Formation Energy in Al-Mg Alloy by Positron Annihilation Lifetime Technique (PALT)

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Abstract

The propose of the present work is to study the interaction of positrons with quenched-in defects and clustered atoms to estimate formation enthalpy in series 50xx of commercial Al-Mg alloys, namely, 5049, 5051,5052 and 5083 at various concentrations: 1.9, 2.09, 2.46 and 4.44 wt % of Mg, respectively. Typically additional impurities were mainly Si, Fe, Cu, Cr and Ti. The monvacancy formation energy of Al-Mg alloys was measured from a trapping model analysis of the T-dependence of the positron lifetime.

Key Words: Lifetime, formation enthalpy, point defects in Al-Mg alloys.

1.   Introduction

When an energetic positron enters a metal it rapidly loses almost all of its initial energy through collisions and comes to thermal equilibrium within the containing medium in a very short lifetime ($\approx$1 ps). After significantly longer period ($\approx$100 ps) the thermalized positron annihilates with an electron. However, the observation [1] that the lifetimes of a small fraction of the positrons in a number of metals in thermal equilibrium is strongly affected by the presence of lattice vacancies has developed into one of the most flourishing application of positron probes to solid state physics. As a result several techniques have come into use to study the electronic and defect structures and their properties (such as formation and migration energies, recovery stages...) [2], one of which being PALT [3]. This technique now plays an important role in defect spectroscopy and electron band structure. Earlier observation showed that positrons can be trapped by defects and could be influenced by changes in the concentration of such defects [4-7]. Advantages of this method in obtaining both qualitative and quantitative data on defect behavior. To explain these results several groups have proposed a simple trapping model [8,9] (which actually had been introduced earlier by Brandt [10]).

The present work aims to investigate the dependence of thermal formation vacancies on the content of Mg atoms in a series of commercial Al-alloys by PALT. McKee et al.[11], Kim et al.[12] and Fluss et al. [13] have estimated the value of the formation enthalpy in Pure Al (5N) to be 0.71 eV, 0.67$\pm$0.03 eV and 0.66$\pm$0.09 eV, respectively.

2.   Experimental procedure

The composition of the commercially Al-Mg alloys used in the present investigation are given in Table 1.

Table 1. The composition of the commercially Al-Mg alloys used in the present investigation in detail in wt. %.

Al-Alloy	Mg	Si	Fe	Cu	Mn	Cr	Na	Ti
5049	1.9	0.17	0.35	0.08	0.6 - 0.9	0.05 - 0.2	0.0004	0.05
5051	2.09	0.09	0.28	0.008	0.26	0.073	0.0003	0.021
5052	2.46	0.15	0.35	0.008	0.022	0.08	0.0005	0.013
5083	4.44	0.15	0.21	0.003	0.6 - 0.8	0.12	0.0004	0.025

