Positron-lifetime study of secondary-defect formation in quenched aluminum

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Positron-annihilation lifetime measurements were made on quenched aluminum as a function of isochronal annealing in the (130—450)-K temperature range. Secondary-defect formation was detected at 210 K. The appearance of a separate long-lifetime component in the lifetime spectra above 280 K showed the presence of small three-dimensional vacancy clusters in the samples. The annealing of vacancy clusters results in the formation of dislocation loops showing strong temperature-dependent trapping of positrons. These defects are interpreted as shallow traps for positrons.

INTRODUCTION

The recovery of quenched metals and alloys was intensively studied during the 1960s mainly by electrical resistivity and transmission electron microscopy (TEM) measurements. It was established that the recovery of frozen supersaturated vacancies takes place in two stages in pure aluminum.[1–3] The first stage in the (200—300)-K temperature range is believed to be the condensation of lattice vacancies to secondary defects, which could roughly be classified into two groups according to their shape. Various dislocation loops and small three-dimensional voids were discovered by TEM investigations.[4] At sufficiently high temperatures these defects become unstable. The second stage at 370—470 K is known to be associated with the elimination of secondary defects.

Positron-annihilation techniques are now regarded to be useful in studying lattice defects and their recovery behavior, and the amorphous structure of metals and alloys.[5,6] Positrons injected into solids lose their kinetic energy and reach thermal equilibrium with their surroundings at a time that is short compared to their lifetime. The thermalized positrons respond sensitively to the presence of open-volume lattice defects. The absence of ion cores at defects gives rise to an effective attractive potential and the positron localization at lattice defects becomes energetically advantageous.

The annihilation signal of bound-state annihilations differs markedly from those characterizing "free" annihilation in the bulk of the material. The narrowing of the momentum or energy density distribution measured by angular correlation or Doppler broadening of the annihilation gamma lines, respectively, and the appearance of long-lifetime components in the lifetime spectra indicate considerable positron trapping at open volumes.

Calculations show a strong dependence of the annihilation characteristics on the size of open-volume defects.[7,8] The line-shape parameters (S and h parameters) and the positron lifetime (τ) are progressively increasing functions of the size of small spherical microvoids up to 5 Å in radius. Above this size the annihilation parameters undergo virtually no further change probably because positron bound states appear on the inner surfaces of the microvoids. Positron localization is even more favorable to more extended open volumes, and the trapping rate is expected to be proportional to the volume of the small voids and proportional to the surface for larger voids.[9]

In the past few years positron physicists have shown much interest in the vacancy-clustering phenomenon in quenched aluminum and various aluminum alloys because the nucleation of vacancy clusters cannot easily be studied by TEM since the size of the small clusters is less than the resolving power of conventional electron microscopes (10 Å). For this reason, investigation of the initial stages of vacancy agglomeration is an area that has proved to be especially fruitful for positron studies.

In the Doppler-broadening studies of Wampler and Gauster[10] and Alam *et al.*,[11] it has been shown that the vacancy-cluster growth can be observed above the 200-K annealing temperature in quenched aluminum. The increase of the line-shape parameter (S parameter) from the value characterizing saturation trapping at single vacancies was detected and attributed to the occurrence of vacancy agglomerates, in qualitative agreement with the results of the above-mentioned theoretical considerations.

Experimental evidence has been found which indicates that a small amount of various impurities even enhances the observed effects.[11–16] Most of this research has been done by the Doppler-broadening technique, and the more time-consuming positron-lifetime measurements have rarely been use despite the possibility of achieving additional information about the nucleated vacancy clusters. Here, we have applied the lifetime technique to obtain information on the nucleation, growth, dissolution, and nature of secondary defects in the various annealing stages of pure quenched aluminum.

EXPERIMENTAL

Positron-lifetime measurements were performed with a fast-slow coincidence system with XP 1023 photomultipliers with NE 111 plastic scintillators and Ortec electronics. The double energy-gating technique was employed to eliminate (0.5—0.5)-MeV random coincidences around the spectrum peak and to improve the peak height-to-background ratio to about 2000:1.[17] This modification al-

TABLE I. Typical rough spectrum of quenched aluminum annealed up to 210 K, the extracted source term, and the result of the analysis with source correction.

