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The influence of positron diffusion on positron trapping at voids in molybdenum

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Abstract. The temperature dependence of positron trapping at voids in molybdenum has been carefully studied from 7 to 360 K. The trapping was studied before and after decorating the voids with hydrogen or nitrogen. The influence of positron-diffusion-limited trapping was extracted and found to be independent of void decoration, as expected. The voids were also studied by transmission electron microscopy and the results confirm that $4\pi r n D_+$ is the correct term for describing the diffusion-limited trapping rate at spherical defects.

1. Introduction

The positron annihilation technique (PAT) is well established as a sensitive tool for the study of atomic defects in solids; see, e.g., West (1979). The study of defects is inextricably bound up with the study of the positron–defect interaction and *vice versa*. It is therefore of general interest to study the temperature dependence of positron–defect interactions. This may not only improve the understanding of these interactions, but may also give information about the defects themselves.

The trapping of positrons at defects may be limited by two factors: diffusion and transition (Seeger 1974). After implantation and thermalization the positron must diffuse towards the defect and finally must transit from a delocalized bulk state into a localized trapped state at the defect.

One way of distinguishing between the two limiting processes is to study the temperature dependence of the positron trapping, and to extract the rates for the two processes due to different expected temperature dependencies. However, several difficulties emerge at this point: (i) theoretical and experimental results concerning the temperature dependencies of the rates are not always in agreement; (ii) it is not always possible to alter the rate of one process without altering the rate of the other too (e.g. by annealing of the defects); and finally, (iii) PAT may often be applied in isolation in defect studies without additional data from other techniques.

In the present work these difficulties have all been overcome by studying the positron trapping at voids in molybdenum; this defect–metal combination was chosen because the problem concerning the temperature dependence of positron diffusion seemed to have been solved experimentally for molybdenum (Huomo *et al* 1987) and is in agreement with theory. In their work Huomo *et al* found D_+ to be proportional to $1/\sqrt{T}$, the

positron mobility thereby being governed by acoustic phonon scattering (Bergersen *et al* 1974). With regard to the second difficulty, it is known that voids can be decorated in a controlled way by hydrogen or by nitrogen (Nielsen *et al* 1985, Bentzon *et al* 1984, Hansen *et al* 1982a, 1982b). As described later, we have used these procedures to alter the transition-limited trapping rate at voids without changing the diffusion-limited trapping rate. For a review of gas-defect interactions in metals studied by positrons see Linderoth (1989).

Finally, as in other important applications of PAT to defects in metals, we have monitored the void substructure by transmission electron microscopy (TEM). In the following sections of this study into the positron-void interaction for clean and decorated voids, the TEM evidence will be seen to provide important corroboration of the data less directly deduced from the PAT results.

2. Experimental techniques

A molybdenum single crystal of purity 4N was irradiated to a dose of 25×10^{18} fast neutrons cm^{-2} at 325 K. The crystal was isochronally annealed, 50 K h^{-1} , up to 1200 K in a high vacuum, $p \leq 10^{-8}$ mbar. This procedure to produce a defect substructure dominated by voids was originally demonstrated by Evans *et al* (1972) and Petersen *et al* (1974), and has been widely used for PAT studies of voids.

Positron lifetime spectroscopy (PLS) was performed on this sample using a fast-fast time spectrometer with a resolution of 220 ps (FWHM). One time spectrum typically contained 3×10^6 events. The sample was placed in the usual sample-source-sample geometry in a liquid helium cryostat. The temperature was measured by a Pt-100 resistor calibrated at 4.2, 77 and 273 K, and was varied from 7 to 360 K, with lifetime spectra taken at appropriate temperature intervals.

This sequence of measurements was carried out on the same sample, first as-annealed, secondly after hydrogen charging, and finally after annealing in nitrogen.

The hydrogen was introduced into the sample by electrolytic charging following the same procedure as Nielsen *et al* (1985). Though the amount of hydrogen introduced is not known, the charging strongly affects the positron trapping rate at voids (chemisorbed hydrogen) and the lifetime of the trapped positron (hydrogen gas) (Nielsen *et al* 1985). The final treatment, annealing in nitrogen at 1 bar and 1125 K for one hour, removes the hydrogen and allows the uptake of the soluble nitrogen into the molybdenum. As the treatment was kept well below the original 1200 K anneal, no change in void parameters was expected. Using the data of Evans and Eyre (1969), the treatment was calculated to give an equilibrium concentration of 10 ppm at the anneal temperature. Although cooling induces some nitrogen precipitation, the voids act as traps for the mobile nitrogen giving rise to a strong influence on the positron lifetime (Hansen *et al* 1982b). It is worth noting that both here and for the hydrogen treatment the fact that positron effects are seen, hence changing the transition-limited trapping rate at voids, is of more interest than their magnitude.

