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POSITRON ANNIHILATION SPECTROSCOPY OF DEFECTS IN METALS - AN ASSESSMENT*

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Positron annihilation spectroscopy (PAS) has made significant contributions to our knowledge regarding lattice defects in metals in two areas: (i) the determination of atomic defect properties, particularly those of monovacancies, and (ii) the monitoring and characterization of vacancy-like microstructure development during post-irradiation or post-quench annealing. The application of PAS to the study of defects in metals is selectively reviewed and critically assessed within the context of other available techniques for such investigations. Possibilities for using the positron as a localized probe of the structure of atomic defects are discussed. Finally, the present status and future potential of PAS as a tool for the study of defects in metals are considered relative to other available techniques.

1. INTRODUCTION

The application of positron annihilation spectroscopy (PAS) to the study of defects in metals has grown rapidly since the first realizations [1-3] of the sensitivity of positrons to lattice defects. During the past decade, PAS has become an increasingly important tool within the metal defects research community [4-6], and it is now an accepted technique for the characterization of defect microstructures [7]. At this time, and by invitation of the Conference Organizers to do so, it seems appropriate to assess the role that positron annihilation spectroscopy has played in the field of defects in metals, and to look at its strengths and weaknesses, both as a technique unto itself and as a complement to the other experimental methods available to the materials scientist for such studies.

The applicability of PAS to the study of defects in metals rests with the ability of positrons to be trapped in localized, bound states in a variety of vacancy-like defects, from which they subsequently annihilate. In most metals, positrons are very sensitive to defect regions of significantly lower-than-average electron density, such as vacancies, small vacancy clusters, and voids, at which they can form rather deeply bound states. Positrons are also sensitive to dislocations, grain boundaries, and interfaces, which in general represent somewhat smaller negative perturbations to the average electron density in a metal than the vacancy-type defects. However, these extended defects may contain defects themselves (e.g., jogs on a dislocation line) that can trap positrons more deeply. Since positrons are generally repelled from regions of higher-than-average electron density in the metal (e.g., an interstitial atom or small interstitial cluster), PAS is able to distinguish between the defect clustering processes that involve vacancies or interstitials in irradiated metals, a particularly useful feature of PAS as compared with a number of other techniques.

The PAS techniques (lifetime, Doppler broadening, and angular correlation) can yield two types of information regarding the defects that trap positrons. First, for sufficiently low defect concentrations, from about 10^{-6} to 10^{-4} in the case of vacancies, for example, the probability of positron trapping at the defects prior to annihilation changes with concentration, approaching unity for vacancy concentrations $>10^{-4}$. Since the positron annihilation characteristics are significantly different in the defect (longer lifetimes, narrower, more peaked Doppler-broadened and angular-correlation spectra) than in the defect-free lattice, these defect concentration changes can be rather precisely monitored within this range. Second, since the defect-trapped positron-annihilation characteristics, the positron lifetime or the shape of the Doppler-broadened or angular-correlation spectrum, are defect specific in a given metal, the nature of the defect or defects trapping the positrons can be distinguished. This is true even when the positron trapping is saturated, i.e., when the trapping probability is unity. This type of defect-specific information is available, in a practical manner, only as long as either a given defect type is dominant or the defect ensemble under investigation is sufficiently simple, i.e., usually containing no more than two types of defects, that a deconvolution of the PAS spectra can be made. Hence, PAS is capable of directly following changes in both the concentration and defect-specific nature of vacancy-like defect ensembles in metals. This combination of available information, and the general applicability of these techniques to most metals, has allowed PAS to make a significant impact upon the study of defects in metals during the past decade.

The contributions that PAS has made to the characterization of defects in metals have been primarily in two areas: (i) the determination of properties of atomic defects, particularly those of monovacancies, and (ii) the monotoring and characterization of vacancy-like microstructure development during post-irradiation or post-quench annealing. Most often, these investigations have been performed on pure metals. However, applications to the study of defects in alloys have increased markedly in recent years. Defect studies in metals and alloys are useful for a variety of reasons. Two of the most important of these are: (i) the elucidation of the atomic-defect mechanisms responsible for mass transport (diffusion) under conditions of essentially thermodynamic equilibrium, and (ii) the need to understand how this mass transport is affected under the nonequilibrium conditions of energetic-particle (e.g., electron, neutron, ion) irradiation. A number of defect-related phenomena such as the spatial redistribution of solute elements, induced phase instability, and dimensional swelling and distortion can be caused by irradiaton, often with deleterious effects upon the pertinent physical properties of the material in question. Before discussing the rôle that PAS has played in the study of defects in metals, it may be useful to first consider briefly some extant problems in this research area to which the positron annihilation techniques may be usefully applied in the future.

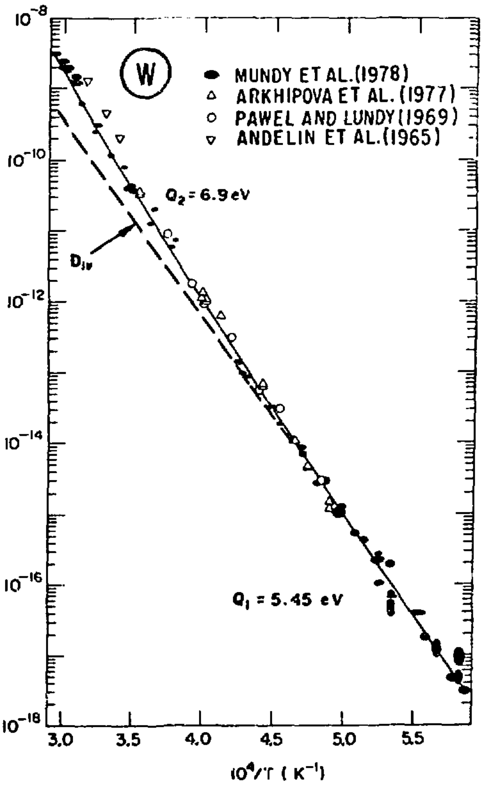

Fig. 1. Self-diffusion in tungsten; logarithm of the tracer self-diffusion coefficient as a function of reciprocal temperature [11-14]. The expected behavior from atomic exchange with monovacancies, D_{1v}, is indicated, as are the low- and high-temperature activation enthalpies, Q_l and Q_2, respectively. After Ref. [11].

The atomic-defect mechanisms of self-diffusion in metals have been investigated for many years by a combination of radiotracer diffusion measurements and a variety of experimental techniques for the study of vacancy defects. These investigations have clearly demonstrated that atomic exchange with monovacancies is the dominant mechanism by which atoms undergo transport in metals [8-10], except as the metal approaches its melting temperature, T_m. In essentially all metals, as T_m is approached, self-diffusion is increasingly enhanced over that which can be attributed to simple atom-monovacancy exchange [10]. This enhancement appears as a positive curvature in an Arrhenius plot (ln D versus T^{-1}) of the temperature dependence of the self-diffusion coefficient. For the face-centered-cubic (fcc) metals, this enhancement at T_m ranges from about a factor of 1.25 for nickel to a factor of 3 for aluminum. The more recently measured self-diffusion behavior in the refractory body-centered-cubic (bcc) metals, an example of which is shown in Fig. 1 for tungsten, indicates enhancements of more than about a factor of 10 at T_m [10].

Evidence exists for some fcc metals, notably aluminum, platinum, and gold, that this diffusion enhancement is caused by the presence of an increasing population of divacancies in the equilibrium vacancy ensemble with increasing temperature. For example, the temperature dependence of the total vacancy concentration in aluminum, deduced from a combination of differential dilatometry and quenching experiments [20], is shown in Fig. 2. Not only are there thus more vacancy defects present with which atoms can exchange, but also the divacancy is known to be more mobile than the monovacancy in the fcc structure. In the refractory bcc metals, such as tungsten and molybdenum, on the other hand, there now appears to be rather convincing evidence that the considerably larger high-temperature diffusion enhancement found in these metals cannot be attributed, at least solely, to the presence of divacancies [10]. The possibility that self-interstitial atoms may contribute significantly to atomic transport in both fcc and bcc metals under essentially equilibrium conditions at high temperatures has been suggested as an alternative or supplemental mechanism for this diffusion enhancement. One important aspect of clarifying this situation is to be able to elucidate the nature of the high-temperature equilibrium vacancy