The samples were prepared in the dimensions $0.25 \times 2 \times 2.5$ cm from a rod of $5 \times 5 \times 10$ cm using a low speed diamond saw (Struers Minitor). The samples were polished by silicon carbide polishing papers of successive grit sizes 80, 120, 220, 800, 1000 and 1200 and cleaned by electropolishing in a solution of 75% of methanol and 25% nitric acid [14] by (Lectrupol-5) struers; rinsed in pure acetone (99.9%); then rinsed in distilled water and dried. All samples were homogenized for 10 h at 823K, and annealed for 90-min. (1.5 h) before quenched in water (3 °C). Subsequent positron-lifetime studies were performed at room temperature using a Fast-Fast coincidence system with a time resolution about 281 ps (FWHM). The block diagram of this system is shown in Figure 1, and described elsewhere [15]. The resolution function of the system can be estimated by using a ^{60}Co-source, because there is no time difference between the two γ-rays emitted from the decay of ^{60}Co. The 1.274 MeV γ-ray is taken as a start signal for the TPHC, while one of the 0.511 MeV annihilation γ-rays is the stop signal from the TPHC fed into the MCA for storage. That is, the 1.274 MeV γ-ray marks the birth of the positron, and the 0.511 MeV γ-ray marks the annihilation of the positron. Thus the time interval between the above two γ-rays is the lifetime of the positron in the material. The 1 mci positron source was made by placing then evaporating a free carrier ^{22}Nacl Aqua solution on a 7.5 μm thick kapton foil. Sample was then wrapped in a thin Al foil. Figure 2 represents the experimental arrangement. Positron lifetime was measured in 10 pairs for each concentration ratio of Al-Mg alloy samples. Measurements were performed one time for 9×10^3 sec each during which about 1.2×10^5 coincident events were accumulated. The lifetime spectra were analyzed using the program POSITRONFIT [16]. The spectra were satisfactorily analyzed as a single lifetime component after subtraction of the background and the source components.
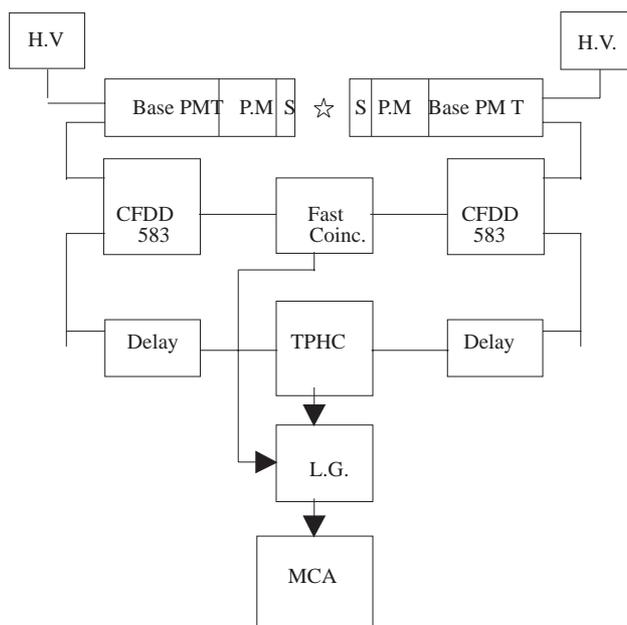
Figure 1. The conventional Fast-Fast timing coincidence block diagram system used in measuring the lifetime.
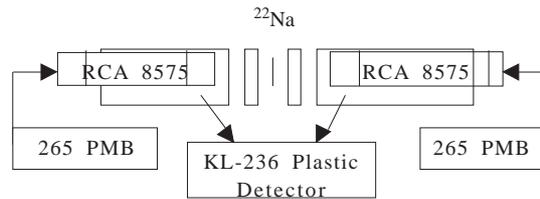
Figure 2. The experimental arrangement for sample source configuration.