When the PLS studies were completed, two 3 mm discs were cut from the sample and prepared by normal electrochemical thinning techniques for TEM observations which were carried out on a Philips EM400 operating at 100 kV.

3. Results

The positron lifetime spectra were analysed by applying the computer program POSITRONFIT (Kirkegaard *et al* 1981). After subtracting that part of the spectrum arising

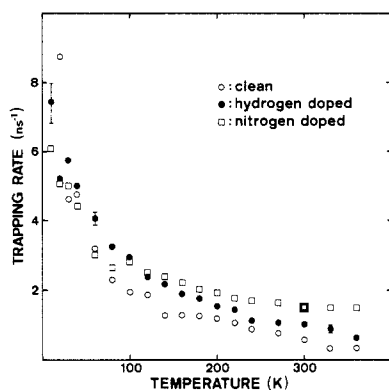


Figure 1. The temperature dependence of positron trapping at loops; before and after loading the sample with hydrogen or nitrogen, respectively.

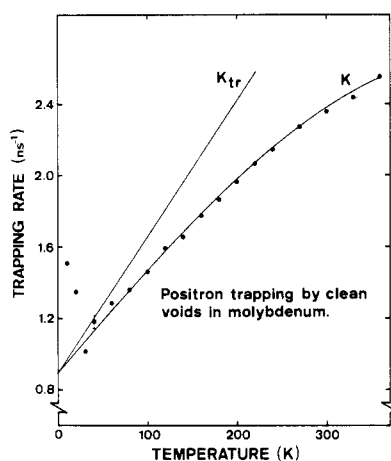


Figure 2. The temperature dependence of positron trapping at voids before decorating with hydrogen or nitrogen.

from positrons annihilating in the source material, the spectra could be resolved into three components corresponding to free positrons annihilating in bulk (τ_1), trapped positrons annihilating in loops (τ_2) or voids (τ_3). Output parameters from POSITRONFIT (τ_2, I_2, τ_3, I_3) were then applied to calculate the trapping rates at the two types of trap according to a three-state trapping model with time-independent trapping rates (Brandt 1974).

The longest positron lifetime τ_3 was ascribed to positrons annihilating in the voids and had a value of 492 ps as annealed, 482 ps after decorating by hydrogen and 629 ps after decoration by nitrogen, in agreement with Hansen *et al* (1982b). A medium lifetime τ_2 around 155 ps was ascribed to positrons annihilating in loops; a similar lifetime was found by Nielsen and Petersen (1982).

A short lifetime τ_1 was due to untrapped positrons and appeared to be in good agreement with the reduced bulk lifetime calculated from the trapping model. As expected, τ_2 and τ_3 did not show up any variation with temperature. The measured trapping rates at the two different types of defect, loops and voids, are shown in figures 1 to 4.

The data on trapping at loops as a function of measurement temperature are given in figure 1 and appear to be only slightly affected by the hydrogen/nitrogen treatment.

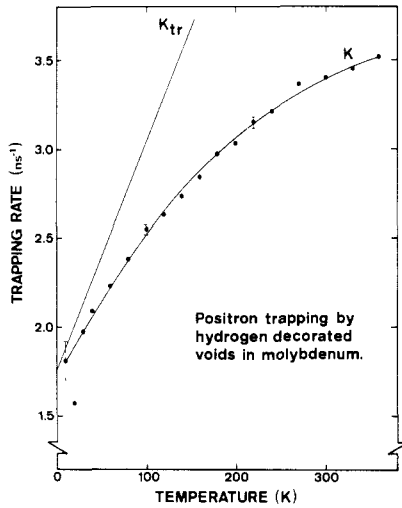


Figure 3. The temperature dependence of positron trapping at voids decorated with hydrogen.

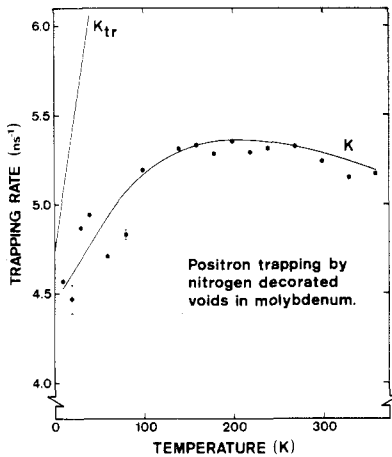


Figure 4. The temperature dependence of positron trapping at voids decorated with nitrogen. The difference between the trapping rates shown in figures 2, 3 and 4 is due to (i) void decoration changing the parameter K_0 in the transition-limited trapping rate and (ii) a change in the transition-limited trapping rate altering the relative influence of the diffusion-limited trapping rate.

