

# Binding Energies between a Vacancy and a Cadmium, Indium or Tin Atom in Al-10wt%Zn, Al-3.0wt%Ag and Al-3.0wt%Cu Alloys

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The changes of electrical resistivity of several alloys, that is, Al-10wt%Zn, Al-10wt%Zn-0.01wt%Cd, Al-10wt%Zn-0.01wt%In, Al-10wt%Zn-0.01wt%Sn, Al-3.0wt%Ag, Al-3.0wt%Ag-0.01wt%Cd, Al-3.0wt%Ag-0.01wt%In, Al-3.0wt%Ag-0.01wt%Sn, Al-3.0wt%Cu, Al-3.0wt%Cu-0.01wt%Cd and Al-3.0wt%Cu-0.01wt%In, during isothermal aging after quenching were measured. The interactions between a vacancy and a cadmium, indium or tin atom in Al-10wt%Zn, Al-3.0wt%Ag and Al-3.0wt%Cu alloys were estimated. Binding energies obtained for Al-Zn, Al-Ag and Al-Cu base ternary alloys agree within experimental accuracy with each other.

## § 1. Introduction

There are many studies concerning to the binding energy between a vacancy and an impurity atom in metals. Since the equilibrium concentration of vacancies, the rate of annealing out of super-saturated vacancies, the rate of diffusion and etc. are all affected by the binding energy, it is of fundamental importance. It also plays important roles in understanding the phenomena of aging and the change of mechanical properties of metals by quenching or irradiation.

Binding energy between a vacancy and an impurity atom in aluminium was known for several impurity elements. For instance, Kimura, Kimura and Hasiguti<sup>(1)</sup> studied an Al-Cu alloy using the initial rate of aging and deduced the binding energy between a vacancy and a copper atom as 0.2 eV. Panseri and Federighi<sup>(2)</sup> studied the clustering in Al-10wt%Zn alloy and the binding energy between a vacancy and a zinc atom was estimated to be 0.06 eV. On the other hand, the binding energy between a vacancy and a zinc atom or silicon atom was estimated to be 0.18 or 0.28 eV, respectively, with the quenching method by Takamura et al.<sup>(3)(4)</sup>. Also, Kimura and Hasiguti<sup>(5)</sup> studied Al-Sn alloy using the quenching method and deduced the binding energy between a vacancy and a tin atom as 0.42 eV. Beaman, Balluffi and Simmons<sup>(6)(7)</sup> studied the dilute Al-Ag and Al-Mg binary alloys. They measured the equilibrium vacancy concentration at high tempera-

tures and estimated the binding energy between a vacancy and a silver atom or magnesium atom as 0.08 or 0.01 eV, respectively. Panseri and Federighi<sup>(8)</sup> studied a ternary Al-Zn-Mg alloy and obtained the binding energy between a vacancy and a magnesium atom as 0.54 eV. For this value, Takamura, Okazaki and Greenfield<sup>(9)</sup> obtained ~0.2 eV for dilute Al-Mg binary alloys by the quenching experiments.

In a previous paper<sup>(10)</sup>, it was shown that the ratio of time,  $t_{Mt}$ , required to reach the maximum of electrical resistivity in isothermal aging curves of an Al-Zn base ternary alloy to that time,  $t_{Mb}$ , in the binary alloy might be inversely proportional to the ratio of the concentration of vacancies bound to zinc atoms,  $C'_{vt}$ , immediately after quenching in the ternary alloy to that concentration,  $C'_{vb}$ , in the binary alloy, when an atom of third element did not interact with zinc atom. That is

$$\frac{C'_{vt}}{C'_{vb}} \approx \frac{t_{Mb}}{t_{Mt}} \quad (1)$$

If 0.18 eV is adopted as the binding energy between a vacancy and a zinc atom<sup>(3)</sup>, the binding energy between a vacancy and a Cu, Ag, Ca, Cd, In, Si, Ge, Zr, Sn or Mn atom in aluminium were estimated to be <0.23, <0.23, 0.27 ± 0.05, 0.32 ± 0.05, 0.39 ± 0.05, 0.28 ± 0.05, 0.33 ± 0.05, 0.33 ± 0.05, 0.43 ± 0.05 and <0.23 eV, respectively<sup>(10)~(15)</sup>. These values agree with those obtained by other authors. For instance, the binding energy between a silicon atom and a vacancy was estimated to be 0.28 eV by this

method. On the other hand, the binding energy between a silicon atom and a vacancy was estimated to be 0.27 eV with the quenching method by Okazaki and Takamura<sup>(4)</sup>. Agreement of both values is very good. Furthermore, the binding energy between a tin atom and a vacancy was 0.43 eV by this method, and Kimura and Hasiguti<sup>(5)</sup> estimated this binding energy as 0.42 eV. Again agreement of both values is very good.

In both Al-Zn and Al-Ag binary alloys, the spherical zones are formed and their size is of the same order when aged at room temperature. Thus behaviours of clustering of Al-Ag alloy are quite similar to those of Al-Zn alloys. Therefore, it is considered that the binding energy between a vacancy and a silver atom can be obtained using Eq. (1), when the binding energy between a vacancy and an atom of third element is known. In a previous experiment<sup>(16)</sup>, the binding energy between a vacancy and a silver atom was estimated to be  $0.25 \pm 0.05$  eV, when germanium, indium or tin was added as the third element in Al-Ag binary alloy. In this experiment, the values of binding energy of Ge-V, In-V and Sn-V were used, those which were estimated from the study of Al-Zn binary alloy and Al-Zn-X ternary alloys<sup>(10)(12)</sup>.

In Al-Cu alloy, the shape of G. P. zones is plate like and there are fairly large strain field around these G. P. zones. Therefore, the aging experiments of long time are not desirable. But the experimental equation for the change of electrical resistance in initial aging is obtained by DeSorbo, Treafis and Turnbull<sup>(17)</sup>. Therefore, the binding energy between a vacancy and an impurity atom in aluminium can be estimated using the similar method as Kimura, Kimura and Hasiguti's<sup>(1)</sup>.

