Memoirs of the School of Engineering Okayama University Vol. 10, No. 1, July 1975

On the Vacancy-Zn Atom Binding Energy in Al

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(Received June, 6, 1975)

Synopsis

Binding energy between a vacancy and a Zn atom in Al was investigated by measurement of as-quenched resistivity in Al-0.021at%Zn and pure-Al, with the estimation of vacancy loss during quenching. The contribution of clusters to resistivity in Al-0.021at%Zn was also investigated.

Their results are summarized as follows:
(1) The results of isothermal and isochronal annealing indicate that clusters in Al-0.021at%Zn could not be detected beyond the experimental errors.
(2) The model applied to estimate the vacancy loss in pure-Al has enough validity.

The quantitative estimation of clusters and the improvement in experimental conditions are greatly desired, which enable the more detailed analysis of the data.

1. Introduction

Up to now, many experimental and theoretical works which lead to the knowledge of the interactions between defects and impurities in

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metals have been carried out. Yet, they have not led to a general agreement, for instance, on the binding energy between a vacancy and a solute atom. This can be well illustrated by some quenching experiments on the binding energy between a vacancy and a Zn atom.

Panceri and Federighi[1] measured the apparent vacancy formation energy from the isothermal aging of Al-10at%Zn alloy. Their results were interpreted in terms of binding energy between a vacancy and a Zn atom amounting to 0.06eV. Perry and Entwistle[2] studied the influence of small additions of Zn on the initial rate of zone growth in Al-Cu alloy, and derived vacancy-Zn atom binding energy of 0.21eV. Recently, Takamura et al.[3] measured the apparent vacancy formation energy from as-quenched resistivity in dilute Al-Zn alloys, using their method of extrapolation to infinitive small specimen size. They concluded that vacancy-Zn atom binding energy was only 0.02± 0.02eV.

In this work, vacancy-Zn atom binding energy was investigated by measuring the as-quenched resistivity in dilute Al-Zn binary alloy (Al-0.021at%Zn) and pure-Al. At temperature T, vacancy concentration which exists in thermal equilibrium in pure-Al will be given as follows,

$$C = A\exp(-E_f/kT) \qquad (1)$$

and in dilute binary alloy, according to Lomer's[4] expression

$$C = A\exp(-E_f/kT)(1-12X+12X\exp(E_b/kT)) \qquad (2)$$

where A, E_f, k, X and E_b denote entropy factor, vacancy formation energy, Boltzmann constant, atom fraction of solute and vacancy-solute atom binding energy, respectively.

In analyzing the data obtained from quenching experiments, it is usually assumed that there is a proportional relationship between the vacancy concentration and the resistivity change. Quenching experiments, however, arise the problem of vacancy loss during quenching. Here, a simple kinetic model was introduced in order to estimate the vacancy loss.

In case of dilute binary alloy, the data must be analyzed with care, unless only vacancies contribute to as-quenched resistivity. The determination of the resistivity reference state where the quenched-in vacancy concentration is negligible will prove to be an important factor, when the resistivity increment due to vacancies is estimated. Ohta and Hashimoto[5] have shown in their resistometric study on Al-Zn alloys that resistivity reaches a metastable value ρ_e' in a short time when annealed at temperatures higher than the solvus

temperature for G.P.zone and lower than the solvus temperature of phase diagram, and the values of ρ_e' are on the extrapolated part of the ρ_0-T_q curve. They have then concluded that the state corresponding to ρ_e' might be a solid solution which contains clusters quite different from G.P.zones. Kanadani[6] reported that the contribution of clusters to resistivity was observed even in Al-0.1wt%Zn, which contains Zn atoms twice as much as Al-0.021at%Zn used in this work. The results of the investigation on the clusters are also reported, since the clusters are thus thought to give not a little contribution to as-quenched resistivity.

