

Gas-defect interactions in metals

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1989 J. Phys.: Condens. Matter 1 SA55

(<http://iopscience.iop.org/0953-8984/1/SA/007>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 27/05/2010 at 11:09

Please note that [terms and conditions apply](#).

Gas-defect interactions in metals

Søren Linderorth

Laboratory of Applied Physics, Technical University of Denmark, DK-2800 Lyngby, Denmark

Received 1 December 1988, in final form 14 March 1989

Abstract. The application of positron annihilation spectroscopy to the study of gas-defect interactions in metals is reviewed. Examples of hydrogen interactions with vacancies or voids in Al, Fe, Ni and Mo are presented. The effect of thermal vacancies on the hydrogen diffusivity in Al is discussed. Results on noble gases in Al, Cu and Mo are presented as well as the effect of nitrogen on vacancy migration in Mo.

1. Introduction

Experimental and theoretical studies of gases in metals have become a subject of increasing interest in recent years [1, 2], created by the important technological consequences of the interactions of gases with defects. Hydrogen has a considerable effect on the mechanical properties of metals: hydrogen concentrations of a few ppm may cause severe embrittlement and change in the ductility of metals [3]. Noble gases are practically insoluble in metals and therefore tend to precipitate as bubbles [2]. The noble gas bubbles have strong effects on the physical and mechanical properties of metals; hence, it is important to develop an understanding of their behaviour.

Many experimental techniques have been developed to gain an understanding of gas-defect interactions. Gas release and permeation studies, ion beam analysis, electrical resistivity and lattice change measurements are methods that have been widely employed for such investigations. These methods give mainly macroscopic information about the system. When they are used in conjunction with theoretical approaches, it is possible to gain insight into the microscopic nature of the gas-defect interactions. Ion beam channelling, transmission electron microscopy (TEM), perturbed angular correlation (PAC) and positron annihilation spectroscopy (PAS) studies give more direct information about the reactions on the microscopic level. In particular, PAS has been established as a method that is sensitive on the atomic scale [4, 5].

Positron annihilation spectroscopy has been developed to become a defect spectroscopy method that is selectively sensitive to lattice defects such as vacancies, dislocations and voids [4, 5]. In the presence of vacancy-type defects the positron is trapped and its lifetime increases, compared to that in the bulk state, due to a decreased electron density felt by the positron. The gas impurities are trapped by the same open-structured defects that trap positrons. The electronic structure in the defect is changed by the presence of impurities; hence the positron annihilation or trapping rates characteristic of the type of defect are altered [6-8]. This provides a powerful tool for a direct study of gas-defect

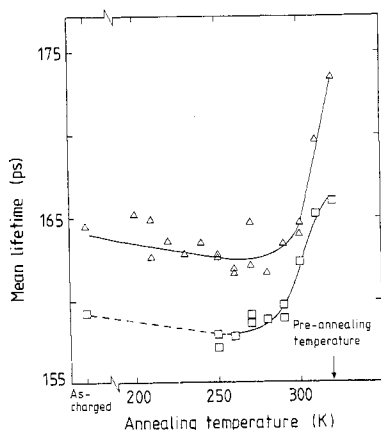


Figure 1. The mean positron lifetime versus annealing temperature for H-doped Ni for two different chargings (§ 2.1). Prior to the chargings Frenkel pairs were introduced by proton irradiation. The samples were annealed at 320 K before hydrogen was injected by an electrochemical method. The isochronal annealing was performed with increments of 30 K h⁻¹. All measurements were performed at 77 K. From [9].

interactions. In the following we shall present PAS studies on H, He, Ar, Kr and N interacting with defects in different metals.

2. Hydrogen-defect interactions

A hydrogen atom being trapped at a defect may retain mobility in one of three ways: (i) the hydrogen atom detraps below a temperature at which the defect is mobile; (ii) the hydrogen-defect centre migrates as a whole; (iii) the hydrogen stabilises the defect until a break-up occurs at a temperature where both species are mobile. Situation (ii) may be difficult to distinguish from (iii). Examples will be given for hydrogen release from monovacancies below and above stage III (the temperature region where monovacancies become mobile). The influence of hydrogen on the defect nucleation processes will be discussed. Also hydrogen in large three-dimensional vacancy clusters changes the annihilation characteristics dramatically; results demonstrating trapping and release of hydrogen at voids will be presented.

