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Investigation of the annealing kinetics of quenched-in vacancies in the Al-0.1 wt % Mn alloy

D. P. LAHIRI*, T. R. RAMACHANDRAN, A. K. JENA
Department of Metallurgical Engineering, Indian Institute of Technology, Kanpur, India

Isochronal and isothermal annealing characteristics of Al–0.1 wt % Mn alloy quenched from the temperature range 400 to 600° C are investigated by electrical resistivity measurements. The two recovery stages in the alloy are similar to those found in pure aluminium excepting that the temperatures at which these stages occur in the alloy are higher than those in the pure metal. The isothermal annealing of vacancies in pure aluminium and the alloy quenched from 445° C obey first order kinetics. By comparing the rate constants for annealing of vacancies in pure aluminium and the alloy, the manganese–vacancy binding energy is calculated to be 0.12 eV. Deviation from the first order kinetics is observed in the alloy when the quenching temperature is 500° C. The annealing of vacancies in this case is analysed by computer simulation on the basis of a model where the migration of both divacancies and single vacancies to sinks are considered. This analysis also indicates that the manganese–vacancy binding energy is of the order of 0.1 eV. It is concluded that the value of binding energy obtained by the kinetic method is more reliable than that obtained by the equilibrium method.

1. Introduction

The binding energy of the manganese–vacancy complex in aluminium–manganese alloys is expected to be high on the basis of the high activation energy for the diffusion of manganese in aluminium [1] and the low rates of precipitation of manganese even at temperatures of the order of 350° C [2, 3]. A quantitative study of the retardation of the clustering kinetics in Al–Zn alloys by trace additions of manganese yields values for the manganese–vacancy binding energy of 0.23 ± 0.05 eV [4] and 0.27 ± 0.02 eV [5]. However, from the temperature dependence of the quenched-in resistivity, the binding energy is evaluated to be in the range o.15 to 0.3 eV [6–8] and from the maximum solubility of manganese in aluminium, the binding energy can be roughly estimated to be 0.11 eV [9]. In the investigation reported here the manganese–vacancy binding energy is determined by the kinetic method [10]. Wire samples of aluminium and Al–0.1 wt % Mn alloy are quenched from high temperatures and the isochronal and isothermal annealing of the quenched-in vacancies are followed by electrical resistivity measurements. The isothermal annealing data are analysed for calculating the manganese–vacancy binding energy.

2. Experimental procedure

The Al–0.1 wt % Mn alloy was prepared by melting 5 N pure aluminium and a master alloy of Al–1.0 wt % Mn. The alloys were melted in an induction furnace under an argon atmosphere using a high pruity graphite crucible. After homogenization, the ingots were cold-forged, swaged and rolled with intermediate annealing treatments to $1.25 \times 1.25\,\text{mm}^2$ sections. A part of these wires was further rolled to $0.85 \times 0.85\,\text{mm}^2$ section while the rest was drawn to wires of 0.9 mm diameter. Spectroscopic analysis of the alloy wires

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*Present address: Defence Metallurgical Research Laboratory, Hyderabad, India.

revealed that the alloy contained 0.1 wt % Mn with traces of (< 0.001%) Si, Cu and Ti. The elements Fe, Mg, Ni, Cr and Cd were not detected in the analysis. Pure aluminium wires of 0.85 x 0.85 mm^2 section were prepared by the same process from pure aluminium rods.

The specimens for electrical resistivity measurements were in the form of helical coils of about 7 mm i.d. with the ratio of the length to cross-sectional area lying in the range 7.85 to 8.56 x 10^3 cm^{-1}. The lead wires were of the same composition and size as the specimen wires; they were fused to each end of the sample by using a flux [8]. Electrical resistivity measurements were carried out with a precision Kelvin bridge with a sensitivity of 1 $\mu\Omega$. It was capable of detecting a change in the resistivity of the specimens of about 1.25 x 10^{-10} Ωcm.