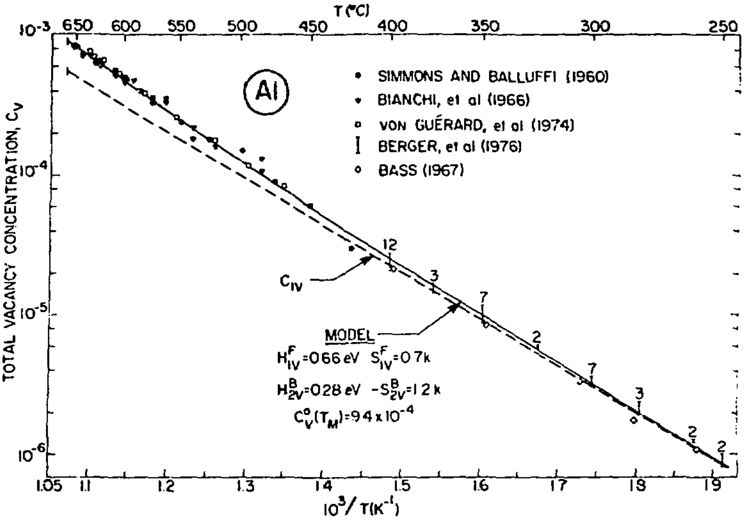

Fig. 2. The total equilibrium vacancy concentration in aluminum; logarithm of C_v as a function of reciprocal temperature. The post-quench resistivity data [15,16] are scaled to the C_v values measured by differential dilatometry [17-19] using a vacancy resistivity of 1.0 x 10^{-4} Ω cm. The number and range of measurements at each temperature from [15] are indicated. The data are compared with a model curve for $C_v(T)$ using the vacancy parameters shown; the monovacancy concentration $C_{1v}(T)$ is also indicated. From Ref. [20].

ensemble. PAS has been one of our most valuable tools in determining the formation properties of monovacancies in metals; its application to the defect-specific study of the high-temperature vacancy ensemble appears now to also be viable, as will be discussed below. Furthermore, PAS studies of the mobility of vacancy defects might be fruitfully extended from those on monovacancies to investigations of high-order mobile clusters, such as divacancies.

Many of the effects of energetic-particle irradiation upon the microstructure of metals and alloys, and the concomitant changes induced in their physical properties, are already quite well known [21]. These effects include: (i) radiation-enhanced diffusion, (ii) radiation-induced segregation of elemental constitutents, (iii) void formation leading to swelling, and (iv) radiation-induced instability and spatial redistribution of alloy phases. These defect-related phenomena can sometimes have a rather complex relationship to the fundamental physical properties of the atomic defects that control them. Nevertheless, an understanding of the underlying defect properties and interactions is imperative if these phenomena are to be eventually understood and controlled. Two examples will suffice here to demonstrate the nature of the microstructural effects that can ensue from energetic-particle irradiation and the rôle that PAS might play in providing fundamental information regarding these effects.

Radiation-induced segregation of solute elements to defect sinks (i.e., annihilation sites), such as the surface, grain boundaries, and dislocation loops, can occur in alloys under any energetic-particle irradiation that produces excess mobile defects. Radiation-induced segregation, which can dramatically alter the physical and mechanical properties of an alloy, results from the coupling of a flux of solute atoms to the flux of radiation-induced excess defects diffusing to the sinks. This coupling exists by virtue of an interaction between the solute element and an atomic defect. The magnitude of such an effect depends upon a number of defect-related properties, including the degree of defect-solute binding, the defect mobilities, and the defect production rate compared with the equilibrium defect concentrations. Owing to the sensitivity of the positron in most metals to the presence of vacancy defects, and the ability of the positron to distinguish between vacancy- and interstitial-type imperfections, PAS can directly provide much of the needed basic information regarding these defect-related properties pertaining to vacancy defects. Indirectly, by comparison with experiments that do not distinguish between vacancies and interstitials, such as electrical resistometry, PAS investigations can yield fundamental information regarding interstitials as well.

Void formation in irradiated metals, and the concomitant dimensional swelling of the material, is caused by the precipitation of the excess vacancies that result from an imbalance in the net annihilation rates at defect sinks (mainly dislocations) of the vacancies and interstitials produced by the energetic-particle irradiation. It is a major and costly problem in the use of metals for fuel cladding in nuclear reactors. The rate and magnitude of void swelling depend upon a variety of defect properties, such as equilibrium vacancy concentrations, vacancy and interstitial mobilities, vacancy-cluster binding energies, defect-solute interactions, etc. The morphologies of the void distributions formed during irradiation are normally investigated using transmission electron microscopy (TEM). TEM offers the most direct information available regarding the size, density, and distribution of these vacancy clusters, as long as they are above the normal

TEM resolution limit ($\gtrsim$20 Å in diameter) for voids. PAS cannot, and has no need to, compete with TEM for such morphological observations. Nevertheless, PAS can contribute to the investigation of the void formation and swelling problem in a number of significant ways. These range from the study of the properties of vacancies in metals and alloys, including their interactions with solute elements and extended defects, to the study of the earliest stages of the vacancy precipitation process itself, for which PAS has unique capabilities. The effects of both substitutional and interstitial solute atoms upon this vacancy precipitation process can also be investigated by PAS.

The present paper will consider primarily the investigation of vacancy formation, migration, and clustering by PAS in comparison with the other available techniques for these defect studies. By means of such comparisons, it is hoped that both the particular strengths and weaknesses of PAS as a method for the study and characterization of defect microstructures will be made clear.

2. PROPERTIES OF MONOVACANCIES

2.1 Monovacancy formation

The study of vacancy formation in metals has been actively pursued for more than 20 years using differential dilatometry, quenching, and, more recently, positron annihilation spectroscopy techniques [20]. Differential dilatometry, which is based upon the measurement of the relative macroscopic length change ($\Delta L/L$) and microscopic lattice-parameter change ($\Delta a/a$) in a crystal, is normally carried out as a function of temperature under conditions of thermodynamic equilibrium. These measurements have the virtue of being rather straightforward in that they yield a value for the total vacancy concentration at each temperature by means of the relation $C_v = 3\ [(\Delta L/L)-(\Delta a/a)]$, which pertains for an isotropic (i.e., cubic) metal. For anisotropic (e.g., hexagonal) metals, length and lattice-parameter changes along each unique lattice direction must be measured. The practical drawback to differential dilatometry is the precision with which the ($\Delta a/a$) measurements can presently be performed, usually to no better than 5 parts in 10^5. Thus, the technique is limited to measurements of $C_v > 5 \times 10^{-5}$. For most metals this is a rather severe limitation, since vacancy concentrations at the melting temperature are of order of magnitude 10^{-4} to 10^{-3}. Thus, either a sufficiently wide temperature and vacancy-concentration range is unavailable to allow for the precise determination of vacancy formation enthalpies (See Fig. 3.) or, if the vacancy concentration at T_m is relatively high, the likelihood of contributions to the measurements from higher-order vacancy clusters (principally divacancies) cannot be ignored (See Fig. 2.).

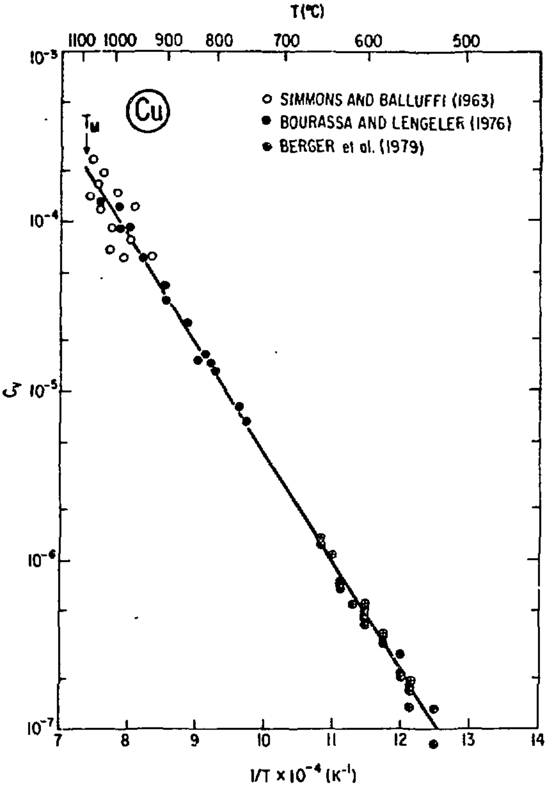

Fig. 3. The total equilibrium vacancy concentration in copper; logarithm of C_v as a function of reciprocal temperature. The post-quench resistivity data [23,24] are scaled to the C_v values measured by differential dilatometry [22] using a vacancy resistivity of 0.62×10^4 Ω cm. After Ref. [24].