2.1. Hydrogen in nickel

Hydrogen trapping and release at vacancies have been studied in Ni [9]. Frenkel pairs were first introduced at 20 K by high-energy protons. The sample set was then pre-annealed at 320 K. This is below stage III in nickel and the vacancies created during the irradiation therefore remain immobile and no vacancy clustering should occur. The specimens were doped with hydrogen by electrochemical methods at room temperature, and quickly quenched to 77 K. The positron lifetime spectra were also measured at 77 K. The doping caused the mean positron lifetime to decrease by about 5–10 ps, in agreement with theoretical calculations that predict the positron lifetime in a H-decorated vacancy to be lowered by 8–25 ps [4]. The annealing curve in figure 1 shows a rapid recovery of the mean positron lifetime around 305 K, at a temperature below the pre-annealing temperature. Hence the change must be ascribed to hydrogen detrapping from the vacancies slightly below stage III. This temperature for hydrogen release agrees well with results from ion beam experiments [10]. There two release stages for deuterium have been observed; one around 260 K attributed to deuterium detrapping from self-

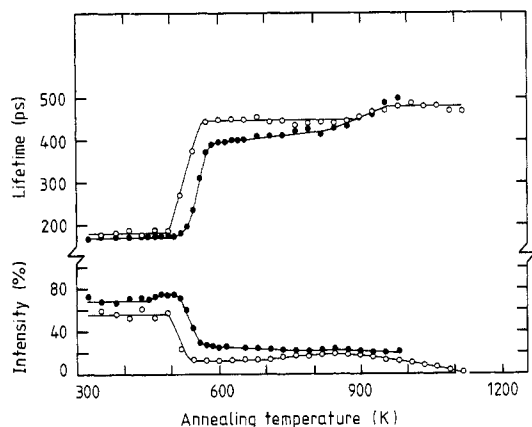


Figure 2. Variation with temperature of the positron lifetime parameters for the long-lived component in electron-irradiated Mo: ○○○, pure; ●●●, H-doped. The annealing rate was 30 K h^{-1} . From [13].

interstitials [11] or from vacancies [10] and another stage around 305 K attributed to release from vacancy clusters [12] or monovacancies [10]. The information obtained by the method of ion beam analysis is primarily macroscopic and the defect structure is not well known. Positron lifetime experiments can more easily be designed to study the particular defect of interest and the positron lifetime results suggest that the 305 K stage found from ion beam analysis is due to deuterium release from monovacancies.

2.2. Hydrogen in molybdenum

An experiment similar to that on Ni has been carried out on Mo [13], where Frenkel pairs were created by 2 MeV electron irradiations at room temperature. Two-component fittings of the positron spectra, obtained at room temperature, yielded 180 ps for the long-lived component, corresponding to positron annihilation from a monovacancy in Mo. Doping with hydrogen decreased this lifetime to 165 ps. Computer simulations have predicted [7] that the positron lifetime in a vacancy decorated by one, two or four H atoms decreases to 175, 165 and 146 ps, respectively, with the H atoms positioned in the nearly octahedral site suggested by ion channelling experiments [14]. The lifetime of 165 ps is thus reproduced with about two hydrogen atoms per vacancy.

The variations of the positron lifetime parameters with annealing temperature are shown in figure 2. The presence of H in vacancies is seen to immobilise the vacancies to slightly higher temperatures than in the undoped specimen. The H-vacancy complexes dissociate at 540 K.

Positron lifetime results for hydrogen in Mo have also revealed a release temperature of around 540 K for chemisorbed hydrogen [15]. The binding energy of H to voids is expected to be only slightly larger than for hydrogen binding to monovacancies [16]. This strongly suggests that the H-vacancy complexes do indeed dissociate around 540 K rather than migrate as a whole [13].

The dissociation energy, E_d , for a H-defect complex may be estimated from

$$E_d = k_B T_r \ln(\nu t / \ln 2) \quad (1)$$

employing a one-step detrapping model, i.e. where repeated hydrogen trapping is neglected. In equation (1) k_B is the Boltzmann constant, T_r the temperature where half the hydrogen is assumed to be released, ν the escape attempt frequency (taken to equal

Table 1. Deduced H-defect binding energies E_b for different metals obtained from equation (2) using dissociation energy E_d from equation (1). The release temperatures T_r are taken from figures in the quoted references. The hydrogen migration energies used are taken from refs. [18, 23–26]. The uncertainties in the estimated binding energies are believed to be less than about 0.1 eV. The experimental data are compared with results E_b^{theor} of theoretical calculations using the effective-medium theory.