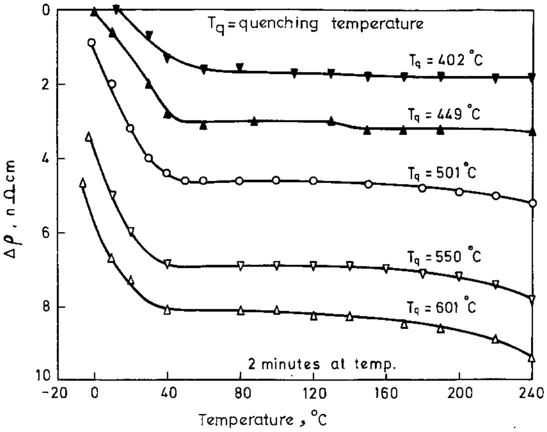

Figure 1 Isochronal annealing of quenched Al–0.10 wt % Mn alloy.

All the specimens were initially annealed at 600° C for 2 h and then air-cooled. They were heated in a vertical muffle furnace to the desired temperature, soaked there for about 15 min and quenched in an iced $CaCl_2$ bath maintained at −2° C. They were immediately transferred to the liquid nitrogen bath. Isochronal and isothermal annealing treatments were carried out in a Colora thermostatic bath (± 0.01° C) for temperatures up to 100° C and in an oil bath (± 0.1° C) for higher temperatures. The resistivity measurements were carried out at liquid nitrogen temperature.

3. Results

Isochronal annealing of the samples quenched from 402, 449, 501, 550 and 601° C was carried out by the measurement of electrical resistivities immediately after quenching and annealing at a series of progressively higher temperatures; the

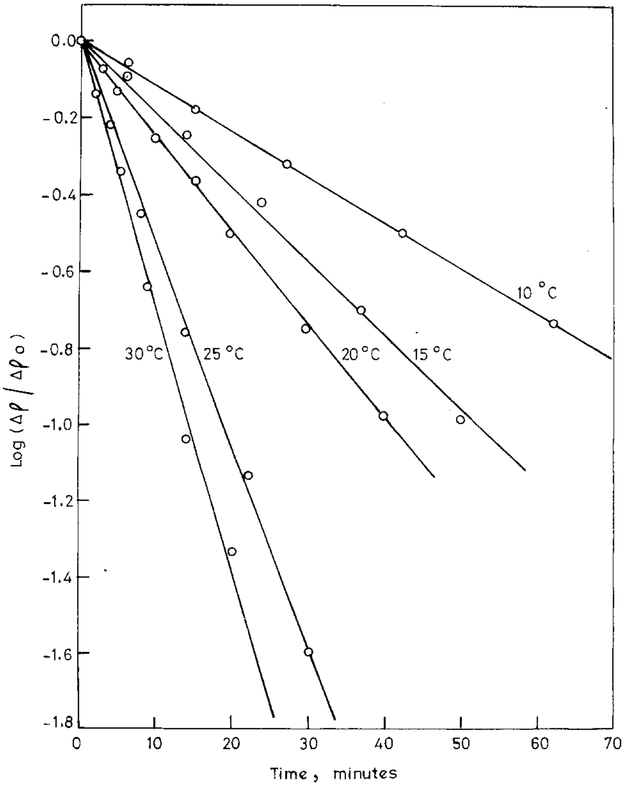

Figure 2 Isothermal annealing plots for pure aluminium quenched from 445° C.

