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To Study Grain Boundaries in Nanocomposite Alloys by Positron Diffusion

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***Abstract* - The mechanism of positron annihilation in ferrite nanocomposite alloys has been discussed in terms of diffusion of positrons inside the grains and trapping into the grain boundaries and thermal vacancies. The diffusion trapping model has been used to calculate mean lifetime of positrons ($\bar{\tau}$) as a function of grain size and temperature in Fe-B-Si, Fe_2O_3, Fe-Zr and Fe-Si-Nb nanocomposites. The decrease in $\bar{\tau}$ with increase in the size of the grains is due to the fact that the density of grain boundary decreases gradually as the grain grows thus reducing the trapping centers. The calculations are done for two different temperature regions, low and high temperatures. The calculations of $\bar{\tau}$ shows that at low temperature $\bar{\tau}$ decreases with temperature. While the same increases with the temperature in the high temperature region. This increase in $\bar{\tau}$ has been ascribed to the increase in the number of thermally generated vacancies at higher temperatures. . In Nb and Zr based alloys a strong segregation at grain boundaries occurs, which stabilizes the nanostructure and leads to a decrease of the grain boundary diffusivity and diffusion is closely linked with thermal defect formation. Thus, information regarding thermal vacancies concentration in nanocrystallites could be obtained from positron lifetime data.**

Keywords: Grain boundaries. Positron annihilation. Thermal vacancies. Nanoparticle.

1. INTRODUCTION

In understanding the novel properties of nanocrystalline materials, special emphasis has been laid on the study of the atomic arrangement on the ultrafine grained boundaries. The properties of nanocrystalline ferrites is a subject of intense research in recent years.[1] These ferrites are novel materials for applications in a variety of areas like information storage, color imaging, ferro-fluids, microwave devices and communication technology. When these ferrites are reduced to ultra fine grain sizes the anomalous changes in their fundamental properties have attracted great interest.[2]

The high temperature properties of nanocrystalline materials are of the fundamental importance because the formation of thermal vacancies in nanocrystalline materials is closely linked to general problems of solid state physics, namely size effect in fine-dispersed systems and clusters[3,4] and characteristics of thermal defects in disordered systems, such as interfaces and grain boundaries.[5]

In recent years positron annihilation spectroscopy (PAS) has been employed to investigate the electronic structural aspects of nanocrystalline grain interfaces. Pioneer work in this direction was done by Hidalgo et al.[6] These authors investigated the temperature dependence of the positron trapping at grain boundaries in fine grain sample of Zn-Al-Mg. They found that the trapping mechanism at grain boundary is diffusion controlled. Dupasquier et al.[7] explained the positron trapping at grain boundaries employing the standard trapping model. Similarly grain boundaries are also expected to act as trapping sites for positrons since, they are regions of low atomic density. By virtue of their rapid thermalization on entering a grain the positrons exhibit remarkable advantage of diffusing out to the grain surfaces before annihilating with the electron. Tong et al.[8] performed the positron lifetime measurements in nanoscale grain size Fe-B-Si alloy. Significant changes in the structure and properties of grain boundaries and intercrystalline regions were observed when grain was reduced below 25 nm. Chakrabati et al.[9] studied the positron lifetime and Doppler broadening line shape parameter in Fe_2O_3 nanocrystalline alloy. They observed that the positron lifetime at the grain boundaries reduces with increasing grain size, implying a reduction of the total interfacial defect volume.

Detailed high temperature study of positron lifetime at grain boundaries, atomic free volumes and vacancies in the ultrafine grained alloys was performed by Wurschum et al.[10]. The studies were made over a wide temperature range i.e. up to 1200K on various metallic systems with different types of microstructures and interfaces. Thermal formation of the lattice vacancies have been found in ultrafine grained Cu. In an earlier study Wurschum et al.[11] reported the results of combined high temperature studies of positron lifetime and ^{59}Fe tracer diffusion in the nanocrystallites of intermetallic amorphous Fe-Si-B-Nb-Cu nanocomposites. The results showed a substantial variation of the diffusion behaviour and the thermal vacancy formation with the temperature. Thus, suggesting the thermal vacancy formation and rapid self diffusion in the nanocrystallites.