Metal	Defect	T_r (K)	E_d (eV)	E_b (eV)	E_b^{theor} (eV)
Al	Vacancy	295 [19]	0.95	0.43	0.52 [11]
Fe	Void	275 [17]	1.03	0.97	0.99 [20, 21]
Ni	Vacancy	305 [9]	0.98	0.58	0.52 [10]
Nb	Vacancy	400 [22]	1.3	1.2	—
Mo	Vacancy	540 [13]	1.75	1.6	0.96 [16]
Mo	Void	540 [15]	1.75	1.6	0.98 [16]
Ta	Vacancy	480 [22]	1.6	1.4	—

the Debye frequency) and t the annealing time around the release temperature. The effect of hydrogen retrapping is to increase the release temperature and thereby the deduced dissociation energy. This effect is thought to be small as very similar release temperatures are found from positron annihilation spectroscopy and ion beam analysis experiments, in spite of defect concentrations that differ by orders of magnitude [17].

For hydrogen in vacancies in Mo a dissociation energy of 1.75 ± 0.05 eV can then be deduced. With a migration energy E_m for hydrogen in the Mo lattice of 0.11 eV [18] the H-defect binding energy is obtained from

$$E_b = E_d - E_m \quad (2)$$

this being around 1.64 eV. This is tabulated in table 1, together with estimates for other metals; theoretical calculations are also included.

In ion beam analysis measurements, deuterium release was also observed between 500 and 600 K [16]. These results were treated by nineteen coupled differential equations, which yielded a binding energy of 1.03 ± 0.15 eV for this release stage. From ion beam analysis measurements with a less complicated treatment the binding energy was estimated to be around 1.5 eV [27]. From chemisorption and solubility data [18, 28, 29] the binding energy to large voids is deduced to be 1.3 eV.

After the vacancies have migrated and formed clusters at approximately 600 K (cf. figure 2), the positron lifetime is shorter and its intensity greater in the doped sample than in a similarly irradiated pure sample. As hydrogen is released from voids around 540 K this difference cannot be ascribed to hydrogen in the voids, but is due rather to the influence of hydrogen on the nucleation process [13]. The shorter lifetime and the greater intensity in the doped sample means that the voids are smaller but more numerous than in the undoped sample. This suggests that vacancies occupied by hydrogen act as nucleation centres and change the nucleation process. The nucleation centres are more likely to be vacancies with multiple hydrogen occupancy as these are immobilised more effectively. They are not allowed to migrate before complete release of hydrogen from the vacancy. The lifetime of around 400 ps corresponds to about 10 vacancies per cluster [4]. This lifetime increases slowly between 600 and 900 K due to coarsening, reaching a value of about 465 ps, which corresponds to more than 30 vacancies per void [4].

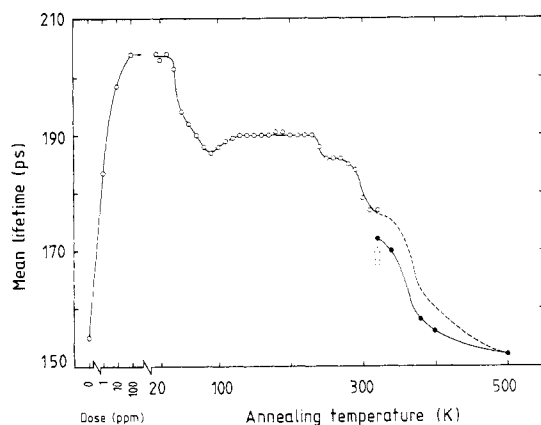


Figure 3. Annealing of proton-implanted Al followed by positron lifetime measurements. The annealing rate was 25 K h^{-1} . Measuring temperature: \circ , 15 K; \triangle , 50 K; \bullet , 80 K; \square , 100 K. From [19].

2.3. Hydrogen in aluminium

In positron studies the gases of interest are normally introduced either by annealing in an atmosphere of the gas and either quenched [30] or slowly cooled [22] depending on the heat of solution for the gas in the metal, or by electrochemical methods [9, 13, 15]. Recently, a method has been applied in which the gas atoms are injected by implantation [19, 31]. By this process the defects with which the gas atoms interact are produced simultaneously with the gas doping. The primary defects are Frenkel pairs. The method has been used to study hydrogen in aluminium [19]: protons were implanted below 20 K and the recovery processes during annealing at elevated temperatures was followed. The increase in the mean positron lifetime due to vacancies created during the implantations is shown in figure 3. In the subsequent annealing sequence, the recovery stages up to 250 K are all attributed to defect-defect interactions, and are not particularly influenced by the presence of hydrogen in the sample [21, 32]. This has been verified by similar studies on samples in which Frenkel defects were introduced by penetrating protons [21, 32]. In the latter experiment, complete recovery occurred around 230 K where monovacancies become free to move. In figure 3 only a small recovery stage is seen around 230 K while a new stage appears at 295 K. The hydrogen atoms have blocked the migration of the vacancies until the H-vacancy pairs migrate or dissociate [21]. When dissociation is assumed to occur E_d is deduced to be 0.95 eV [19], in agreement with ion beam analysis experiments where E_d was found to be 0.94 eV [33].