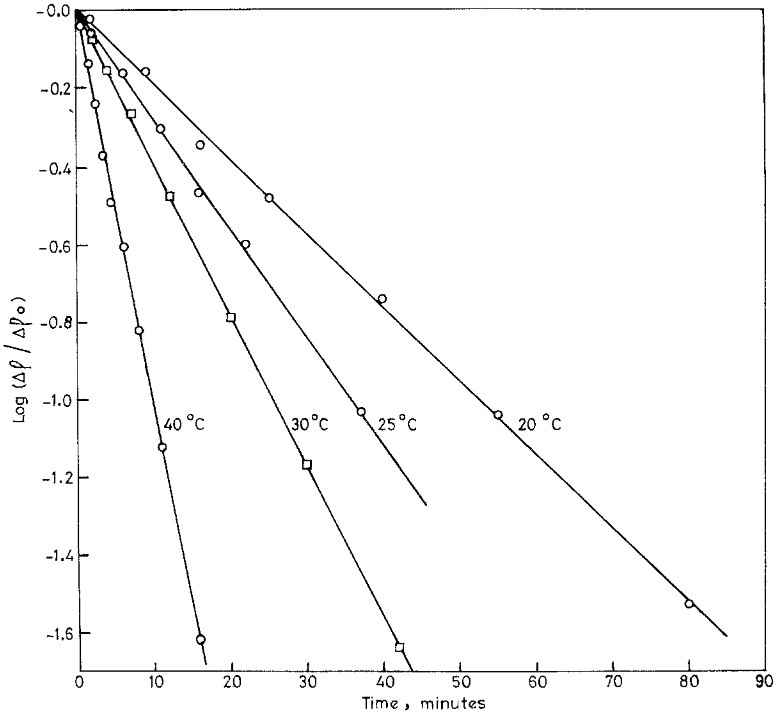

Figure 3 Isothermal annealing plots for Al–0.10 wt % Mn alloy quenched from 445° C.

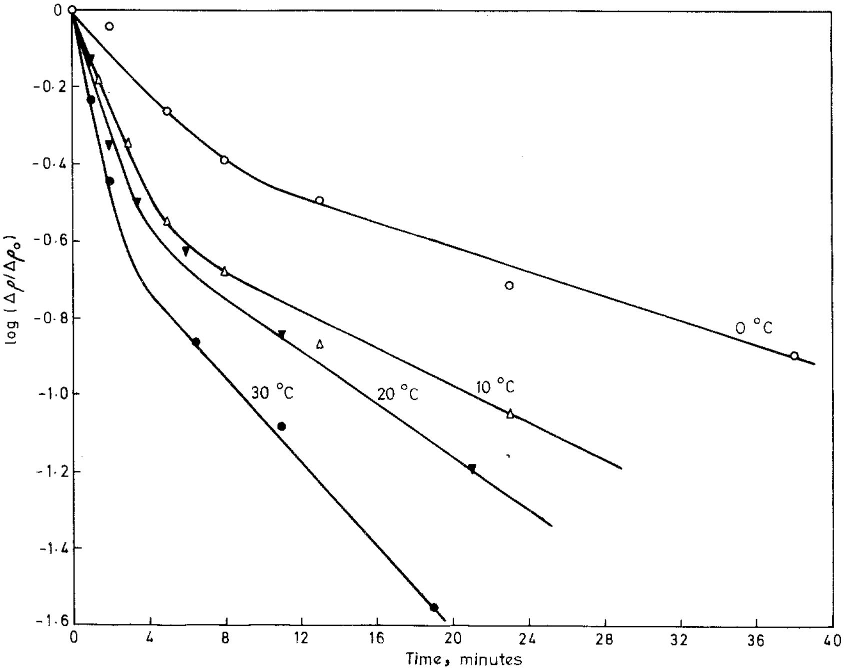

Figure 4 Isothermal annealing curves for Al–0.10 wt % Mn alloy quenched from 500° C.

time of annealing at any particular temperature was 2 min. The results are shown in Fig. 1; $\Delta\rho$ is the difference in the resistivities immediately after quenching and after annealing at a particular temperature. Two recovery stages are clearly observed. The first stage in which a large part of the resistivity is recovered occurs below 50° C. The second stage appears above 120° C in specimens quenched from temperatures above 550° C.

