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Positron annihilation at grain boundaries in Zn–22 wt% Al alloy

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Abstract. A series of samples of Zn–22 wt% Al alloy with different fine grain sizes are studied using Doppler broadening and lifetime spectra of positron annihilation. It is reasonable to assume that the lifetime of positron trapping at the grain boundaries is about 240 ps. The relationship between the mean positron lifetime and the inverse grain size is linear only when the grain size is larger than 0.5 μm.

1. Introduction

It is known that the positron annihilation technique can be applied to the study of lattice defects such as vacancies, voids and dislocations. Similarly, grain boundaries would be expected to serve as trapping sites for positrons since they are regions of low atomic density.

Until now, the structure of grain boundaries in alloys has not been revealed clearly. However, some information on grain boundaries can be obtained by the positron annihilation technique. Some investigations have been carried out previously.

Mckee *et al* [1] studied the positron lifetime and S-parameter for Doppler broadening of positron annihilation radiation as a function of mean grain size in a Zn–Al alloy and they obtained clear evidence of trapping at grain boundaries.

Hidalgo and de Diego [2] proposed a model for positron trapping at grain boundaries. They suggested a linear relationship between any linear annihilation parameter and the inverse mean grain size, but this relationship is dependent on the condition that $L > 2D_p$, where L is the mean grain size and D_p is the mean positron diffusion length.

The purpose of this paper is to study the mean positron lifetime τ as a function of the inverse mean grain size of fine-grained Zn–22 wt% Al alloy so that we can obtain more information on grain boundaries.

2. Experimental details

Zn–22 wt% Al alloy with the eutectoid composition was prepared in the form of a sheet, 1.4 mm thick. First, a group of samples were treated for 3 h at 370 °C and then quenched

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Table 1. Heat treatment conditions and the mean grain sizes for the Zn–Al alloy samples.

Sample	Annealing time at 250 °C (min)	Mean grain size L (μm)
0	0	0.319 ± 0.003
1	2	0.361 ± 0.003
2	5	0.387 ± 0.003
3	10	0.411 ± 0.004
4	20	0.452 ± 0.004
5	40	0.548 ± 0.005
6	80	0.653 ± 0.007
7	160	0.757 ± 0.007
8	360	0.824 ± 0.010
9	540	0.990 ± 0.010
10	720	1.155 ± 0.010

into a mixture of ice and water. After rapid quenching, they transformed to the two-phase structure consisting of fine equiaxed grains at room temperature. Larger grains were obtained by annealing at 250 °C to obtain grain coarsening. After annealing, the samples were cooled to room temperature in the furnace. The grain sizes were measured by the intercept method using electron microscopy. In the measurement, each sample is etched chemically so that we can measure the sizes in a two-dimensional plane.

Before the positron measurement, the samples were mechanically polished. Then a chemical etch (HNO_3 : HF : HCl, 1 : 1 : 1) was used to remove the surface layer damaged during the polishing.

A positron source of about 3.7×10^5 Bq of ^{22}Na, deposited from an aqueous solution of the chloride onto a Kapton foil, was used in the measurements. The source enclosed by the foil was sandwiched between duplicated samples.

Measurements of Doppler broadening were made using a high-purity Ge detector with a resolution (FWHM) which was less than 1.3 keV at 514 keV. The accumulation was more than 10^6 events in the full-energy peak in a measurement time of 1 h. A line-shape parameter S has been extracted from the Doppler-broadening data as a simple one-parameter characterization of the momentum distribution. It is defined as the ratio C/A where C is the area under the central channels and A is the area of the two wings.

The positron lifetime measurements were made using a fast–fast coincidence system. The resolution was 260 ps. The accumulation was also more than 10^6 events in a measurement time of 2 h. The lifetime spectra were analysed with source correction using the computer program POSITRONFIT [3]. The source correction component lifetime was 381 ps and the intensity was 23%. This correction comes from several measurements of single-crystal Zn (which should only have a single lifetime of 160 ps) and was attributed to the source and the foil. The third component τ_3 from the three-component fit is the weak ($I_3 < 1\%$) long-lived surface component.