The diffusivity of hydrogen in metals is normally measured at high temperatures to achieve high hydrogen solubility. In metals with low vacancy formation energies compared with the dissociation energy of H-vacancy pairs, the measured hydrogen diffusivity can be influenced by thermally created vacancies due to there being a high probability of the hydrogen atoms residing in vacancies. Calculations suggest that close to the melting point of aluminium the hydrogen atoms spend about half their time in vacancies and that the diffusivity is lowered by a factor of two compared with a vacancy-free lattice [23]. Thus, the effective migration energy measured in permeation experiments is also lower than the true migration energy. The variation of the effective migration energy with temperature calculated for three different hydrogen migration energies in Al is shown in figure 4. Positron annihilation spectroscopy results for the H-vacancy dissociation energy, the entropy and the energy for vacancy formation combined with hydrogen diffusivity results yields [23] a true hydrogen migration energy of $E_m =$

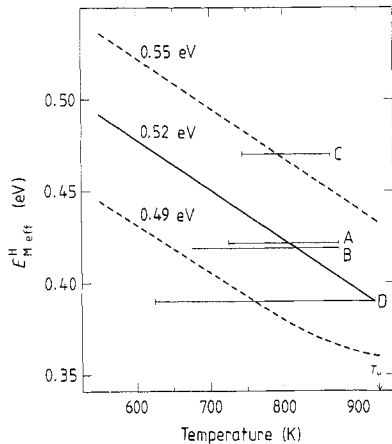


Figure 4. The effective migration energy for H in Al as a function of temperature, calculated for three different energies of hydrogen migration in a vacancy-free lattice. From [23].

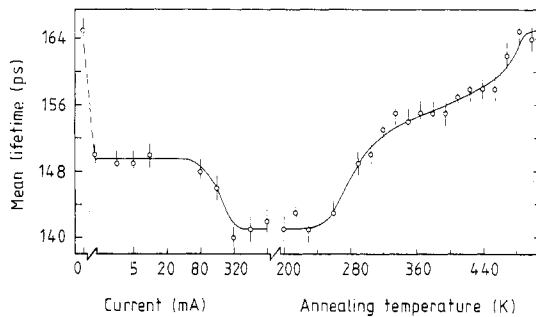


Figure 5. The mean positron lifetime as a function of H-dose and subsequent annealing for Fe containing voids. The H doping was performed by an electrochemical method. The isochronal annealing rate was 30 K h^{-1} . From [17].

(0.52 ± 0.07) eV and a pre-exponential factor of $D_0 \approx 8 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$. These values are in agreement with very recent diffusivity results obtained around room temperature [34], where the influence of thermally created vacancies is insignificant.

2.4. Hydrogen in iron

Hydrogen in large three-dimensional vacancy agglomerates can also be detected by PAS [15, 17]. Figure 5 shows how the mean positron lifetime depends on H doping for a Fe sample containing voids [17]. $\bar{\tau}$ decreases by up to 25 ps and three-component decompositions have shown that this is the result of a reduced trapping rate to the voids by a factor of four [17]. Annealing between 200 and 500 K, with measurements at 77 K, show a recovery stage around 280 K due to hydrogen release from the voids. As has also been observed in ion beam analysis measurements [33], a surface layer obstructs the complete release from the sample until about 460 K. Also, hydrogen in voids has been studied in Mo by PAS and the positron lifetime in Mo voids has been reduced by more than 100 ps due to trapped hydrogen [15]. Hydrogen in large vacancy clusters may therefore easily be studied by PAS.

3. Noble gas–defect interactions in metals

The subject of noble gases in metals has attracted much attention in recent years and much effort has been put into theoretical and experimental studies of e.g. bubble

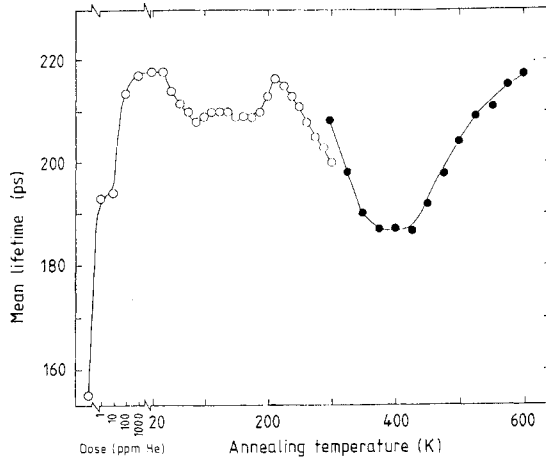


Figure 6. The evolution of the mean positron lifetime with annealing temperature for He-implanted Al. The isochronal annealing rate was 25 K h^{-1} . From ref. [21]. Measuring temperature: $\circ\circ\circ$, 15 K; $\bullet\bullet\bullet$, 80 K.

formation, density and pressure of the noble gases in the bubbles and their influence on the evolution of defects [2, 35]. The positron annihilation spectroscopists have also entered this area and a few results will now be presented in brief.