The kinetics of annealing of the quenched-in vacancies in the first recovery stage were investigated by using two quenching temperatures, 445 and 500° C. After measuring the as-quenched resistivity, the samples were annealed isothermally for varying lengths of time and their resistivities measured. When the rate of fall of resistivity became very small, isothermal annealing was discontinued. The samples were then annealed at 80° C for 3 min in order to complete the first stage of annealing (Fig. 1) and the resistivities ρ_{final} were measured. Isothermal annealing plots for pure aluminium and Al–0.1 wt % Mn alloy quenched from 445° C are shown in Figs. 2 and 3 as plots of log $(\Delta\rho/\Delta\rho_0)$ against time where $\Delta\rho = \rho_t - \rho_{\text{final}}$ and $\Delta\rho_0 = (\rho_{\text{quenched}} - \rho_{\text{final}})$; ρ_t is the resistivity of the sample after annealing for time t and ρ_{quenched} is the as-quenched resistivity. The isothermal annealing data for the alloy quenched from 500° C are shown in Fig. 4; the difference in the nature of the annealing curves for the two quenching temperatures is evident from Figs. 3 and 4.

4. Discussion

4.1. Annealing stages

The recovery stages observed in the isochronal annealing of the Al–0.1 wt % Mn alloy are consistent with those observed in pure aluminium [11], Al–0.35 wt % Mn and Al–1.0 wt % Mn alloys [3]. As expected, the temperature ranges of the two stages in the alloy are higher than those observed in pure aluminium. For example for a quenching temperature of 450° C stage one in aluminium begins at −50° C [11] whereas in the alloy it starts at 10° C. Similarly, when the quenching temperature is 600° C the second stage is completed at 200° C in aluminium and at 240° C in the alloy. The resisitivity recovery in the second stage for both aluminium and the alloys is about 18%. The first stage is due to the annealing of vacancies to sinks and the second stage is associated with the annealing of dislocation loops.

4.2. Isothermal annealing kinetics of samples quenched from 445° C

The data presented in Figs. 2 and 3 indicate that the isothermal annealing kinetics of samples quenched from 445° C can be represented by the following equation

$$\Delta\rho = \Delta\rho_0 \exp(-Kt). \qquad (1)$$

The values for the rate constant K in the above equation can be obtained from the slopes of the linear plots. The temperature dependence of the rate constants for the pure metal and the alloy is shown in Fig. 5. The plots in this figure are linear. The activation energies for the pure metal and the alloy are calculated to be 0.67 ± 0.05 and 0.67 ± 0.04 eV, respectively.

When aluminium is quenched from a low temperature, e.g. 445° C, single vacancies are expected to be the predominant defects. The process which occurs during annealing is the exponential decay