In a previous studies, Al-10wt%Zn binary alloy and Al-10wt%Zn base ternary alloys were mainly used. In a present study, the binding energies between a vacancy and an atom of third element were estimated using Al-3.0wt%Ag binary alloy, Al-3.0wt%Ag base ternary alloys, Al-3.0wt%Cu binary alloy and Al-3.0wt%Cu base ternary alloys as specimens and these values were compared with the values obtained by the experiments of Al-Zn base ternary alloys. And the method used and the values obtained for Al-Zn base ternary alloys was reexamined from these results.

## § 2. Experimental Procedure

Specimens were made from 99.996wt% pure aluminium, 99.999wt% pure zinc, 99.999wt% pure silver, 99.999wt% pure copper, 99.999wt% pure tin, 99.999wt% pure cadmium and 99.999wt% pure indium. Each alloy was melted in the high alumina crucible in the air. Nominal weight compositions of alloys were Al-10wt%Zn, Al-3.0wt%Ag, Al-3.0wt%Cu, Al-10wt%Zn-0.01wt%Cd, Al-10wt%Zn-0.01wt%In, Al-10wt%Zn-0.01wt%Sn, Al-3.0wt%Ag-0.01wt%Cd, Al-3.0wt%Ag-0.01wt%In, Al-3.0wt%Ag-0.01wt%Sn, Al-3.0wt%Cu-0.01wt%Cd and Al-3.0wt%Cu-0.01wt%In. Ingots of the each alloys were hot forged to the sheets of about 5mm thick and then cold rolled to the strips of 0.4mm thick and the specimens were cut down from these strips with current and potential lead wires. Each specimen were about 0.5 mm wide and about 50mm long.

Specimens were heated in a horizontal furnace with a temperature controlled within  $\pm 0.5^\circ\text{C}$ . Temperature was measured at aluminium block in a furnace and the specimen was attached closely to this block. Specimens were always kept at the quenching temperature for at least 30 minutes for the equilibrium state at this quenching temperature to be obtained.

The quenching was performed by quickly extracting the specimen out of the furnace and immersing it into the ice water at  $0^\circ\text{C}$ . After the quenching it was transformed quickly into liquid nitrogen. The time elapsed during these procedures was shorter than 2/10 second and the quenching rate of specimen would be fairly large. Aging treatments were performed by transferring the specimen into an acetone bath ( $0^\circ\text{C}$  and below) or a water bath (above  $0^\circ\text{C}$ ) and after aging treatment the specimen was again transferred to the liquid nitrogen bath and the measurements of electrical resistivity were carried out.

The measurement of electrical resistivity was performed by the potentiometer method and the errors caused by various electromotive forces were removed by the usual method. The accuracy of measurements was about 1/10000.

## § 3. Results

Isothermal aging curves of Al-10wt%Zn binary alloy, Al-10wt%Zn-0.01wt%Cd, Al-10wt%Zn-0.01wt%In and Al-10wt%Zn-0.01wt%Sn ternary

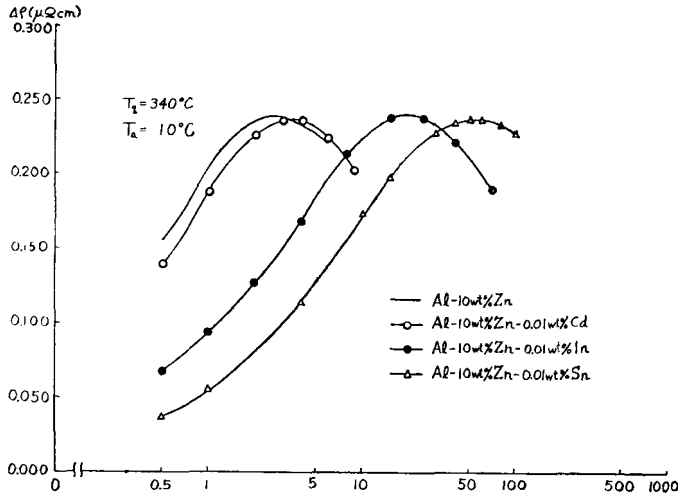


Fig. 1 Isothermal aging curves of Al-10wt%Zn binary alloy, Al-10wt%Zn-0.01wt%Cd, Al-10wt%Zn-0.01wt%In and Al-10wt%Zn-0.01wt%Sn ternary alloys at  $10^\circ\text{C}$  after quenching from  $340^\circ\text{C}$ .

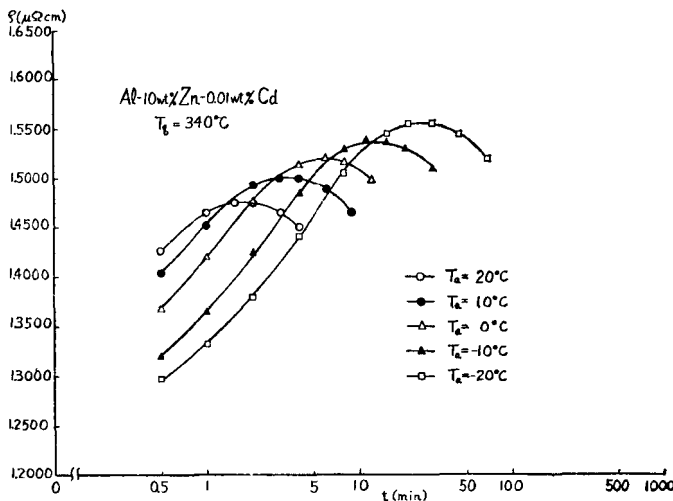


Fig. 2 Isothermal aging curves of Al-10wt%Zn-0.01wt%Cd ternary alloy at several temperatures after quenching from  $340^\circ\text{C}$ .

ry alloys at  $10^\circ\text{C}$  after quenching from  $340^\circ\text{C}$  are shown in Fig. 1. The electrical resistivity increase initially, reaches a maximum value and then decreases. In Al-Zn binary alloy and Al-Zn base ternary alloys, the form of curves obtained are quite similar and the increment of electrical resistivity in all curves are about  $240 \text{ m}\mu\Omega\text{cm}$ . If there were the interaction between an atom of second element and an atom of third element, the form of isothermal aging curves might be different from that for the binary alloy. Therefore, these facts show that an atom of second element does not interact with an atom of third element in these ternary alloys.

