. Two channels of positron annihilation were shown to be important in case of ceramics: positron trapping (two components) and ortho-positronium (o-Ps) decaying (one or two components) [16]. 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–positronium traps become mutually interconnected resulting in a significant complication of PAL data. This occurs provided the input of one of the above annihilation channels will be significantly changed. In addition, adsorbed water influences on processes of physical and chemical adsorption of water near grain boundaries in the MgO–Al₂O₃ ceramics.

Early we used PAL method to study influence of sintering conditions in the MgO–Al₂O₃ ceramics in general (to characterization of MgO–Al₂O₃ ceramics sintered at 1100–1400°C) and water-sorption processes in nanopores of these materials (at analysis of third and fourth com-
ponents of PAL spectra) [10, 17]. In this work, to clarify this feature, we shall analyze physical water-sorption process near grain boundaries in the modified MgO–Al₂O₃ ceramics using positron–positronium trapping algorithm proposed in [18] (at interpretation of three-component treatment of PAL spectra) in comparison with chemical water-sorption process at decomposition of PAL spectra into four components.

2. Experimental

The modified MgO–Al₂O₃ ceramics were prepared using traditional ceramic route at maximal temperatures ($T_s$) of 1100–1400°C during 2 h as it was described in [7–11, 17, 19]. In respect to X-ray diffraction measurements [7], the ceramics prepared at lower $T_s = 1100–1200$°C are composed of main spinel phase and large amount of additional MgO and Al₂O₃ phases (up to 12%), while the ceramics sintered at high $T_s$ of 1300°C and 1400°C contain additionally only MgO phase in the amount of 3.5 and 1.5%, respectively.

The PAL measurements were performed with the ORTEC instrument ($^{22}$Na source) [17]. The first experiment were performed at 22°С and relative humidity RH = 35% after immersion of ceramic samples into distilled water for 12 h. Then, the PAL measurements were repeated once more with water-immersed ceramics at the same conditions. In the second case PAL measurement for ceramic samples was carried out at 22°C and relative humidity RH = 35% after 1 day of water exposure (water wetting in distiller at RH = 100%) and drying in a vacuum at 120°C during 4 h [17].

Each PAL spectrum was collected to analyze short and intermediate PAL components. Further processing of PAL spectra was performed with LT 9.0 program [20] considering the three- or four-component treatment [7, 17, 21]. In spinel ceramics the lifetime $\tau_2$ is related to the size of free-volume defects (or voids) near grain boundaries, and $I_2$ intensity reflects their amount [17]. The third and fourth components ($\tau_3, I_3$) and ($\tau_4, I_4$) originate from annihilation of o-Ps atoms in intrinsic nanopores of MgO–Al₂O₃ ceramics. Using positron trapping parameters, the positron trapping modes (average positron lifetimes $\tau_{av}$, positron lifetime in defect-free bulk $\tau_0$ and positron trapping rate in defects $\kappa_d$) were calculated within two-state positron trapping model [9, 22].

The effects caused by physical-adsorbed water in modified MgO–Al₂O₃ ceramics were studied using the positron–positronium trapping algorithm detail described in [18] (in the case of three-component treatment of PAL spectra). This method is a test-indicator in terms of transformation of positronium sites in the initial MgO–Al₂O₃ matrix towards positron trapping sites in MgO–Al₂O₃ ceramics with absorbed water. In respect to algorithm described in [18], physical parameterization water-related sites can be finally performed taking ($\tau_{int}, I_{int}$) as corresponding components of the generalized two-

3. Results and discussion

Typical PAL spectra reconstructed on three components for modified MgO–Al₂O₃ ceramics prepared at 1400°C are shown in Fig. 1. As it was established early in [7, 11] the MgO–Al₂O₃ ceramics are characterized by good adsorption capacity, which is provided by branched porous structure and specificity formation of grains and grain boundaries. But desorption processes in ceramics are more interesting to investigation, since part of absorbed water remains in the internal structure of material localized near grain boundaries and in small nanopores. Schematic cut-section diagram illustrating water-adsorption processes in ceramics is shown in Fig. 2.
Positron trapping parameters and modes in “dry” (investigated at 20°C and 35% of relative humidity) and “immersed” ceramics sintered at different $T_s$ is shown in Table I. It is established that the third largest component is affected by the biggest changes. The filling of nanopores of ceramics by water is manifested in increase of intensity $I_3$ from 0.02 to 0.12–0.15, which reflects more intense annihilation of $\alpha$-Ps in nanopores filled by water.