3. Results and Discussion

The lifetime spectra were analyzed via least-squares in exponential terms. The long lifetime is due to annihilation in the source while the short lifetime is a mixture of the lifetime components from bulk lattice, vacancy and grain boundary. The mean lifetime τ reflects the characteristic of the defect formation and recovery processes and is a function of the quenching temperature (QT). The results of the positron annihilation experiments are normally analyzed in terms of a two state trapping model. This model assumes that the positron exits in one of only two states in the materials: the free states and the defect trapped states. The dominant second component of the lifetime is plotted in Figures 3-6 as a function of the quenching temperature.
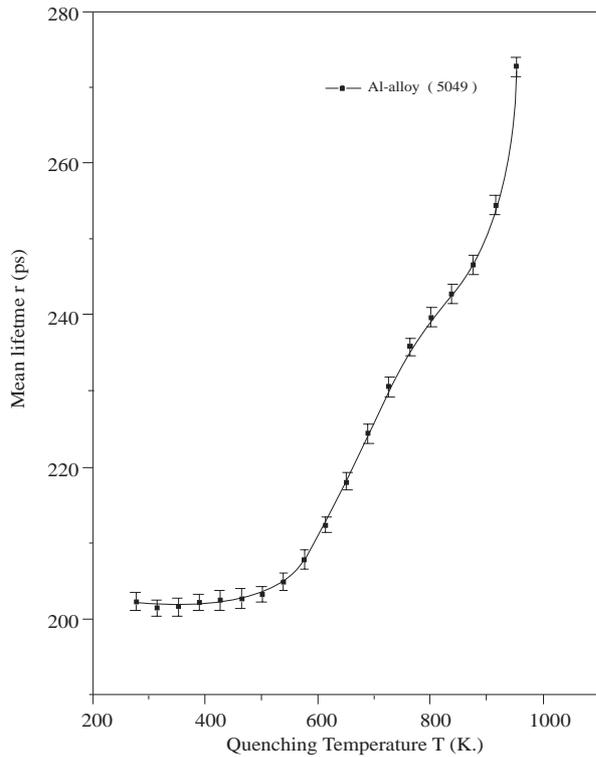
Figure 3. The mean lifetime as a function of temperature T (K) for Al-alloy (5049).
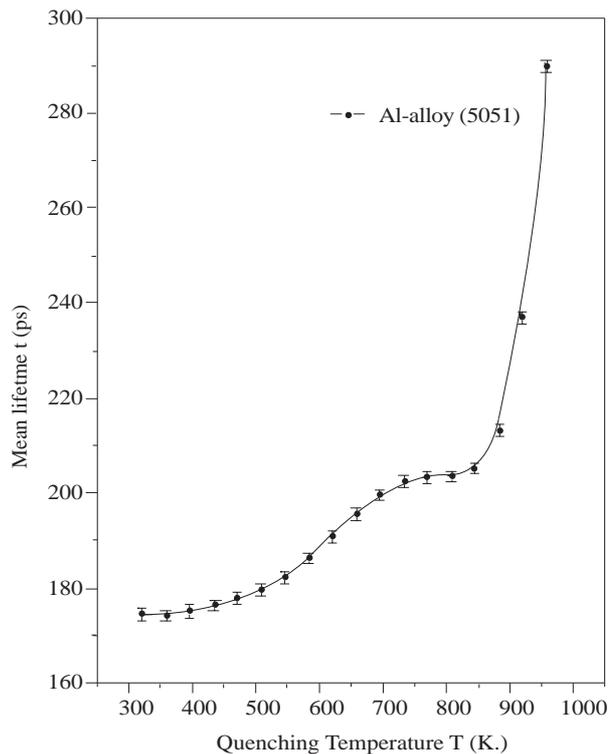
Figure 4. The mean lifetime as a function of temperature T (K) for Al-alloy (5051).

3.1. Data Analysis

3.1.1. Trapping Model

The majority of data on the T_c -dependence of annihilation parameters has been supplied by measurements of lifetime τ. In turn the bulk of this data have been analyzed by a sample 2-state trapping model, with the

extraction of monovacancy formation energy the primary objective. The model provides the relationships [17,18]
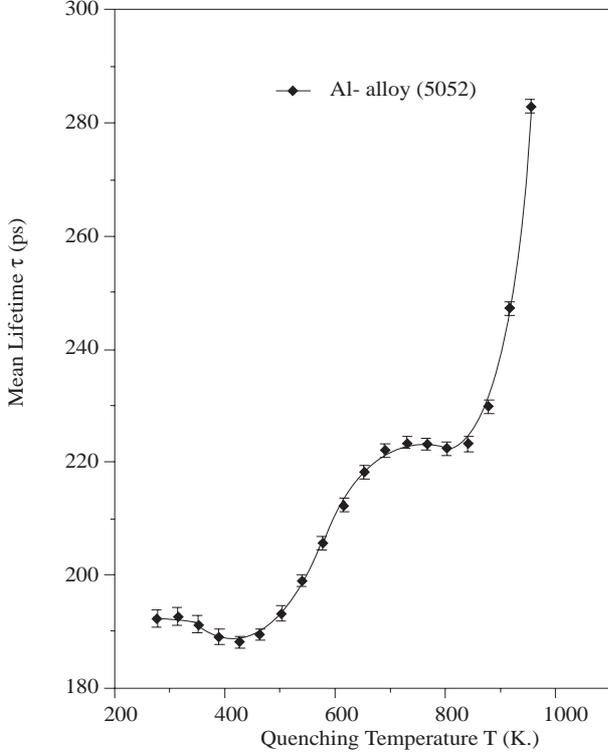
Figure 5. The mean lifetime as a function of temperature T (K) for Al-alloy (5052).
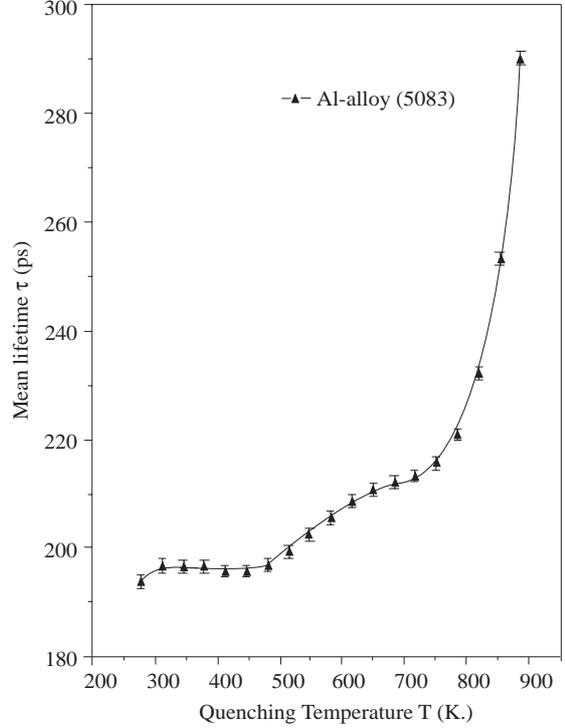
Figure 6. The mean lifetime as a function of temperature T (K) for Al-alloy (5083).