	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	I_2 (%)	I_3 (%)	Variance of the fit
Without source correction	241±2					5.90
	231±2	751±30		2.4±0.1		1.42
	226±2	442±18	1633±80	5.4±0.3	0.5±0.03	1.35
With source correction	228±1					1.46
Source term	300±8	900±30		20.0±1.1		1.45

lows the application of a relatively high-activity positron source thereby reducing the accumulation time and minimizing the errors associated with time-zero instabilities. The self-resolution of the system was around 300-ps full width at half maximum (FWHM) with 30% energy side ^{22}Na window settings as determined by a ^{60}Co source. A 7×10^5-Bq activity ^{22}Na positron source in the form of a carrier-free ^{22}NaCl solution deposited between two Mylar foils ~1 mg/cm^2 was applied in the usual sample-source sandwich arrangement. A typical spectrum (2×10^6 counts at 39 ps/channel) was obtained in one day.

The samples were $(1\times1\times0.08)$-cm^3 plates prepared from 99.999% pure polycrystalline aluminum. They were annealed at 823 K in air for one hour, then quenched in a vertical furnace in cold water; after rapid drying ($\sim$4—6 s) they were then quenched in liquid nitrogen. The measurements were performed at 120 K in a liquid-nitrogen cryostat up to a 320-K aging temperature; above this temperature they were done at room temperature. 30-minute isochronal heat treatments were performed *in situ* in the cryostat: The actual temperature values were controlled to ±1 K.

For the evaluation of the lifetime spectra we used the POSITRONFIT EXTENDED computer program.[18] The extraction of the true lifetime and intensities from the spectra is a very delicate problem, as has been pointed out by many authors.[19–21] Considerable efforts were made to use the best approximation for the time resolution of the spectra. The experimentally determined ^{60}Co curves (^{22}Na windows) were quite well fitted by a single [296 ps full width at half maximum (FWHM)] or eventually by two Gaussians but could markedly differ from the resolution during lifetime measurements.[22] They were used as first approximations for the actual time resolution of the spectra.

The best working fit for the "prompt" curves was obtained by the variation of the FWHM's and the intensity ratio in the case of two Gaussians with unconstrained correction-free analyses of the spectra. By approaching the actual time resolution the extracted parameters—especially the shortest lifetime value and the relative intensities of the components—tend to become rather insensitive to the variation of the starting channel of the fitting.

Extreme care was taken to determine the "source component" which arises from positron annihilation occurring in the positron source itself, in the source-supporting foils, and in the foil-sample interfaces. Even though the three-component lifetime spectrum of Mylar foils[23] proved to be suitable for room-temperature measurements, it could not have been utilized to correct low-temperature spectra because the annihilation parameters of Mylar are extremely temperature dependent.[24] We obtained the source-surface component from the measured spectra below the 200-K annealing temperature by reversed analysis: Since it was clear from the correction-free analyses that these spectra contain only one main component, this component was given as a source term with an intensity above 90%. The remaining analyzed part proved to be nearly the same for the first six spectra, and the average was accepted as the source correction. A typical spectrum with and without the source correction and the source term is shown in Table I.

The extracted source-surface component is in qualitative agreement with our measured component referring to multilayered Mylar foils at 120 K (Table II), and with the spectra obtained by room-temperature measurements.[23] The main difference is the disappearance of the longest orthopositronium component at low temperatures. The variation of τ_1 in the 280—440 ps, τ_2 in the 900—1800 ps, and I_2 in the 12—20% range caused the ±2% variation of the determined lifetimes and the considerable increase in the variance. The fraction of positrons annihilating in the foils and interfaces was estimated to be 7%,[23] and indeed the use of the above source-surface term has given a minimum in the variance of the fit in the 7—8% range for most of the spectra measured at 120 K.

The measuring temperature change at 340 K perturbed both the measured lifetimes (as will be discussed later) and the source-surface contribution. The latter is due to the temperature-dependent positron parameters of Mylar foils. As a consequence, attempts to use the same source-correction term for the spectra obtained at low and room temperature failed. However, the use of different source terms on the two sides of such a critical point could eventually lead to the distortion of the extracted parameters

TABLE II. Experimentally determined source-surface contribution measured on multilayered Mylar foils at 120 K.