3. Results

The range of mean grain sizes of the samples is from 0.3 to 1.2 μm. Table 1 lists the heat treatment conditions and the mean grain sizes measured for the various samples.

Table 2. Results from the analyses of positron lifetime measurements for the various samples. A and B refer to two different data analyses.

	Data analysis A			Data analysis B	
Sample	τ_1 (ps)	τ_2 (ps)	I_2 (%)	τ_1 (ps)	I_2 (%)
0	151 ± 32	244 ± 9	79 ± 11	125 ± 12	87 ± 1
1	122 ± 15	240 ± 5	78 ± 3	114 ± 6	80 ± 1
2	111 ± 12	239 ± 4	74 ± 2	119 ± 5	72 ± 1
3	133 ± 12	241 ± 7	62 ± 4	134 ± 4	62 ± 1
4	132 ± 13	229 ± 8	65 ± 6	149 ± 4	51 ± 1
5	141 ± 9	241 ± 10	49 ± 6	141 ± 3	49 ± 1
6	141 ± 9	241 ± 11	46 ± 6	140 ± 3	46 ± 1
7	136 ± 8	240 ± 10	49 ± 5	137 ± 3	47 ± 1
8	142 ± 8	242 ± 12	41 ± 6	142 ± 3	41 ± 1
9	133 ± 8	228 ± 9	49 ± 6	143 ± 2	39 ± 1
10	140 ± 9	236 ± 13	40 ± 6	144 ± 3	36 ± 1

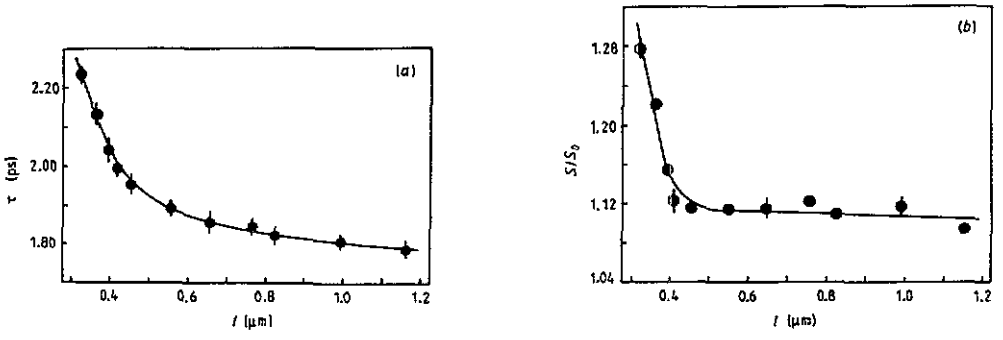

Figure 1. (*a*) Mean positron lifetime τ versus mean grain size L. (*b*) Doppler broadening parameter S versus mean grain size L, where S_0 is the S-parameter of single-crystal Zn.

The lifetime spectra were analysed and the results are summarized in table 2.

The results for data analysis A are from the decomposition of the lifetime spectra. The second component τ_2 seems to be independent of grain size with a mean value of 240 ps. We attribute this to the annihilation at grain boundaries, i.e. $\tau_t = 240$ ps. The results for data analysis B are from the analyses of lifetime spectra with the constraint $\tau_2 = 240$ ps.

From the data analysis B, we can obtain the mean lifetime τ of the two main components. The mean lifetime τ is shown in figure 1(*a*) as a function of mean grain size L. In figure 1(*b*), the S-parameter of the Doppler broadening lineshape measurements is also shown as a function of mean grain size L, and the S-parameter in the figure has been normalized to the value S_0 of single-crystal Zn.

The mean positron lifetime τ is plotted versus the inverse mean grain size L^{-1} in figure 2. This shows that the mean positron lifetime varies linearly with the inverse mean grain size in the range of $L > 0.5\ \mu$m. A positron lifetime relating to $L = \infty$ has been

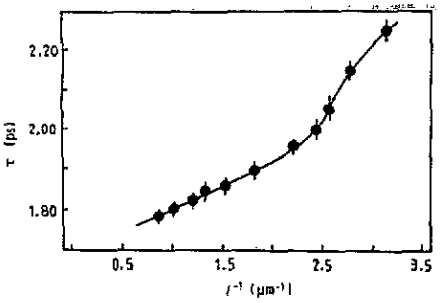

Figure 2. Mean positron lifetime τ versus inverse mean grain size L^{-1}.