$$\left(\frac{\tau - \tau_f}{\tau_f\left(\tau_t - \tau\right)}\right) = A \exp\left(-\frac{H_{1v}^f}{T}\right) \tag{1}$$

and

$$A = \frac{\mu}{\lambda_f} \exp\left(\frac{S_{1v}^f}{K_B}\right) \tag{2}$$

Here, τ_f and τ_t are the annihilation parameters for extreme cases of "free" and trapped positron, respectively; τ is the mean positron lifetime value at intermediate temperature T and is given by $\tau = (I_o\tau_o + I_1\tau_1)$; the time constants τ_o and τ_1 with the relative intensities I_o and $I_1 = 1 - I_o$ can be determined from the numerical analyses of the positron lifetime spectra, and A is a constant with a value of about 10^{15} for all metals. The vacancy concentration appears in the exponential terms, $H_{1\nu}^f$ being formation energy and $H_{1\nu}^f$ the formation entropy; μ (4×10^{14}) is the bulk trapping probability, and λ_f is the positron decay rate. By fitting Eqn. (1) to data such as those of figures (3- 6) one extracts the vacancy properties of λ_f and $H_{1\nu}^f$. Figures 7-10 show the result of the fitting process, from their slopes we can calculate the formation enthalpy $H_{1\nu}^f$ for our Al-alloys. Figure 11 shows the fitting for all data samples. The weaknesses of this model reside partly in the need to assume specific T-dependence for the quantities τ_f, τ_t, μ and in its neglect of divacancies and of detrapping at high temperature.
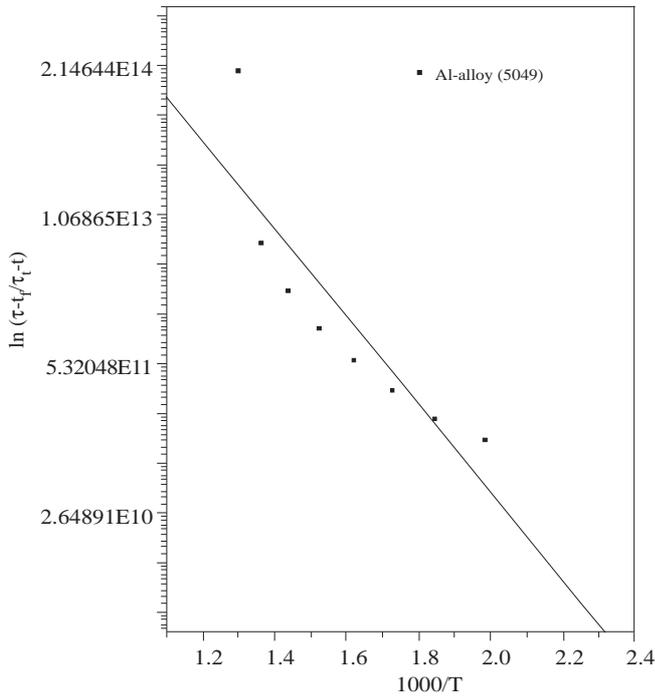
Figure 7. The relation between ln $(\tau - \tau_f/\tau_t - \tau)$ and the Q.T. (K) for Al-alloy (5049).
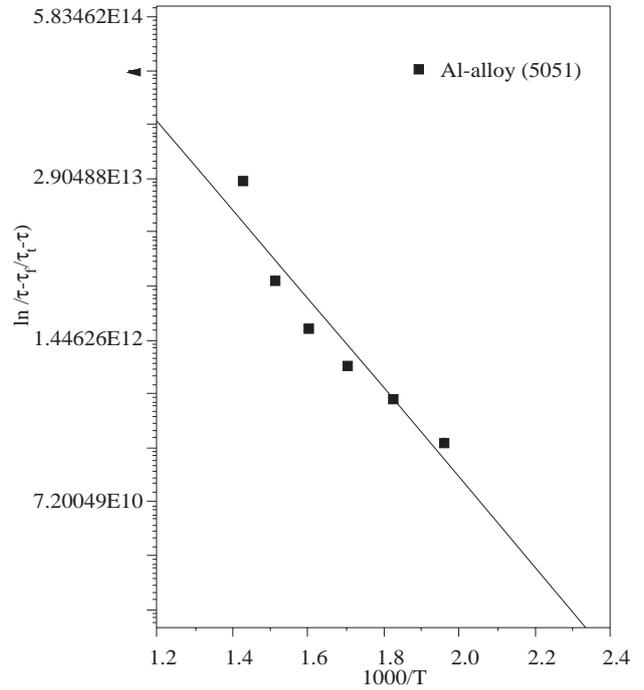
Figure 8. The relation between ln $(\tau - \tau_f/\tau_t - \tau)$ and the Q.T. (K) for Al-alloy (5051).
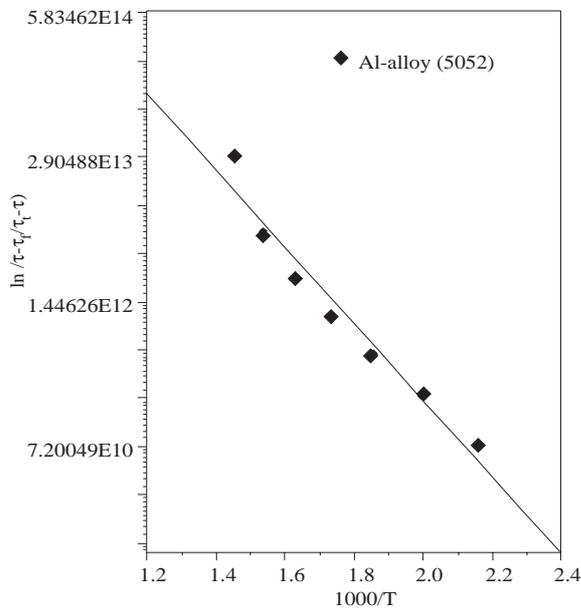
Figure 9. The relation between ln $(\tau - \tau_f/\tau_t - \tau)$ and the Q.T. (K) for Al-alloy (5052).
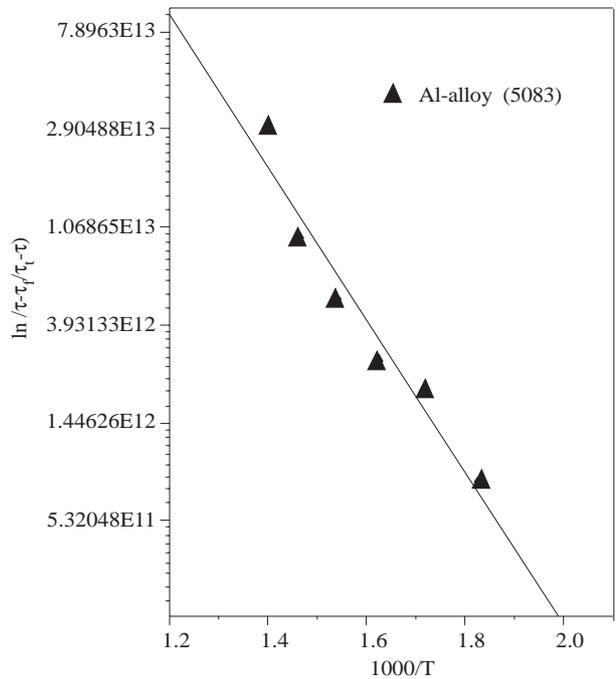
Figure 10. The relation between ln $(\tau - \tau_f/\tau_t - \tau)$ and the Q.T. (K) for Al-alloy (5083).