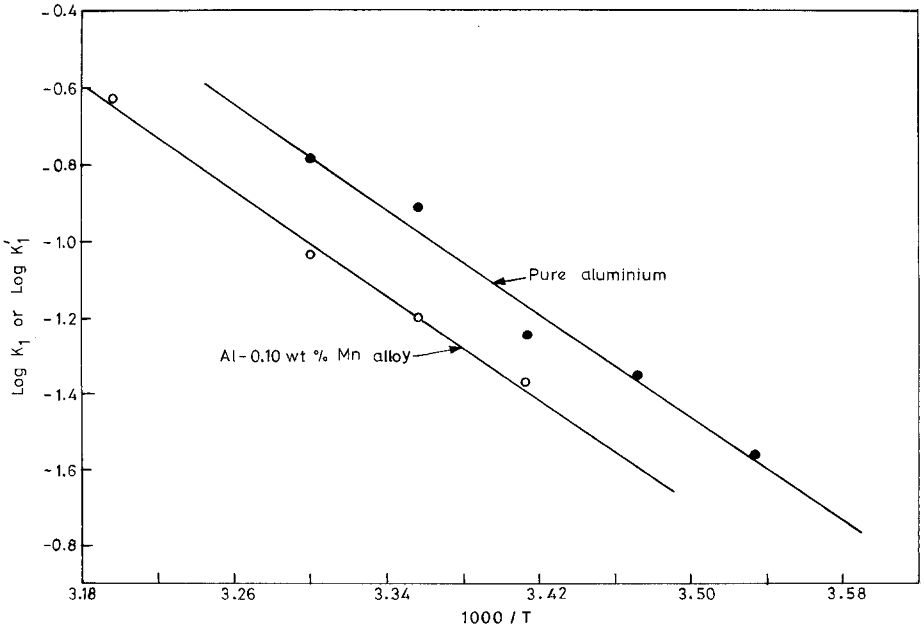

Figure 5 Temperature dependence of the rate constants for the annealing of vacancies in pure aluminium and Al–0.10 wt % Mn alloy.

of single vacancies v_1 to sinks represented by the equation

$$v_1 \xrightarrow{K_1} \text{sinks}. \qquad \text{(a)}$$

The rate constant K_1 in this process is given by [12]

$$K_1 = \alpha v \lambda^2 \exp\left(-\frac{E_{m1}}{kT}\right) \qquad (2)$$

where α is the sink density, v is the vibration frequency, λ is the jump distance, E_{m1} is the migration energy of a single vacancy and k is the Boltzmann constant. The single vacancy migration energy is, therefore, 0.67 ± 0.05 eV which is in reasonable agreement with the reported values which fall in the range 0.60 to 0.65 eV [11].

During the annealing of the dilute alloy the single vacancies go to sinks and simultaneously react with solutes i to form complexes c. Therefore the additional process which occurs with rate constants K_2 and K_3 is:

$$v_1 + i \underset{K_3}{\overset{K_2}{\rightleftharpoons}} c. \qquad \text{(b)}$$

Under these conditions the apparent rate constant K'_1 obtained from the slope $[\mathrm{d}\log(\Delta\rho/\Delta\rho_0)/\mathrm{d}t]$ is given by [12]

$$K'_1 = \frac{K_1}{1 + 12I\exp(B_{vi}/kT)} \qquad (3)$$

where I is the solute concentration and B_{vi} is the solute vacancy binding energy. If K_1 and K'_1 are known for the same annealing temperature, then B_{vi} can be calculated. The values of B_{vi} calculated from the best values of K_1 and K'_1 taken from the Arrhenius plots are listed in Table I. The average value of the binding energy is 0.12 eV.

It follows from Equation 3 that the activation energy E'_m obtained from the Arrhenius plot for the alloy is given by

$$E'_m = E_{m1} + \frac{12IB_{vi}\exp\dfrac{B_{vi}}{kT}}{1 + 12I\exp\dfrac{B_{vi}}{kT}}. \qquad (4)$$

The difference between the values of E'_m and E_{m1} for $B_{vi} = 0.12$ eV, $T = 293$ K (the mean of the annealing temperatures) and $I = 500$ ppm is 0.05 which is well within the experimental errors. It may be noted that the values of E'_m and E_{m1} are nearly the same because of the small value of the binding energy. All the results are, therefore, internally consistent.

TABLE I Rate constants for the annealing of vacancies in pure aluminium and Al–0.1 wt % Mn alloy quenched from 445° C and manganese–vacancy binding energies

Temperature (°C)	K_1 (min^{-1})	K'_1 (min^{-1})	B_{vi} (eV)
10	0.026 62	0.016 08	0.11
15	0.043 22	0.025 91	0.12
20	0.068 57	0.041 07	0.12
25	0.107 0	0.064 10	0.12
30	0.165 9	0.098 60	0.12
35	0.251 5	0.149 5	0.13
40	0.377 2	0.223 8	0.13

