MEMOIRS OF THE SCHOOL OF ENGINEERING, OKAYAMA UNIVERSITY, Vol. 3, No. 1, SEPTEMBER, 1968

Binding Energy between a Vacancy and an Atom of Third Element and their Effects on the Initial Aging of Aluminium Binary Alloys

Matsuo OHTA, Fumio HASHIMOTO and Tadashi TANIMOTO

Department of Iudustrial Science

(Received, March 15, 1968)

Al-Zn, Al-Ag and Al-Cu base ternary alloys were studied by measurement of electrical resistivity. An approximate methods to estimate the binding energy between an atom of a third element and a vacancy was derived. The binding energy between a vacancy and an atom of Cu, Ag, Au, Be, Ca, Cd, In, Si, Ti, Ge, Zr, Sn, Pb or Mn was estimated to be <0.23, $0.25,>$ 0.35, 0.28, 0.27, 0.32, 0.39, 0.28, 0.30, 0.33, 0.33, 0.43, >0.38 or <0.23 (± 0.05) eV, respectively. The results may be summarized as follows:

(1) The ratio of the time required to reach the maximum electrical resistivity in isothermal aging curves of the Al-Zn-X or Al-Ag-X ternary alloy to that in the Al-Zn or Al-Ag binary alloy may be inversely proportional to the ratio of the concentration of vacancies bound to Zn or Ag atoms immediately after quenching in the ternary alloy to that in the binary alloy. And also the ratio of initial rate of clustering for Al-Cu-X ternary alloy to that in the binary alloy may be inversely proportional to the ratio of the concentration of vacancies bound to Cu atoms immediately after quenching in the ternary alloy to that in the binary alloy. It is possible to deduce the binding energy between an atom of X element and a vacancy using this relations.

(2) The effect of the valence of the solute element on the binding energy between an atom of a third element and a vacancy was remarkable.

(3) The effect of the radius of an atom of the solute element on the binding energy is also observed, but this effect is smaller than that of the valence.

§ 1. Introduction

There are many investigation on the mechanism of aging in various alloys quenched from a high temperature, dealing mainly with binary alloys. The sequence of precipitation, mechanism of hardening, change of physical properties and factors governing these changes are known, and the role of frozen-in vacancies are also discussed by many authors. Furthermore, there are many works on the effect of a third element, but most of them are related to the change in properties, crystal structures and sequence of precipitation. However, it is obvious that frozen-in vacancies must also play an important role in these cases, though the situation may become more complex owing to the presence of a third element.

Kimura and Hasiguti[1] studied effects of the addition of Sn on the rate of aging in Al-Cu alloys, and succeeded in explaining a low rate of clustering of Cu atoms. They attributed this phenomenon to the decrease in the concentration of vacancies bound to Cu atoms due to a large binding energy between a Sn atom and a vacancy.

Effects of the addition of Mg on the rate of clustering of Zn atoms in Al-10 wt% Zn alloys were first studied by Panseri and Federighi[2]. They also attributed the low rate of clustering to a very large binding energy between an Mg atom and a vacancy (0.54 eV). However, there is some evidence which shows that the low rate of clustering does not depend upon the large binding energy between an Mg atom and a vacancy but upon the formation of G. P. zones which are different from those in Al-Zn binary alloys[3,4]. Bartsch[5] also published similar results which could be atributed to the presence of an other type of G. P. zones.

Panseri and Federighi replied to Bartsch's paper in Acta Met.[6], but they did not refer to any new experimental results or new interpretations. It may not be suitable to explain the low rate of clustering of Zn atoms in Al-Zn-Mg alloys by the large binding energy between an Mg atom and a vacancy.

As shown by one of the present authors[7,8] in the case of low temperature aging in Al-Cu-Mn alloys, the effect of a third element on the rate of clustering of atoms of the main solute element will be large when the binding energy between an atom of main solute element and a vacancy, B_1, is small. Since the binding energy between a Cu atom and a vacancy is estimated to be 0.2 eV by Kimura et al.[9], it is impossible to estimate the value of binding energy between an atom of a third element and a vacancy which is smaller than about 0.25 eV[7]. Therefore, the use of alloys whose main solute atom has a small binding energy with a vacancy is more favorable to study the binding energy between an atom of a third element and a vacancy.

Panseri and Federighi[10] studied the initial stage of low temperature aging in Al-10wt%Zn alloy resistometrically, and estimated the value of binding energy between a Zn atom and a vacancy to be 0.06 eV. On the other hand, Shimizu and Takamura[11] estimated this value to be 0.18 eV which would be a more reliable value.