Mackenizie and Lichtenberger [19] define a trapping threshold temperature T_c as the interaction of linear fits to the prevacancy and early vacancy parts of the S-AlMg.

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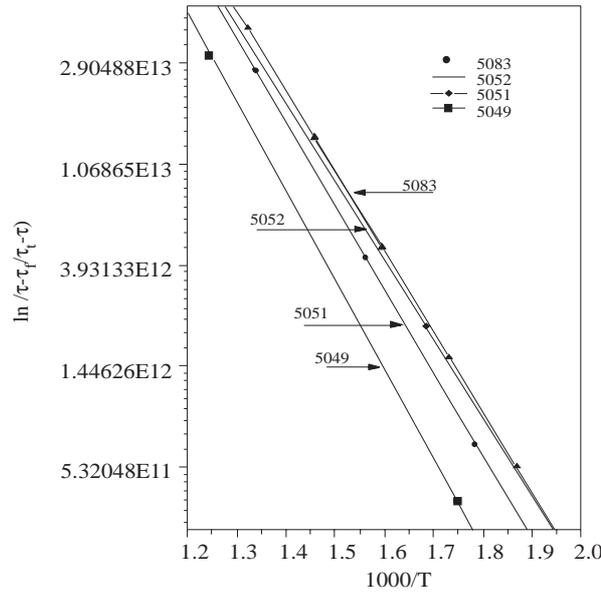
Figure 11. The relation between ln $(\tau - \tau_f/\tau_t - \tau)$ and the Q.T. (K) for Al-Mg alloys.

3.1.2. Correlation between T_c and Q^{SD}

The main correlation discussed lies between T_c and the activation energy for self-diffusion Q^{SD} (which is the summation of formation $H_{1\nu}^{f}$ and migration $H_{1\nu}^{M}$ enthalpies for a simple vacancy diffusion mechanism proposed by Damsk [20]) and we have attempted to include it in the present work of Al-alloys. Mackenizie and Lichtenberger observed that the linear relationship between T_c and Q^{SD} was consistent with the assumptions that $H_{1\nu}^{f}$ would completely dominate over the other factors that influence T_c and that $H_{1\nu}^{f} = $ b Q^{SD}, where b is the numerical constant (approximately **0.5**). Kim and Buyers [21] demonstrated analytically (by expanding Eqn. (1) in a Taylor series) that when A, τ_f and τ_t are assumed T-independent, Eqn. (1) reduces to Eqn. (3) as follows:

$$H_{iv}^{f} = \frac{[\ln A]}{[\ln A - 2]} K_B T_c \tag{3}$$

Attribution to τ_f and τ_t of linear T-dependence, typically of those observed experimentally for τ_t in the prevacancy region, does not significantly change the significance of Eqn. (3) viz. that a linear relation between