τ_1 (ps)	τ_2 (ps)	I_1 (%)	I_2 (%)
300±8	1320±60	88±1	12±1

with the result that any observed large change of the average lifetime would be questionable. This point was explored most carefully, and numerous analyses were carried out in an endeavor to find the proper spectrum evaluations. At this point we must emphasize that the general shape of the recovery curve for correction-free evaluations is similar to the final one and that the drastic decrease of the average lifetime at 340 K is to be found in correction-free evaluations too. This strongly suggests that there is only negligible mixing of some low-intensity source component with the extracted average lifetime and if indeed this mixing takes place it does not greatly perturb the lifetime values.

We calculated the average lifetimes, $\bar{\tau}=\sum_i I_i\tau_i$ for all spectra. The average lifetime is statistically a much more suitable parameter and is more insensitive to uncertainties in the spectrum-evaluation procedure than the individual lifetime components. This parameter reflects reliably the changes of the defect structure having standard deviation at around ± 2 ps which is of extreme importance in analyzing small changes in the lifetime distribution. It must be pointed out, however, that the decomposed parameters offer much more information on the defect configuration than the average lifetime alone.

RESULTS AND DISCUSSION

The average lifetime as a function of the annealing temperature is shown in Fig. 1. The lifetime spectra could satisfactorily be fitted with one component up to 220 K and above 300 K, whereas at intermediate annealing temperatures they show essentially two lifetime components. The initial value of the average lifetime (one-component fit) $\bar{\tau}=228\pm 2$ ps is significantly lower than the lifetime characterizing saturation trapping of positrons at monovacancies in pure aluminum, namely, $\tau_v^{\mathrm{Al}}=245\pm 10$ ps;[25–27] $\bar{\tau}$ is unchanged up to 210-K annealing temperature. At 230 K the slight increase of the average lifetime is followed by a steep decrease in this parameter from 230 to 260 K. Above this temperature $\bar{\tau}$ increases significantly as a consequence of the appearance of a low-intensity, long-lifetime component $\tau_2=560$ ps in the lifetime spectra, whereas at 300 K, $\bar{\tau}$ reaches a plateau with the value 197 ± 2 ps. The drop in the average lifetime at 340 K is due to the change in the measuring temperature above which temperature $\bar{\tau}$ decreases slowly to 400 K where it reaches the value characteristic for positron annihilations from defect-free aluminum, namely, $\tau_f^{\mathrm{Al}}=166\pm 3$ ps.

Although significant differences appear, the behavior of the average lifetime qualitatively resembles that of the S parameter in the Doppler-broadening studies of the annealing of quenched aluminum.[10,11] In the 200–250-K temperature range only a slight, if any, increase of the average lifetime is observed instead of the pronounced peak in the line-shape (S) parameter. The steep decrease of the average lifetime observed in the 230–260-K temperature range is delayed to the 250–300-K range, whereas the peak of $\bar{\tau}$ at the 260–300-K range is totally absent in the S parameter curve.

It is clear from the lifetime value measured below 210 K that the achieved vacancy concentration is below the value which enables saturation positron trapping at single vacancies.

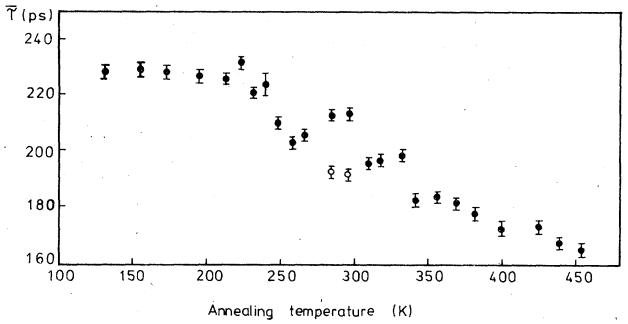

FIG. 1. Average lifetime of positrons in quenched aluminum versus annealing temperature (●). Open circles (○) indicate the τ_1 values.

In seeking the stage where the major vacancy loss occurs during the quench, additional quenches were carried out. The direct quench from high temperature to 200 K resulted in near-saturation positron trapping in frozen-in vacancies. The achieved single-vacancy lifetime, $\tau\simeq 240$ ps, indicates that the majority of these defects had reached the sinks during the short aging (4–6 s) at room temperature in our primary samples.