3.1. Helium in aluminium

Figure 6 shows results for ^3He -implanted Al at 20 K. The implantation causes Frenkel pairs to be created and the highly mobile helium is thought to be trapped already in the implantation stage [21, 36]. During the course of annealing, stages I, II and III are observed at about 40 K, 90 K and 200 K, respectively [32, 36]. Due to a high vacancy concentration small vacancy clusters are formed in stage III, causing the mean positron lifetime to increase, but this is subsequently followed by a decrease due to thermal instability of the small vacancy clusters. A minimum in the mean positron lifetime is reached at about 400 K. A two-component analysis also shows a minimum of τ_2 around 400 K with a value of about 207 ps [36]. This value is well below the positron lifetime in a pure monovacancy (250 ps). The value of 207 ps is assigned to positron annihilation from He-vacancy pairs, in agreement with the theoretical prediction of 203 ps [8]. The mean positron lifetime increases again above 400 K, this being explained by migration and nucleation of He-vacancy pairs [36]. A He-vacancy migration energy of $1.3 \pm 0.1 \text{ eV}$ has been estimated [21, 36], this being in agreement with results from thermal desorption experiments where the activation energy was determined to be 1.35 eV [37]. This is interpreted in terms of diffusion of substitutional He through the vacancy mechanism [36, 37]. τ_2 rises to above 300 ps at 600 K and annealing to 900 K further increases τ_2 to 470 ps due to bubble growth. He bubbles have proved to be stable up to two degrees below the melting point of Al [38] at least.

The positron lifetime in bubbles of He in Al has been calculated as a function of He density [8]. For large bubbles (>30 vacancies) deviation of the positron lifetime from that in pure voids is due to the presence of He. The lifetime has been calculated [8] to decrease with increasing He density, n_{He} , following the simple relation:

$$\tau = 500 - 23.5 n_{\text{He}} \quad (3)$$

where τ is in units of ps and n_{He} in units of 10^{28} m^{-3} . From this relation it is possible to

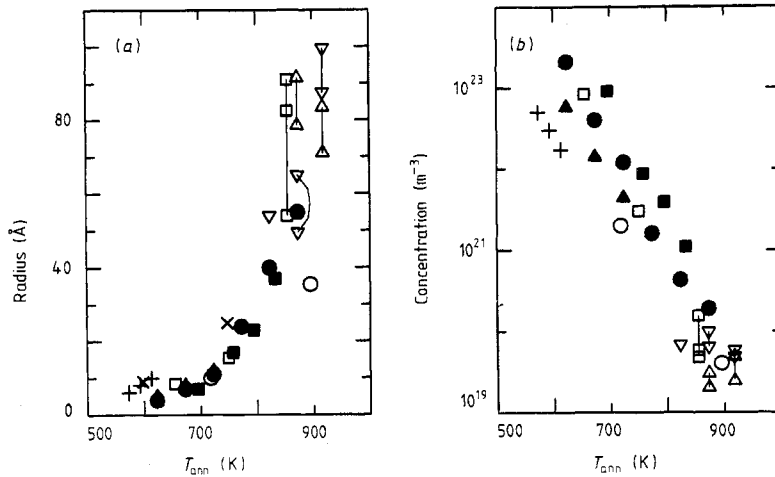


Figure 7. (a) Radius and (b) concentration of He bubbles in Al versus annealing temperature as deduced from positron lifetime (full symbols) and transmission electron microscopy (open symbols) studies. The reader is referred to [39] for details.

estimate the He density inside the bubbles, a quantity that can be estimated only by a few other methods like electron energy-loss spectroscopy and vacuum-ultraviolet absorption spectroscopy. Positron annihilation spectroscopy has the advantage of being able to provide information of the size and concentration of bubbles, as well as the He density [39]. Figure 7 shows results of positron lifetime and transmission electron microscopy (TEM) determinations of bubble radii and concentrations, good agreement being observed between the two techniques. The bubble sizes may also be estimated from the knowledge of the He density when employing the equation of state (EOS), assuming that the bubbles are in thermal equilibrium [36, 39]. Due to uncertainties in the EOS and in the positron lifetime data [36], rather large uncertainties appear in equation (3). However, good agreement between PAS and TEM measurements has been obtained [36, 39].