The results of differential dilatometry measurements of C_v in copper [22] are shown in Fig. 3, along with the results from two quenching studies [23,24]. These latter, nonequilibrium measurements of the residual resistivity increments (at 4.2 K) from quenched-in vacancies have avoided one of the most problematic pitfalls of quenching investigations of vacancy formation [25], that of the loss of vacancies to existing sinks (primarily dislocations) during the rapid quench from high temperatures. This has been accomplished by starting with very low dislocation density single crystals [23] or by quenching from sufficiently low temperatures that this loss can be shown to be negligible [24]. The results of these differential dilatometry and quenching studies together are seen to provide a rather consistent description of vacancy formation in copper. A similarly self-consistent description exists for two other fcc metals, aluminum [20], as shown in Fig. 2, and gold [25,26]. In the case of copper (Fig. 3) these data give no indication of an enhancement

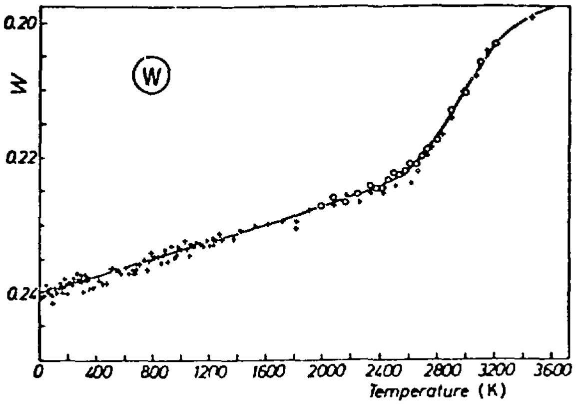

Fig. 4. Doppler-broadening lineshape parameter W(T) for tungsten as a function of temperature, and the trapping model fit to these data. From Ref. [31].

in C_v at high temperatures from the presence of divacancies in the equilibrium vacancy ensemble, whereas for aluminum and gold such an enhancement is clearly evident [20]. However, the problems with performing reliable quenching experiments are considerable, and relating the nonequilibrium quenched-in vacancy ensemble back to the equilibrium vacancy ensemble of interest in these vacancy formation studies can be rather difficult.

PAS has provided a means, for the first time, to study vacancy formation in metals under equilibrium conditions with sufficient sensitivity to monitor the changing concentration of vacancies with temperature over the range in which monovacancies dominate the equilibrium vacancy ensemble. This is a result of the positron being sensitive to vacancy concentration changes in the range of $<10^{-6}$ to 10^{-4} in most metals. Measurements of the temperature dependence of positron annihilation, through the application of the two-state trapping model [27-29], have resulted in determinations of the monovacancy formation enthalpy, H^F_{1v}, in a wide variety of metals [30]. The intrinsic temperature dependence of the positron annihilation characteristics, such as that shown in Fig. 4 for tungsten [31], appears to be now rather well understood. At low temperatures, above about one third the Debye temperature, a positron annihilation parameter (positron lifetime or Doppler-broadening or angular-correlation lineshape) will vary linearly with temperature owing to the positron's response in its delocalized Bloch state to a combinaton of lattice expansion and positron-phonon-electron coupling [32,33]. The positron annihilation parameter departs exponentially from this linear behavior as equilibrium vacancies at concentrations of $>10^{-7}$ are introduced into the metal. As the melting temperature of the metal is approached, and the equilibrium vacancy concentration becomes $\sim 10^{-4}$ to 10^{-3}, the positron's response tends toward a saturation as the probability for positron trapping prior to annihilation approaches unity. For the positron's localized state in the vacancy, the temperature dependence of the positron annihilation parameter is expected to be weaker than it is for the positron's delocalized Bloch state, since the phonon coupling is no longer extant. For high-purity metal samples maintained under carefully well-annealed conditions, such an intrinsic temperature dependence of the positron annihilation parameters can be measured, as shown in Fig. 5 for nickel [34], for example.

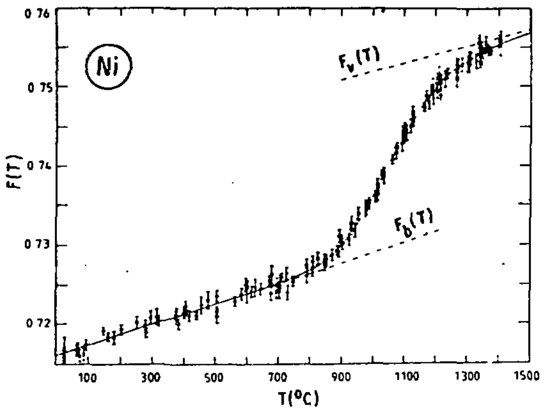

Fig. 5. Doppler-broadening lineshape parameter F(T) for nickel as a function of temperature. The trapping model fit to these data is shown, along with the temperature dependences of its limiting states, the Bloch state, $F_b(T)$, and the vacancy-trapped state, $F_v(T)$. From Ref. [34].

Difficulties can arise, however, which may lead to departures from such an idealized picture. An example is shown in Fig. 6, also for nickel [35], which admittedly can be a rather difficult metal to both obtain and maintain under the conditions necessary for the measurement of such intrinsic behavior, since interstitital

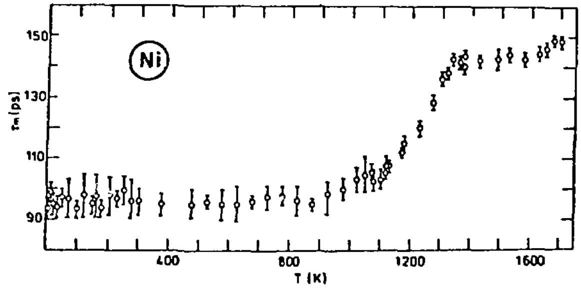

Fig. 6. Positron lifetime in nickel, from a single-lifetime fit, as a function of temperature. From Ref. [35].

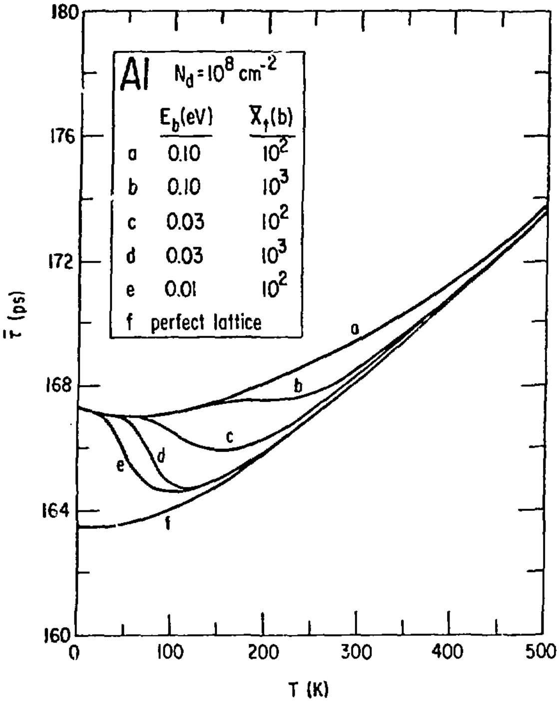

Fig. 7. Calculated mean positron lifetime as a function of temperature in aluminum containing a dislocation density of 10^8 cm^{-2}, for various mean spacings $\bar{X}_t$ between deep traps along the dislocation lines (in units of the Burgers vector b) and positron-trap binding energies, compared with the perfect aluminum lattice. After Ref. [37].

impurities are readily absorbed which can pin dislocations and prevent or slow their annealing. The most striking feature of these data is the temperature independence of the positron lifetime below ~ 900 K. While the positron lifetime and the Doppler-broadening parameter shown in Fig. 5 are not expected to have the same temperature dependences, they would both be expected to vary linearly with temperature below ~ 900 K. It has been suggested that such behavior, which has been rather widely observed [36], can be explained on the basis of positron trapping in dislocations at low temperatures. A model for this has been proposed [37], based upon weak positron trapping at dislocation lines and stronger trapping at sites such as jogs along these lines, which yields predictions in qualitative agreement with the behavior observed for a variety of metals, as can be seen from Fig. 7. It would appear at this writing that the various experimental observations of the temperature dependence of positron annihilation in metals, even in anisotropic metals such as cadmium [38-40], in the so-called "prevacancy region" (i.e., at temperatures below the onset of the sensitivity of PAS to the presence of vacancies) can be attributed either to the theoretically expected intrinsic behavior [32,33] or to extrinsic factors, such as the presence of dislocations as low-temperature positron traps. Fortunately, however, the increased uncertainties introduced by this extrinsic behavior in determining vacancy formation enthalpies by PAS are often within the practical error limits (about ± 5%) of the technique itself [41], although lower values of H^F_{1v} tend to result from this behavior owing to erroneous extrapolation of the prevacancy temperature dependence into the vacancy-sensitive region.

Measurements of the monovacancy formation enthalpy using PAS can yield the most reliable values for H^F_{1v}, but they do agree well with those obtained from careful quenching studies, when available. A comparison of H^F_{1v} values obtained from PAS and quenching studies is presented in Table 1 for a few selected fcc and refractory bcc metals. For such metals, to which PAS can be applied in a straightforward manner using the two-state trapping model, positron annihilation has provided rather precise and accurate values for H^F_{1v}. However, the application of PAS to such determinations is not always so straightforward. For metals which undergo phase transitions within the temperature range of the sigmoidal response of PAS, such as iron [51] for example, there is an increased uncertainty in the application of PAS to the determination of H^F_{1v}. Nevertheless, while not as accurate as one might like, the values obtained may still be the best available, since other techniques would be even more difficult to apply. A similar situation holds for the group VB refractory bcc metals, vanadium, niobium, and tantalum, for which an additional assumption regarding positron detrapping from vacancies at high temperatures has been used in deducing H^F_{1v} values from PAS data [31], although the results of theoretical calculations [52] indicate that such detrapping is highly improbable in these metals. Despite these and other practical problems in applying PAS to the study of vacancy formation in metals, the positron annihilation techniques have become our most useful tool for such studies, a situation that is unlikely to change in the forseeable future.

