Water-sensitive positron trapping modes in nanoporous magnesium aluminate ceramics

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Abstract. The water-sensitive positron trapping modes in nanoporous MgAl₂O₄ ceramics with a spinel structure are studied. It is shown that water-sorption processes in magnesium aluminate 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. The fixation of all water-dependent positron trapping inputs allow to refine the most significant changes in positron trapping rate of extended defects.

1. Introduction
Nanoporous magnesium aluminate spinel-type MgAl₂O₄ ceramics are perspective materials for humidity sensors due to formation of the uniform porous structure of the surface, which promotes effective cooperative adsorption of water molecular [1-4]. In other worlds, the humidity-sensing application of these ceramics are known to be determinant of chemical and physical water-sorption processes occurring within inner pores in ceramics bulk [2,5]. The presence of open porosity permits greater conductivity due to the enhancement of the specific surface area available for water adsorption [4-6]. Recently, it was shown that amount of adsorbed water in these ceramics affects not only their electrical conductivity, but also other physical-chemical parameters. Such parameters can be the positron trapping modes of extended free-volume defects studied by positron annihilation lifetime (PAL) spectroscopy – one of the most powerful experimental methods for studying of structurally intrinsic voids in solids, which was effectively used earlier for investigation of vacancy-like defects and some their extended modifications (clusters, agglomerates, micro- and nanopores, etc.) [7,8].

The PAL method based on the fact that the unstable positron-electron system (positronium Ps) is repelled from ionic cores of atoms and tends to location in open pores [8,9]. In the ground state, the Ps exists as singlet para-positronium p-Ps and triplet ortho-positronium o-Ps. In matter, since the positron wave function overlaps with electrons outside the o-Ps. The latter process is called “pick-off” annihilation [8-13].

As was shown early [7,14,15], positrons injected in the studied MgAl₂O₄ ceramics can undergo two different processes such as positron trapping (two components) and o-Ps decaying (one component) obtained at three-component fitting procedure. Within this approach, the shortest component of
deconvoluted PAL spectra with positron lifetime $\tau_1$ reflects mainly microstructure specificity of the spinel structure and the middle component with positron lifetime $\tau_2$ corresponds to extended defects near intergranular boundaries. The third component with lifetime $\tau_3$ is due to “pick-off” annihilation of o-Ps in the intergranular nanopores filled by adsorbed water. It is established that the content of these adsorbed water influences on positron trapping modes of MgAl$_2$O$_4$ ceramics.

With this in mind, we shall try to develop new methodological approach in treatment of PAL data in MgAl$_2$O$_4$ ceramics in terms of water-sensitive positron trapping modes tested with positron annihilation technique.

2. Experimental

The studied spinel-type MgAl$_2$O$_4$ ceramics were sintered from fine-dispersive Al$_2$O$_3$ and MgO powders using a special regime with maximal temperatures of 1400 °C, the total duration being 2 h [7,14,16]. In a result, the humidity-sensitive ceramics with a so-called trimodal pore size distribution and character values of pore radiuses centered near $\sim$0.003, 0.09 and 0.4 µm were obtained [7,16]. The phase composition of ceramics obtained with X-ray diffraction [7,16] was established that the studied ceramics contained the main spinel phase and small quantity of MgO phase (1.54 %).

Experimental positron annihilation lifetime measurements were performed with an ORTEC spectrometer ($^{22}$Na source placed between two sandwiched ceramic samples) at 20 °C within row of relative humidity RH of 40-60-98 % and 5 % in He atmosphere. Special testing procedure with a set of standard thermally-treated non-defected Ni and Al probes was performed to correctly account for source input and other positron trapping channels in the measured lifetime spectra.

The obtained data were mathematically treated with known LT computer program of J. Kansy [17] at three-component fitting procedure with the fixed positron lifetimes of the first and second PAL components ($\tau_1$ and $\tau_2$). 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):

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

where $\kappa_d$ is positron trapping rate in defect, $\tau_0$ – positron lifetime in defect-free bulk and $\tau_{av}$ – average positron lifetime. In addition, the difference ($\tau_2 - \tau_0$) 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 $\tau_2/\tau_0$ ratio represents the nature of these defects [18,19].