Baur and Gerold[12] studied an Al-Ag binary alloy by measuring scattering of X-ray by zones at small angle range and estimated the binding energy between a vacancy and an Ag atom as <0.4 eV. Recently Beaman, Balluffi and Simmons[13] studied dilute Al-Ag alloys. They measured the equilibrium vacancy concentration at high temperatures and estimated the binding energy between a vacancy and an Ag atom as 0.08 eV.

In the present paper, the results on Al-Zn-X, Al-Ag-X and Al-Cu-X ternary alloys*) are summarized and the effects of small amount of Cu, Ag, Be, Ca, Cd, In, Si, Ti, Ge, Zr, Sn, Pb and Mn on the clustering of Zn, Ag and Cu atoms in Al-Zn, Al-Ag and Al-Cu binary alloys and the binding energy between an atom of these elements and a vacancy are discussed.

§ 2. Binding Energy

As shown by Kimura and Hasiguti[1], the initial rate of clustering of main solute atoms is decreased by addition of a third element having a large binding energy with a vacancy, since the concentration of vacancies bound to Cu atoms is decreased by the absorption of them by atoms of a third element. Therefore, it is necessary to measure the initial rate of aging. However, it is not very easy to determine the initial rate of aging even when the experimental equation for relations between the change in suitable property and time is known as in the Al-Cu alloy. Clustering of solute atoms during quenching cannot be avoided and the earliest stage of aging is hardly observable in practive. In Al-Zn and Al-Ag alloys, since such a experimental equation is not known, it will be more difficult to measure the initial rate of aging.

During the low temperature aging of Al-Zn binary alloys, the electrical resistivity increases until it reaches a maximum value, and then decreases. When the maximum value has been reached, the radius of zones is about 8 Å[22,23] and is independent of the aging temperature. On the other hand, the maximum value increases as the aging temperature decreases. Therefore, it may be reasonably assumed that the number of zones is increased when the aging temperature is decreased and the total number of jumps by Zn atoms until the resistivity attained a maximum is always equal and independent of the aging temperature, since the stability of zones decreases with temperature. Then the time required to attain the maximum value of resistivity, t_M, may be a measure of the concentration of vacancies bound to Zn atoms immediately after quenching. Thus, by comparing t_M for the ternary alloy, t_{Mt}, with that for the binary alloy, t_{Mb}, it will be possible to estimate the binding energy between an atom of a third element and a vacancy. The details are as follows:

In the binary alloy at the quenching temperature, T_q, the concentration of vacancies C_{vb}, is given as follows:[24]

$$C_{vb} = \exp(-E_f/kT_q)\{1 - zc_1 + zc_1 \exp(B_1/kT_q)\}, \quad (1)$$

where E_f is the energy of formation of vacancies in pure metal (Al), c_1 the concentration of solute element, z the co-ordination number and k Boltzmann's constant. All entropy terms are assumed to be unity. This

equation can be used when zc_1 is smaller than unity.

If main solute atoms do not interact with atoms of a third element in ternary alloys, equation (1) can be applied to ternary solid solution. Hence, the total concentration of vacancies at the quenching temperature will be

$$C_{vt} = \exp(-E_f/kT_q)[1-z(c_1+c_2) + \{c_1\exp(B_1/kT_q)+c_2\exp(B_2/kT_q)\}], \quad (2)$$

where B_2 is the binding energy between an atom of a third element and a vacancy, and c_2 the concentration of a third element. Of course, if main solute atoms interact with atoms of a third element, equation (2) cannot be used.

Since C_{vb} and C_{vt} in equation (1) and (2) are total equilibrium concentrations of vacancies at the quenching temperature, T_q, these vacancies must be frozen-in by quenching. However, there will be a difference in the distribution of vacancies between the nearest neighbouring sites of solute atoms and the sites apart from solute atoms during quenching, even if the quenching rate is fairly high and the total concentration of vacancies is not changed. If the distribution of vacancies reached equilibrium at the aging temperature, T_a, without any loss of the total concentration of vacancies, the concentration of vacancies bound to main solute atoms, C'_{vt}, may be written as follows:

$$C'_{vt} = \{zc_1\exp(B_1/kT_a)C_{vt}\}/[1-z(c_1+c_2) +z\{c_1\exp(B_1/kT_a)+c_2\exp(B_2/kT_a)\}]. \quad (3)$$

If values of B_1 and B_2 are not very small, the redistribution of vacancies will occur quickly, and it may be reasonably assumed that this distribution is practically attained immediately after quenching. In equation (3), free vacancies which are not bound to main solute atoms or atoms of a third element are considered, but when B_1 and B_2 are not very small, the concentration of these free vacancies are very low. Hence,

$$C'_{vt} \simeq \{(c_1/c_2)\exp(-\Delta B/kT_a)C_{vt}\}/\{1+(c_1/c_2)\exp(-\Delta B/kT_a)\}, \quad (4)$$

where $\Delta B = B_2 - B_1$.

