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POSITRON LIFETIMES IN VOIDS AND OTHER DEFECTS IN
ANNEALED, NEUTRON-IRRADIATED ALUMINUM*

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ABSTRACT

MASTER

We have measured positron lifetimes in neutron-irradiated high-purity aluminum single crystals, and have performed companion small-angle x-ray scattering experiments to determine the radius of gyration and volume fraction of radiation-induced voids. The lifetime data are consistent with a model in which positrons are trapped both in voids and in other defects which are tentatively identified as vacancy clusters bound to transmutation-produced silicon. The lifetime in the latter defects increased from 230 psec to 430 psec as the voids annealed out (around 306°C), suggesting that the clusters grow in size as voids disappear. The lifetime in voids remained constant at (550 ± 30) psec.

INTRODUCTION

Positron techniques were first used to study neutron-irradiation induced voids in molybdenum [1,2] and in aluminum [3,4]. In this paper we present a correlation of positron lifetimes with void parameters as determined by small-angle x-ray scattering in irradiated aluminum. Our samples were annealed at successively higher temperatures, with data being collected after some of these temperatures. The present experiments are a continuation of our studies aimed at elucidating the mechanisms of nucleation and growth and the properties of voids in neutron-irradiated aluminum single crystals. Earlier work with transmission electron microscopy [5], small-angle x-ray scattering [5], small-angle neutron scattering [6,7], and positron annihilation [3,4] has been reported previously. An expanded report of the present research, including results from angular correlation of annihilation radiation, will appear elsewhere [8].

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EXPERIMENTAL TECHNIQUE

Sample Preparation

The sample, a 31 mm × 6 mm × 0.9 mm single crystal grown from 99.9999+% starting material,* was prepared as one of the sequence described by Epperson et al.[5]. It was irradiated in the hydraulic tube of the Oak Ridge High Flux Isotope Reactor in contact with the cooling water at a temperature of $55 \pm 5^\circ\text{C}$ to a thermal fluence of 1.17×10^{22} neutrons/cm² ($E < 25.3$ MeV) and a fast fluence of 4.96×10^{21} neutrons/cm² ($E > 0.1$ meV).

Pieces of the specimen were annealed at successively higher temperatures in an attempt to vary the concentration and size of the voids. Isochronal one-hour anneals were done in 25°C steps between 150 and 275°C . Thereafter, 20-minute isochronal anneals were done in 6°C steps up to a temperature of 319°C , and a final one-hour anneal was done at 350°C . The annealing was done in a well-regulated tube furnace under an argon atmosphere, and the temperature was maintained constant to within $\pm 1^\circ\text{C}$.

Small-Angle X-Ray Scattering

We have characterized the void distributions in the specimens by determining the sample radius of gyration (R_g) and swelling ($\Delta V/V$) on the ORNL 10-meter small-angle x-ray scattering spectrometer [9]. This device utilizes a 6 kilowatt rotating anode x-ray source, pin-hole collimation (1 mm × 1 mm square slit at the specimen), and a 20 cm × 20 cm two-dimensional position-sensitive proportional counter with up to 200 × 200 resolution elements (1 mm spatial resolution FWHM). The measurements were obtained in 4000 sec per sample. The analysis of the data followed the procedures described earlier [6].

Lifetime Measurements

Lifetime spectra were taken after the anneal to 250°C and after all anneals above 293°C . A sodium-22 source mounted on 3.8 μm Mylar film was sandwiched between two pieces of the sample. This was viewed by Pilot U scintillators mounted on XP1021 phototubes. The scintillators were in the shape of truncated cones 25 mm high, 25 mm in base diameter, and 6.4 mm in apex diameter. A standard fast-slow electronic system utilized constant-fraction fast discriminators and an ORTEC 437 TAC to give timing information, and DDL amplifiers and timing single channel analyzers to give energy information to gate the multichannel analyzer.

*Obtained from Cominco American Inc., Spokane, WN, USA.

The time calibration was 11.15 psec/channel as determined by an ORTEC 462 time calibrator. Each run lasted about 6×10^5 seconds; drifts in the peak channel during the run were detected and compensated for.

The overall prompt resolution of our system was determined with a Cobalt-60 source. When the energy windows on the SCA's were set for the upper 20% of the cobalt γ -ray spectrum, the FWHM of the resolution curve was 200 psec. When 20% windows were set at the experimental settings, the FWHM was 340 psec. The shape of the resolution curve matched a Gaussian quite well.

THEORY

The positron lifetime spectrum from the unannealed sample shows three exponentially-decaying components, which may be attributed to annihilations in the bulk and in two distinct types of defects. In the simplest possible trapping model, the defects trap the positrons with trapping rates α and β , respectively, and no detrapping occurs. If the numbers of positrons in the bulk metal and the two types of defect are N_1 , N_2 , and N_3 , respectively, and the respective annihilation rates are λ_f , λ_2 , and λ_3 , solution of the rate equations, under the initial conditions $N_1 = 1$ and $N_2 = N_3 = 0$, yields

$$N = N_1 + N_2 + N_3 = Ae^{-\lambda_1 t} + Be^{-\lambda_2 t} + Ce^{-\lambda_3 t} \quad (1)$$

with

$$\alpha = B(\lambda_1 - \lambda_2), \quad \beta = C(\lambda_1 - \lambda_3) \quad (2)$$

and

$$\lambda_f = \lambda_1 - \alpha - \beta, \quad (3)$$

where λ_1 is the total disappearance rate of positrons from the bulk; that is $dN_1/dt = -\lambda_1 N_1$.