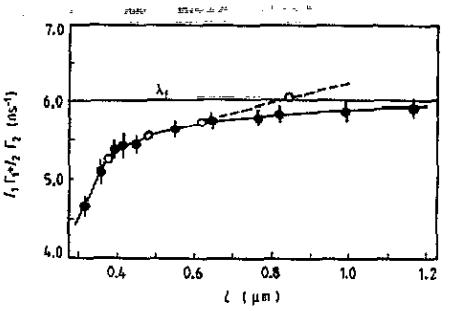

Figure 3. The relationship between $I_1\Gamma_1 + I_2\Gamma_2$ and mean grain size L: ●, our experimental results; ○, experimental results of Mckee *et al* [1]. The horizontal line is the level for λ_f (6 ns^{-1}).

deduced, yielding a value of 167 ps, and it is regarded as τ_f, the positron lifetime of a free state in the alloy. The curve deviates from the straight line when $L < 0.5\ \mu$m.

In the simple trapping model (STM), the value of $I_1\Gamma_1 + I_2\Gamma_2$ ($\Gamma_1 = 1/\tau_1$, $\Gamma_2 = 1/\tau_2$) should be equal to a constant λ_f ($= 1/\tau_f$). The values of $I_1\Gamma_1 + I_2\Gamma_2$ for the various samples have been calculated using the data analysis B in table 2 and the relationship between $I_1\Gamma_1 + I_2\Gamma_2$ and the grain size L is shown in figure 3. The experimental results do not agree with the STM. The results of Mckee *et al* are also plotted in figure 3 for comparison.

4. Discussion

From the analyses of positron lifetime measurements, it is reasonable to assume that the lifetime $\tau_2 = 240$ ps arises from positron annihilation at grain boundaries in Zn–Al alloy, and it is an approximate mean value for the lifetimes of positrons trapped at grain boundaries in these samples. It seems that there is no other explanation for the lifetime component. The vacancies retained in the samples after quenching and other defects can be excluded because of the subsequent annealing at 250 °C. Further interpretations have been considered by Mckee *et al* [1]. The positron lifetime of 240 ps at grain boundaries is comparable with that of vacancies or dislocations; so we suggest that the grain boundaries are composed of vacancies or dislocations. In figure 1, the mean positron lifetime τ and the Doppler parameter S/S_0 decrease with increasing mean grain size L. This shows that the density of grain boundaries decreases gradually when the grain grows.

In figure 3, the values of $I_1\Gamma_1 + I_2\Gamma_2$ for the various samples are not the same; therefore the STM is not applicable to the problem of grain boundaries. The experimental values are lower than the constant λ_f. The smaller the mean grain size L, the lower is the value of $I_1\Gamma_1 + I_2\Gamma_2$. Perhaps, if the grain size becomes very large, the agreement between the STM and experimental results on the grain boundary might become fairly good. This curve does not fit the linear relationship proposed by Hidalgo and de Diego [2] (see figure 2) and, in particular when the grain size $L < 0.5\ \mu$m, the results deviate from the straight line. It is interesting that, if we make use of the formula $L = 2D_p$ [2]

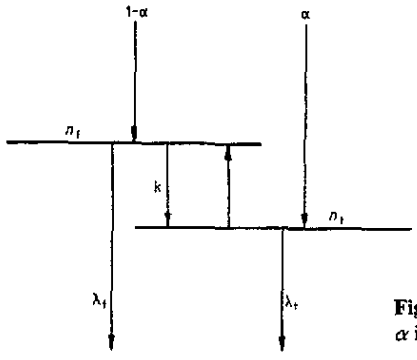

Figure 4. Positron-trapping model for 3D defects. α is the volume fraction occupied by the defects.

and set $L = 0.45\ \mu$m, the mean positron diffusion length D_p can be deduced yielding a value of $0.225\ \mu$m. This value is almost the same as that obtained by Bergersen *et al* [4].