3. Results and Discussion

Let’s try to discuss the new methodological approach in treatment of PAL data in MgAl$_2$O$_4$ ceramics in terms of water-sensitive positron trapping modes. So the previous PAL measurements in the studied ceramics sintered at 1400 °C was performed at 20 °C and 35 % relative humidity without special testing procedure without standard thermally-treated non-defected Ni and Al probes. The best results were obtained at three-component fitting procedure with corresponding positron lifetimes and intensities ($\tau_1 = 0.17$ ns, $I_1 = 0.74$; $\tau_2 = 0.35$ ns, $I_2 = 0.23$ and $\tau_3 = 1.83$ ns, $I_3 = 0.02$). 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 in different porous substances whichever their structural type [18,19]. It can be surmised this component is owing to predominant o-Ps “pick-off” decaying in the intergranular nanopores filled with absorbed water [7]. Since the water sorption reveals catalytic effect on positron trapping modes in MgAl$_2$O$_4$ ceramics [7], in our next investigations, we decided to fix all water-dependent positron trapping inputs in humidity-sensitive MgAl$_2$O$_4$ ceramics with the different contest of adsorbed water.
This approach can be well realized by fixing short positron lifetime $\tau_1$, which reflects microstructure specificity of spinel ceramics, as well as middle defect-related positron lifetime $\tau_2$, which corresponds to extended defects located near intergranal boundaries, where the studied ceramics are more defective [7,14,15]. In respect to our previous XRD measurements [7], the MgAl2O4 ceramics sintered at 1400 °C contains the prevailing spinel-type phase. The spinel structure of such ceramics is not changed at adsorption water by their nanopores. Therefore, the $\tau_1$ lifetime can be fixed on a typical for these ceramics values.

It was shown in [7], the positrons are trapped in the same extended defects located near intergranal boundaries both in as-prepared and water-moistened ceramic samples. In accordance with these data, the lifetime $\tau_2$ can be also fixed. At such methodological approach, changes in the fitting parameters of the first and second lifetime components of PAL spectra connecting with the different amount of adsorbed water in ceramics will be reflected in intensities $I_1$ and $I_2$.

Within this approach and taking into account the previous data obtained for the studied ceramics sintered at 1400 °C, the lifetimes $\tau_1$ and $\tau_2$ were fixed at the levels of 0.17 and 0.35 ns, respectively. In addition, with the aim of obtaining of minimal FIT, the lifetimes of these two components were also fixed on a typical for MgAl2O4 ceramics values, such as 0.18-0.19 ns (for $\tau_1$ lifetime) and 0.30-0.33-0.36-0.39 ns (for $\tau_2$ lifetime). Nevertheless, the best FIT was obtained at fixed lifetimes $\tau_1 = 0.17$ ns and $\tau_2 = 0.35$ ns. It should be noted that these results are in well agreement with the previous data obtained without non-defected Ni and Al probes at natural conditions (20 °C and 35 % relative humidity).

It is shown (see table 1) that in our case the intensity $I_1$ decrease with relative humidity, while the intensity $I_2$ increase. Obviously, these changes connected with increasing of content of adsorbed water in ceramics. Thus, the positron trapping in water-filled defects occurs more intensive.

| RH, % | $\tau_1$, ns | $I_1$, a.u. | $\tau_2$, ns | $I_2$, a.u. | $\tau_3$, ns | $I_3$, a.u. | $\tau_3I_3$, ns | $\tau_3I_3$, ns | $\tau_3I_3$, ns |
|-------|--------------|-------------|--------------|-------------|--------------|-------------|----------------|----------------|----------------|
| 5     | 0.17         | 0.76        | 0.35         | 0.22        | 2.13         | 0.02        | 0.13           | 0.08           | 0.03           |
| 40    | 0.17         | 0.75        | 0.35         | 0.24        | 2.38         | 0.01        | 0.13           | 0.08           | 0.03           |
| 60    | 0.17         | 0.68        | 0.35         | 0.31        | 2.52         | 0.01        | 0.12           | 0.11           | 0.03           |
| 98    | 0.17         | 0.63        | 0.35         | 0.36        | 2.70         | 0.01        | 0.11           | 0.13           | 0.03           |

The third longest non-fixed component in the deconvoluted lifetime spectra for the studied MgAl2O4 ceramics can be attributed to “pick-off” annihilation of o-Ps [5]. As is followed from table 1, the lifetime $\tau_3$ increase from 2.38 to 2.70 ns with increase of RH from 40 to 98 %, but $I_3$ intensity leaves at the same level close to 1-2 %. Nevertheless, the input of this third component ($\tau_3I_3$) is not change and closed to 0.03. Thus, this channel is non-significant during process of water sorption.