2. Experimental Procedure

Electrical resistivity was measured by using the specimens made from Al-0.021at%Zn alloy and pure-Al. One master alloy (Al-2wt%Zn) was prepared by melting together the required amounts of Al and Zn in a high alumina crucible in air, the starting materials being 99.996% Al and 99.999%Zn. This alloy was homogenized for two days at 400°C in air. Al-0.021at%Zn alloy was prepared by the same technique using sections from this master alloy with the required additions of pure-Al. The homogenized castings were hot-forged to sheets of about 3mm thick and then cold-rolled to strips of 0.4mm thick. Specimens were cut down from these strips with current and potential lead wires. On the other hand, specimens of pure-Al were prepared using sections cut down from the starting materials.

Specimens were solution-treated for 1hr. at 500°C in a furnace installed with aluminium block to which specimens were attached closely. Then, specimens were cooled in the furnace to the quenching temperatures (controlled within ±0.5°C) and held there for 1hr. The quenching was performed by quickly extracting the specimens out of the furnace and immersing it into iced water bath. It was then transferred to a liquid nitrogen bath. Isothermal or isochronal annealing treatments were made by transferring the specimens into an ethanol bath (0°C or below), a water bath (from 10°C to 60°C) and a silicon oil bath (from 70°C upwards).

All resistivity measurements were made at liquid nitrogen temperature by the potentiometric method and the errors caused by various electromotive forces were minimized by the usual method. The dummy was used in order to allow a first-order correction to be made for

small fluctuations in the bath temperature. In this manner, the resistivity could be determined with a precision of about 1×10^{-4}.

Cooling rate during quenching was measured by passing a constant current of about 0.6 ampere through the specimen and recording the voltage developed across it as a function of time on an electromagnetic oscillograph with a direct current amplifier. An example of cooling curves obtained is illustrated schematically in Fig.1. When the quenching temperature is lowered, the curve changes in the manner as indicated with a broken line.

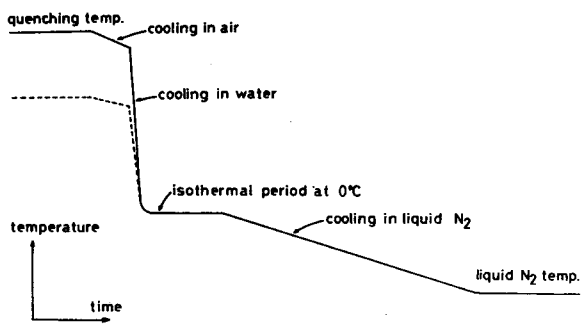

Fig.1 Schematic illustration of cooling curve obtained.

3. Estimation of vacancy loss and determination of E_f and E_b

In pure-Al, vacancy loss during quenching is assumed to arise through monovacancies migrating to fixed sinks, each by making j jumps during its lifetime. The vacancy loss will be given by integrating

$$dC/dt = -f(C-C^*)/j \qquad (3)$$

where f is the vacancy jump frequency and C^* is the equilibrium vacancy concentration at the current temperature T given by eq.(1). Now, $f = f_o A_m \exp(-E_m/kT)$, where E_m is the jump energy of a monovacancy, A_m is the entropy factor for migration and f_o is the Einstein frequency. With A = 8[7], $A_m = 1$, $E_m = 0.60$eV and $j = 10^8$ jumps/sec, equation (3) can be solved numerically by a program fed into the Niac computer under conditions where the temperature fell step-like. Actually, the air- and water-cooling periods of the cooling curves were devided into a hundred parts equally. Here the vacancy loss in liquid nitrogen was neglected. The value of E_m was quoted from Federighi's[8] review, in which he proposed that the migration energy of a monovacancy was 0.62±0.02eV. The value of A_m was quoted according to Perry et al.[9] as $A_m = 1$. The value of j is derived, assuming that vacancies annihilate only at pre-existing

dislocations and migrate to the nearest dislocations by ramdom walk. The density of dislocations is that in well annealed pure-Al.

If one assumes a value of E_f, the retained vacancy concentration C_r for each quenches will be calculated. E_f' would be temporarily obtained from the plots of C_r against reciplocal of quenching temperature T_q (hereafter this will be called Arrhenius plots for short). Vacancy formation energy E_f was derived by repeated computation for the value of E_f' to consist with E_f^o which is obtained from the Arrhenius plots of as-quenched resistivity increment $\Delta\rho_o$ vs. T_q. $\Delta\rho_o$ is defined as the resistivity increment due to quenched-in vacancies.