$H_{1\nu}^{f}$ and T_c is a necessary outcome of the trapping model of Eqn. (1). The correlation is insensitive to variation in A. Previous formulations of the T_c versus Q^{SD} correlation [19,21] have used Q^{SD} values obtained as slopes of Arrhenius plots in tracer self-diffusion experiments. Figure 12 shows the linear relation between the threshold temperature T_c and the formation enthalpy $H_{1\nu}^{f}$. The Arrhenius plot is now observed to have two distinct components, usually identified with monovacancies and divacancies, the latter contributing curvature near the melting temperature. The monovacancy self-diffusion energies Q_{1v} that are the slopes of the major component, and are generally less than the previously used mean slopes Q^{SD}. Figure 13 shows the values of Q_{1v} which are obtained from two-component fits to Arrhenius plots. The resulting correlation is fitted by
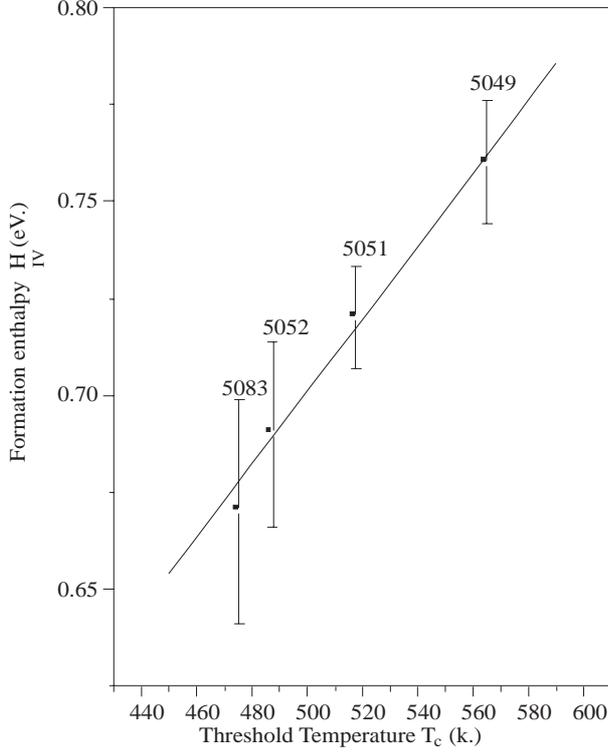
Figure 12. The linear correlation between formation enthalpy $H_{1\nu}^f$ and the threshold temperature T_c (K) for Al-Mg alloys.
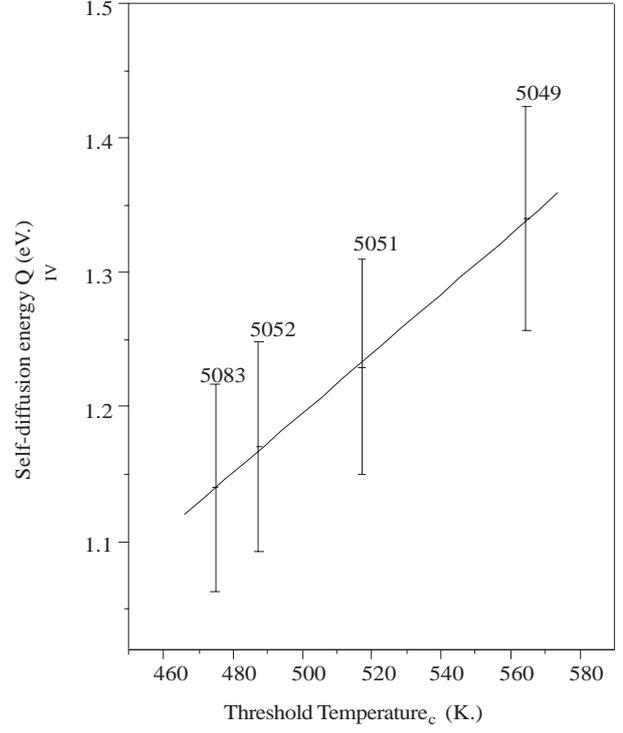
Figure 13. The linear correlation between the self-diffusion enthalpy and the threshold temperature T_c (K) for Al-Mg samples.

$$Q_{1v} = (0.107 \pm 0.049) + (21.8 \pm 0.6)T_c \times 10^{-4}. \tag{4a}$$

If the line is forced to pass through the origin, then

$$Q_{1v} = (0.079 \pm 0.042) + (21.1 \pm 0.5)T_c \times 10^{-4}. \tag{4b}$$

In Table 2 we collect the required data. The vacancy formation enthalpy for Al-Mg alloys are those measured by us from Arrhenius plot of Eqn. (1).