2.2 Monovacancy migration

Vacancy migration in metals has been fruitfully investigated by two methods, which have most often, but not always, yielded results consistent with one another. One method has been the essentially direct measurement of vacancy mobility by monitoring the temperature-dependent annealing of a nonequilibrium ensemble of vacancies introduced into the metal by quenching or energetic-particle (preferably electron) irradiation [53]. The other method has been the more indirect, but often preferable, one of combining the results of monovacancy formation and low-

Table 1. Monovacancy formation enthalpies, H^F_{1v}, from PAS compared with those from quenching. The 'best' values for H^F_{1v} are subtracted from the activation enthalpies for low-temperature diffusion, Q_1, to yield values for the monovacancy migration enthalpy, H^M_{1v} [10].

Metal	H^F_{1v}(eV)			Q_1(eV)	H^M_{1v}(eV)
	PAS	Quenching	'Best'		
Al	0.66 ± 0.02 [42]	0.66 ± 0.01 [43]	0.66	1.28	0.62
Ag	1.11 ± 0.05 [44]	1.10 [45]	1.11	1.76	0.65
Au	0.97 ± 0.01 [46]	0.94 ± 0.02 [26]	0.94	1.78	0.84
Cu	1.31 ± 0.05 [47]	1.30 ± 0.05 [24]	1.31	2.07	0.76
Ni	1.8 ± 0.1 [34]	1.6 [48]	1.8	2.88	1.1
Mo	3.0 ± 0.2 [31]	3.2 [49]	3.2	4.5	1.3
W	4.0 ± 0.3 [31]	3.6 ± 0.2 [50]	3.6	5.4	1.8

temperature radiotracer diffusion studies to deduce monovacancy migration enthalpies [8,20]. In the first method, as long as the nonequilibrium defect ensemble introduced into the metal by quenching or irradiation is not too complex, as it can often be in the cases of heavy-particle (neutron, ion) irradiation or mechanical deformation, the defect annealing can be interpreted in terms of the mobilities of the individual defects comprising the ensemble [54]. The experimental techniques used to monitor this annealing behavior have been diverse, including electrical resistometry, anelastic measurements, TEM, diffuse X-ray scattering, field ion microscopy (FIM), ion channeling, Mössbauer spectroscopy, and perturbed angular correlation (PAC). PAS has found its niche in both of these methods to deduce the migration properties of vacancy defects.

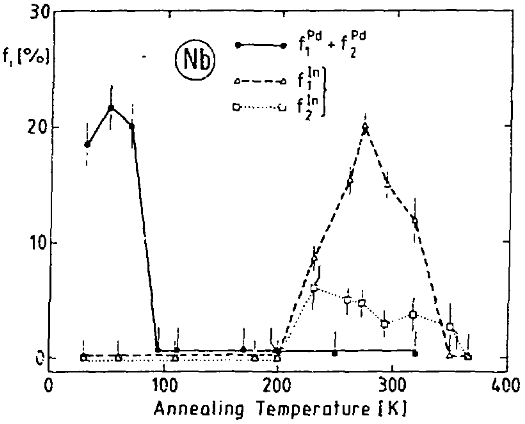

Fig. 8. Perturbed angular correlation study in niobium of defect annealing after heavy-ion irradiation at 30 K. Fractions f_i of ^{100}Pd and ^{111}In probe atoms which have trapped mobile defects of type i as a function of annealing temperature. From Ref. [57].

Since the activation enthalpy for self-diffusion by atomic exchange with monovacancies is given by $Q_1 = H^F_{1v} + H^M_{1v}$, precise measurements of Q_1 by radiotracer diffusion or nuclear magnetic resonance methods can be combined with similarly precise measurements of H^F_{1v} to yield values for the monovacancy migration enthalpy, H^M_{1v}. Some examples are presented in Table 1. When the measurements of Q_1 and H^F_{1v} are straightforward, as for the examples given in Table 1, requiring no ad hoc assumptions in the analysis of either the diffusion or vacancy-formation data, this method for determining H^M_{1v}, basically under equilibrium conditions and a rather simple defect situation, can yield the most accurate values available for this migration enthalpy. These values also agree well with those available from post-quench and post-irradiation annealing studies [53]. On the other hand, when the determination of either Q_1 or H^F_{1v}, or both, requires a more complex and model-dependent analysis than usual, as in the case of metals undergoing high-temperature phase transitions [51,55] or when positron detrapping from vacancies is suspected [31], this method can yield results which are considerably less reliable than those available from the more direct studies of vacancy mobility in quenched or electron-irradiated metals.

As a case in point, PAS data for niobium have been analyzed under an assumption of positron detrapping from vacancies to yield a value for the monovacancy formation enthalpy [31], the only value that has been measured for this metal. This value, when subtracted from the measured low-temperature activation enthalpy for radiotracer diffusion [56], yielded a value for the monovacancy migration enthalpy that indicated a minimum temperature for vacancy migration of 480 K in niobium [31]. However, recent

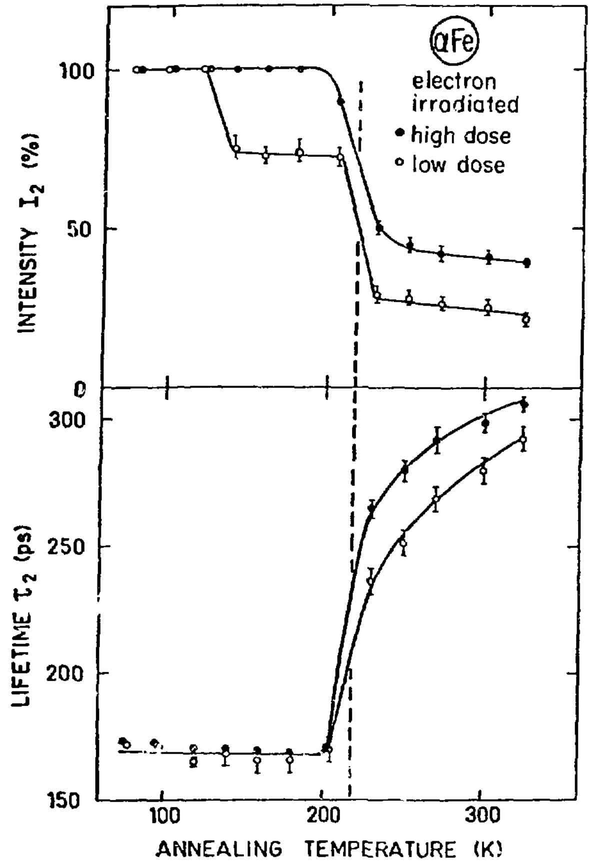

Fig. 9. The lifetime τ_2 of trapped positrons, and the intensity I_2 of this component, in electron-irradiated alpha iron as a function of annealing temperature. After Ref. [60].

PAC measurements [57] of post-irradiation annealing in niobium, shown in Fig. 8, indicate rather convincingly that vacancies are mobile at about 250 K where they are seen to become trapped by the oversized In probe atoms, but not by the undersized Pd probe atoms. This PAC observation of vacancy mobility in Nb at about 250 K is consistent with previous observations of a post-irradiation annealing stage at this temperature by both electrical resistometry [58] and PAS [59], and furthermore indicates that the value of H^F_{1v} derived from the equilibrium PAS measurements [31] may indeed be too low. A possible reason for this low deduced value of the monovacancy formation enthalpy could be the incorporation of positron detrapping from vacancies into the model used to analyze the PAS data, an effect which appears to be theoretically unjustified [52] for niobium.

PAS has been particularly useful in monitoring vacancy annealing in metals after irradiation or quenching, owing to the rather unique sensitivity of the positron to vacancy defects. Thus, even in a defect ensemble containing both vacancies and interstitials, produced by energetic-particle irradiation, PAS is able to distinguish those temperature regions in which vacancies are mobile and form clusters from those in which vacancy-interstitial recombinaton occurs. This defect-specific sensitivity of the positron has consequently helped significantly in confirming that mobile vacancies are responsible for what is normally called Stage III annealing in irradiated metals [53]. A controversy existed for a number of years regarding this annealing stage, owing in part to the lack of defect-specificity of previously used techniques, such as electrical resistometry, which allowed for interpretation of this annealing in terms of either vacancies or interstitials.

