Fine-Grained Material and Diffusion Trapping Model

(print view)

(Written by Jerzy Dryzek)

It is well known that a positron prior the annihilation with an electron in condensed matter spends a finite time:100 ps – 300 ps, randomly walking with thermal energies. This is well visible in the slow positron beam experiments, with the increasing entered positron energy the surface contribution to the measured positron annihilation characteristics decreases. In the conventional experiments based on the direct implantation of positrons emitted from the external radioactive source into the sample, the diffusion process is also present but well visible in fine grain samples where the size of the grain is comparable with the positron diffusion length defined as follows: $L_+ = \sqrt{D_+ \tau}$, where D_+ is the positron diffusion coefficient and τ is the positron lifetime. In metals L_+ it is about 0.1 μ m and in semiconductors 0.2 μ m.

The first attempt at observation of the effect how the size grains influences the positron lifetime tagging the positron diffusion in the polycrystalline Cu was performed by Lynn et al. 1974. The bimetallic samples consisting of many thin Ag and Cd layers obtained by the evaporation technique have been used for detection of the diffusive movements of thermal positrons in the angular distribution of annihilation photons (Świątkowski et al. 1975). However, quite reasonable results were obtained by McKee et al. 1980 and then repeated by Dong et al. 1991 who used the samples of the eutectoid fine grained Zn-22 wt.% Al alloy. In the latter the authors established the positron lifetime at a grain boundary is about 240 ps showing also that the mean positron lifetime and the inverse grain size is linear only when the grain size is larger than 0.5 μ m.

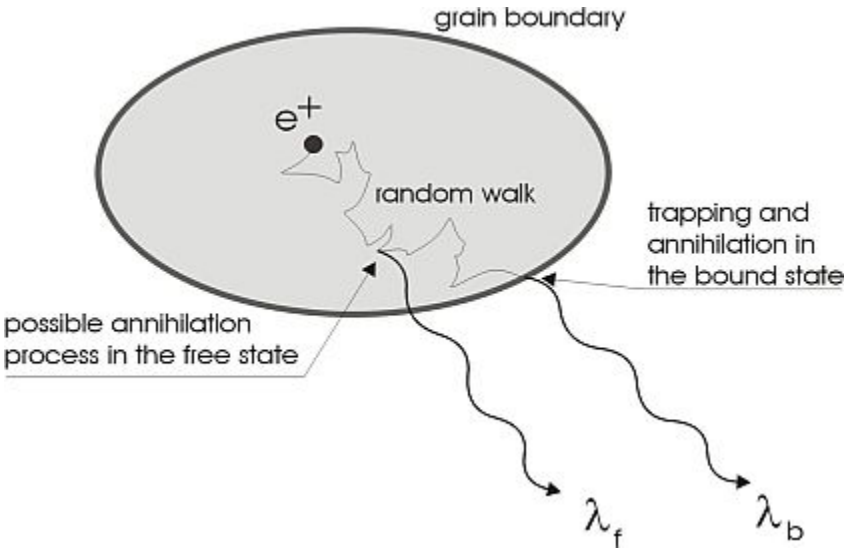

Fig.1 The presentation of the DTM assumptions.

The theoretical description of the phenomena of the positron diffusion comprises two approaches. In the first, the simplest one, it is assumed that during thermalization process the positrons are located in two distinct regions of a sample, e.g., grain and its boundary, in which they next annihilate (Hidalgo et al. 1982, Dong et al. 1991). Therefore, only the volume ratio of the two regions is important and the positron diffusion process could be neglected. In the second approach the positron diffusion is taken into account but at certain level of calculations the approximations were introduced to reduce the

solution to the well known results obtained within standard trapping model where diffusion is neglected (Brandt, Paulin 1972). Nevertheless, several authors have obtained the solution of the positron diffusion equation for particular cases, (Nieminen et al. 1979, Dupasquier et al. 1993). A Monte-Carlo simulation of the positron diffusion in spherical and ellipsoidal grains was carried out by Hübner et al. 1994 as well. However, the problem of the positron diffusion contribution on the measured characteristics is studied currently intensively due to the interest in fine grained and nanocrystaline materials (Schaefer (1992)).