The positron trapping parameters caused by residual water (or humidity) were estimated using the positron–positronium trapping algorithm, early used to study evolution of voids in Ge–Ga–Se glasses caused by their “cold” crystallization [23]. Water-immersed (“immersed”) MgO–Al₂O₃ ceramics sintered at different $T_s$ were taken as modified matrix and “dry” ceramics sintered at the same temperatures — as initial matrix. Comparative analysis parameters of own positron trapping and corresponding parameters for modified matrix is shown in Table II.

### Table I

<table>
<thead>
<tr>
<th>$T_s$ [°C]</th>
<th>Matrix pre-history</th>
<th>Fitting parameters</th>
<th>Positron trapping modes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\tau_1$ [ns]</td>
<td>$I_1$ [a.u.]</td>
</tr>
<tr>
<td>1100</td>
<td>“dry”</td>
<td>0.24</td>
<td>0.68</td>
</tr>
<tr>
<td>1200</td>
<td>“immersed”</td>
<td>0.24</td>
<td>0.56</td>
</tr>
<tr>
<td>1300</td>
<td>“dry”</td>
<td>0.23</td>
<td>0.70</td>
</tr>
<tr>
<td>1400</td>
<td>“immersed”</td>
<td>0.23</td>
<td>0.59</td>
</tr>
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</table>

### Table II

Comparison of own positron trapping parameters with corresponding parameters for the modified (“dry”) matrix of MgO–Al₂O₃ ceramics (calculated within positron–positronium trapping algorithm)

<table>
<thead>
<tr>
<th>$T_s$ [°C]</th>
<th>Fitting parameters and positron trapping modes for modified (“dry”) matrix</th>
<th>Own positron trapping parameters and modes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\tau_2$ [ns]</td>
<td>$I_2$ [a.u.]</td>
</tr>
<tr>
<td>1100</td>
<td>0.50</td>
<td>0.30</td>
</tr>
<tr>
<td>1200</td>
<td>0.47</td>
<td>0.28</td>
</tr>
<tr>
<td>1300</td>
<td>0.44</td>
<td>0.26</td>
</tr>
<tr>
<td>1400</td>
<td>0.36</td>
<td>0.22</td>
</tr>
</tbody>
</table>

### Table III

Positron trapping parameters and modes for “water-wetted” and “dried” MgO–Al₂O₃ ceramics sintered at different $T_s$

<table>
<thead>
<tr>
<th>Matrix pre-history</th>
<th>$\tau_1$ [ns]</th>
<th>$I_1$ [a.u.]</th>
<th>$\tau_2$ [ns]</th>
<th>$I_2$ [a.u.]</th>
<th>$\tau_3$ [ns]</th>
<th>$I_3$ [a.u.]</th>
<th>$\tau_4$ [ns]</th>
<th>$I_4$ [a.u.]</th>
<th>$\tau_{av.}$ [ns]</th>
<th>$\tau_b$ [ns]</th>
<th>$\kappa_d$ [ns⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1100°C “water-wetted”</td>
<td>0.17</td>
<td>0.66</td>
<td>0.48</td>
<td>0.28</td>
<td>1.820</td>
<td>0.044</td>
<td>53.05</td>
<td>0.009</td>
<td>0.263</td>
<td>0.21</td>
<td>1.15</td>
</tr>
<tr>
<td>1100°C “dried”</td>
<td>0.17</td>
<td>0.68</td>
<td>0.45</td>
<td>0.29</td>
<td>2.215</td>
<td>0.021</td>
<td>68.29</td>
<td>0.019</td>
<td>0.257</td>
<td>0.21</td>
<td>1.08</td>
</tr>
<tr>
<td>1200°C “water-wetted”</td>
<td>0.17</td>
<td>0.64</td>
<td>0.42</td>
<td>0.31</td>
<td>2.047</td>
<td>0.038</td>
<td>58.67</td>
<td>0.004</td>
<td>0.252</td>
<td>0.21</td>
<td>1.19</td>
</tr>
<tr>
<td>1200°C “dried”</td>
<td>0.16</td>
<td>0.72</td>
<td>0.43</td>
<td>0.23</td>
<td>2.290</td>
<td>0.031</td>
<td>68.87</td>
<td>0.017</td>
<td>0.229</td>
<td>0.19</td>
<td>0.93</td>
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<tr>
<td>1300°C “water-wetted”</td>
<td>0.16</td>
<td>0.76</td>
<td>0.40</td>
<td>0.21</td>
<td>2.619</td>
<td>0.018</td>
<td>58.33</td>
<td>0.007</td>
<td>0.213</td>
<td>0.19</td>
<td>0.80</td>
</tr>
<tr>
<td>1300°C “dried”</td>
<td>0.15</td>
<td>0.82</td>
<td>0.42</td>
<td>0.15</td>
<td>2.448</td>
<td>0.007</td>
<td>68.17</td>
<td>0.014</td>
<td>0.198</td>
<td>0.17</td>
<td>0.63</td>
</tr>
<tr>
<td>1400°C “water-wetted”</td>
<td>0.16</td>
<td>0.77</td>
<td>0.41</td>
<td>0.20</td>
<td>2.562</td>
<td>0.022</td>
<td>57.35</td>
<td>0.006</td>
<td>0.211</td>
<td>0.18</td>
<td>0.78</td>
</tr>
<tr>
<td>1400°C “dried”</td>
<td>0.15</td>
<td>0.89</td>
<td>0.40</td>
<td>0.10</td>
<td>2.539</td>
<td>0.007</td>
<td>61.85</td>
<td>0.008</td>
<td>0.179</td>
<td>0.16</td>
<td>0.40</td>
</tr>
</tbody>
</table>