An example of the application of the PAS lifetime technique to the direct study [60] of vacancy mobility in electron-irradiated αFe is shown in Fig. 9. In this study, the observed post-irradiation annealing of the defect-trapped positron lifetime τ_2 and the intensity I_2 of this component in the lifetime spectrum clearly indicates that vacancies are mobile at about 220 K in αFe. The annealing of I_2 in the low-dose sample at 140 K, along with the absence of any concomitant change in τ_2 at this temperature, suggests that vacancy-interstitial recombination has occurred in this annealing stage. The annealing of I_2 at 220 K, in both the high- and low-dose irradiated samples, along with the concomitant increase of τ_2 from that value attributable to monovacancies (about 175 ps) to those values representative of small vacancy clusters, show clearly that vacancy precipitation is taking place at this temperature. This direct observation of vacancy mobility at about 220 K in αFe is at odds with the indirect deduction of a monovacancy mobility in αFe from a combination of equilibrium PAS [51] and radio-tracer diffusion [55] results, which suggests that the monovacancy in αFe only becomes mobile at considerably higher temperatures. However, this appears to be a good case in point for the greater reliability of the more direct measurement of vacancy mobility by PAS compared with the indirect method for a metal which undergoes multiple high-temperature phase transitions. This can be more fully appreciated in the light of the complex diffusion [55] and vacancy formation [51] behavior in Fe shown in Figs. 10 and 11, respectively. Recent measurements using a variety of techniques, including PAS, TEM, magnetic after-effect measurements, and electrical resistometry, have confirmed the low-temperature mobility of the vacancy in αFe [64].

Positron lifetime measurements of vacancy mobility, such as those on αFe [60], have a distinct advantage at present over either angular correlation or Doppler-broadening investigations, since the positron lifetime in a

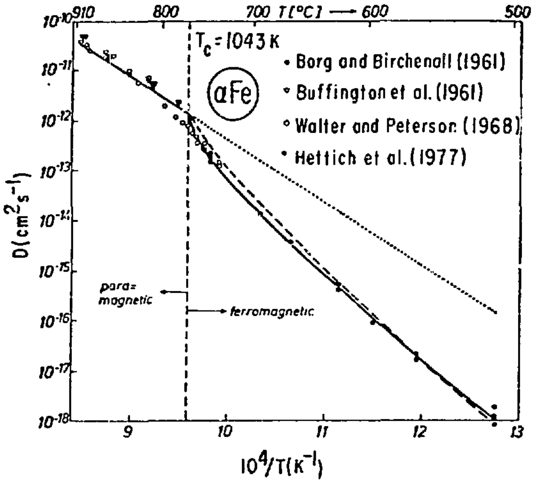

Fig. 10. Self-diffusion in paramagnetic and ferromagnetic alpha iron; logarithm of the tracer self-diffusion coefficient as a function of reciprocal temperature [55,61-63]. After Ref. [55].

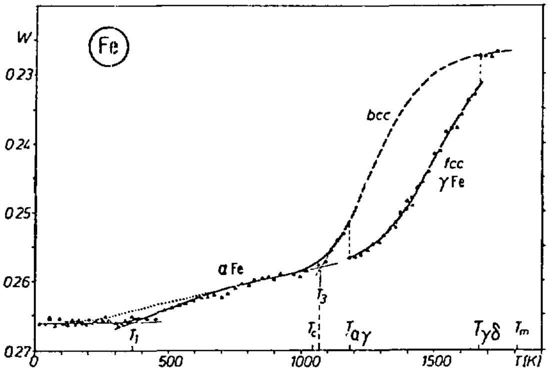

Fig. 11. Doppler-broadening lineshape parameter W(T) for the alpha, gamma, and delta phases of iron as a function of temperature. From Ref. [51].

particular defect-trapped state is a better-defined physical quantity than the various momentum-distribution shape parameters in use, and it can also be theoretically estimated with reasonable certainty. However, the PAS momentum techniques can also be usefully applied to the study of vacancy mobility. As shown in Fig. 12, it has been possible to define [65] a ratio (R parameter) of measured lineshape-parameter differences that is defect-type specific, but essentially defect-concentration independent. The variation of this parameter with annealing temperature has been used to confirm that vacancy precipitation occurs at about 280 K in electron-irradiated copper [65] by comparison with results for quenched copper [66], which of course contains only vacancies that precipitate upon ageing at about the same temperature [24]. While such momentum measurements have not been widely used as yet for defect mobility studies, it can be expected that in the near future, with the advent of increasingly realistic theoretical calculations of defect-trapped positron annihilation spectra [67,68], even more defect-specific shape parameters will be developed to facilitate such investigations.

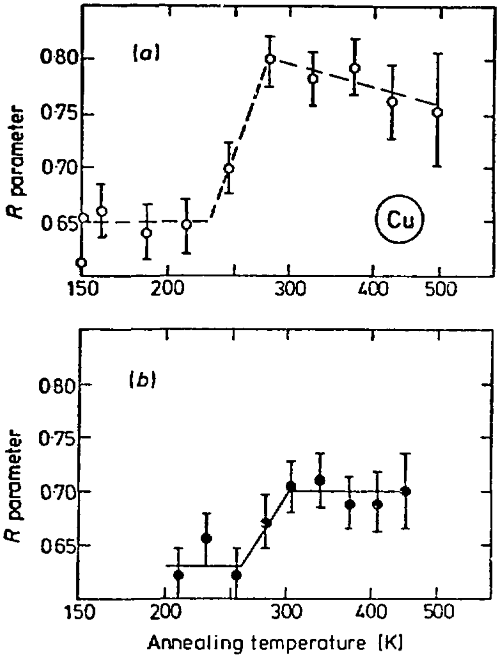

Fig. 12. Ratio (R-parameter) of Doppler-broadening lineshape-parameter differences for (a) electron-irradiated copper as a function of annealing temperature, compared with that for (b) quenched copper. From Ref. [66].

Before proceeding to a consideration of divacancies in metals, it may be useful to point out a feature of direct measurements of vacancy mobility using PAS of which full advantage has not been taken. PAS measurements of vacancy mobility in nonequilibrium defect ensembles have concentrated upon determining the temperature range in which vacancies become mobile, which is qualitively useful information. However, they have not gone beyond this to quantitatively determine a vacancy migration enthalpy, which is necessary input in the modeling of complex defect-related behavior found in real materials. Although more tedious than isochronal annealing studies, as that shown in Fig. 9, isothermal annealing measurements at a variety of temperatures within the defect-mobile region can yield quantitative measurements [54] of the vacancy migration enthalpy by PAS, as they have using electrical resistometry and TEM. Such measurements would be particularly useful, of course, for those metals (e.g., αFe, V, Nb, Ta) in which the comparison of the results of low-temperature diffusion studies and monovacancy formation enthalpy measurements have yielded questionable [69] values for the monovacancy *migration enthalpy [31,51]*.

3. DIVACANCIES

As discussed in the Introduction, self-diffusion in metals is generally observed to be enhanced at high temperatures over that expected from atomic exchange with monovacancies [10]. This effect is usually attributed [8,70] to the presence of significant concentrations of divacancies in the equilibrium vacancy ensemble. As a result, PAS data, such as those shown in Fig. 5, have also been analyzed for evidence of contributions from these higher-order vacancy clusters. Such attempts at deducing information regarding divacancies, however, yield results that appear to lack uniqueness. Doppler-broadening data for copper shown in Fig. 13 were analyzed in detail by fitting to a trapping model containing monovacancies alone (1v), or in combination with increasing concentrations of divacancies (1v-2v) [47]. It was concluded that no *unique information regarding the presence of* divacancies in the equilibrium vacancy ensemble could be obtained from this type of positron annihilation data using parametric trapping-model fits. This may be a particularly difficult problem for copper, which has a rather low vacancy concentration at T_m and for which the data shown in Fig. 3 give no evidence for an enhanced divacancy concentration at high temperatures. The difficulty in obtaining information regarding divacancies from such data as shown in Fig. 13 results from a lack of knowledge regarding the temperature-dependent annihilation characteristics for the monovacancy- and divacancy-trapped positrons, and hence, a lack of knowledge regarding the limiting high-temperature behavior, $F_v(T)$, of the sigmoidal curve. Fortunately, the application of PAS to the problem of the high-temperature equilibrium vacancy ensemble in metals is not limited to such measurements. Two aspects of PAS, one experimental and one theoretical, seem to have now matured to the point where it appears that a successful approach to this problem is at hand.

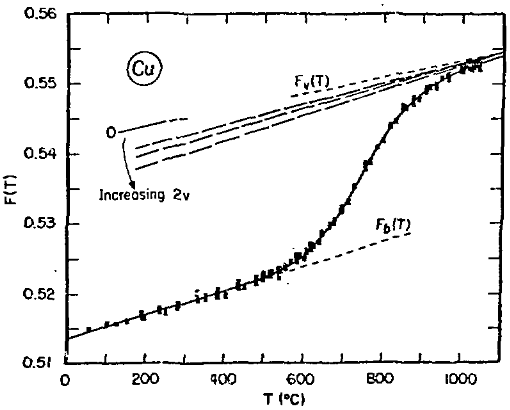

Fig. 13. Doppler-broadening lineshape parameter F(T) for copper as a function of temperature, and four statistically indistinguishable trapping-model fits to the data [47]. The $F_v(T)$ deduced from these fits (1v or 1v-2v) are seen to accommodate to the uncertainties regarding the high-temperature vacancy ensemble.