The main assumption of the so called Diffusion Trapping Model (DTM) is based on the fact that the grain boundary is a perfect sink for positrons in which they are localized and then annihilate with the rate: $\lambda_b = 1/\tau_b < \lambda_f$, (this is so called Smoluchowski boundary condition). In the interior of the grain positrons may randomly walk and annihilate with the rate: $\lambda_f = 1/\tau_f$, where τ_f is the positron lifetime in a free state, Fig.1. The transition rate from the free to the localized state is described by the α parameter equal to the width of the boundary times the trapping rate parameter which is related with the cross section for absorption of positrons by the grain surface. The number of trapped positrons at the grain boundary, denoted as n_b, is a function of time. The same is with the local positron concentration within the grain: $C(\vec{r},t)$. Both functions must fulfil the following set of equations (Dryzek et al. 1998):

$$\begin{cases} \dfrac{\partial}{\partial t} C(\vec{r},t) = D_+ \nabla^2 C(\vec{r},t) - \dfrac{1}{\tau_f} C(\vec{r},t) \\ \dfrac{d}{dt} n_b(t) = \alpha \cdot \oiint_{\Sigma} dS\, C(\vec{r},t) - \dfrac{1}{\tau_b} n_b(t) \\ D_+ \cdot \oiint_{\Sigma} d\vec{S} \cdot \nabla C(\vec{r},t) + \alpha \cdot \oiint_{\Sigma} dS\, C(\vec{r},t) = 0 \end{cases}, \quad (1)$$

where Σ is the grain boundary. The first equation is a diffusion equation for positrons which can also annihilate in the grain interior. The second one is the rate equation for the trapped positrons, and the third one exhibits the fact that only the positrons which pass through the surface are able to be localized there. This last equation is the boundary condition for the first and second ones. The set of equations (1) is valid for the arbitrary grain shape.

Assuming that at the initial time positrons are uniformly distributed in the spherical grain interior, it is the case of conventional positron experiments because the positron implantation profile is much larger than grain size and the diffusion length, one can get the analytical, simple expression for the value of the positron annihilation characteristics. For the spherical grain of radius R the mean positron lifetime can be expressed as follows:

$$\bar{\tau} = \tau_f + (\tau_b - \tau_f) \frac{3L_+}{R} \frac{L(R/L_+)}{1 + \dfrac{L_+}{\alpha \tau_f} \cdot L(R/L_+)}, \quad (2)$$

where $L(z) = \coth(z) - 1/z$, is the Langevin function.

Similar for the value of the S-parameter:

$$S = S_f + (S_b - S_f)\frac{3L_+}{R}\frac{L(R/L_+)}{1+\frac{L_+}{\alpha\tau_f}\cdot L(R/L_+)}, \quad (3)$$

where S_f and S_b represent the values of the S-parameter associated with the positron annihilation in the free and bound state, respectively. More detail calculations can give the relation for the positron lifetime spectrum:

$$-\frac{dn(t)}{dt} = 3\frac{L_+}{R}\frac{1}{\sqrt{\tau_b^2-\tau_b\tau_f}}\frac{L(\sqrt{1-\tau_f/\tau_b}\cdot R/L_+)}{1+\sqrt{1-\tau_f/\tau_b}\cdot\frac{L_+}{\alpha\tau_f}L(\sqrt{1-\tau_f/\tau_b}\cdot R/L_+)}\cdot\exp\left(-\frac{t}{\tau_b}\right)$$

$$+6\left(\frac{\tau_b}{\tau_f}-1\right)\cdot\sum_{i=1}^{\infty}\frac{\left(1+\frac{L_+^2}{R^2}\varsigma_i^2\right)}{\left(\tau_b-\tau_f+\frac{L_+^2\tau_b}{R^2}\varsigma_i^2\right)\left[1-\frac{D_+}{\alpha R}+\left(\frac{D_+}{\alpha R}\right)^2\varsigma_i^2\right]\varsigma_i^2}\cdot\exp\left[-\frac{t}{\tau_f}\left(1+\frac{L_+^2}{R^2}\varsigma_i^2\right)\right], \quad (4)$$

where ς_{i_i} is the solution of the transcendental equation: $j\varsigma_i\cdot L(j\varsigma_i)+\frac{\alpha\tau_f R}{L_+^2}=0$, and $j=\sqrt{-1}$. (We should mentione that in the newest version of t he LT program for deconvolution of the positron lifetime spectra the option with the DTM is included.)