In order to interpret the experimental results, we propose the annihilation mechanism illustrated in figure 4.

Here we assume that

(i) the grain boundary is a kind of three-dimensional composite defect which occupies a volume fraction α,

(ii) all positrons thermalized are distributed uniformly in the alloy, and thereby a fraction α of the positrons are already trapped at grain boundaries when they are thermalized,

(iii) there are no other kinds of defect and

(iv) the detrapping rate can be neglected.

Denoting by $n_f(t)$ and $n_t(t)$ the occupation probabilities of free positrons and positrons trapped at the grain boundaries, respectively, at time t, the rate equations can be written as

$$\begin{aligned} \mathrm{d}n_f/\mathrm{d}t &= -\lambda_f n_f(t) - k n_f(t) \\ \mathrm{d}n_t/\mathrm{d}t &= -\lambda_t n_t(t) - k n_f(t) \end{aligned} \tag{1}$$

where λ_f and λ_t are the positron annihilation rates in the bulk and at grain boundaries, respectively, defined by $\lambda_f = 1/\tau_f$ and $\lambda_t = 1/\tau_t$. k is the positron-trapping rate for the grain boundaries.

Let $t = 0$ correspond to the time when positrons are completely thermalized; so the initial conditions are

$$\begin{aligned} n_f(0) &= 1 - \alpha \\ n_t(0) &= \alpha. \end{aligned} \tag{2}$$

From the solutions of equations (1) and (2), the following formulae can be obtained:

$$I_1\Gamma_1 + I_2\Gamma_2 = \lambda_f - (\lambda_f - \lambda_t)\alpha \tag{3}$$

$$\tau = \tau_f(1 + k\tau_t)/(1 + k\tau_f) + [(\tau_t - \tau_f)/(1 + k\tau_f)]\alpha. \tag{4}$$

Making use of equation (3), the results in figure 3 can be interpreted very well. The smaller the mean grain size of the sample, the larger is the volume fraction α of grain

Table 3. The α, d- and w-values for the samples.

Sample	Volume fraction of grain boundaries α (%)	Mean size of grain boundaries d (μm)	Thickness of grain boundaries w (μm)
0	72 ± 6	0.23 ± 0.02	0.071 ± 0.010
1	50 ± 5	0.18 ± 0.02	0.047 ± 0.007
2	35 ± 5	0.14 ± 0.02	0.033 ± 0.006
3	31 ± 5	0.13 ± 0.02	0.030 ± 0.006
4	31 ± 5	0.14 ± 0.02	0.034 ± 0.007
5	18 ± 4	0.10 ± 0.02	0.022 ± 0.006
6	12 ± 5	0.08 ± 0.03	0.017 ± 0.007
7	8 ± 5	0.06 ± 0.04	0.014 ± 0.008
8	7 ± 5	0.06 ± 0.04	0.013 ± 0.009
9	5 ± 3	0.05 ± 0.03	0.010 ± 0.008
10	3 ± 5	0.03 ± 0.06	0.007 ± 0.013

boundaries in the alloy and the greater is the difference between the value of $I_1\Gamma_1 + I_2\Gamma_2$ and the constant λ_f. The results of Mckee *et al* [1] in figure 3 also support our discussion.

In the measurement by the intercept method, L is defined to be the mean grain size (including the grain boundary):

$$L = \sum_{i=1}^{m} l_i \Big/ \left(M \sum_{i=1}^{m} n_i \right) \tag{5}$$

where M is the magnification of the electron microscope l_i and n_i are the length of the scale and the number of grains, respectively, in the ith measurement and m is the number of measurements ($m > 10$). Define d to be the mean size of the grain boundaries. By using a measurement formula similar to that for L, d is only the mean value of the boundary size in all directions (not only in a vertical direction to the boundary); so the value of d is larger than the real thickness of the grain boundaries. In fact, it is very difficult to distinguish the grain boundary from the grain because the width of the grain boundary apparent through etching varies with the etch time; the value of d cannot be obtained directly from measurement. d can be found from $\alpha = d/L$ by using the basic stereology formula [5]. Then the following equation can be obtained from (4):

$$\tau = \tau_f(1 + k\tau_t)/(1 + k\tau_f) + [(\tau_t - \tau_f)/(1 + k\tau_f)](d/L). \tag{6}$$

The relationship between τ and L is shown in equation (6). It is different from the relationship proposed by Hidalgo and de Diego [2].