Within such methodological approach, the main numerical parameters (the average $\tau_m$, and defect-free bulk $\tau_0$ lifetimes and difference $\tau_2 - \tau_0$) are practically non-changed at increasing of relative humidity (see table 2). In addition, the positron trapping centre ($\tau_2/\tau_0$) is formed on a typical for MgAl2O4 ceramics level of ~1.75 [7,14], which testify to the same nature of trapping sites whichever the content of adsorbed water.

In contrast, the positron trapping rate in defect $\kappa_d$, considerable increases from 0.68 ns$^{-1}$ at 5 % RH to 1.1 ns$^{-1}$ at 98 % RH (see table 2). It means that water-sorption processes in nanopores act catalytically on positron trapping in MgAl2O4 ceramics. Thus, all water-sorption influences on positron trapping will be represented in positron trapping rate in defect located near intergranal boundaries and this $\kappa_d$ parameter will be determined as the main water-sensitive positron trapping modes in MgAl2O4 ceramics.
| RH, % | $\tau_{av}$, ns | $\tau_b$, ns | $\kappa_d$, ns$^{-1}$ | $\tau_2 - \tau_b$, ns | $\tau_2/\tau_b$ |
|-------|----------------|-----------|----------------|----------------|----------------|
| 5     | 0.21           | 0.19      | 0.68           | 0.16           | 1.82           |
| 40    | 0.21           | 0.19      | 0.74           | 0.16           | 1.80           |
| 60    | 0.23           | 0.20      | 0.94           | 0.15           | 1.73           |
| 98    | 0.24           | 0.21      | 1.10           | 0.14           | 1.67           |

The further development of this approach should be spread for humidity-sensitive spinel-type MgAl$_2$O$_4$ ceramics obtained at different sintering temperature 1100, 1200, 1300 and 1400 °C. No more important will be experimental study of sorption-desorption water processes in MgAl$_2$O$_4$ ceramics within row of relative humidity of 40-60-80-80-60-40 %.

4. Conclusions

The fixation of all water-dependent positron trapping inputs allow to refine the most significant changes in positron trapping rate of extended defects 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.

References

[1] Laobuthee A, Wongkasemjit S, Traversa E and Laine R M 2000 J. Europ. Ceram. Soc. 20 91
[2] Traversa E 1995 Sensor and Actuators B 23 135
[3] Chang M F, Gijsbertus de With, Stephen C P 2001 J. Am. Ceram. Soc. 84(7) 1553
[4] Gusmano G, Montesperelli G, Traversa E, Bearzotti A, Petrocco G, D’Amico A and Di Natale C 1992 Sensor and Actuators B 7 460
[5] Ichinose N 1985 Am. Ceram. Soc. Bull. 64(12) 1581
[6] Schreyeck L, Wlosik A and Fuzellier H 2001 J. Mater. Chem. 11 483
[7] Klym H, Ingram A, Shpotyuk O, Filipecki J and Hadzaman I 2007 Phys.Stat. Sol. (c) 4(3) 715
[8] Krause-Rehberg R and Leipner H S 1999 Positron Annihilation in Semiconductors. Defect Studies (Springer-Verlag, Berlin-Heidelberg-New York) p 378
[9] Consolati G, Dotelly G and Quaso F 2001 J. Am. Ceram. Soc. 84(1) 227
[10] Dryzyk J 1999 Acta Phys. Polonica (a) 95 539
[11] Shpotyuk O and Filipecki J 2003 Free volume in vitreous chalcogenide semiconductors: possibilities of positron annihilation lifetime study (Wydawnictwo Wyzszej Szkoły Pedagogicznej w Czestochowie) p 144
[12] Salgueiro A, Somoza O, Cabrera G and Consolati G 2004 Cement and Concres. Res. 34, 91
[13] Jasinska A, Dawidowicz T, Goworek S and Radkiewicz A L 2000 Phys. Chem. Chem. Phys. 2, 3269
[14] Balitska V, Filipecki J, Ingram A and Shpotyuk O 2007 Phys. Stat. Sol. (c) 4(3) 1317
[15] Shpotyuk O, Ingram A, Klym H, Vakiv M, Hadzaman I, and Filipecki J 2005 J. Europ. Ceram. Soc. 25, 2981
[16] Vynnyk I B, Hadzaman I V, Klym H I, Mrooz O Ya and Shpotyuk O I 2006 Technology and Design in Electronics. 2 60
[17] Kansy J 2000 Radiation Physics and Chemistry 58 427
[18] Ghosh S, Nambissan P M G and Bhattacharya R 2004 Phys. Lett. A 325 301
[19] Nambissan P M G, Upadhyay C and Verma H C 2003 J. Appl. Phys. 93 6320