Isothermal aging curves of Al-10wt%Zn-0.01wt%Cd and Al-10wt%Zn-0.01wt%In ternary alloys at several aging temperatures after quenching from  $340^\circ\text{C}$  are shown in Fig. 2 and Fig. 3, respectively. Also, the similar aging curves were obtained for Al-10wt%Zn-0.01wt%Sn ternary alloy.

The influence of addition of cadmium, indium and tin in Al-Zn binary alloy can be seen in Fig. 4, where  $\log t_M$  are plotted against the reciprocal of aging temperature  $T_a$ . From these results the activation energies of clustering in Al-10wt%Zn binary alloy, Al-10wt%Zn-0.01wt%Cd, Al-10wt%Zn-0.01wt%In and Al-10wt%Zn-0.01wt%Sn ternary alloys are estimated to be about 0.43, 0.45, 0.57, and 0.63 eV, respectively.

Isothermal aging curves of Al-3.0wt%Ag binary alloy, Al-3.0wt%Ag-0.01wt%Cd, Al-3.0wt%Ag-0.01wt%In and Al-3.0wt%Ag-0.01wt%Sn ternary alloys at  $-10^\circ\text{C}$  after quenching from  $320^\circ\text{C}$  are shown in Fig. 5.

Isothermal aging curves of Al-3.0wt%Ag-0.01wt%Cd ternary alloy at the several aging temperatures after quenching from  $320^\circ\text{C}$  are shown in Fig. 6. The similar aging curves in Al-3.0wt%Ag-0.01wt%In and Al-3.0wt%Ag-0.01wt%Sn ternary alloys were obtained<sup>(16)</sup>. From Fig. 5

and 6, it seems that the behaviours of clustering of Al-Ag alloys are quite similar to those of Al-Zn alloys.

The influence of addition of cadmium, indium and tin in Al-Ag binary can be seen in Fig. 7, where  $\log t_M$  are plotted against the reciprocal of the aging temperature  $T_a$ . It seems that these plots for each alloy lie on approximately straight lines. From these results the activation energies of clustering in Al-3.0wt%Ag binary alloy, Al-3.0wt%Ag-0.01wt%Cd, Al-3.0wt%Ag-0.01wt%In and Al-3.0wt%Ag-0.01wt%Sn ternary alloys are estimated to be about 0.50, 0.53, 0.63, and 0.64 eV, respectively.

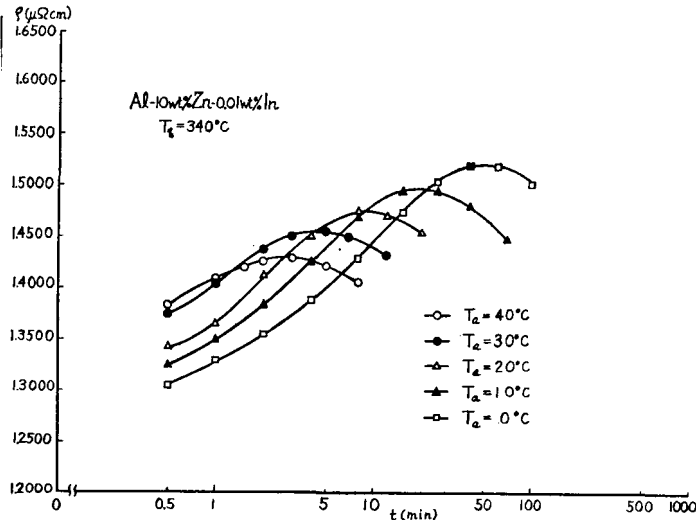


Fig. 3 Isothermal aging curves of Al-10wt%Zn-0.01wt%In ternary alloy at several temperatures after quenching from 340°C.

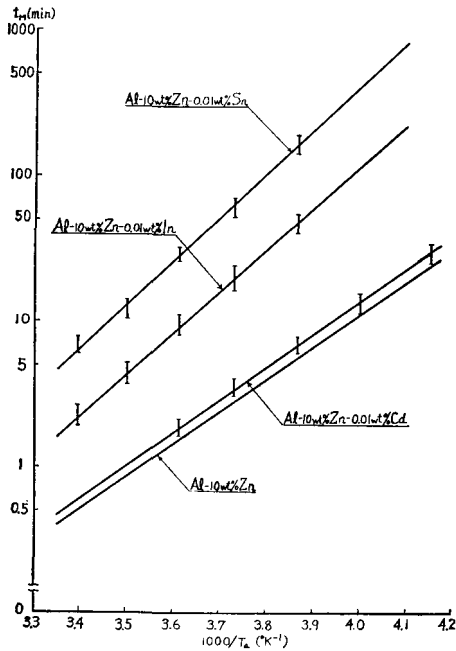


Fig. 4 Logarithmic plotting of  $t_{0r}$  of Al-10wt%Zn binary alloy, Al-10wt%Zn-0.01wt%Cd, Al-10wt%Zn-0.01wt%In and Al-10wt%Zn-0.01wt%Sn ternary alloys after quenching from 340°C against the reciprocal of absolute aging temperature  $T_a$ .