Lot of experimental work has been already done for understanding the magnetic behavior of nanoparticles. On theoretical side, however, little work has been done to understand the positron behaviour in nanoparticle systems. Dryzek et al.[12] developed a diffusion transition model of the trapping and annihilation of the positrons in the grain

boundaries. The model was employed to explain the positron lifetime spectrum in nanocrystalline systems. However, these authors did not consider the temperature dependence of the positron lifetime spectrum In the present work, our endeavor is to understand the temperature dependence of positron lifetime in nanocrystalline materials. The high temperature behaviour is widely determined by atomic diffusion and thermal vacancy formation. We have developed a model that considers the diffusion of positrons in fine-grained particles and trapping of positrons at the grain boundaries and into the thermally induced vacancies. The three dimensional diffusion equation has been solved and the rate equations are set up to describe the tapping of positrons at the grain boundaries and into the thermal vacancies. The model has been also applied to calculate the mean positron lifetime ($\bar{\tau}$) in Fe-B-Si, Fe_2O_3, Fe-Zr, and Fe-Si-Nb as a function of grain size and temperature.

2. FORMULATION OF THE MODEL

In the following the diffusion-trapping model has been developed and applied to calculate positron lifetime in nanoparticle systems. The following processes control the trapping of positrons in the nanoparticle grains. First the diffusion towards the trap and second the transition from the free to localized state. The grain boundaries serve as trapping sites for positrons since they are regions of low atomic density.[8] Besides these the positrons are also expected to trap at thermally formed vacancies in the nanocrystallites.[11] In the present work, we consider the solution of diffusion model in the diffusion transition regime by considering the grains having a symmetric form. We consider that the positrons captured within the grains can thermally diffuse out to the surfaces prior to annihilation, as the grain size is smaller than the thermal diffusion length of positrons.[13] On the grain surfaces they are trapped at grain boundaries. Thus the lifetime is characteristics of the nature of grain interface, interfacial defect structures and the thermally generated vacancies.

In the model considered, we assume that positrons diffuse in the perfect grain in which they annihilate with annihilation rate of free positrons in the sample λ_f *(=1/*τ_f*)*. Let *C(r,t)* is the local positron density with in the grain. The change in the positron concentration inside a grain with time and space is described by the three dimensional diffusion equation:

$$D_+\nabla^2 C(r,t) - \lambda_f C(r,t) = \frac{\partial C(r,t)}{\partial t} \qquad (1)$$

For the present calculation, we assume that at *t = 0* the positrons are uniformly distributed within the grain and there are no positrons trapped at the grain boundary and into the thermal vacancy. Thus, the diffusion equation is solved subjected to the boundary conditions:

$$\left.\begin{aligned} C(r,0) &= \frac{1}{V_\Omega} \qquad \text{for } r < R \\ C(r,0) &= 0 \qquad\quad \text{for } r \geq R \end{aligned}\right\} \qquad (2)$$

where V_Ω is the volume of the grain having radius *R*. Thus, we obtain the solution of equation (1)

$$C(r,t) = \sum_{n=0}^{\infty} \frac{(2n+1)}{V_\Omega}\left(\frac{r}{R}\right)^{2n} \exp -\left\{D_+\left(\frac{3\pi}{R}\right)^2 + \lambda_f\right\}t \qquad (3)$$

When a beam of monoenergetic positrons is implanted from vacuum into the grain, the positron survives before annihilation either as a free positron or trapped at the grain boundary or into the thermally induced vacancy. These are described by the following rate equations

$$\frac{\partial n_f(t)}{\partial t} = -\alpha_g n_f(t) - N(t) \qquad (4)$$

where $\alpha_g = \lambda_f + \alpha_{fv}$

$$\frac{\partial n_{fg}(t)}{\partial t} = -\lambda_g n_{fg}(t) + N(t) \qquad (5)$$

$$\frac{\partial n_{fv}(t)}{\partial t} = -\alpha_{vf} n_{fv}(t) + \alpha_{fv} n_f(t) \qquad (6)$$

$$\frac{\partial n_{vf}(t)}{\partial t} = -\lambda_v n_{vf}(t) + \alpha_{vf} n_{fv}(t) \qquad (7)$$

In the above equations n_f, n_{fg}, n_{fv} represent the fraction of positrons in free state, trapped at the grain boundaries and into the thermal vacancies respectively. n_{vf} represents the fraction that detrapped from vacancy to free state. α_{fg}, α_{fv} and α_{vf} represent the transition rate from free to grain boundary, free to the thermal vacancy and from vacancy to free state respectively. λ_g and λ_v are the positron annihilation rate at the grain boundary and into the thermal vacancy respectively. The total number of positrons reaching at the grain boundary is given by

$$N(t) = \alpha_{fg} \iint ds\, C(r,t) \qquad (8)$$

In solving the above, the following boundary conditions have been used: (a) corresponding to low temperature (*T < 350 K*) behavior of $\bar{\tau}$; *C(R,t) = 0* at *r = R* and (b) corresponding to high temperature range *(T > 350 K)*; $C(L_+,t) = 0$ at $r = L_+$. Thus, assuming that at high *T* all positrons annihilate inside the grains before reaching at the surface.
The solution gives