The full momentum-density information available from two-dimensional angular correlation of annihilation radiation (2D-ACAR), previously used for electronic structure investigations of defect-free metals [71], can be used for the study of positrons annihilating from vacancy-defect-trapped states within the high-temperature equilibrium vacancy ensemble. In addition, it is now possible to make realistic theoretical calculations of the positron-annihilation characteristics from monovacancy- and divacancy-trapped *states in a metal, based upon* a self-consistent, local density functional formalism [72] incorporating many-body enhance*ment effects and carried out for vacancy defects* within a supercell [73]. An investigation of the equilibrium vacancy ensemble in aluminum using a combination of these 2D-ACAR experimental and theoretical PAS techniques has very recently been performed [67], and is described schematically in Fig. 14. The 2D-ACAR surfaces measured in single-crystal aluminum at 20°C, 500°C, and 630°C are shown in Fig. 14. These are referred to a set of 1D-ACAR peak-count measurements as a function of temperature, by means of which the fraction of trapped positrons contributing to the high-temperature 2D-ACAR data could be ascertained. The theoretically calculated 2D-ACAR spectra for positrons annihilating from the Bloch state and the monovacancy- and divacancy-trapped states, to which the data have been compared, are also presented. The Bloch-state calculation [72] agrees well with the experimentally measured surface at 20°C; the surfaces measured at 500°C and 630°C are observed to lie between the theoretical spectra for the monovacancy- and divacancy-trapped states in terms of both their shape and magnitude.

The preliminary reports [67] of this study are quite encouraging, in that they indicate that these combined experimental and theoretical results are consistent with a significant population of divacancies in the equilibrium vacancy ensemble, which increases with increasing temperature. Such behavior of the equilibrium vacancy ensemble in aluminum is to be expected [20] from a combination of vacancy formation studies (See Fig. 2.) using differential dilatometry, quenching, and PAS. Aluminum, which has a total vacancy

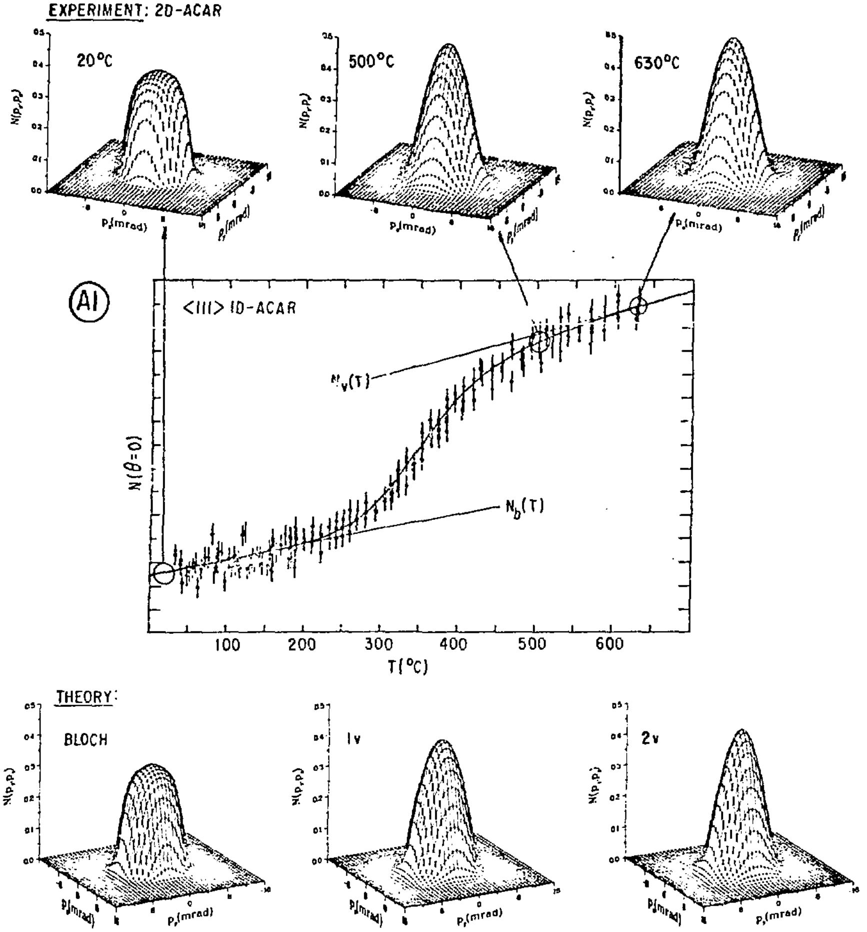

Fig. 14. Schematic of a 2D-ACAR investigation of the equilibrium vacancy ensemble in aluminum [67]. The experimental 2D-ACAR surfaces for an Al single crystal at 20°C, 500°C, and 630°C, measured at Brandeis University, are compared with the theoretical 2D-ACAR spectra, calculated for 0 K and convoluted with the experimental resolution, for the Bloch state and the monovacancy (1v) and divacancy (2v) trapped states of the positron. The p_z and p_y axes correspond to <110> directions for the experiment and <100> directions for the theory; the representations are rotated accordingly. The 2D-ACAR data are referred here to a set of measured p_z = <111>, 1D-ACAR (long-slit) data as a function of temperature for convenience of visualization.

concentration at T_m of 9.4 x 10^{-4}, is thought to have [20] about 40% of its vacant lattice sites in the form of divacancies at T_m, about 20% at 500°C, and an almost negligible amount at 300°C. In addition, post-quench resistivity annealing studies [3,74], an example of which is shown in Fig. 15, clearly indicate that an increasing concentration of highly mobile vacancy defects (presumably divacancies) are present in the quenched-in vacancy ensemble as the quench temperature is increased. The presence of divacancies, having higher mobility than monovacancies, in the high-temperature vacancy ensemble is also consistent with the rather strong diffusion enhancement observed at high temperatures in aluminum [8-10]. Nevertheless, a unique "fingerprint" of the divacancy has not yet been found in this 2D-ACAR study [67], although a full analysis of the data has not yet been completed. A number of temperature-dependent effects must still be incorporated into the theoretical calculations, in order to take full advantage of these data. While this initial 2D-ACAR PAS study of an equilibrium vacancy ensemble has been carried out for aluminum, owing to the previously available vacancy-defect information regarding divacancies, neither the experimental nor theoretical techniques used in this study are limited to this simple metal; the techniques can be applied to any metal, even the refractory bcc metals. It is anticipated that such 2D-ACAR investigations, combining both theory and experiment, will allow for defect-specific, spectroscopic observations of the

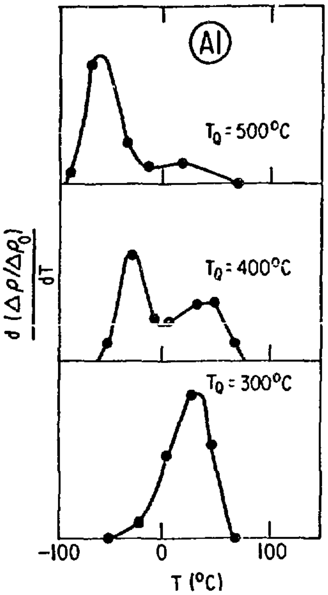

Fig. 15. Isochronal resistivity (ρ) annealing spectra in aluminum quenched from various temperatures T_Q. After Ref. [74].

equilibrium vacancy ensembles in a variety of metals in the future, which can answer a number of important questions regarding their defect-related behavior. Furthermore, it may be expected that such observations can be extended to the study of vacancy-solute interactions in dilute alloys as well, to yield information regarding the change in the electronic structure of a vacancy when it is bound to an impurity. This, of course, is the fundamental information required to understand vacancy-solute interactions in general.

4. VACANCIES IN ALLOYS

Studies of vacancy-solute interactions in dilute alloys have been carried out using the same techniques that have been usefully applied to the study of vacancy formation in pure metals, differential dilatometry, quenching, and PAS [75]. Generally, the measurements performed under equilibrium conditions, either using differential dilatometry or PAS, have indicated rather small interactions between substitutional impurities and vacancies; these results are also consistent with radiotracer measurements of solute diffusion in metals [5]. On the other hand, the nonequilibrium, quenching measurements of vacancy-solute interactions have often indicated considerably larger effects [76]. Although the complexity of the defect ensembles in these quenched dilute alloys sometimes precludes a clear analysis, these effects may often be attributable to the stronger interactions among higher-order vacancy and solute clusters, which would not be found to any significant degree in the equilibrium defect ensemble. As in the case of vacancy formation in pure metals, the equilibrium techniques for investigating vacancy-solute interactions are to be preferred.