3.1.3. Correlation between T_c and $H_{1\nu}^f$

Kuribayashi et al. [22] were the first to point out explicitly a further correlation between the

$H_{1\nu}^f$ obtained from conventional analyses of vacancy trapping curves and the threshold temperatures T_c at which the onset of the vacancy trapping effects is first apparent. As has been demonstrated analytically by Kim and Buyers [23] and by Nanas et. al. [24], two state trapping model as expressed in Eqn. (1) reduces to a linear relationship between T_c and $H_{1\nu}^f$, since we have demonstrated empirically that T_c and Q^{SD} are linearly related ($H_{1\nu}^f = b\ Q^{SD}$). The implication of $H_{1\nu}^f$ correlating to T_c has attracted interest is the possibility of using it as a means of determining $H_{1\nu}^f$ values for Al-Mg alloys by the rather simple expedient of measuring T_c. This presumes that one has 'calibrated' via values of $H_{1\nu}^f$ that are already known. The simultaneous presentation of both $H_{1\nu}^f$ and T_c vs. T_m is based on the commonly adopted Mackenzie and Lichtenberger [25] and then improved by Schulte and Campbell [26]. These authors found That

$$H_{1\nu}^f = (-0.098 \pm 0.057) + (15.2 \pm 0.7) \times 10^{-4} T_c, \tag{5}$$

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where T_c is the threshold temperature determined experimentally from the intersection of straight-line approximations to the prevacancy and monovacancy. In Table 2 we collect the required data, the trapping threshold temperatures T_c, the vacancy formation enthalpy $H_{1\nu}^f$ as measured by us from Eqns. (1) and (5), and the self diffusion energy Q_{1v} as calculated from Eqn. (4a) for Al-Mg alloys.

Table 2. Shows the trapping threshold temperatures T_c, the vacancy formation enthalpy $H_{1\nu}^f$ (as measured from Eqns. (1) and (6)) the self diffusion energy Q_{1v} (calculated from Eqn. (5a)) and the activation energy for self-diffusion energy for Al-Mg alloys.

Al-alloy Sample	$T_c(K)$	Arrhenius method $H_{1\nu}^f$ [eV]	Q_{iv} [eV]	Q_{sd} [eV]	Threshold method $H_{1\nu}^f$ [eV]
5049	564.7	0.76 ± 0.016	1.34 ± 0.083	1.53	0.85 ± 0.045
5051	514.2	0.72 ± 0.013	1.23 ± 0.080	1.43	0.77 ± 0.041
5052	487.5	0.69 ± 0.024	1.17 ± 0.078	1.38	0.73 ± 0.040
5083	475.1	0.67 ± 0.028	1.14 ± 0.077	1.34	0.71 ± 0.0389

In that work, and from Table (3), the addition of Mg to Al reduces $H_{1\nu}^f$ to results similarly observed in the angular correlation data for Cu-Mn alloys obtained by Fukushima and Doyama [27]. The reduction in $H_{1\nu}^f$ means an increase in the vacancy concentration, which may have relvance respectively to the effect observed by Kuper et al. [28] in which the order-disorder transition affected the diffusion coefficient of Cu, Zn, and Sn in β-brass.

A clear decrease in the activation energy for self-diffusion was observed as the alloy went from the disordered to the ordered state. The activation energy for self-diffusion is the sum of $H_{1\nu}^f$ and H_{1v}^m (the migration energy of vacancies) and it is possible that both these parameters are affected by the ordering process. Also, the self-diffusion for monovacancy Q_{iv} is decreased with the increase of the Mg content. Peterson [29] estimated the value of Q_{iv} for pure Al to be 1.28 eV, The values of obtained from T_c and from the trapping model analysisis, respectively, quite good for the alloy.

4. Conclusions

The temperature dependence of the positron lifetime has been measured in Al-Mg alloys, namely 5049, 5051, 5052 and 5083, in the temperature range 297 < T < 750 K, and shows the following characteristics:

- The mean lifetime values show a predominantly linear increase with two regions of different slope (below and above the f.c.c → b.c.c transformation temperature).

- The mean lifetime exhibits a linear increase over the entire temperature range.

- No indications of effects that ascribe to the generation of thermal equilibrium vacancies were observed before the transformation temperature.

- The formation enthalpy is decreasing with increasing Mg concentration and decreasing the bias of aluminum in the low concentrations of Mg.

- Two slowly increasing regions of mean lifetime can be recognized, first, in the prevacancy region and the latter the monovacancy region.

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