$$N(t) = \sum_{n=0}^{\infty} B_n \exp -(b_n t) \qquad (9)$$

where $B_n = \frac{4\pi\alpha_{fg}(2n+1)R^2}{V_\Omega}$ (10)

$$b_n = D_+\left(\frac{3\pi}{R}\right)^2 + \lambda_f \quad \text{(for low } T\text{)} \qquad (11)$$

and $$b_n = D_+\left(\frac{3\pi}{L_+}\right)^2 + \lambda_f \quad \text{(for high T)} \qquad (12)$$

The mean positron lifetime ($\bar{\tau}$) in the nanocrystalline samples can be written as:

$$\bar{\tau} = \int_0^\infty n_f(t)dt + \int_0^\infty n_{fg}(t)dt + \int_0^\infty n_{fv}(t)dt + \int_0^\infty n_{vf}(t)dt \quad (13)$$

Thus, one gets

$$\bar{\tau} = \frac{1}{\alpha_g} + \sum_{n=0}^{\infty} \frac{B_n}{b_n}\left(\frac{1}{\lambda_g} - \frac{1}{\alpha_g} + \frac{\alpha_{fv}}{\alpha_g \alpha_{vf}} + \frac{\alpha_{fv}}{\alpha_g \alpha_v}\right) \quad (14)$$

3. RESULTS AND DISCUSSION

Employing the procedure as described above, the $\bar{\tau}$ have been calculated in Fe-B-Si, Fe_2O_3, Fe-Zr, and Fe-Si-Nb nanocrystalline alloys a function of grain size and temperature. In the calculations, we have considered the symmetrical grain of spherical shape. The different transition rates in equations (4-7) have been calculated as follows: The transition rate α_{fg} is understood to be proportional to D_+, whose dependence on the temperature is given by $D_+ \propto T^{-1/2}$ (Ref. 6). If the diffusion length L_+ competes the size of the grain the probability of the transition rate from free to grain boundary is high. Thus, α_{fg} could be described as[12]

$$\alpha_{fg} = 100\frac{L_+}{\tau_f} \quad \text{,where } L_+ = \sqrt{D_+ \tau_f} \quad (15)$$

Pasquini et al.[14] have shown that the trapping coefficient for the thermal vacancy shows an increasing trend as temperature rises. Further, the trapping rate is expected to be proportional to the thermal vacancy concentration. Therefore, the trapping rate of positrons in thermal vacancies is written as

$$\alpha_{fv} = \sigma_1 \exp\left(\frac{S_v}{K_b} - \frac{H_v}{K_b T}\right) \quad (16)$$

where, H_v and S_v are the effective vacancy formation enthalpy and entropy respectively. K_b is the Boltzmann constant. The thermally activated detrapping of positrons is given by[15]

$$\alpha_{vf} = \sigma_2 T^{3/2} \exp -\left(\frac{E_b}{K_b T}\right) \quad (17)$$

where, E_b is the binding energy of the positrons into the thermal vacancy for the nanocrystallites with pre-exponential factor σ_2. The values of the different parameters used in the evaluation of $\bar{\tau}$ have been taken from experimental observations. Few constants have been estimated to give good results.

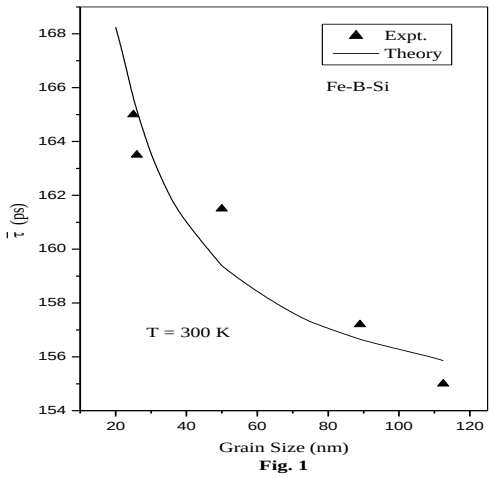

Fig. 1

Fig. 1: Comparison of calculated mean positron lifetime ($\bar{\tau}$) as a function of grain size in Fe-B-Si nanocrystalline alloy with the experimental observations of Tong et al.[9]