On the other hand, the positron trapping at voids (figures 2 to 4) is observed to be strongly dependent on temperature and thus clearly influenced by the decoration of voids by hydrogen and nitrogen, not only in absolute value but also in qualitative behaviour. The uncertainties shown are those induced by statistics and these dominate at high temperatures. At low temperatures, the strong increase in K_{loop} leads to a decrease in τ_1 and I_1 making small instabilities and variations in the time spectrometer resolution function important. These uncertainties are not shown in the figures, but appear to be of the same order of magnitude at the lowest temperatures.

TEM observations on the two prepared samples showed that each contained an identical homogeneous distribution of small voids identified by their typical light to dark through-focus behaviour. In order to obtain good data on the void size distribution and density, electron micrographs were taken on various areas with $g = 110$, $s = 0$, and with $g = 330$ diffracting conditions. The first condition gives the characteristic thickness

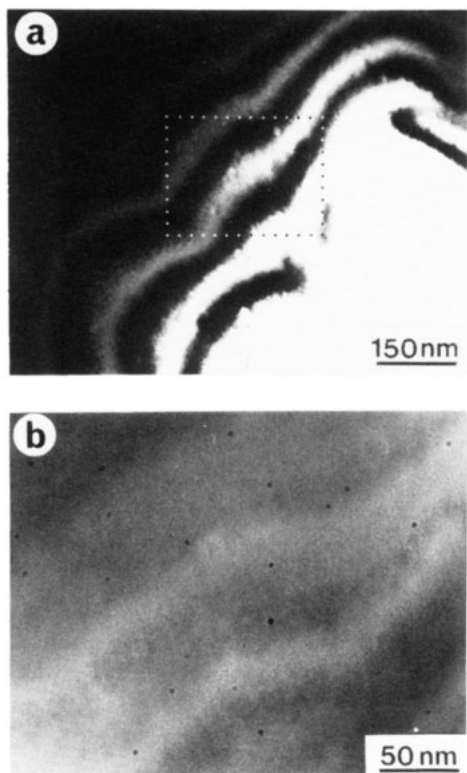


Figure 5. (a) Electron micrograph showing characteristic thickness fringes for diffraction conditions $g = 110$, $s = 0$. (b) Higher-magnification micrograph of outlined area in (a) showing over focused (dark) void images; $g = 330$.

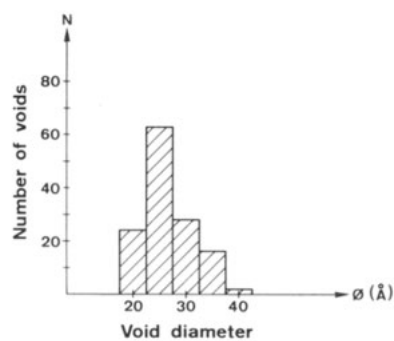


Figure 6. Size distribution of voids. The data are taken from several TEM micrographs using the same diffraction conditions as in 5(b).

fringes, figure 5(a) which allow accurate void density estimates, while the second condition allows sharp images to be obtained for size measurements. In figure 5(b) a higher-magnification micrograph of the outlined area in figure 5(a) shows the typical over focused dark void images. The size distribution of voids is given in figure 6. The mean void radius was 1.33 ± 0.05 nm while the void density in both samples was $(5.3 \pm 1.0) \times 10^{21} \text{ m}^{-3}$.

4. Discussion

When the positron trapping at spherical defects is limited by diffusion as well as by transition, the trapping rate is time dependent and can be expressed as (Seeger 1974):

$$K(t) = K(\infty)[1 + \rho r / (\rho + 1) \sqrt{\pi D_+ t} \dots] \quad (1)$$

$$K(\infty) = K_{\text{tr}} K_{\text{diff}} / (K_{\text{tr}} + K_{\text{diff}}) \quad (2)$$

$$\rho = K_{\text{tr}} / K_{\text{diff}}. \quad (3)$$

t is time, r is the radius of the spherical defect, D_+ is the positron diffusion coefficient,