According to DeSorbo, Treafitis and Turnbull<sup>(17)</sup> the change of electrical resistance due to clustering of copper atoms in Al-Cu alloy is

$$\Delta R = \frac{1}{b} \log(a + bt) \quad (2)$$

where  $\Delta R$  is the change of electrical resistance due to clustering of copper atoms,  $a$  and  $b$

constants, and  $t$  the aging time. Fig. 8 shows an example of the results observed on an Al-3.0wt%Cu binary alloy quenched from 530°C and aged at 0°C. A similar relation was found for Al-Cu-Cd and Al-Cu-In ternary alloys. Fig. 9 shows an example for an Al-3.0wt%Cu-0.01wt%Cd ternary alloy quenched from 530°C and aged at 0°C, while Fig. 10 shows an example for an Al-3.0wt%Cu-0.01wt%In ternary alloy quenched from 530°C and aged at 0°C. Curves in these figures were calculated according to Eq. (2).

It is known that the initial rate of aging is proportional to the initial concentration of quenched-in vacancies banded to copper atoms and the aging temperature as well. Therefore, the comparison of initial rates of aging between Al-Cu alloy and Al-Cu-X alloys would make possible to examine the interaction between an X atom and a vacancy, i. e., the effect of additional X to the Al-Cu alloy, when the quenching temperature and the aging temperature are identical for both alloys. The initial rate of clustering is given as follows:

$$\frac{1}{R_0} \left( \frac{dR}{dt} \right)_{t=t_0} = \frac{1}{R_0} \frac{1}{a + bt} \quad (3)$$

where  $R_0$  is the resistance of a specimen which is properly quenched and does not contain any cluster and  $t_0$  is the time of the above mentioned quenching. It is necessary to know  $R_0$  and  $t_0$  in order to obtain the initial rate of clustering. However, it appears impossible to obtain these values experimentally. Furthermore, it is very

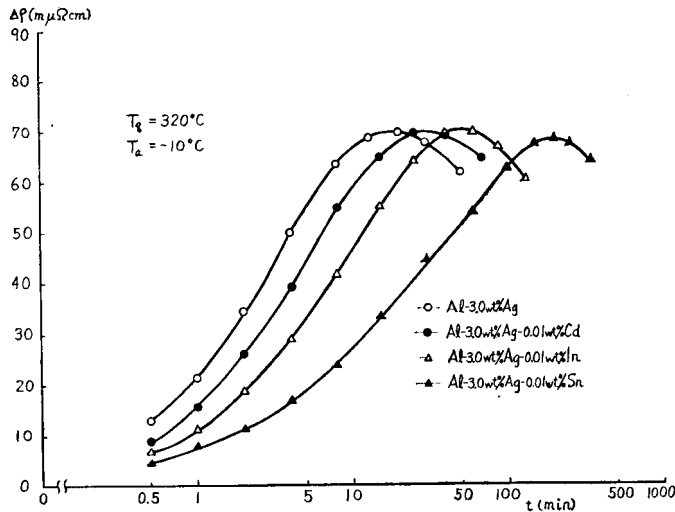


Fig. 5 Isothermal aging curves of Al-3.0wt%Ag binary alloy, Al-3.0wt%Ag-0.01wt%Cd, Al-3.0wt%Ag-0.01wt%In and Al-3.0wt%Ag-0.01wt%Sn ternary alloys at  $-10^{\circ}\text{C}$  after quenching from  $320^{\circ}\text{C}$ .

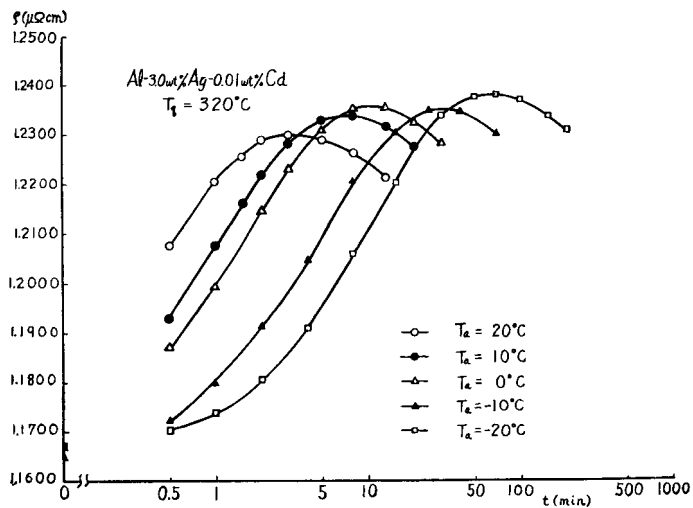


Fig. 6 Isothermal aging curves of Al-3.0wt%Ag-0.01wt%Cd ternary alloy at several temperatures after quenching from  $320^{\circ}\text{C}$ .

difficult to estimate these values from the known parameters, because of unknown contributions of copper-vacancy, X-vacancy, X-copper pairs, and clusters to the resistance during quenching. Kimura, Kimura and Hasiguti<sup>(1)</sup> assumed  $R_0$  to be an intermediate value between the as-quenched value and the value after reversion of the low temperature aging, and extrapolated resistance versus time curves to  $R_0$  in order to obtain  $t_0$ . In the present investigation, the as-quenched value of resistance was regarded as  $R_0$ . Of course, these values must correspond to the condition containing a small number of clusters, and the initial rate of aging

determined from the Eq. (3),  $R_0$ , and  $t_0$  determined by these assumptions correspond to the rate at a little later stage of aging.

The influence of addition of cadmium and indium in Al-Cu binary alloy can be seen in Fig. 11, where the logarithms of initial rate are plotted against the reciprocal of the aging temperature  $T_a$ . From these results the activation energies of clustering in Al-3.0wt%Cu binary alloy, Al-3.0wt%Cu-0.01wt%Cd and Al-3.0wt%Cu-0.01wt%In ternary alloys are estimated to be about 0.42, 0.54 and 0.56 eV, respectively.