Since the relative effect on the vacancy concentration enhancement from the presence of vacancy-solute bound states in the equilibrium vacancy ensemble is greatest at lower temperatures [77], and since any contributions from higher-order vacancy clusters are minimized at such temperatures, PAS measurements of equilibrium vacancy formation in dilute alloys have significant advantages over other available techniques for the study of vacancy-solute interactions in metals. An example of such a measurement [78,79] in Ni(1 at.% Ge) is shown in Fig. 16. Radiation-induced Ge solute segregation has been observed in Ni(Ge) alloys, and attributed to rather strong vacancy-Ge binding [80]. However, the recent PAS measurements of

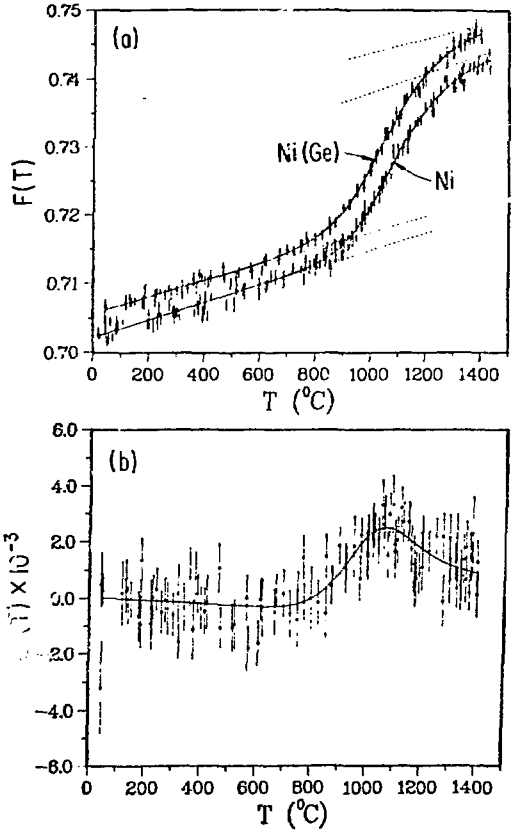

Fig. 16. (a) Doppler-broadening lineshape parameter F(T) for Ni and Ni(1 at.% Ge) as a function of temperature, and the trapping model fits to these data. From Ref. [78]. (b) The difference ΔF(T) between the data for the Ni(1 at.% Ge) and the Ni shown in (a) as a function of temperature. From Ref. [79]. This difference has been set to zero at the lowest temperature.

vacancy formation in Ni(Ge) alloys with various Ge concentrations indicate that this binding enthalpy is only 0.25 ± 0.09 eV [79]. This value is rather small in comparison with the monovacancy formation enthalpy of 1.8 eV in pure Ni [34], but nevertheless may still be sufficiently large to explain the experimentally observed solute-segregation in these alloys.

Even though PAS measurements have definite advantages over other techniques for these investigations, the results presented in Fig. 16 give a good indication of the difficulty of determining vacancy-solute binding enthalpies using such PAS data. The solute enhancement in the equilibrium vacancy concentration is generally quite small in the case of substitutional solute elements and the positron-annihilation parameter measurements must have sufficient precision to distinguish these small changes. However, the maximum effect from the solute-bound vacancies as seen by the positron, shown in Fig. 16b, is well suited to such measurements. A problem that does have to be given due consideration in these PAS measurements, even more so than for pure metals, is that of positron trapping in dislocations in the prevacancy region [36]. This effect, which can be more of a problem in alloys owing to the additional difficulty in the annealing of solute-pinned dislocations, can lead to an erroneous extrapolation of the low-temperature behavior of the lineshape parameter into the vacancy region and, hence, a deduced vacancy-solute binding enthalpy that is larger than that in reality [79]. Nevertheless, carefully performed PAS investigations of vacancy formation in dilute alloys, and in concentrated alloys as well, can provide much needed fundamental information regarding the defect-related behavior of such materials.

The study of vacancies in concentrated alloys has been only recently pursued with much activity [81], using most of the same experimental techniques that have been applied to pure metals and dilute alloys. A number of these studies can be found in Ref. [6] and in these Proceedings. The advantages of PAS over the other techniques are once again its high sensitivity and defect specificity. While in a dilute alloy one is seeking information of an incremental nature regarding the interaction between a solute atom or atoms and a vacancy (or interstitial), which can be a rather difficult task as mentioned above, in a concentrated alloy one is dealing in general with an average or effective defect property. In the most complete study of vacancy formation in concentrated alloys to date [82], the results of which are shown in Fig. 17, a systematic decrease in the effective vacancy formation enthalpy with increasing electron-to-atom ratio was demonstrated for a number of concentrated copper alloys. These measurements show considerable promise for PAS investigations of vacancies in concentrated alloy systems. However, a greater fundamental understanding of how the positron is distributed in such alloys and, as such, how it samples the defects present will be required in order to obtain full value from such measurements.

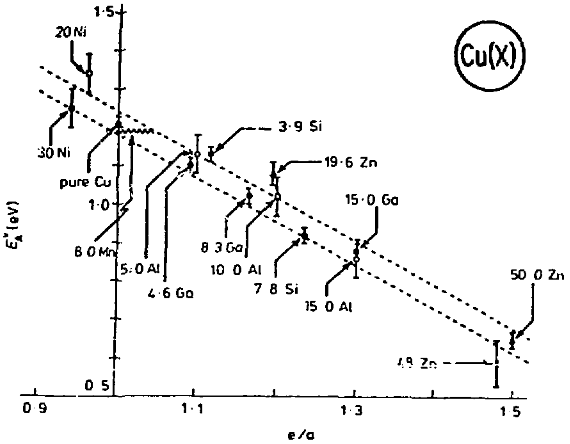

Fig. 17. Apparent vacancy formation enthalpies E_A^V in concentrated copper alloys, Cu(X), containing a variety of solute elements, X, as a function of electron-to-atom ratio (e/a). From Ref. [82].

5. VACANCY CLUSTERING

Vacancy clustering in metals, leading to the formation of dislocation loops, voids, or bubbles, has been widely studied by TEM, by a combination of electrical resistometry and TEM, and, more recently, by PAS. Diffuse X-ray scattering, FIM, and ion channeling have also been used for such studies, but only in a few selected cases. Reviews of many of these applications can be found in Ref. [7]. Transmission electron microscopy has been the technique of choice in most studies of vacancy clustering, since it yields direct information regarding the size, nature, and spatial distribution of the clusters, with good sampling statistics, if done appropriately. TEM can also yield the relationship between such information and that of other microstructural features of interest in the material (e.g., dislocations, grain boundaries, surfaces). In these areas of microstructural observation, no other technique competes effectively with TEM. An example of the utility of TEM for the observation of void distributions is presented in Fig. 18, in which a dramatic ordering is shown of the normal random distribution of voids in irradiated niobium resulting for oxygen concentrations $\gtrsim$ 0.04 at.% [83]. PAS would be rather insensitive to even such a dramatic morphological change as this. The limitations of TEM in performing these tasks are primarily its lack of resolution of very small vacancy clusters ($\lesssim$ 20 Å) and its inability to monitor the earliest stages of the segregation

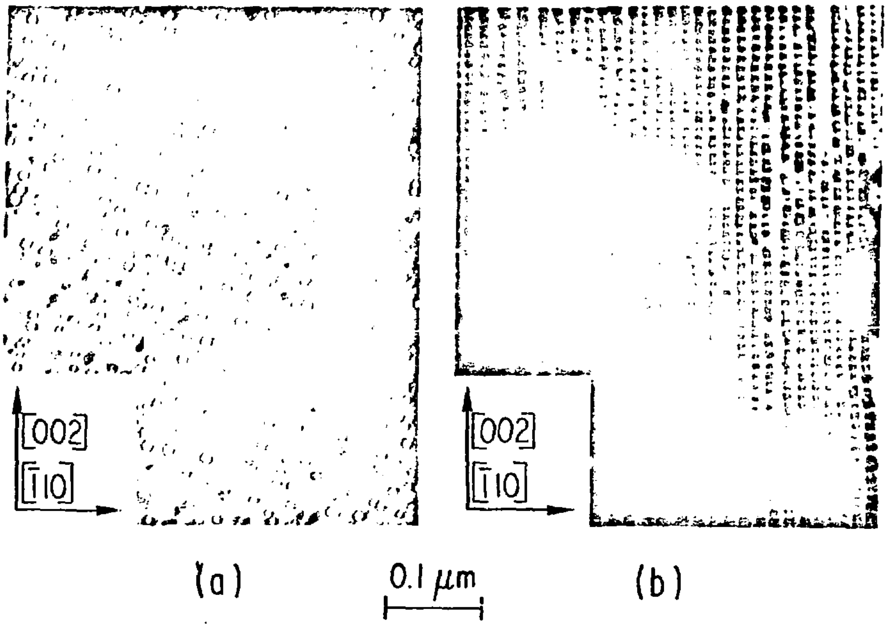

Fig. 18. Transmission electron micrographs of void distributions in niobium containing (a) 0.004 at.% oxygen or (b) 0.039 at.% oxygen after nickel-ion irradiation at 1050 K. From Ref. [83].

of impurities, either substitutional or interstitial, to these clusters. While FIM can, in principal, owing to its atomic resolution and analytical capabilities [84], complement TEM in these areas, its sampling statistics are too limited to high-density events for general applicability. Positron annihilation spectroscopy, by virtue of (i) the positron's unique sensitivity to vacancy defects in the complete range from single vacancies to small vacancy clusters to clusters of vacancies large enough to be observed by TEM and (ii) its ability to distinguish the chemical environment of these vacancy defects, both with good sampling statistics, can complement TEM investigations of vacancy clusters as no other technique available to the materials scientist can. However, much of this potential is as yet unrealized, although this situation appears to be changing rapidly.