$K_{\text{diff}} = 4\pi r n D_+$ is the diffusion-limited trapping rate after the transient has died out, K_{tr} is the transition-limited trapping rate, and n is the density of voids. An effective (time-averaged) trapping rate is calculated as:

$$K_{\text{eff}} = \int_0^{\infty} K(t) \exp(-\lambda_1 t) dt / \int_0^{\infty} \exp(-\lambda_1 t) dt \quad (4)$$

where λ_1 is the rate of positron disappearance from the bulk state. Assuming the worst case for the parameter $\rho (\gg 1)$ we get:

$$K_{\text{eff}} = K(\infty)(1 + r/\sqrt{D_+ \tau_1}) \quad (5)$$

by neglecting the time dependence of $\tau_1 = 1/\lambda_1 = 1/(\lambda_b + \Sigma K(t))$, where λ_b is the annihilation rate for positrons in bulk and $\Sigma K(t)$ is the sum of all trapping rates.

Inserting values for the studied sample ($r = 1.33$ nm, $D_+ = 1.2$ cm² s⁻¹, $\tau_1 = 60$ ps) we find from equation (5) that $K(\infty)$ deviates from the effective trapping rate by less than 2%. This implies that the trapping rate at these voids can be considered as time independent. The calculation of trapping rates, based on a three state trapping model with time-independent trapping rates, is therefore valid in this experiment.

The transition limited trapping rate is often found, or assumed, to increase linearly with temperature:

$$K_{\text{tr}} = K_0(1 + \alpha T). \quad (6)$$

This is most clearly demonstrated when the studied sample contains a high concentration of small voids (Bentzon *et al* 1985). Nieminen *et al* (1979) have proposed a model where the positron wave may reflect at the void surface, leading to an increase in trapping rate with increasing temperature. However, the model of Nieminen *et al* presumes a positron wavelength smaller than the void, and the de Broglie wavelength of a thermal positron is $\lambda_+ = h/p = h/\sqrt{3mk_B T} = 6.2$ nm at 300 K which is obviously bigger than the voids studied in this work. Since we have no model describing the linear temperature dependence of the transition-limited trapping rate at this category of voids, we cannot extract the information present in this rate prior to, as well as after, the decoration. However, decorating the voids will change the state of the trapped positron and, therefore, K_{tr} too.

The diffusion-limited trapping rate can be expressed as (Seeger 1974):

$$K_{\text{diff}} = 4\pi r n D_+. \quad (7)$$

Due to its nature, the diffusion-limited trapping will not be influenced by decorating the voids with impurities. Inserting the expressions for K_{tr} and K_{diff} in equation (2) gives:

$$K \approx K(\infty) = 4\pi r n D_+ K_0(1 + \alpha T)/(4\pi r n D_+ + K_0(1 + \alpha T)). \quad (8)$$

The results in figures 2, 3 and 4 have been fitted by equation (8) and the three free parameters K_0 , α and $4\pi r n D_+(300 \text{ K})$ extracted. $D_+(T)$ was taken to be proportional to $1/\sqrt{T}$, as found experimentally by Huomo *et al* (1987) and which is in agreement with theory (Bergersen *et al* 1974). The fitted values are given in table 1.

The numbers in table 1 show that K_0 is extremely sensitive to decoration by gas impurities, while the other parameter describing the transition-limited trapping rate, α , is unaffected.

The agreement between the diffusion-limiting term, $4\pi r n D_+(300 \text{ K})$, for the three experiments confirms the correctness of the applied model. Of equal significance is the agreement between the absolute value found and the value calculated applying our TEM

Table 1. Parameters describing the transition- and diffusion-limiting trapping at voids. The parameters are extracted from the data shown in figures 2, 3 and 4. The full curves in these figures represent the fitted trapping rate. The straight lines represent the transition-limited trapping rate $K_{tr} = K_0(1 + \alpha T)$.

Decoration	K_0 (ns ⁻¹)	α (kK ⁻¹)	$4\pi r n D_+$ (300 K) (ns ⁻¹)
None	0.85 ± 0.07	9.3 ± 1.8	9.0 ± 1.5
Hydrogen	1.75 ± 0.04	7.4 ± 0.6	8.5 ± 0.9
Nitrogen	4.7 ± 0.3	7.2 ± 0.9	8.2 ± 0.4
TEM results	—	—	10.6 ± 3.3

results ($r = 1.33$ nm, $n = 5.3 \times 10^{21}$ m⁻³) and the value for $D_+(300$ K) = 1.2 cm² s⁻¹ found by Huomo *et al* (1987). This combination of PAT and TEM appears to give the first experimental evidence that the term $4\pi r n D_+$ describes the diffusion-limited trapping rate for positron trapping at spherical defects.