In Fig. 2 there presented the main feature of the DTM prediction: the mean positron lifetime and the intensity of the longest lifetime component associated with the positron annihilation at the grain surface depend upon the radius of the grain or the positron diffusion length L_+ .The another interesting feature is the positron lifetime spectrum contains an infinity number of lifetime components. It is worth pointing out that for the infinity radius of the grain or small value of the positron diffusion length the results tends to the well known results from the Standard Trapping Model.

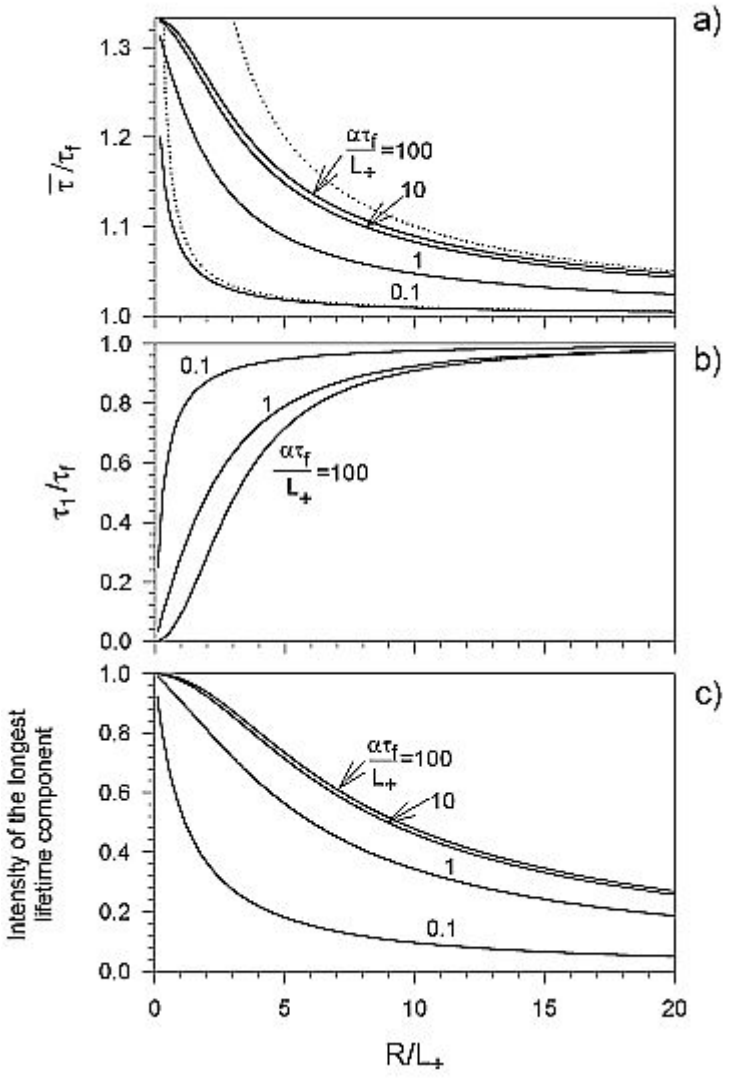

Fig. 2 The mean positron lifetime (a), the first lifetime component of the sum in (4) normalised to the τ_f value (b) and the intensity of the lifetime component associated with the positron annihilation at the grain boundary (c). The calculations were performed for the spheres of different $\alpha\tau_f/L_+$ values, as a function of the grain radius divided by the diffusion length L_+. The dotted upper and lower lines present the asymptotic relations. In the calculations it was assumed that $\tau_b/\tau_f = 4/3$.

In the paper given by Dryzek et al. 1998 one can find the solution of (1) for the grain in the shape of the layer and cylinder and the general case where the spherical grain contains the vacancies which can also localize positrons (see also Würschum, Seeger, (1996),). The solution of the set (1) for arbitrary grain shape is available as well (Dryzek, Czapla,1998).

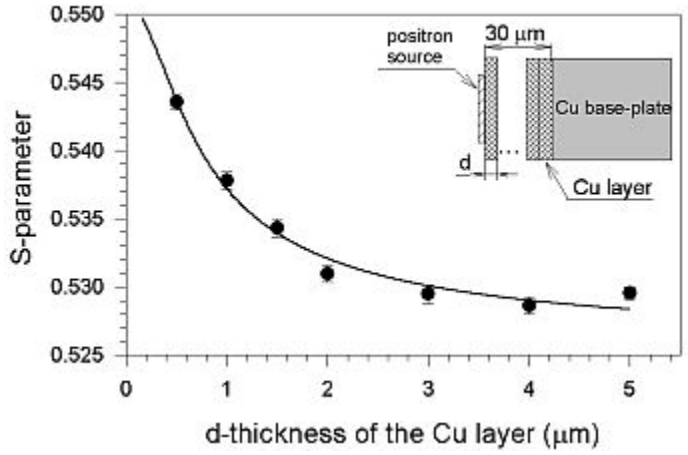

Fig.3 The value of the S-parameter of the annihilation line measured versus the thickness of the copper layer d in the multilayer samples obtained by electrodeposition process. Solid line presents the best fit of the dependence predicted by the DTM (3).