The average lifetime is practically unchanged up to 210 K, despite the apparent statistical scatter of the values. At 220 K a slight increase of this same parameter is observed. However, it must be emphasized that the 6-ps increase of the average lifetime is at the limit of the detectable change of this parameter. It would be regarded only as a qualitative indication on the lifetime change direction.

As pointed out in the Introduction, calculations and earlier positron-annihilation studies of aluminum and other metals showed[7] that the presence of small three-dimensional imperfections might lead to lifetime values that are higher than those characterizing positron annihilation in single vacancies. The electron density in such crystal defects is lower than that in smaller-volume defects, which feature in turn results in longer lifetimes of positrons localized in vacancy clusters.

In this sense the slight increase of the average lifetime at 220 K allows us to detect the formation of secondary defects, such as small three-dimensional vacancy clusters, during the course of 30-min annealing at this temperature.

The concentration of such small aggregated multivacancy configurations might be sufficiently high and comparable with the retained single-vacancy concentration: Otherwise their presence would not be manifested in a detectable lifetime change.

The steep decrease of the average lifetime observed above the 230-K annealing temperature is accompanied by the splitting of the lifetime spectra into two lifetime components. The results of the computer analysis are shown in Table III. The uncertainty values indicate the statistical scatter of the data.

It is apparent that the second lifetime value is approximately constant in the (230–260)-K temperature range and that τ_2 oscillates at around the lifetime value which

TABLE III. Results of separating the lifetime spectra into two components in the (230—300)-K annealing temperature range.

Annealing temperature T (K)	τ_1 (ps)	τ_2 (ps)	I_2 (%)	Variance of the fit
231	106±24	236± 3	88.4± 2.8	1.24
239	178±15	255±10	60.0±14.5	1.35
248	110±13	237± 3	78.9± 3.1	1.34
258	136± 7	244± 4	62.5± 4.3	1.55
266	179± 4	332±17	17.5± 3.5	1.16
284	193± 1	558±28	5.4± 0.6	1.49
295	192± 1	549±16	6.0± 0.4	1.84

characterizes saturation trapping of positrons in single vacancies, viz., $\tau_v^{\mathrm{Al}}=245\pm10$ ps. The intensity of this component is a monotonously decreasing function of the annealing temperature whereas the first lifetime component is an increasing function of the same quantity.

Such behavior of the lifetime parameters indicates a decrease in the retained single-vacancy and vacancy-cluster concentration. It is noteworthy that the values of these parameters do not satisfy a simple two-state trapping model, since there is a strong deviation from the $\lambda_1=\lambda_f+(\lambda_f-\lambda_v)I_2/(1-I_2)$ relation [between λ_1, the annihilation rate of the first component, and $I_2/(1-I_2)$] expected on the basis of the model.[21] The more complex correlation between the annihilation parameters strongly suggests the presence of traps other than single vacancies in the samples after the given heat treatments at ambient temperatures. However, the concentration of such imperfections might be low in comparison with the single-vacancy concentration, since it was not manifested as an increase of the longer lifetime values.

The overall changes in the lifetime parameters in the (210—260)-K temperature range are in good agreement with the recent studies of quenched aluminum utilizing the Doppler-broadening technique of positron annihilation.[10—13] An increase of the line-shape parameter in the (200—250)-K temperature range was found and it was attributed to the formation of vacancy clusters during heat treatments at the given temperatures. The explanation for the line-shape increase is based on the theoretical expectation that higher-volume defects result in higher values of the line-shape parameters.[7,8] In the (250—300)-K temperature range the line-shape parameters decrease, which in turn could be explained by the growth of vacancy clusters and the considerable diminution in the concentration of smaller ones.

As the average lifetime carries essentially the same integral information as the line-shape parameters defined in the cited papers, comparison of our results with these earlier ones is not contraindicated.

Our data closely resemble those in Refs. 10 and 11, although we find that the effects on the annealing temperature are not so pronounced. The slight peak at 220 K and the subsequent strong decrease of the average lifetime led us to similar conclusions as referred to above (see Refs. 10 and 11).

It should be noted that our samples might contain a considerable number of sinks for migrating vacancies and small vacancy agglomerates and that these sinks may well be responsible for the moderate effect found around 220 K. Above this temperature a strong diminution of the defect concentration is found which is explainable by the same effect.