The constancy of the parameter α , despite the decoration, is conspicuous; other results (Bentzon 1987) show that α increases during high-temperature annealing, when coarsening of the void population can take place. Therefore it seems likely that α is associated with the size of the void. However, an explanation of the linear temperature dependence of K_{tr} still seems to lack a good model.

The positron trapping rate at loops is found to have a very typical ‘loop shape’: strongly decreasing with temperature below 100 K and levelling off at higher temperatures (see e.g. Smedskjær *et al* 1980; Linderoth *et al* 1985). This type of defect is not as well defined as spherical voids, and a quantitative analysis of the results may be difficult. We end the discussion here by noting that the concentration of loops and other dislocation-type defects observed by TEM in the studied sample was very low compared with that of voids. The specific trapping rate for this kind of defect, therefore, has to be very high, and positron diffusion may also be important for positron trapping at this type of defect.

5. Conclusion

The temperature dependence of positron trapping at voids has been studied for neutron-irradiated molybdenum annealed at 1200 K. The voids were decorated by either hydrogen or nitrogen. The results show that the positron trapping is limited by diffusion and by transition. The diffusion-limiting term, $4\pi r n D_+$, is not affected by the decoration and is found to have an absolute value in agreement with our TEM results and the existing independently determined values of D_+ . This confirms that $4\pi r n D_+$ is the correct term for diffusion-limited trapping of positrons at spherical defects.

The transition-limited trapping rate could be expressed as $K_{tr} = K_0(1 + \alpha T)$, and while α was unaffected by the decoration, K_0 increased by factors of 2 and 5 when the voids were decorated by hydrogen and nitrogen, respectively. Although a model

explaining the linear temperature dependence of K_{tr} is lacking, α is associated with the size of the void.

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References

- Bentzon M D 1987 *PhD thesis* Technical University of Denmark
- Bentzon M D, Hansen H E, Linderroth S, Nielsen B, Nielsen H K and Petersen K 1984 *Microstructural Characterization of Materials by Non-Microscopical Techniques* ed N Hessel Andersen, M Eldrup, N Hansen, D Juul Jensen, T Leffers, H Lilholt, O B Pedersen and B N Singh (Roskilde: Risø National Laboratory) p 199
- Bentzon M D, Linderroth S and Petersen K 1985 *Positron Annihilation* ed P C Jain, R M Singru and K P Gopinathan (Singapore: World Scientific) p 485
- Bergersen B, Pajanne E, Kubica P, Stott M J and Hodges C H 1974 *Solid State Commun.* **15** 1377
- Brandt W 1974 *Appl. Phys.* **5** 1
- Evans J H and Eyre B L 1969 *Acta Metall.* **17** 1109
- Evans J H, Mahajan S and Eyre B L 1972 *Phil. Mag.* **26** 813
- Hansen H E, Linderroth S, Wierzchowski W and Petersen K 1982a *Appl. Phys. A* **27** 247
- Hansen H E, Nielsen B, Trumpy G and Petersen K 1982b *Positron Annihilation* ed P G Coleman, S C Sharma and L M Diana (Amsterdam: North-Holland) p 435
- Huomo H, Vehanen A, Bentzon M D and Hautojärvi P 1987 *Phys. Rev. B* **35** 8252
- Kirkegaard P, Eldrup M, Mogensen O E and Pedersen N J 1981 *Comput. Phys. Commun.* **23** 307
- Linderroth S 1989 *J. Phys.: Condens. Matter* **1** SA55
- Linderroth S, Bentzon M D, Hansen H E and Petersen K 1985 *Positron Annihilation* ed P C Jain, R M Singru and K P Gopinathan (Singapore: World Scientific) p 494
- Nielsen B, Hansen H E, Nielsen H K, Bentzon M D and Petersen K 1985 *Positron Annihilation* ed P C Jain, R M Singru and K P Gopinathan (Singapore: World Scientific) p 497
- Nielsen B and Petersen K 1982 *Phys. Lett.* **92A** 85
- Nieminen R M, Laakonen J, Hautojärvi P and Vehanen A 1979 *Phys. Rev. B* **19** 1397
- Petersen K, Thrane N and Cotterill R M J 1974 *Phil. Mag.* **29** 9
- Seeger A 1974 *Appl. Phys.* **4** 183
- Smedskjær L C, Manninen M and Fluss M 1980 *J. Phys. F: Met. Phys.* **10** 2237
- West R 1979 *Positron Annihilation (Topics in Current Physics 12)* ed P Hautojärvi (Heidelberg: Springer)