From equation (3) and $\alpha = d/L$, the volume fraction α and the mean size d of the grain boundaries for the various samples can be calculated, making use of $\tau_t = 240$ ps and $\tau_f = 167$ ps. Table 3 lists the a- and d-values for the samples.

The mean size d of the grain boundaries is not the real thickness of the grain boundaries. In order to obtain the order of thickness, an approximation has to be made as follows. Suppose that each grain is spherical and the grain boundary is a case around the sphere. Define R and w to be the radius of the spherical grain and the thickness of

the case, respectively. Combining the basic relationships $\alpha = 1 - [R/(R + w)]^3$ and $L = \pi(R + w)/2$ (appendices 1 and 2), the following formula can be easily deduced:

$$w = 2L[1 - (1 - \alpha)^{1/3}]/\pi. \tag{7}$$

By making use of equation (7), we can easily estimate the order of thickness of the grain boundaries. All these values of w for the sample are listed in table 3. It is obviously found that the thickness w of the grain boundaries decreases with increasing grain size. Perhaps, the larger the curvature of grain, the larger the number of defects around the grain is, increasing the width of the crystalline disorder region associated with a grain boundary.

From the above discussion, the conclusions are summarized as follows. Clear evidence of trapping at grain boundaries in Zn–Al alloy is observed. The positron trapping lifetime at a grain boundary is about 240 ps. Our experimental results show that the relationship between the mean positron lifetime τ in the alloy and the inverse mean grain size L^{-1} is not linear. The experimental points deviate from a straight line when the grain sizes are very small. The free lifetime of the positron in the alloy is deduced, yielding a value of 167 ps. In order to interpret the experimental results, it is assumed that a fraction α of the positrons are already trapped at $t = 0$ (when they are thermalized) and the fraction α and the thickness of grain boundaries have been estimated to obtain quantitative information on grain boundaries.

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Appendix 1

Assume that each grain is a sphere and that the grain boundary is a case around the grain (figure A1). The total volume V_t and the volume V_b of grain boundaries are as follows:

$$V_t = 4\pi(R + w)^3/3$$
$$V_b = 4\pi(R + w)^3/3 - 4\pi R^3/3.$$

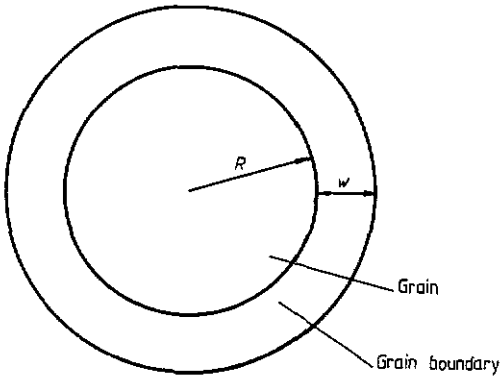

Figure A1. A spherical grain and its grain boundary.

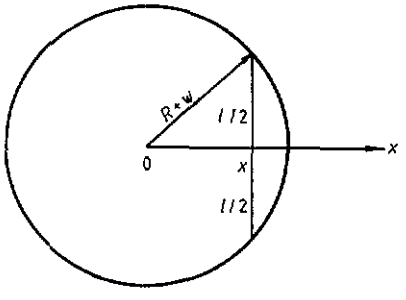

Figure A2. Scheme for calculating any grain size l.

So

$$\alpha = V_b/V_t = 1 - [R/(R + w)]^3.$$

Appendix 2

In the measurement of the mean grain size L, L is the mean value of all the measured sizes l (figure A2). It is easily found that

$$l = 2[(R + w)^2 - x^2]^{1/2}$$

and

$$L = \langle l \rangle = \frac{1}{R + w} \int_0^{R+w} l \, dx = \frac{\pi(R + w)}{2}.$$

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