4.3. Isothermal annealing kinetics of samples quenched from 500° C

The annealing behaviour of the alloy quenched from 500° C does not obey the first order kinetics. This can be attributed to the presence of vacancy clusters and collapsed vacancy clusters which are normally present when the quenching temperatures are high. Amongst the vacancy clusters divancancies v_2 are expected to be most prominent. Therefore, the processes which would occur during annealing are the following in addition to processes (a) and (b)

$$v_1 + v_1 \underset{K_6}{\overset{K_4}{\rightleftharpoons}} v_2 \qquad \text{(c)}$$

$$v_2 \xrightarrow{K_5} \text{sink} \qquad \text{(d)}$$

where K_4, K_5 and K_6 are the rate constants. Under these conditions the change in defect concentration during annealing in a dilute f c c alloy containing v_1, v_2 and c in concentrations of V_1, V_2 and C respectively can be expressed by the following equations:

$$\frac{\mathrm{d}V_1}{\mathrm{d}t} = -K_1V_1 - K_2V_1(I_0 - C) + K_3C - K_6V_1^2 + K_4V_2 \qquad (5)$$

$$\frac{\mathrm{d}V_2}{\mathrm{d}t} = \frac{1}{2}K_6V_1^2 - \frac{1}{2}K_4V_2 - K_5V_2 \qquad (6)$$

$$\frac{\mathrm{d}C}{\mathrm{d}t} = K_2V_1(I_0 - C) - K_3C \qquad (7)$$

$$\frac{\mathrm{d}N}{\mathrm{d}t} = -K_1V_1 - 2K_5V_2 \qquad (8)$$

where I_0 is the initial solute concentration, N is the total vacancy concentration $(V_1 + 2V_2 + C)$ and the rate constants are defined by the following expressions [12].

$$K_2 = K_6 = 84\,v \exp\left(-\frac{E_{m1}}{kT}\right) \tag{9}$$

$$K_3 = 7\,v \exp\left(-\frac{E_{m1} + B_{vi}}{kT}\right) \tag{10}$$

$$K_4 = 14\,v \exp\left(-\frac{E_{m1} + B_{2v}}{kT}\right) \tag{11}$$

$$K_5 = \alpha v \lambda^2 \exp\left(-\frac{E_{m2}}{kT}\right). \tag{12}$$

Here B_{2v} and E_{m2} are the binding energy and migration energy respectively of a divacancy. The differential Equations 5 to 8 have been solved in an I.B.M. 7044 computer to obtain the variation of the defect concentrations with time for isothermal annealing temperatures of 273, 283, 293 and 303 K for the Al–0.1 wt % Mn alloy quenched from 500° C using various values for B_{vi}. The values for B_{2v}, E_{m2} and E_{m1} have been chosen from the literature as 0.17, 0.5 and 0.6 eV respectively [13].

The results obtained for the early stages of the annealing process at 0° C with the solute-vacancy binding energy of 0.1 eV are shown in Fig. 6. The concentrations of divancancies and solute vacancy complexes initially increase rapidly at the expense of single vacancies to establish between the quenched in defects the equilibrium characteristic of the annealing temperature. This process is complete within the first few seconds. After these initial transients the concentrations of the single vacancies, divacancies and complexes decrease slowly with time. The results for the later stages of the annealing process at 20° C are presented as a plot of N/N_0 against time in Fig. 7 where N_0 is