Both C^* and f will be affected by vacancy binding with solute atom in the alloy. The total vacancy concentration has been given by eq.(2). The equilibrium ratio of unassociated vacancy concentration to the total concentration will be

$$r = (1-12X)/(1-12X+12X\exp(E_b/kT)) \qquad (4)$$

In this model, it is assumed that during quenching the equilibrium vacancy distribution indicated by eq.(4) is always accomplished and unassociated vacancies behave similarly as in pure-Al. The supersatulated vacancy concentration term ($C-C^*$) in eq.(3) times r will be unassociated portion of the supersaturated concentration in the alloy.

Here, substituting E_f determined for pure-Al and assuming a value of E_b, C_r can be caluculated. Then, the apparent vacancy formation energy Q_f' will be temporarily obtained from Arrhenius plots of C_r vs. T_q. E_b will be determined by repeated computation for the value of Q_f' to consist with Q_f^o, which is obtained from Arrhenius plots of $\Delta\rho_o$ vs. T_q. Again, $\Delta\rho_o$ is defined as the resistivity increment due to quenched-in vacancies only. A least-square method was used in each Arrhenius plots.

4. Results and Discussion

a) clusters

Fig.2 shows variations in as-quenched resistivity ρ_o with quenching temperature T_q of pure-Al and Al-0.021at%Zn. When T_q is higher than about 250°C, ρ_o increases exponentially with T_q. When T_q is lower than about 200°C, ρ_o is almost constant. The increment of ρ_o due to clusters when T_q is lower is predicted to be quite small in Al-0.021at%Zn alloy because of extremely small content of Zn[6], and

the results do not show a distinct increment of ρ_0 in the low quenching temperature range in the figure.

Isothermal annealings have been performed to make a quantitative estimation of the contribution of clusters to resistivity. Fig.3 shows isothermal annealing curves of pure-Al and Al-0.021at% Zn at each temperature T_a indicated in the figure after quenching from 400 °C. Resistivity decreases monotonically and reaches a metastable value ρ_e. Fig.4 shows resistivity change from as-quenched value by plotting of the same data in Fig.3. The extent of scattering of ρ_e in Al-0.021at%Zn is fairly large and is approximately equal to that in pure-Al. As described in the Introduction, the values of ρ_e would be on the extrapolated parts of ρ_0-T_q curves, and would increase as T_a is lowered. But such a relation is not clearly observed.

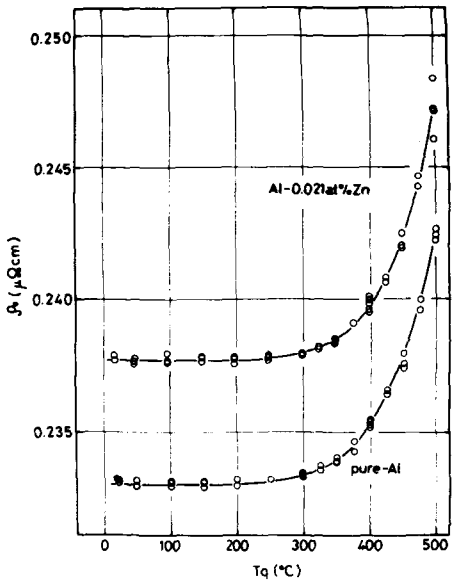

Fig.2 Variation in as-quenched resistivity with quenching temperature.