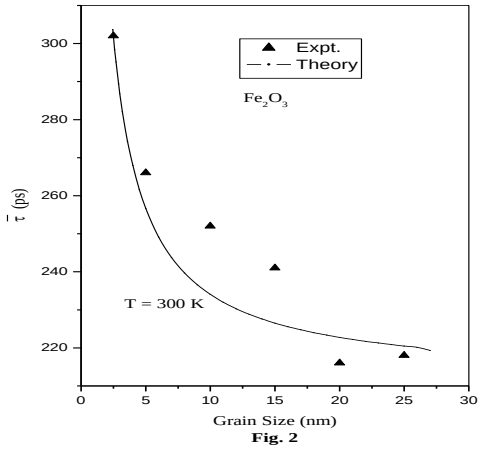

Fig. 2

Fig. 2: Comparison of calculated mean positron lifetime ($\bar{\tau}$) as a function of grain size in Fe_2O_3 nanocrystalline alloy with the experimental observations of Chakrabarti et al.[8]

The Fig. 1 and 2 show the calculated mean positron lifetime as a function of grain size in Fe-B-Si and Fe_2O_3 nanocrystalline alloys with the experimental values taken from Tong et al.[8] and Chakrabati et al.[9] respectively for comparison. The figures show that the $\bar{\tau}$ decreases with increase in the size of the grain. This could be understood from the fact that the density of grain boundary decreases gradually as the grain grows thus reducing the trapping centers. The $\bar{\tau}$ falls rapidly at low grain size, after this it decreases slowly. This is consistent with the observation of Mukherjee et al.[13] that if the size of the grain is less than thermal diffusion length of positrons they will diffuse out of the grains and become trapped at the grain interface. In case of nanocrystalline alloys when the size of the grain becomes close to diffusion length, the lifetime becomes comparable to that in the bulk V. Thakur et.al.[16].

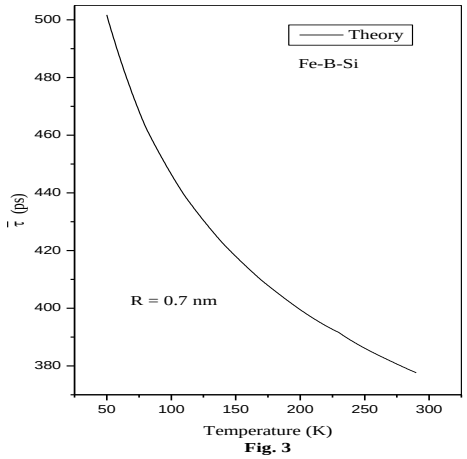

Fig. 3: Calculated mean positron lifetime ($\bar{\tau}$) as a function of temperature in Fe-B-Si nanocrystalline alloy for R = 0.7 nm.

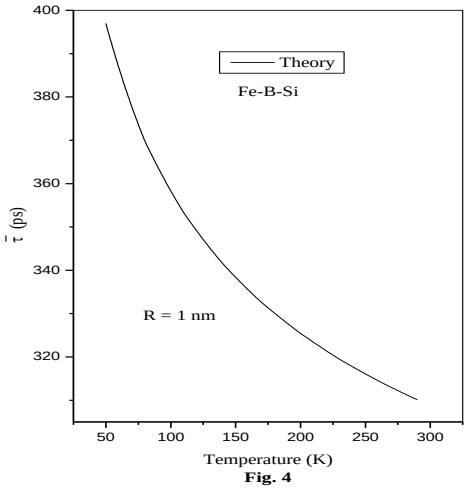

Fig. 4: Calculated mean positron lifetime ($\bar{\tau}$) as a function of temperature in Fe-B-Si nanocrystalline alloy for R = 0.7 nm.

Beside the above, we have also calculated the $\bar{\tau}$ as a function of temperature in Fe-B-Si nanocrystalline alloy for different grain size i.e. $R = 0.7\ \mu m$ and $R = 1\ \mu m$. The results are presented in Figs. 3 and 4. The figures show that the positron lifetime decreases with the increase in the temperature ($T < 350\ K$). The decrease in lifetime with temperature is due to the fact that the D_+ and L_+ decrease with the increase in temperature as given by Eqn. (15). This indicates that the transition rate of positrons reaching at the grain boundary decreases with increase in temperature and more positrons annihilate in side the grain. As far as the effect of grain size is concerned the lifetime has been found to be smaller corresponding to the larger grains. However, the nature of the curves remains same for the different grain sizes.