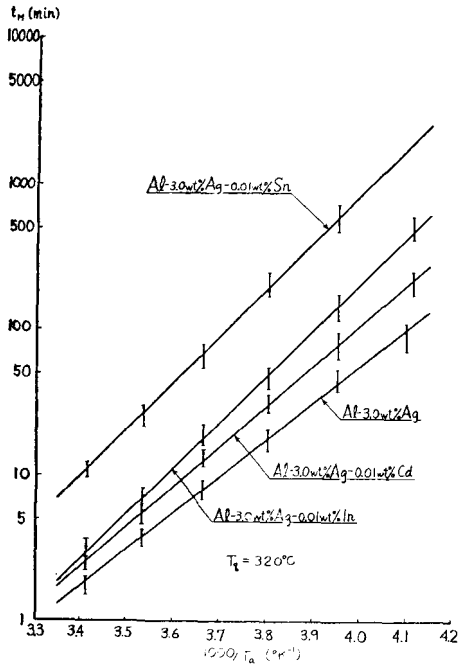


Fig. 7 Logarithmic plotting of  $t_m$  of Al-3.0wt%Ag binary alloy, Al-3.0wt%Ag-0.01wt%Cd, Al-3.0wt%Ag-0.01wt%In and Al-3.0wt%Ag-0.01wt%Sn ternary alloys after quenching from 320°C against the reciprocal of absolute aging temperature  $T_a$ .

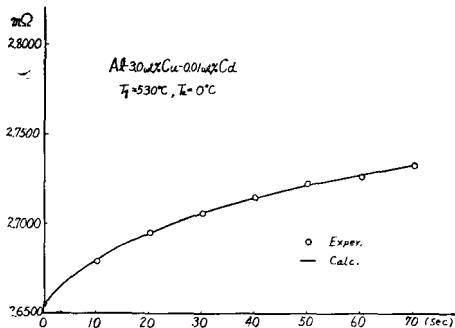


Fig. 8 Isothermal aging curve of Al-3.0wt%Cu binary alloy at 0°C after quenching from 530°C.

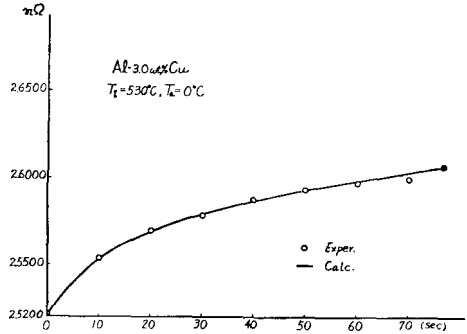


Fig. 9 Isothermal aging curve of Al-3.0wt%Cu-0.01wt%Cd ternary alloy at 0°C after quenching from 530°C.

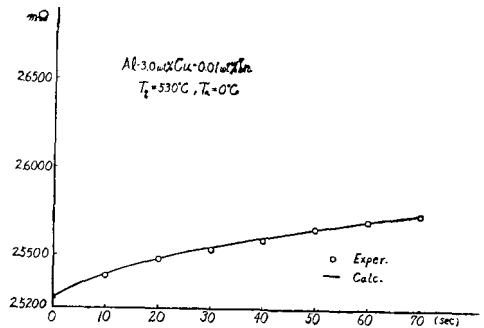


Fig. 10 Isothermal aging curve of Al-3.0wt%Cu-0.01wt%In ternary alloy at 0°C after quenching from 530°C.

§ 4. Discussion

4. 1. Al-Zn base alloys

As shown in Fig. 1, the form of aging curves of ternary alloy are quite similar to those of the binary alloy and the increment of resistivity in ternary alloys are about the same value as that of each binary alloy. These facts are considered to show that general features of clustering in the ternary and binary alloys are same. If so it might be possible to obtain some informations concerning the interaction between an atom of

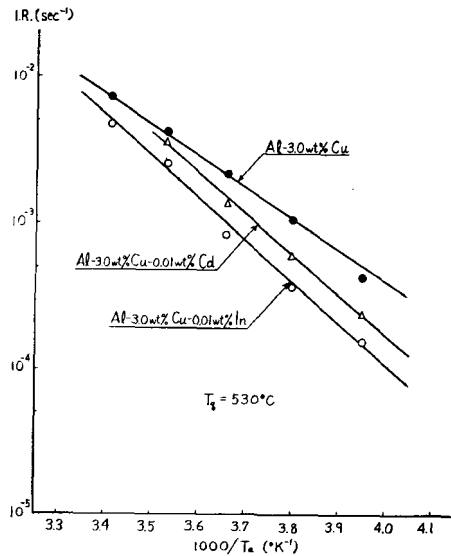


Fig. 11 Logarithmic plotting of initial rate of Al-3.0wt%Cu binary alloy, Al-3.0wt%Cu-0.01wt%Cd and Al-3.0wt%Cu-0.01wt%In ternary alloys after quenching from 530°C against the reciprocal of absolute aging temperature  $T_a$ .

third element and a vacancy.

The experimental results in Fig. 1, Fig. 2 and Fig. 3 can be explained, if it is assumed that all zones have about the same radius at every instance and grow with the same rate or, in other word, that zones all begin to grow at the same time after quenching and grow with the same rate during the isothermal aging and the number of zones is increased when aging temperature is lowered. And furthermore it is assumed that the total number of jumps made by zinc atoms until the maximum value of electrical resistivity being reached are always equal and independent of the aging temperature, since radius of zones at maximum resistivity is constant and independent of aging temperature and the stability of zones will decrease when the temperature is raised.