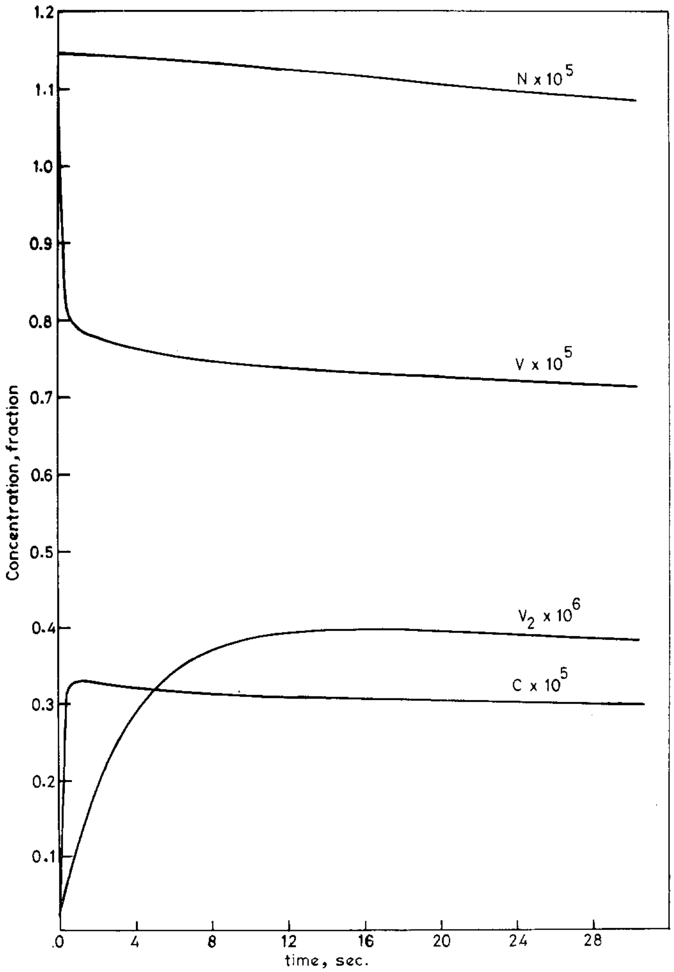

Figure 6 Computer calculated variation of the defect concentrations during the initial stages of isothermal annealing of Al–0.10 wt % Mn alloy quenched from 500° C.

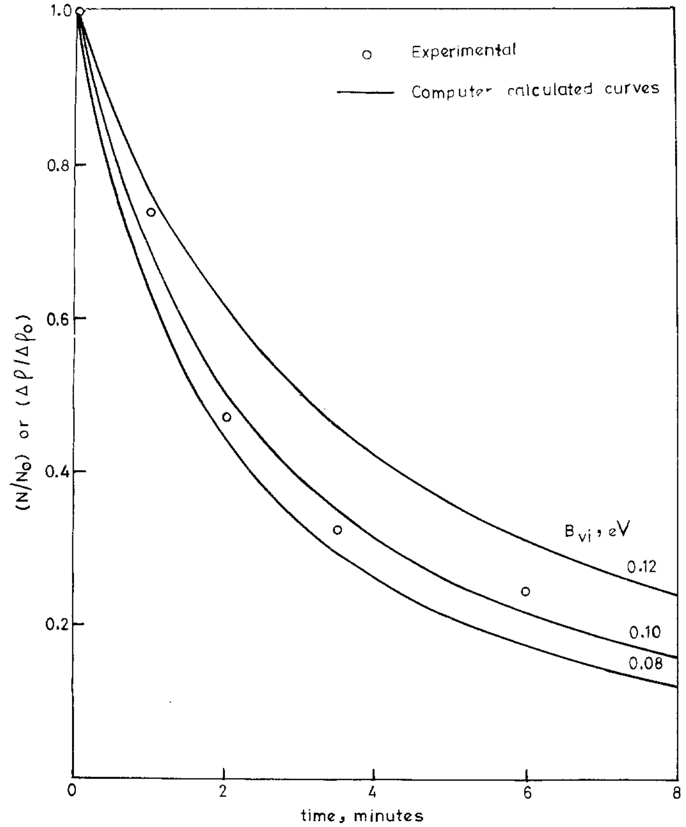

Figure 7 Computer simulated and experimental isothermal annealing curves for the Al–0.10 wt %Mn alloy quenched from 500° C and annealed at 20° C.

the total vacancy concentration at zero time assuming that no vacancies are lost during quenching.