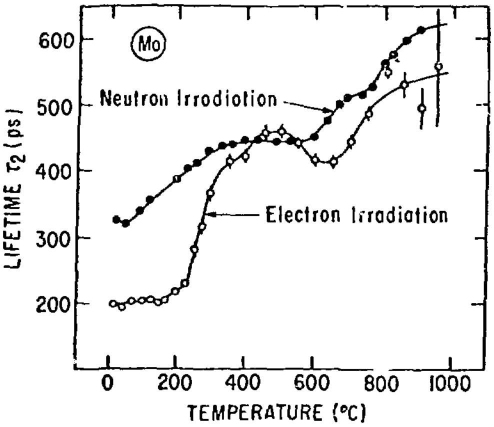

Fig. 19. Annealing behavior of the trapped-positron lifetime τ_2 in electron [85] and neutron [86] irradiated molybdenum. After Ref. [87].

Examples of the application of PAS to the investigation of vacancy clustering in electron [85] and neutron [86] irradiated molybdenum are shown in Fig. 19. The defect-trapped positron lifetime τ_2 is seen to vary continuously with annealing in the electron-irradiated sample from that value (200 ps) representative of monovacancies in Mo to about 450 ps, which is representative of well defined voids [88] in this material. This observed variation of τ_2 with post-irradiation annealing temperature led to two subsequent investigations: one [88], a quantitative analysis of the vacancy clustering process in terms of calculated positron lifetimes in voids in Mo as a function of void size, the other [85], within the context of the original investigation, a confirmation of the PAS-observed void formation by means of TEM. The voids observed by TEM were about 30 Å in diameter and at a density of about 1 to 5 x 10^{13} voids cm^{-3}, close to the limits of both the resolution and sampling capabilities of conventional TEM. The ability of PAS to distinguish between differing states of vacancy clustering in samples that have undergone different irradiation conditions is clearly shown by a comparison of the initial post-irradiation states of the vacancies in the electron and neutron irradiated samples as seen by the positron. The larger initial value of τ_2 in the latter case as compared with the former, distinguishes rather clearly between the void-like nature of the depleted zones present after neutron irradiation and the monovacancies present after electron irradiation, which results in rather simple Frenkel-pair (i.e., vacancy plus interstitial) production.

The increase in τ_2 above 450 ps, shown in Fig. 19, observed for both the electron and neutron irradiated molybdenum at annealing temperatures in excess of 600°C was subsequently shown [87] to have been due to impurity contamination of the voids from the gaseous annealing atmosphere, argon containing 200 ppm nitrogen. The results of a recent PAS lifetime investigation [89] of the effects of the addition of 200 ppm nitrogen upon the defect production and recovery in electron-irradiated molybdenum are shown in Fig. 20. PAS can be seen to be very sensitive to a number of these effects, such as the increased defect production, the suppression of vacancy mobility, and the formation of voids containing nitrogen. A comparison of the positron lifetimes in the voids in the pure and nitrogen-doped Mo clearly confirms the nitrogen contamination during high-temperature annealing in the previous work [85-87] shown in Fig. 19. The demonstrated sensitivity of PAS to such impurity effects can have considerable impact on the study of the earliest stages of solute segregation to voids and its eventual influence upon the void formation and swelling problem in alloys. While such applications of PAS have been somewhat slowly realized, it can now be anticipated from several recent studies reported in these Proceedings that PAS investigations of impurity segregation at voids will provide an important complement to the large number of TEM investigations of this technologically important problem, since TEM after all can only observe the later stages of these segregation processes.

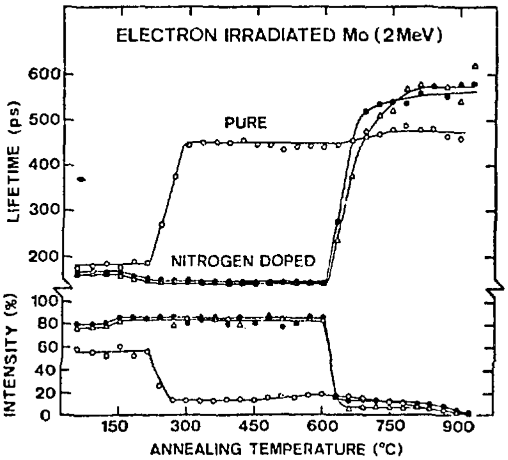

Fig. 20. The lifetime of trapped positrons, and the intensity of this component, in electron-irradiated, pure and nitrogen-doped molybdenum. From Ref. [89].

The investigation of vacancy clustering by PAS is not limited to the lifetime technique, although this technique has clearly been the most useful one in this area to date. The PAS momentum techniques, Doppler broadening and angular correlation, can be similarly applied to these problems, with the particular advantage that specific chemical environments related to these defect clusters may be more effectively probed than with lifetime measurements. In order to fully utilize the potential of these momentum measurements, however, defect-specific parameters of the positron annihilation spectra must be developed and calibrated. With the recent advent of realistic calculations of the positron-annihilation parameters in defect-trapped states [67,68], it can be anticipated that the PAS momentum techniques will become much more powerful tools for these applications to vacancy clustering phenomena in the near future.

6. CONCLUSIONS

The present paper, which is based in part upon another recent paper by this author [90], has focused upon the investigation of vacancy formation, vacancy migration, and vacancy clustering in metals by PAS in comparison with other experimental techniques available for such studies. These areas of application within the field of defects in metals were selected, since they represent the areas in which PAS has made the most significant contributions to date and in which it will likely do so in the relatively near future. Positron annihilation studies of deformed metals and alloys have also been carried out, and the sensitivity of the positron to the defect microstructures thus produced have been clearly demonstrated. Unfortunately, at this time there is an insufficient understanding of the way in which the positron interacts competitively with the variety of potential positron trap states in the rather complex defect ensembles produced by mechanical deformation. Much the same thing might be said at present regarding the application of PAS to complex irradiation-induced defect ensembles. While PAS can indeed be very useful in qualitatively monitoring the gross changes which may occur in such complex defect ensembles, it is unlikely that much defect-specific information can be deduced from these changes until the response of the positron to a number of possible defect-trap states can be elucidated.

For example, the response of positrons to trapping in dislocation lines vis-à-vis jogs along these dislocation lines has been considered theoretically [37]. It has been suggested that weak positron trapping at the dislocation, in conjunction with stronger trapping at jog sites, may explain a number of the prevacancy effects observed even in supposedly well-annealed metals [36], which of course always contain some residual dislocations. While this suggestion seems to account for many of these observations, a clear experimental demonstration of the differing positron trapping and annihilation response to dislocation lines and jogs along these lines is still lacking. The realistic interpretation of PAS data in deformed metals would naturally depend rather heavily on the clarification of this problem. Similar questions remain in terms of the positron's response to other extended defects in metals, such as grain boundaries, and interfaces between phases in alloys. Careful investigations by PAS of microstructures previously characterized by TEM, for example, would be exceedingly valuable in this regard.

Whether PAS will become as valuable a technique for the study of more complex defect-related behavior in metals and alloys as it has been for the study of the properties of vacancies, is a question that remains to be answered. There appear, however, to be rather few a priori limitations to the application of PAS to the study of defects in metals and alloys, either by itself or as a complement to other available experimental techniques. These applications will undoubtedly be given even a broader scope with the recent availability of slow positron beam sources with positron acceleration capabilities [91,92]. These positron sources can be used to probe near-surface defects in a depth-dependent fashion, and possibly laterally-dispersed defects, as well, using focused positron beams, in the future. A major factor in determining how far PAS can be eventually taken in its effective applicability to the study of defects in metals may well be the degree to which realistic theoretical calculations of positron response to various defect types can be carried practically. Just as transmission electron microscopy has relied upon calculations of the expected diffraction contrast from various defects for its most sophisticated applications to the observation of defect microstructures, so positron annihilation spectroscopy may ultimately depend upon a combination of theory and experiment for a utilization of its full potential for the study of defects in metals. At this writing, the future of these applications of PAS looks rather bright.

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