In a previous paper<sup>(10)</sup>, it was shown that the ratio of time,  $t_{Mt}$ , required to reach the maximum of electrical resistivity in isothermal aging curves of Al-Zn base ternary alloy to that time,  $t_{Mb}$ , in the binary alloy might be inversely proportional to the ratio of concentration of vacancies bound to zinc atoms,  $C'_{vt}$ , immediately after quenching in the ternary alloy to that concentration,  $C'_{vb}$ , in the binary alloy, when an atom of third element did not interact with zinc atom. That is

$$\frac{C'_{vb}}{C'_{vt}} = \left[ \frac{1 - \frac{12C_2\{1 - \exp(B_2/kT_a)\}}{1 - 12C_1\{1 - \exp(B_1/kT_a)\}}}{1 - \frac{12C_2\{1 - \exp(B_2/kT_q)\}}{1 - 12C_1\{1 - \exp(B_1/kT_q)\}}} \right] \frac{t_{Mt}}{t_{Mb}} \quad (4)$$

where  $C_1$  and  $C_2$  are the atomic fraction of second element and third element, respectively,  $B_1$  and  $B_2$  are the binding energy between an atom of second element and an atom of third element and a vacancy, respectively,  $k$  is Boltzmann constant,  $T_q$  is the quenching temperature and  $T_a$  is the aging temperature. All entropy terms are assumed to be unity.

If the third element was added and an atom of it did not interact with a zinc atom, it would be possible to estimate the binding energy between a vacancy and an atom of third element from Eq. (4). Therefore, it is necessary to know whether an atom of third element interact with a zinc atom or not. There are no precise method to decide whether there is interaction or not. For convenience, it is assumed that there is no interaction when the shape of isothermal aging

curve and the increment of resistivity at maximum point under the same condition of heat treatments are same as those for the binary alloy. This assumption might be reasonable, because it was considered that the shape or the increment would be different from those for the binary alloy if there was interaction. For example<sup>(18)(19)</sup>, the isothermal aging curves for Al-10wt%Zn-0.13wt%Mg ternary alloy show two stages, namely, the small convex part appears before reaching the maximum of resistivity and the increment of resistivity becomes larger than that for Al-10wt%Zn binary alloy. As shown in Fig. 1 the form of curves for Al-10wt%Zn-0.01wt%Cd, Al-10wt%Zn-0.01wt%In, and Al-10wt%Zn-0.01wt%Sn ternary alloys are quite similar to those of Al-10wt%Zn binary alloy and the maximum increments of electrical resistivity in all curves are about the same. These facts are considered to show that the general features of clustering in the both ternary and binary alloys are same, that is, electrical resistivity increment depends upon the spherical zones which are the same as those in Al-Zn alloy.

If the atom of a third element does not interact with the zinc atom to form pair, it will be possible to apply Lomer's formula<sup>(20)</sup> to the case of ternary alloys, and the concentration of vacancies,  $C_{vt}$ , at the quenching temperature will be as follows:

$$C_{vt} = \exp(-E_f/kT_q) \{ 1 - 12(C_1 + C_2) + 12C_1 \exp(B_1/kT_q) + 12C_2 \exp(B_2/kT_q) \} \quad (5)$$

where  $E_f$  is the energy of formation of vacancy in the pure aluminium. Furthermore, all entropy terms are assumed to be unity, since they are 1~10 and their effect on the final results is not so large. If all vacancies are frozen-in at their concentration by quenching and are bound to atoms of third element immediately after quenching, the concentration of vacancies bound to zinc atoms,  $C'_{vt}$ , will be given as follows

$$C'_{vt} \approx \left[ \frac{C_1}{C_2} \exp(-\Delta B/kT_a) / \left\{ 1 + \frac{C_1}{C_2} \exp(-\Delta B/kT_a) \right\} \right] C_{vt} \quad (6)$$

where  $\Delta B$  the difference between binding energies of a vacancy with an atom of third element and that with a zinc atom, i. e.  $B_2 - B_1$ .

In Fig. 12, the concentration of vacancies bound to zinc atoms calculated from Eq. (6) are

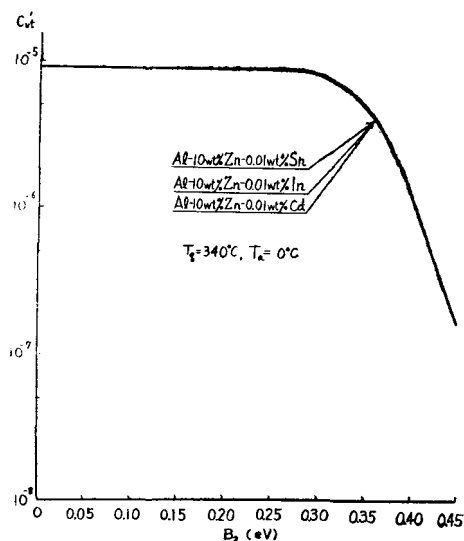


Fig. 12 Change of concentration of vacancies bound to zinc atoms with change of binding energies between an atom of third element (Cd, In or Sn) and a vacancy. Following values were used:  $E_f=0.76$  eV,  $B_1=0.18$  eV,  $T_q=613^\circ\text{K}$  and  $T_a=273^\circ\text{K}$ .

plotted for Al-10wt%Zn-0.01wt%Cd, Al-10wt%Zn-0.01wt%In and Al-10wt%Zn-0.01wt%Sn ternary alloys against the binding energy between an atom of third element and a vacancy. For calculation, the following values were used;  $E_f=0.76$  eV,  $B_1=0.18$  eV,  $T_q=613^\circ\text{K}$  and  $T_a=273^\circ\text{K}$ . Binding energies between a vacancy and a cadmium, indium or tin atom are determined from the points in these curves which are equivalent to the value  $t_{M0}/t_{M1}$ . According to these procedures, the binding energies between a vacancy and a cadmium, indium and tin atom in Al-10wt%Zn alloy were obtained as  $0.32 \pm 0.05$ ,  $0.39 \pm 0.05$  and  $0.43 \pm 0.05$  eV, respectively.