At 220 K and above, the concentration of small vacancy agglomerates is considerable. These imperfections are highly mobile at these temperatures; in particular, divacancies are expected to have higher mobility than single vacancies.[28] Above 220 K these imperfections migrate rapidly to sinks and disappear, and only the higher-volume vacancy clusters remain in the sample. The concentration of the latter clusters is relatively low and their presence in the samples was not manifested directly in the lifetime spectra.

The annihilation parameters changed dramatically when the annealing temperature exceeded 260 K. The structure of the lifetime spectra is markedly different from those below this annealing temperature; a long lifetime of the value $\tau_2\simeq550$ ps of small intensity, namely, $I_2\simeq0.06$, appears in the spectra. The shorter lifetime component is around the value of the average lifetime value of the earlier spectra, namely, $\tau_1\simeq193$ ps, as indicated as circles on the picture. This component could be considered as the average lifetime of "free" and vacancy-trapped positron states, while higher-volume imperfections give rise to the separate long-lifetime component. The appearance of such a separate long-lifetime component is direct evidence of the formation of large three-dimensional vacancy clusters, containing a few tens of vacancies, as only an open volume of this size could result in such a high positron lifetime. The trapping rate of these "open-volume defects" might be comparable with the trapping rate of smaller volume imperfections (vacancies, dislocations, etc.). It shows that a considerable fraction of single vacancies condensed to vacancy clusters at this stage.

Above 300 K the one-component evaluation of the lifetime spectra is favored again. The value of the average lifetime is nearly at the same level as the first lifetime component of the previous spectra, viz., around 197 ps. The disappearance of the second lifetime component could be ascribed to the diminution of higher-volume

three-dimensional vacancy aggregates. One possibility is the collapse of three-dimensional clusters to one- and two-dimensional—type defects such as dislocation loops.[29] As is well documented, the dislocations give similar saturation annihilation parameter values as single vacancies,[21,25] and it is meaningful to expect the average lifetime to approximate the 197-ps value on this basis.

The drop in the average lifetime at 340 K is the consequence of the change in the measuring temperature, since all the spectra below this annealing temperature are measured at 120 K and spectra above are measured at room temperature. The drastic change of the observed average lifetime level could be explained either by a temperature-dependent trapping rate or by the presence of shallow traps in the samples. However, a temperature-dependent trapping rate which is characteristic for three-dimensional defects, as experimentally found in neutron-irradiated aluminum,[30] might result in an opposite change of the average lifetime. The presence of shallow traps offers a plausible explanation for the observed lifetime change. Thus at low temperatures these defects are effective traps whereas at room temperature the electronic potential of the defects is too weak to retain the positrons in trapped states, with the result that thermally activated detrapping of positrons occurs. The fraction of positrons annihilating in "free" or delocalized states is enhanced in this way, thereby decreasing the average lifetime.

In the (370—440)-K temperature range the average lifetime decreases continuously to the value characterizing "free" positron annihilation in aluminum, viz., 166 ps. This result is in good agreement with earlier positron annihilation[10,11] and electrical resistivity[2] studies and is interpreted as the annealing of dislocation loops.

CONCLUSIONS

The behavior of the annihilation parameters in this study of quenched aluminum could well be described as a balance between the growth and dissolution of vacancy clusters and annihilation of vacancies in these three- and other-dimensional defects. Below 200 K vacancies are immobile,[28] and only vacancy agglomerates formed during the course of the quench are present in the samples. At 220 K mobile vacancies either gather and build up small clusters or reach various sinks. As the annealing temperature is raised the effect of sinks becomes predominant. This is due to the high mobility of single vacancies and divacancies. Annealings at higher temperatures lead to the diminution of single vacancies and small clusters whereas more stable, larger clusters grow further. At 280 K the trapping rate of more extended clusters is comparable with that of other defects, which in turn enables the appearance of a separate long component in the lifetime spectra.

At 300 K the three-dimensional vacancy clusters probably collapse to dislocation loops. As the lifetimes of positrons annihilating in single vacancies and dislocations are essentially indistinguishable[21] the collapse of vacancy clusters leads to the disappearance of the second long-lifetime component in the spectra.

The dislocation loops show a strong temperature-dependent response on positrons. The results are consistent with the picture of thermally activated detrapping of positrons at room temperature and they indicate the shallow trap character of these defects. The annealing of dislocation loops takes place in the (370—440)-K temperature range—as suggested by the positron-annihilation data.

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