3.2. Argon in molybdenum

In the preceding sections positron lifetime studies of gas-defect interactions have been discussed. In recent years variable-energy positron beams have been used in studies of defects close to the surface. In this technique the positrons are injected with fairly low energies and the extracted information comes from the fraction of positrons returning to the surface. The information is less direct than from positron lifetime measurements, but the technique provides information about the surface and sub-surface. This is of use in other surface science studies.

Surface cleaning is most often performed using sputtering by noble gases. Figure 8 shows the defect concentration as a function of annealing temperature, after 3 keV Ar⁺-sputtering of Mo at room temperature. The results show that defects created by the sputtering are extremely stable and have not annealed out completely at 1500 K. A rapid recovery stage is seen between 900 and 1200 K. As the recovery occurs well above stage III in Mo, the positron traps are not pure monovacancies, but Ar-vacancy complexes or vacancy clusters [40].

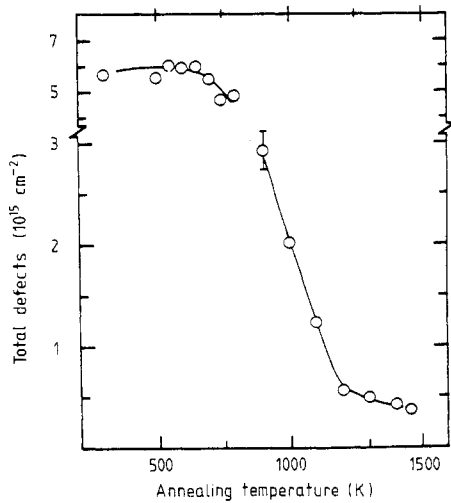


Figure 8. The total concentration of defects versus annealing temperature in Ar-irradiated Mo as deduced from variable-energy positron beam experiments. From [40].

Direct information about the nature of defects is not obtained by this technique, but a very recent development in which it has become possible to perform positron lifetime measurements in variable-energy positron beams [41] makes the variable-energy beam technique very powerful.

3.3. Krypton in copper

Bubbles of Kr in Cu have been produced by a combined implantation and sputtering process [42]. Positron annihilation studies of solid bubbles and their coalescence around the temperature where the bubbles melt have been reported [42]. Using a combination of experimental positron annihilation measurements and theoretical calculations it has been possible to estimate the Kr density inside the bubbles, good agreement with results from other techniques having been obtained. After annealing to 1325 K the Cu samples were expected to contain Kr bubbles of sizes in the range 1–10 μm with Kr pressures of 1–10 atm [43]. At these densities the positron lifetime is only slightly reduced at room temperature, but when the sample is cooled layers of Kr adsorb onto the bubble surfaces, where the positrons are also localised. Figure 9 shows that the adsorption reduces the positron lifetime to 300 ps. This is in accord with theory where a single layer of Kr is found to reduce the positron lifetime from 500 ps to 300 ps [8].

4. Nitrogen-defect interactions in molybdenum

Interstitial nitrogen has been introduced in Mo by quenching the specimen, kept in a pure nitrogen atmosphere at about 2000 K, to room temperature [45]. Frenkel defects were then induced by 2 MeV electron irradiation. Figure 10 shows the annealing curve as measured by the positron lifetime technique. The positron lifetime in vacancies is reduced, compared with a pure sample, from 180 ps to 145 ps, due to the decoration of monovacancies by nitrogen atoms. Theoretical calculations find that a single nitrogen atom placed off-centre in a Mo monovacancy will give rise to a lifetime of 146 ps, while a monovacancy decorated by two nitrogen atoms should not trap positrons [7]. The

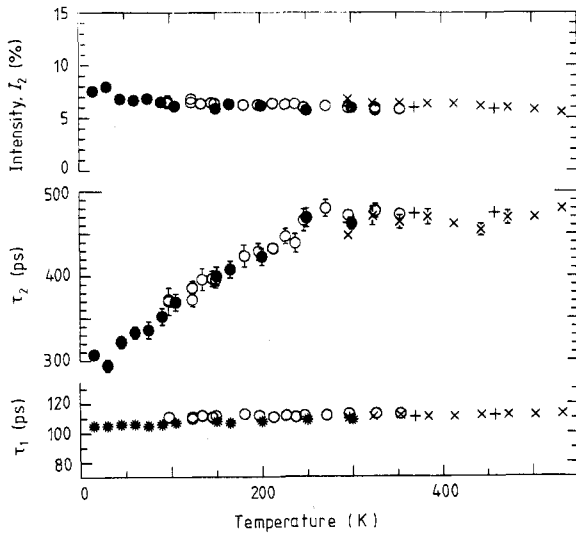


Figure 9. Results of two-component analyses of positron lifetime spectra for Cu samples containing cavities with Kr shown as a function of measuring temperature. The different symbols denote measurements made in different spectrometer set-ups. From [44].