#### 4. 2. Al-Ag base alloys

In the studies of Al-Zn base alloys, an experiment of Al-10wt%Zn-0.13wt%Ag ternary alloy was carried out<sup>(11)</sup>. The form of aging curves, the time required to reach the maximum resistivity and the activation energy of clustering are quite similar to those for Al-10wt%Zn binary alloy and not affected by the addition of  $\sim 0.1$  wt%Ag. From these results, it was considered that one of the two following cases might be possible: (1) silver atom do not exist as isolated atoms in the solid solution and the binding energy between a vacancy and a silver atom is

now unconcerned for clustering process, or (2) the binding energy between a vacancy and a silver atom is not so large and possibly smaller than about 0.23 eV (the binding energy between a zinc atom and a vacancy in eV + 0.05 eV).

In the both Al-Ag and Al-Zn binary alloys, the spherical zones are formed, and their size is of the same order when aged at room temperature. Furthermore, the behaviours of reversion are quite similar. Thus, the behaviours of clustering of Al-Ag binary alloy are quite similar to those of Al-Zn binary alloy. Therefore, it is considered that the binding energy between a vacancy and a silver atom,  $B_1$ , can be obtained using Eq. (4), when the binding energy between a vacancy and an atom of third element is known and fairly large.

As shown in Fig. 5, the forms of curves for Al-3.0wt%Ag-0.01wt%Cd, Al-3.0wt%Ag-0.01wt%In and Al-3.0wt%Ag-0.01wt%Sn ternary alloys are quite similar to those of Al-3.0wt%Ag binary alloy and the maximum increments of electrical resistivity in all curves are about the same. These facts are considered to show that the general features of clustering in the both ternary and binary alloys are same and there is no interaction between silver atoms and atoms of third element.

Therefore, the binding energy between a vacancy and a silver atom can be obtained using Eq. (4), since the binding energy between a vacancy and an indium atom or a tin atom are known as 0.39 or 0.43 eV, respectively<sup>(10)(13)</sup>. From these results, the binding energy between a vacancy and a silver atom was estimated to be  $0.25 \pm 0.05$  eV<sup>(16)</sup>.

Next, conversely, if 0.25 eV was used as the binding energy between a vacancy and a silver atom, the binding energy between a vacancy and a cadmium atom can be estimated. In Fig. 13, the concentration of vacancies bound to silver atoms calculated from Eq. (6) are plotted for Al-3.0wt%Ag-0.01wt%Cd ternary alloys, against the binding energy between an atom of third element and a vacancy. For the calculation, following values were used:  $E_f=0.76$  eV,  $B_1=0.25$  eV,  $T_q=593^\circ\text{K}$  and  $T_a=273^\circ\text{K}$ . Binding energy between a vacancy and a cadmium atom can be determined from the same procedures as in the case of Al-Zn base ternary alloys. As the result, the binding energy between a vacancy and a cadmium atom in Al-3.0wt%Ag alloy was obtained as  $0.32 \pm 0.05$  eV.



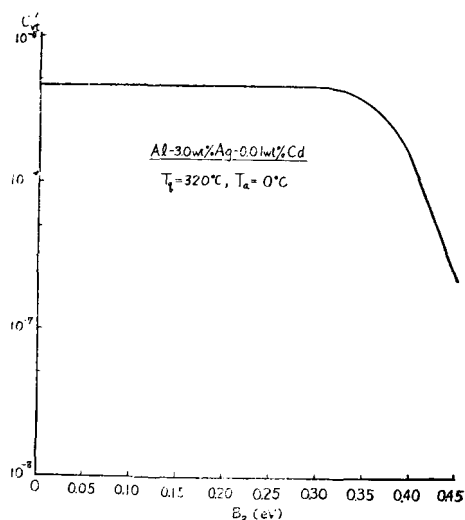


Fig. 13 Change of concentration of vacancies bound to silver atoms with change of binding energies between a cadmium atom and a vacancy. Following values were used:  $E_f=0.76$  eV,  $B_1=0.25$  eV,  $T_q=593^\circ\text{K}$  and  $T_a=273^\circ\text{K}$ .

#### 4. 3. Al-Cu alloys

The increase of resistance in the initial stage of aging of these alloys has generally been attributed to scattering of conduction electrons by lattice distortion due to the G. P. zone themselves, but the details are not clearly known for the present alloys. However, it might be possible to neglect the effect of lattice distortion in the initial stage of clustering. If the same type of G. P. zones are formed in the present alloys, it will be possible to consider that the mechanism of the increase of resistance is same for these alloys. It is shown in Fig. 8, 9, and 10 that the initial clustering of the Al-Cu-Cd and Al-Cu-In ternary alloys can be expressed by the same equation as that in the Al-Cu binary alloy. Therefore, it would be possible to estimate the interactions between a cadmium atom or indium atom and a vacancy from the initial rates of increase of resistance in Al-Cu-Cd, Al-Cu-In ternary alloys and Al-Cu binary alloy.

When the aging temperature is identical for both alloys, it is considered that the initial rates of aging are proportional to the concentration of vacancies bound to copper atoms. The concentration of vacancies bound to copper atoms would decrease if an atom of a third element has a fairly large binding energy with a vacancy. Kimura, Kimura and Hasiguti<sup>(1)</sup> estimated the binding energy between a vacancy and a copper atom to be 0.2 eV. Therefore, all vacancies will

be bound to copper atoms at relatively low temperatures and Eq. (6) can be adopted.