RESULTS AND DISCUSSION

Small-angle x-ray scattering showed that (i) the voids annealed out between 306°C and 319°C, and (ii) the radius of gyration remained constant at 220 Å to 300°C then increased to 272 Å by 319°C. However, analysis of the shape of the scattering curve outside the Guinier region suggests (i) the shape of the void-size distribution curve or (ii) the space-average void shape changed during annealing. It is not possible to distinguish between these possibilities with SAXS. Finally, the temperature range where voids anneal out observed in this work (306–319°C) is somewhat higher than observed by Epperson et al. [5].

The lifetime data were fitted by a routine similar to that described by Kirkegaard and Eldrup [10]. For annealing temperatures below 312°C three exponentials plus a source component were necessary for a good fit. At and above 312°C, two-exponential fits plus a source component were sufficient. Results for all the runs are shown in Fig. 1, where the reciprocals of the rates λ_f , λ_2 , and λ_3 are plotted as mean lifetimes.

The mean lifetime of the third component remained roughly constant at 550 psec while its intensity decreased with increasing annealing temperature, disappearing at 312°C. At this temperature, the SAXS results show that the voids have essentially disappeared. Thus we conclude that this component results from annihilations in surface states in voids as suggested by Hodges and Stott [11]. At the maximum void concentration, about 50% of the positrons annihilated in the void state.

The lifetime in the second type of defect shows much more variation. It increases from 230 psec to 430 psec while the void component is disappearing, and then slowly decreases. The intensity of this component also increases as the voids disappear, and then decreases. This type of defect persists at high annealing temperatures.

The behavior of this component may be explained by reference to silicon-vacancy clusters. An estimated 1900 dpm Si was produced by the reaction $^{27}\text{Al}(n,\gamma)$ with thermal neutrons followed by a β^- decay to ^{26}Si . The solubility of Si in Al is very small — less than 1 ppm at the irradiation temperature of $\sim 55^\circ\text{C}$. It has been observed by TEM that voids in neutron-irradiated aluminum contain silicon precipitates [12], and some silicon is believed to be spread over the surface of the void [7]. In the present case, the process of precipitation of supersaturated Si is complicated by its time-dependent production rate by thermal neutrons as well as by the continuous flux of excess vacancies and interstitials resulting from radiation effects. However, some insight can be gained by qualitative comparisons to work on the nature of indium-vacancy clusters in dilute Al(In) alloys [13,14]. This showed that, at least in dilute Al(In), the distribution of vacancies, impurity atoms, impurity-vacancy pairs, and impurity-vacancy clusters (assumed to be triplets) could be analyzed in terms of the ratio C_{v0}/C_{i0} (where C_{v0} is the total vacancy concentration and C_{i0} is the total impurity concentration). The arguments concerning the nature of the defects should qualitatively apply to Al(Si) alloys, because the impurity-vacancy binding energy is high and the impurity solubility is low in both alloys. During irradiation $C_{v0} \gg C_{i0}$, and virtually all of the impurities were associated in vacancy-impurity complexes which had a relatively high binding energy.

At the end of irradiation, the concentration of vacancies in the matrix (not including those already associated with voids) becomes the thermal equilibrium value for the alloy, and the ratio C_{V0}/C_{Vi} must decrease significantly. Here, the structure shifts to one of a low concentration of complexes, with most defects of the vacancy-impurity dipole type. Thus, at the end of irradiation, in addition to the known voids at which the large excess of Si is precipitated (both on the void surface [7] and in the void corners [5,12]), we would expect the soluble Si to be present mostly in Si-vacancy pairs and some larger clusters. We suggest that these clusters are the trapping sites for the 230 psec component.

Because of the high vacancy-impurity binding energy, and its effect on lowering the surface energy of voids in aluminum [7], the silicon on the void surface stabilizes the void and makes it resistant to annealing. However, as the annealing temperature is increased, the solubility limit of Si increases, and finally the voids and their associated Si precipitates go into solution. It is significant that the temperature at which voids anneal out ($\sim 310^\circ\text{C}$ in this study) is approximately the temperature of the solubility limit at this composition.* During annealing-out of voids, the vacancy concentration, as well as the silicon concentration, increases in the matrix. Because there are many more vacancies than there are Si atoms in a void, the C_{V0}/C_{i0} ratio in the matrix again increases thus shifting the system towards a state in which there are an increasing number of silicon-vacancy complexes. An increase in the size of the clusters would explain the increase in $1/\lambda_2$ with increasing annealing temperature. It is interesting that our values of $1/\lambda_2$ range from 230 psec to 430 psec, while Jena and Singwi [15] have calculated values of 210 psec for monovacancies in aluminum and 399 psec for 8-vacancy clusters. An increase in the number of clusters should be reflected in an increase in the trapping rate α to clusters. From 250°C to 300°C α decreases, suggesting that the number of clusters is being reduced by combination of small ones into larger ones. Above 300° α increases somewhat as virtually all of the silicon goes back into solution thus increasing the number as well as the size of Si-vacancy complexes. (The presence of silicon in these clusters cannot at present be verified by positron techniques.)

*This argument also explains the slight increase ($10\text{--}20^\circ\text{C}$) in the temperature at which voids anneal out as determined here compared to the lower temperatures found in crystals irradiated to lower fluences and thus containing less transmutation-produced Si.

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FIGURE CAPTION

Meanlives and intensities of the exponential components $A(o)$, $B(\Delta)$, and $C(x)$, versus isochronal annealing temperature. Where two points are shown for 300°C, the lower was taken after 40 minutes of annealing, and the higher after 60 minutes of annealing. The lines merely indicate the trend of the points.

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