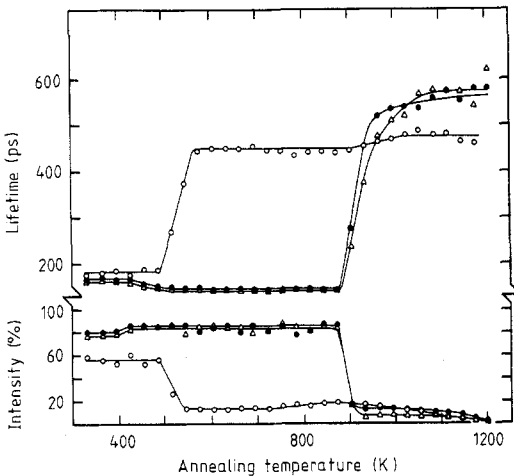


Figure 10. The lifetime and relative intensity of the long-lived component in a two-component analysis of positron lifetime spectra, as a function of annealing temperature: $\circ\circ\circ$, pure; $\bullet\bullet\bullet$ and $\triangle\triangle\triangle$, N-doped Mo. From [45].

vacancy migration stage is delayed by about 350 K to 900 K, where the vacancy–nitrogen pairs are believed to dissociate [45]. From equation (1) the activation energy for dissociation may be estimated to be about 2.9 eV. This is in good agreement with the 2.8 ± 0.2 eV found from ion beam analysis experiments [46] and the 2.55 eV deduced from thermal helium desorption spectroscopy [47].

After the break-up of the N–vacancy complexes, three-dimensional vacancy clusters are formed. The nitrogen atoms can be trapped again at these defects, giving rise to a positron lifetime about 100 ps longer in the N-doped samples than in the undoped specimen [45]. Nitrogen in voids has been shown to give rise to a positron lifetime of about 630 ps, considerably longer than the value of about 475 ps in undecorated voids [48].

5. Conclusion

The use of positron annihilation spectroscopy in studies of interactions between gases and defects in metals has been briefly reviewed. Emphasis has been put more on the application of positrons to the study of gases in metals and the influence of gases on the evolution of defects than on discussions of the specific positron states.

It is evident that positron annihilation spectroscopy is already a very powerful technique for the study of gas-defect interactions and combined with other techniques it can give very useful information that can relate the observed macroscopic behaviours of materials to microscopic processes. The conventional positron lifetime and angular correlation measurements are well suited to measurements on bulk materials. More interesting for surface and sub-surface studies are variable-energy positron beams.

Acknowledgment

M B Madsen is acknowledged for comments on the manuscript.