Isochronal annealings were aimed to study the effects of clusters

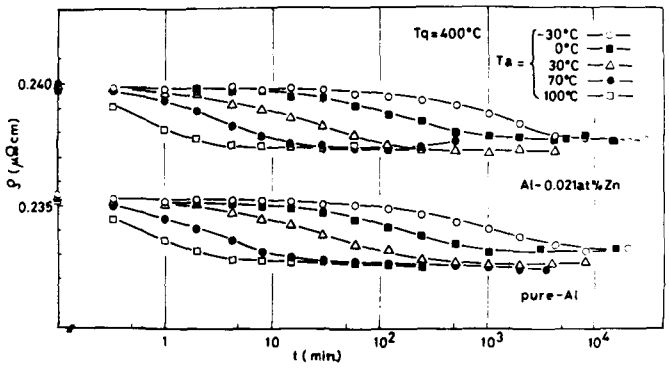

Fig.3 Isothermal annealing curves at various temperature after quenching from 400 °C.

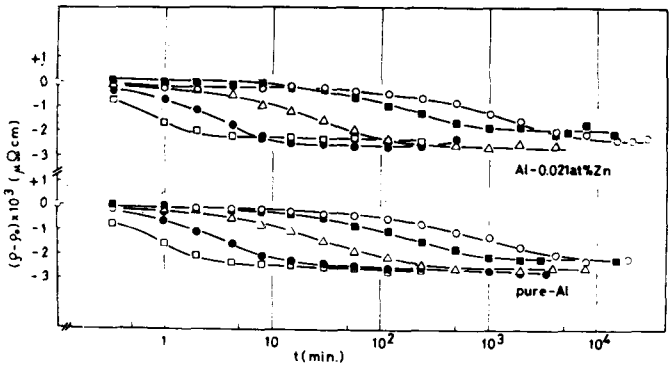

Fig.4 Plots of the data in Fig.3 by resistivity change from as-quenched value.

qualitatively. Fig.5 shows a comparison of the isochronal annealing curves following quenching from 400 °C of pure-Al and Al-0.021at%Zn. The annealing time is always 1 min, and the annealing temperature is set in steps of 10 °C. In each case, resistivity starts to decrease steeply at about 0 °C and relaxes into slower decrease or constant at

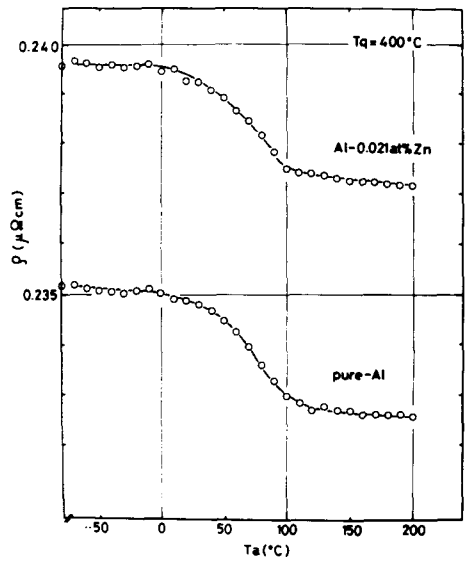

Fig.5 Isochronal annealing curves after quenching from 400 °C. The annealing time is 1 min.

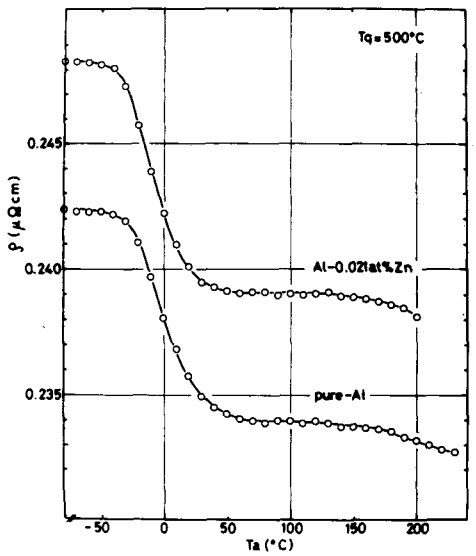

Fig.6 Isochronal annealing curves after quenching from 500 °C.

about 120°C. When T_q is 500°C, as shown in Fig.6, the shape of isochronal curves change greatly, compared with Fig.5. Detailed interpretation of the processes of isochronal recovery is not made here. The interest is placed on the difference between the shapes of the isochrones in Al-0.021at%Zn and in pure-Al. The results do not show large differences, though some small defferences can be found. It is not yet determined whether these small defferences are due to clusters or merely due to the experimental errors. Putting above discussion together, it might be concluded that clusters existing in Al-0.021at%Zn could not be detected beyond the experimental errors of this investigation.