The interesting confirmation of the prediction of the DTM has been found by Dryzek 2002 using the multilayer stacking system of copper obtained by the electrodeposition process. Changing the thickness of the copper layer on the stacking sequence one could control the grain size. Fig. 3 depicts the dependency of the S-parameter versus the thickness of the copper layer which follows perfectly the prediction of the DTM. Fitting the relation (3) it was found the value of the positron diffusion length L_+=94± 20 nm and the transition rate: $\alpha \tau_f / L_+$=(2.83± 1.2)× 10^3. It corresponds well with the positron diffusion length obtained for the polycrystalline copper using the slow positron beam experiment: L_+=121± 7 nm (Dryzek et al. 2001). The measured positron lifetime at the grain boundary equals to 320± 11 ps indicates that the grain in the copper contains the vacancy cluster. This was changing for the other studied multilayer systems (Dryzek 2002 a).

The diffusion accompanies the positron conventional experiments and this should be taken into account in the interpretation of results. For example, the well known experiment for the measurement of the vacancy creation enthalpy should be reinterpreted using the DTM because the average distance between the vacancies is comparable with the positron diffusion length (Dryzek, 1998 a). The DTM can be helpful in the positron studies of recrystalization process in deformed metals where the temperature indicated the grown of the grain is present (Dryzek, 1998 b).

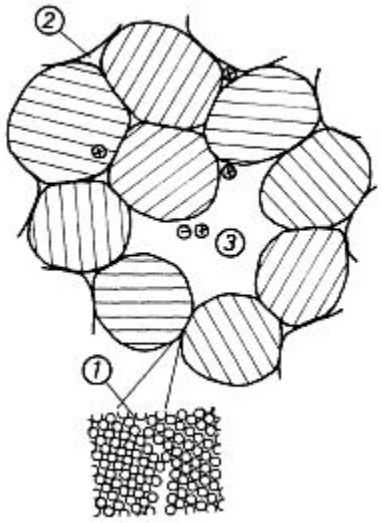

Fig. 4 Schematic two-dimensional arrangement of crystalites in a nanocrystalline material. The hatching indicates the orientation of lattice planes. The atomic structure of the interface is shown schematically in the inset. The various annihilation sites are attribute to the positron lifetimes (1) τ_1=180±15 ps, (2) τ_2=360±30 ps and (3) $1000 \leq \tau_{3,4} \leq 5000$ ps as discussed in the text.

If the grain size is getting much smaller than the diffusion length L_+ then the positrons attain the grain boundary of the small crystallites with high probability and lifetimes longer than that of the "free" delocalized state are observed indicating saturation positron trapping. Thus the DTM is not valid any more and the interpretation of the positron characteristics by positron trapping in interfacial free volumes of the nanocrystalline grains is sufficient. For so called nanocrystalline solids in the positron lifetime spectra even three or four lifetime components all higher than τ_f can be resolved. Schaefer et al. 1988 reported in nanometer-size Fe polycrystals (the average size about 10 nm) four lifetime components. τ_1=180±15 ps is attributed to the free volumes of approximately the size of a monovacancy in the crystallite interfaces of the nanocrystalline material, τ_2=360±30 ps is attributed to the free volumes at the intersections of two or three crystallites interfaces, such volume can be a cluster of 10-15 vacancies with a spherical diameter of about 0.6 nm, τ_3 ≈1300 ps and τ_4 ≈4000 ps indicate the formation of o- Ps at the internal surfaces of larger voids. In Fig.4 there are presented in the schematic the possible mentioned positrons traps in nanocrystalline material. The production procedure has effect significantly on the measured values of positron lifetimes even for the same material, also the temperature treatment and pressure (Schaefer (1992)). Nonocrystalline materials seems to be interesting for the surface positron studies.

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