References

- [1] Alefeld G and Völkl J (ed.) 1978 *Springer Topics in Applied Physics* vols 28–9 (Berlin: Springer)
- [2] Ullmaier H (ed.) 1983 *Radiat. Eff.* **78**
- [3] Thompson A W and Bernstein I M (ed.) 1976 *Effect of Hydrogen on Behavior of Metals* (New York: AIME)
- [4] Hautojärvi P (ed.) 1979 *Springer Topics in Current Physics* vol 12 (Berlin: Springer)
- [5] Brandt W and Dupasquier A (ed.) 1983 *Positron Solid-State Physics* (Amsterdam: North-Holland)
- [6] Puska M J and Nieminen R M 1983 *J. Phys. F: Met. Phys.* **13** 333
- [7] Hansen H E, Nieminen R M and Puska M J 1984 *J. Phys. F: Met. Phys.* **14** 1299
- [8] Jensen K O and Nieminen R M 1987 *Phys. Rev. B* **36** 8219
- [9] Rajainmäki H, Linderöth S, Hansen H E and Nieminen R M 1988 *J. Phys. F: Met. Phys.* **18** 1109
- [10] Myers S M, Nordlander P, Besenbacher F and Nørskov J K 1986 *Phys. Rev. B* **33** 854
- [11] Besenbacher F, Myers S M and Nørskov J K 1985 *Nucl. Instrum. Methods B* **7–8** 55
- [12] Besenbacher F, Böttiger J and Myers S M 1982 *J. Appl. Phys.* **53** 3536
- [13] Linderöth S, Rajainmäki H, Nielsen B, Hansen H E, Nieminen R M and Petersen K 1987 *Mater. Sci. Forum* **15–8** 751
- [14] Picraux S T 1981 *Nucl. Instrum. Methods* **182–3** 413
- [15] 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
- [16] Myers S M and Besenbacher F 1986 *J. Appl. Phys.* **60** 3499
- [17] Linderöth S and Shishkin A V 1987 *Phil. Mag. A* **55** 291
- [18] Katsuta H, McLellan R B and Furukawa K 1982 *J. Phys. Chem. Solids* **43** 533
- [19] Linderöth S, Rajainmäki H and Nieminen R M 1987 *Phys. Rev. B* **35** 5524
- [20] Besenbacher F, Myers S M, Nordlander P and Nørskov J K 1987 *J. Appl. Phys.* **61** 1788
- [21] Linderöth S 1987 *PhD Thesis* Technical University of Denmark (Lyngby)
- [22] Hautojärvi P, Huomo H, Puska M and Vehanen A 1985 *Phys. Rev. B* **32** 4326
- [23] Linderöth S 1988 *Phil. Mag. Lett.* **57** 229
- [24] Kiuchi K and McLellan R B 1983 *Acta Metall.* **31** 961
- [25] Robertson W M 1973 *Z. Metallk.* **64** 436
- [26] Völkl J and Alefeld G 1978 *Springer Topics in Applied Physics* vols 28–9, ed. G Alefeld and J Völkl (Berlin: Springer) p 321
- [27] Böttiger J, Picraux S T, Rud N and Laursen T 1977 *J. Appl. Phys.* **48** 920
- [28] Mahnig M and Schmidt L D 1971 *Z. Phys. Chem.* **80** 71
- [29] Han H R and Schmidt L D 1971 *J. Catal.* **22** 260

- [30] Lengeler B, Mantl S and Triftshäuser W 1978 *J. Phys. F: Met. Phys.* **8** 1691
- [31] Hansen H E, Talja R, Rajainmäki H, Nielsen H K, Nielsen B and Nieminen R M 1985 *Appl. Phys. A* **36** 81
- [32] Rajainmäki H, Linderoth S, Nieminen R M and Hansen H E 1987 *Mater. Sci. Forum* **15-8** 611
- [33] Myers S M, Wampler W R, Besenbacher F, Robinson S L and Moody N R 1985 *Mater. Sci. Eng.* **69** 397
- [34] Ishikawa T and McLellan R B 1986 *Acta Metall.* **34** 1091
- [35] Donnelly S E 1985 *Radiat. Eff.* **90** 1
- [36] Rajainmäki H, Linderoth S, Hansen H E, Nieminen R M and Bentzon M D 1988 *Phys. Rev. B* **38** 1087
- [37] Sciani V and Jung P 1983 *Radiat. Eff.* **78** 87
- [38] Hansen H E, Rajainmäki H, Talja R, Bentzon M D, Nieminen R M and Petersen K 1985 *J. Phys. F.: Met. Phys.* **15** 1
- [39] Jensen K O, Eldrup M, Singh B N and Victoria M 1988 *J. Phys. F: Met. Phys.* **18** 1069
- [40] Bentzon M D, Huomo H, Vehanen A, Hautojärvi P, Lahtinen J and Hautala M 1987 *J. Phys. F: Met. Phys.* **17** 1477
- [41] Schödlbauer D, Sperr P, Kögel G and Triftshäuser W 1988 *Nucl. Instrum. Methods B* **34** 258
- [42] Jensen K O 1987, Eldrup M, Pedersen N J and Evans J H 1988 *J. Phys. F: Met. Phys.* **18** 1703
- [43] Jensen K O 1987 *PhD Thesis* Risø National Laboratory (Roskilde)
- [44] Jensen K O, Eldrup M, Linderoth S and Evans J H 1989 *Positron Annihilation* ed. L Dorikens-Vanpraet, M Dorikens and D Segers (Singapore: World Scientific) at press
- [45] Nielsen B, Veen A, Casper L M, Filius H A, Hansen H E and Petersen K 1982 *Positron Annihilation* ed. P G Coleman, S C Sharma and L M Diana (Amsterdam: North-Holland) p 438
- [46] Hautala M, Anttila A and Hirvonen J 1982 *J. Nucl. Mater.* **105** 172
- [47] Veen A and Caspers L M 1979 *Solid State Commun.* **30** 761
- [48] Hansen H E, Linderoth S, Wierzchowski W and Petersen K 1982 *Appl. Phys. A* **27** 247