b) estimation of vacancy loss

In pure-Al, as-quenched resistivity increment $\Delta\rho_0$ is for the most part due to quenched-in vacancies. Therefore, ρ_b which is defined as the value of ρ_0 in the reference state where the vacancy concentration is negligible was determined by meaning of ρ_0's in the tempera-

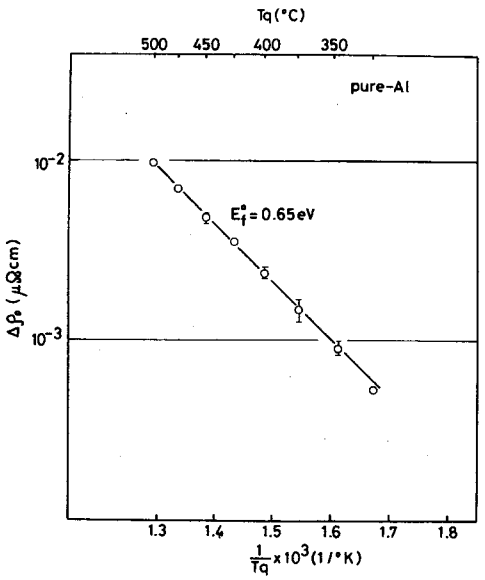

Fig.7 Resistivity increment in pure-Al as function of reciprocal of quenching temperature.

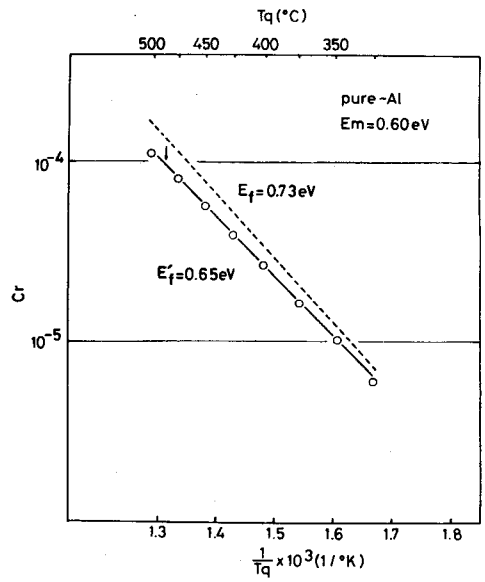

Fig.8 Computed vacancy concentration retained during quenching in pure-Al as function of reciprocal of quenching temperature.

ture range below T_q = 200°C in Fig.2. Then, $\Delta\rho_0$ is given as ρ_0 minus ρ_b. Fig.7 shows Arrhenius plots of $\Delta\rho_0$ vs. T_q. E_f° = 0.65eV was found from this data.

Of course, this is not the true value for vacancy formation energy in Al because of vacancy loss during quenching. With estimation of vacancy loss, E_f' consisted with E_f° when E_f = 0.73eV was assumed. As shown in Fig.8, E_f = 0.73eV was thus obtained(here, the error is evaluated to be about ±0.03eV). This value is nearly in the error range of 0.76±0.03eV[10], which value is now proposed to be valid for the vacancy formation energy in Al. Hence, the model would be applied reasonably to estimated the loss in pure-Al.

c) binding energy between a vacancy and a Zn atom

Kanadani[6] repoted that the effect of G.P.zones formed during quenching was quite small in dilute Al-Zn alloys(which contains lesser than 0.5wt% of Zn). In Al-0.021at%Zn alloy, the contribution of G.P.zones to as-quenched resistivty is assumed to be negligible. Here, the resistivity increment due to quenched-in vacancies was calculated as $\Delta\rho_0 = \rho_0 - \rho_b$. Since the contribution of clusters was not estimated quantitatively, ρ_b was determined as the average of ρ_0's in the temperature range where T_q = 200°C below in Fig.2. Arrhenius plot of $\Delta\rho_0$ vs. T_q is shown in Fig.9, and Q_f° = 0.69eV was obtained. When the retained vacancy concentration C_r was calculated for the assumed values of E_b from 0.02eV to o.15eV and with E_f = 0.73eV derived earlier, the temporarily-obtained apparent formation energy Q_f' varied from 0.65eV to 0.64eV and did not consist with Q_f° = 0.69eV. The value of E_b was thus undetermined.