In Fig. 14, the concentration of vacancies bound to copper atoms calculated from Eq. (6) are plotted for Al-3.0wt%Cu-0.01wt%Cd and Al-3.0wt%Cu-0.01wt%In ternary alloys, against the binding energy between an atom of third element and a vacancy. For the calculation,

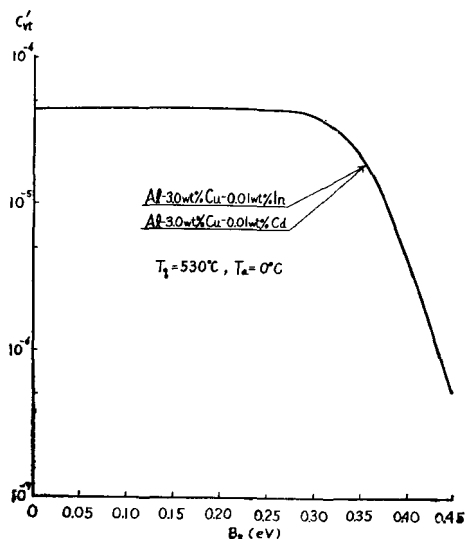


Fig. 14 Change of concentration of vacancies bound to copper atoms with change of binding energies between a cadmium atom or indium atom and a vacancy. Following values were used:  $E_f=0.76$  eV,  $B_1=0.20$  eV,  $T_q=803^\circ\text{K}$  and  $T_a=273^\circ\text{K}$ .

following values were used:  $E_f=0.76$  eV,  $B_1=0.2$  eV,  $T_q=803^\circ\text{K}$  and  $T_a=273^\circ\text{K}$ . Binding energies between a vacancy and a cadmium or indium atom are determined from the points in these curves which are equivalent to the ratio of initial rate of Al-Cu base ternary alloy to the initial rate of Al-Cu binary alloy. According to these procedures, the binding energies between a vacancy and a cadmium or indium atom in Al-3.0wt%Cu alloy are obtained as  $0.33 \pm 0.05$  and  $0.36 \pm 0.05$  eV, respectively.

#### 4. 4. Summary

Table 1 shows the binding energies between a vacancy and a cadmium, indium or tin atom in aluminium which were estimated using Al-Zn, and Al-Ag, and Al-Cu base ternary alloys. The values in parenthesis in this table are the binding energies used when the Ag-V binding energy was estimated and the value in the bracket is the binding energy obtained by

Table 1. Binding energies between a vacancy and a cadmium, indium or tin atom estimated using Al-Zn, Al-Ag and Al-Cu base ternary alloys.

	Cd	In	Sn
Al-Zn-	$0.32 \pm 0.05$	$0.39 \pm 0.05$	$0.43 \pm 0.05$
Al-Ag-	$0.34 \pm 0.05$	$(0.39 \pm 0.05)$	$(0.43 \pm 0.05)$
Al-Cu-	$0.33 \pm 0.05$	$0.36 \pm 0.05$	[0.42]

#### Kimura and Hasiguti<sup>(5)</sup>.

It may be considered that the concentrations of zinc atom in Al-10wt%Zn binary alloy or Al-10wt%Zn base ternary alloys are a little high for Lomer's formula to be adopted. But as shown in Table 1 the Cd-V, In-V and Sn-V, binding energies estimated using Al-Zn, Al-Ag or Al-Cu base ternary alloys agree within experimental accuracy with each other. It is considered from these results that the method used for the case of Al-10%Zn base alloys are correct and the values of binding energies obtained correspond to the binding energies obtained from experiments for Al-X (X is the third element in this paper) binary alloys.

#### References

- 1) H. Kimura, A. Kimura and R. R. Hasiguti: *Acta Met.* 10 (1962) 607.
- 2) C. Panseri and T. Federighi: *Acta Met.* 8 (1960) 217.
- 3) H. Shimizu and J. Takamura: *Suiyokai-shi* 15 (1963) 95.
- 4) K. Okazaki and J. Takamura: *Suiyokai-shi* 15 (1963) 89.
- 5) H. Kimura and R. R. Hasiguti: *Proc. Int. Conf. Crys. Latt. Def.* (1962) *J. Phys. Soc. Japan* 18 Suppl. 111 (1963) 73.
- 6) D. R. Beaman, R. W. Balluffi and R. O. Simmons: *Phys. Rev.* 134 (1964) A 532.
- 7) D. R. Beaman, R. W. Balluffi and R. O. Simmons: *Phys. Rev.* 137 (1965) A 917.
- 8) C. Panseri and T. Federighi: *Acta Met.* 11 (1963) 575.
- 9) J. Takamura, K. Okazaki and I. G. Greenfield: *Proc. Int. Conf. Crys. Latt. Def.* (1962) *J. Phys. Soc. Japan* 18 Suppl. 111 (1963) 78.
- 10) F. Hashimoto and M. Ohta: *J. Phys. Soc. Japan* 19 (1964) 1331.
- 11) M. Ohta and F. Hashimoto: *J. Phys. Soc. Japan* 19 (1964) 133.
- 12) F. Hashimoto and M. Ohta: *J. Phys. Soc. Japan* 19 (1964) 1501.
- 13) M. Ohta and F. Hashimoto: *J. Phys. Soc. Japan* 19 (1964) 1987.
- 14) M. Ohta: *Trans. Japan Inst. Metals* 6 (1965) 4.
- 15) M. Ohta and F. Hashimoto: *Trans. Japan Inst. Metals* 6 (1965) 9.
- 16) F. Hashimoto: *J. Phys. Soc. Japan* 20 (1965) 336.
- 17) W. DeSorbo, H. N. Treafis and D. Turnbull: *Acta Met.* 6 (1958) 401.
- 18) M. Ohta and F. Hashimoto: *J. Phys. Soc. Japan* 19 (1964) 130.
- 19) M. Ohta and F. Hashimoto: *J. Phys. Soc. Japan* 19 (1964) 1337.
- 20) W. L. Lomer: *Inst. of Metals, Monograph and Report Series, London*, 23 (1958) 85.