As was described in [18], the component with defect-related $\tau_{int}$ lifetime can reflect positron trapping sites caused by water. Under accepted prerequisites, these extended defects can be associated with pseudogap voids at the interface between the outer surface layer of agglomerated nanoparticles and innermost layer of surrounding initial matrix (as it well demonstrated in [24, 25]). The bulk positron lifetime can now be attributed to...
bulk positron lifetime of nanoparticle agglomerate. The positron trapping rate of nanoparticle-related traps $\kappa_d$ can be also estimated in terms of known two-state positron trapping formalism [26].

Therefore, the defect-related lifetime $\tau_{int}$ caused by water-immersion in ceramics sintered at different $T_s$, remains the same as lifetime $\tau_2$ for modified (“dry”) matrix (Table II). Other values of positron trapping parameters such as $\tau_{av.}$ and $\tau_b$, lifetimes associated with the positron annihilation in defect-free area in material and positron trapping rate in defects $\kappa_d$ have not essential transformations. However, the intensity of the third component $I_3$ (Table I) in “immersed” ceramics is higher in order in “dry” samples. Such a result can be indicated that physical-adsorbed water fills the nanopores of ceramics, where “pick-off” annihilation of $o$-Ps in water for a “bubble” mechanism occurs (lifetime $\tau_3 \approx 1.88$ ns reflects annihilation of $o$-Ps in water) [27]. However, physical-adsorbed water does not modify positron trapping sites near grain boundaries.

In comparison with the first experiment, the second experiment was performed for MgO–Al₂O₃ ceramics immersed for 1 day in a distiller at 100% of relative humidity and finally dried ceramics in vacuum for 4 h at 120°C (Table III). Obtained effects are described in detail in [17]. The PAL spectra were decomposed in four components, but in this work we shall focus mainly on transformations in the second ($\tau_2$, $I_2$) component.

Structure of MgO–Al₂O₃ ceramics sintered at 1100°C, 1200°C is still not sufficiently developed, and not all adsorbed water is desorbed (part of them clogs voids near grain boundaries). The ceramics obtained at higher temperatures of 1300°C and 1400°C have a developed structure of grains and pores [7, 11].

As shown in Table III, preferential decrease of the lifetime $\tau_2$ in water-wetted MgO–Al₂O₃ ceramics and increase of their intensity $I_2$ demonstrates intensification of positron trapping in defects near grain boundaries filled with water (Table III). The value of defect-related lifetime $\tau_2$ caused by desorption of water is lower than in the case of water-wetted ceramics sintered at 1100°C (Table III). Thus, adsorbed water in ceramics sintered at lower temperature clogs part of voids near grain boundaries (sites where positrons can be trapped).

After drying, the intensities $I_2$ decrease in ceramics sintered at 1300°C and 1400°C, whereas $\tau_2$ lifetimes are larger in ceramics prepared at 1200°C and 1300°C. Thus, most probably the water-desorption processes are accompanied by agglomeration of free-volume voids near grain boundaries in MgO–Al₂O₃ ceramics at water desorption.

4. Conclusions

Water-sorption processes near grain boundaries in the modified MgO–Al₂O₃ ceramics prepared at different temperature are studied using three- and four-component treatment as well as positron–positronium trapping algorithm. Performed analysis allows to suppose that physical-adsorbed water is mainly localized in the nanopores of ceramics and practically does not penetrate into grain boundaries. The chemical-adsorbed water near grain boundaries modifies voids where positrons can be trapped. This process is accompanied by fragmentation of voids at water desorption.

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References