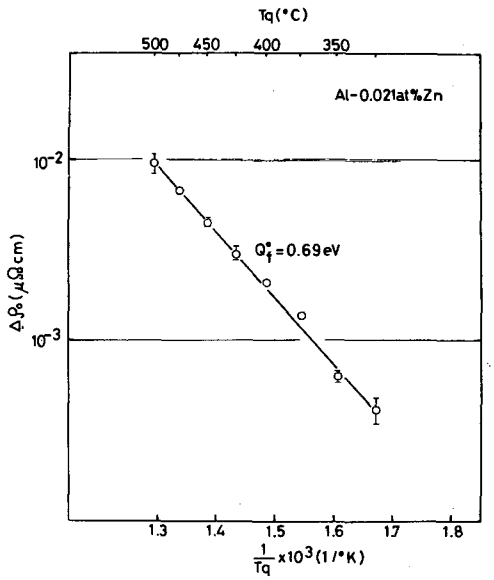

Fig.9 Resistivity increment in Al-0.021at%Zn as function of reciprocal of quenching temperature.

Discussion will be made below for the reason why E_b was not determined.

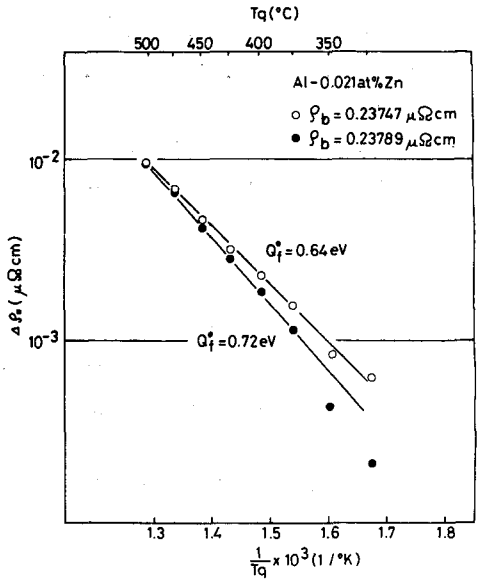

Fig.10 Variation in Q_f when ρ_b is set with the upper and lower limit value of the scattering of ρ_o.

First, it can be pointed out that the analyzing method based on the model for estimating the vacancy loss in alloy is oversimplified. With respect to this problem, though many theoretical works have been carried out to describe the details of the interactions between defects and solute atoms in dilute binary alloys[11], such a theoretical approach must be cautiously applied to experimental results. Second, it is strongly implied that the experimental errors make E_b undetermined. As already discussed, the effects of clusters in Al-0.021at%Zn have not been estimated quantitatively and ρ_b was temporarily determined as the average of ρ_o's. If ρ_b is set with the upper and lower limit value of the scattering of ρ_o in the same temperature range as in Fig.2, Arrhenius plots of corrected $\Delta\rho_o$ versus T_q shows, however, that Q_f° varies from 0.64eV to 0.72eV in Fig.10. Hence, there is such a variation in Q_f° and it is the determination of resistivity reference state that makes E_b undetermined.

It is generally proposed that the larger the solubility limit of solute, the smaller the binding energy[11]. According to phase diagram[12], the solubility limit of Zn atom in Al is found to be almost 67%. thus the binding energy between a vacancy and a Zn atom is predicted to be appreciably small as compared with other solute elements. Actually, a comparison of pure-Al and Al-0.021at%Zn in Fig.2 seems to imply the extremely low binding energy.

In investigating on such the low binding energy, the quantitative estimation of clusters and the improvement in experimental conditions are desired, which enable the more detailed analysis of the data.

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