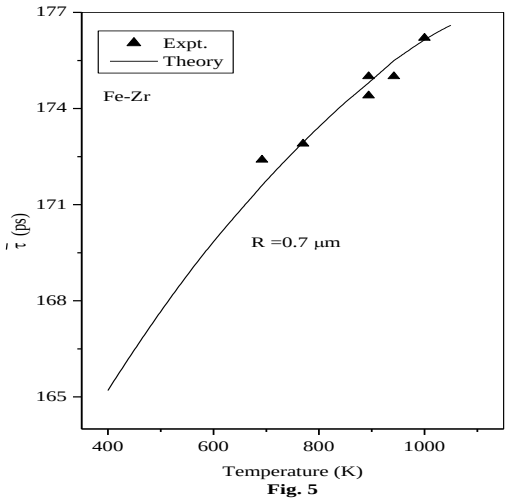

Fig. 5: Comparison of calculated mean positron lifetime ($\bar{\tau}$) as a function of temperature in Fe-Zr nanocrystalline alloy with the experimental observations of Wurschum et al.[10]

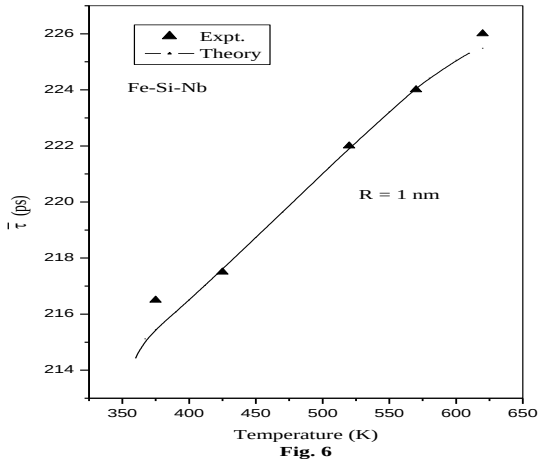

Fig. 6: Comparison of calculated mean positron lifetime ($\bar{\tau}$) as a function of temperature in Fe-Si-Nb nanocrystalline alloy with the experimental observations of Pasquini et al.[14]

4. CONCLUSION

The present calculation shows that

(i) The diffusion of positrons in fine-grained particles coupled with trapping into grain boundaries and thermally generated vacancies in the nanocrystallites could be used to describe the positron annihilation in nanoparticle systems.

(ii) The high temperature studies of the positron lifetime in nanocrystalline grained alloys elucidate the character of the different positron trapping sites including the trapping into thermal vacancies inside the grains.

(iii) Information regarding vacancy concentration in fine-grained samples in principle could be obtained from PAS data.

REFERENCES

1. T. Sato, K. Haneda, M. Seki, and T. Iijima, Appl. Phys. A: Solids Surf. 50, 13 (1990).
2. S. Ghosh, P.M.G. Nambissan, and R. Bhattacharya, Phys. Lett. A 325, 301 (2004).
3. I.D. Morokhov, V.I. Zubov, and V.B. Fedorov, Sov. Phys. Solis State 251, 178 (1983).
4. C. Baladron, J.A. Alonso, and M.P. Iniguez, Phys. Rev. B 37, 8436 (1988).
5. T. Kwok, P.S. Ho, S. Yip, R.W. Balluffi, and A. Brokman, Phys. Rev. Lett. 47, 1148 (1981).
6. C. Hidalgo, N. de Diego, and F. Plazaola, Phys.Rev. B 31, 6941 (1985).
7. A. Dupasquier, R. Romero, and A. Somoza, Phys. Rev. B 48, 9235 (1993).
8. H.Y. Tong, B.Z. Ding, J.T. Wang, K. Lu, J. Jiang, and J. Zhu, J. Appl. Phys. 72, 5124 (1992).
9. S. Chakrabati, S. Chaudhury, and P.M.G. Nambissan, Phys. Rev. B 71, 64105 (2005).
10. R. Wurschum, E. Shapiro, R. Dittmar, and H.E. Schaefer, Phys. Rev. B 62, 12021 (2000).
11. R. Wurschum, P. Farber, R. Dittmar, P. Scharwaechter, W. Frank, and H.E. Schaefer, Phys. Rev. Lett. 79, 4918 (1997).
12. J. Dryzek, A. Czapla, and E. Kusior, J. Phys.: Condens. Matter 10, 10827 (1998).
13. M. Mukherjee, D. Chakravorty, and P.M.G. Nambissan, Phys. Rev. B 57, 848 (1998).
14. L. Pasquini, A.A. Rempel, R. Wurschum, K. Reimann, M.A. Muller, B. Fultz, and H.E. Schaefer, Phys. Rev. B 63, 134114 (2001).
15. R. Wurschum, E.A. Kummerle, K. Badhura Gergen, A. Seeger, Ch. Herzig, and H.E. Schaefer, J. Appl. Phys. B 80, 724 (1996).
16. V.Thakur, S.B.Shrivastava, M.K.Rathore, Nanotechnology, 15, 467 (2004).