The experimental results are available in terms of $\Delta\rho/\Delta\rho_0$ as functions of time. $\Delta\rho$ may be defined by $\Delta\rho = (V_1\rho_{1v} + V_2\rho_{2v} + C\rho_c)$ where ρ_{1v}, ρ_{2v} and ρ_c are contributions to resistivity of single vacancies, divacancies and complexes. Assuming that $\rho_{2v} = 2\rho_{1v}$ and $\rho_c = \rho_{1v}$, $\Delta\rho = \rho_{1v}N$ and $N/N_0 = \Delta\rho/\Delta\rho_0$. The experimental results are superimposed on the computer-produced curves as shown for 20° C in Fig. 7. The best fitting computer plot gives, directly, the values for the manganese–vacancy binding energy to be approximately 0.09, 0.08, 0.10 and 0.11 eV for the annealing temperatures of 0, 10, 20 and 30° C, respectively. These values are in good agreement with those obtained from the isothermal annealing of samples quenched from 445° C.

4.4. Comparison between various reported values of manganese–vacancy binding energy

The reported values for the manganese–vacancy binding energy obtained by the thermodynamic method which involves measurement of the temperature dependence of the as-quenched resistivity are 0.16 eV [7], 0.15 eV [6] and 0.29 eV [8]. The kinetic method employed in the present investigations yields lower values for the binding energy. A similar trend has been observed in the binding energy of the indium–vacancy complex in aluminium where the thermodynamic method gives a value of 0.42 eV [14] and the kinetic method the value of 0.25 eV [15]. The determination of the binding energy from a study of the retardation of the clustering process in Al–Zn alloys [4, 5] is an indirect one and suffers from the disadvantage that complex clusters of solute atoms and vacancies can be present in these alloys.

The thermodynamic technique for the determination of the binding energy has a number of disadvantages associated with it. It assumes that there is no readjustment of equilibirum between the defects during quenching, no vacancies are lost during quenching and quenching strains are absent. It has been shown that the establishment of equilibrium between defects does not change the value of the binding energy provided no vacancies are lost during quenching [8]. The loss of vacancies can be minimized by quenching from a low temperature: however, the fraction of vacancies retained on quenching can vary from experiment to experiment. This can introduce large errors in the values for the as-quenched resistivity. Taking some of these factors into consideration, Hood *et al.* [6] have pointed out that the manganese–vacancy binding energy may be of the order of 0.15 ± 0.15 eV. The kinetic method for the evaluation of the binding energy is relatively free from these errors. If the quenching conditions differ from one sample to another there will be a change in the value of $\Delta\rho_0$ only and this will not affect the rate constant for the annealing process. Consequently, it is suggested that the value of 0.12 eV obtained for the manganese–vacancy binding energy by the kinetic method is a reliable value.

5. Conclusions

(1) The isochronal annealing characteristics of the Al–0.1 wt % Mn alloy are similar to those of pure aluminium except that the temperature ranges at which the two recovery stages occur are higher for the alloy.

(2) The vacancy elimination process in stage I annealing of pure aluminium and the Al–0.1 wt % Mn alloy follows the first order kinetics.

(3) The value of the manganese–vacancy binding energy calculated from the first order annealing rate constants of pure aluminium and the alloy is 0.12 eV.

(4) The annealing of quenched-in vacancies in the alloy does not follow the first order kinetics when the quenching temperature is 500° C.

(5) The isothermal annealing data for the quenching temperature of 500° C are analysed on the basis of a kinetic model where the divacancy concentration is appreciable and both single and divacancies can independently migrate to sinks. The computer produced annealing curves agree well with the experimental curves when the manganese–vacancy binding energy is of the order 0.1 eV.

(6) Considering probable errors in the estimation of the manganese vacancy binding energy by the thermodynamic and kinetic methods it is concluded that the value obtained by the kinetic method is more reliable.

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