When aging treatments are performed, main solute atoms which are bound to vacancies can migrate and most of them will cluster into G. P. zones, while free vacancies will jump at random and some of them will disappear at sinks. It is assumed that only free vacancies do not disappear. The concentration of free vacancies immediately after quenching in the ternary alloy, C''_{vt}, is

$$C''_{vt} = \{1-z(c_1+c_2)\}C_{vt}/[1-z(c_1+c_2) +z\{c_1\exp(B_1/kT_a)+c_2\exp(B_2/kT_a)\}] \equiv \gamma C_{vt}. \quad (5)$$

Then the concentration of vacancies which dissappear one second after quenching may be approximately written as

$$\alpha\nu\lambda^2\exp(-E_m/kT_a)C''_{vt} \equiv K\gamma C_{vt}, \quad (6)$$

where E_m is the activation energy of migration of vacancy, α the vacancy sink concentration of about 10^{10} cm^{-2}, ν the vibration frequency of about 10^{13} and λ 10^{-15} cm^2. Then the total concentration of vacancies after aging of one second is approximately

$$C_{vt} - C''_{vt}K = (1-\gamma K)C_{vt}. \quad (7)$$

Since $\gamma K \ll 1$, the total concentration of vacancies after aging of n seconds can be written as

$$C_{vt}(1-\gamma K)^n \simeq (1-n\gamma K)C_{vt}. \quad (8)$$

Then, the concentration of vacancies bound to main solute atoms after annealing for n seconds, $C'_{vt}(n)$, is

$$C'_{vt}(n) \simeq (1-n\gamma K)C'_{vt}. \quad (9)$$

It t_{Mt} is equal to n, the number of total jumps made by main solute atoms is approximatetly

$$N = \sum_{n=0}^{t_{Mt}} C'_{vt}(n)\exp(-E'_m/kT_a) \simeq C'_{vt}\exp(-E'_m/kT_a)\sum_{n=0}^{t_{Mt}}(1-n\gamma K) \simeq C'_{vt}\exp(-E'_m/kT_a)\frac{2-(t_{Mt}-1)\gamma K}{2}t_{Mt}, \quad (10)$$

where E'_m is the activation energy of migration of a main solute atom.

For binary alloys, N can be obtained in the same way:

$$N \simeq C'_{vb}\exp(-E'_m/kT_a)\frac{2-(t_{Mb}-1)\gamma' K}{2}t_{Mb}, \quad (11)$$

where C'_{vb} is the concentration of vacancies bound to solute atoms immediately after

quenching in the binary alloy, γ' is a factor for the binary alloy corresponding to γ for the ternary alloy. In this equation, the number of total jumps of main solute atoms is equal to that in equation (10) according to the assumption. Dividing equation (10) by equation (11), one obtains

$$1 = \frac{C'_{vt}}{C'_{vb}} \cdot \frac{2-(t_{Mt}-1)\gamma K}{2-(t_{Mb}-1)\gamma' K} \cdot \frac{t_{Mt}}{t_{Mb}} . \qquad (12)$$

Here, γ and γ' are about 10^{-9}, K about 10^{-2}, t_{Mb} and t_{Mt} less than 10^3. Hence it will be reasonable to assume

$$\{2-(t_{Mt}-1)\gamma K\}/\{2-(t_{Mb}-1)\gamma' K\} \simeq 1.$$

Then

$$C'_{vt}/C'_{vb} = t_{Mb}/t_{Mt} . \qquad (13)$$

That is, the ratio of time required to reach the maximum resistivity for the ternary alloy to that for the binary alloy is inversely proportional to the ratio of the concentration of vacancies bound to main solute atoms in the ternary alloy to that in the binary alloy.

Practically, since B_1 is about 0.18 eV and B_2 is larger than B_1, equation (4) can be used. Plotting C'_{vt} against B_2, curves shown in Fig. 1 are obtained. If $B_2 = 0$, C'_{vt} is equal to C'_{vb}. From these curves and equation (13), it is possible to obtain B_2.

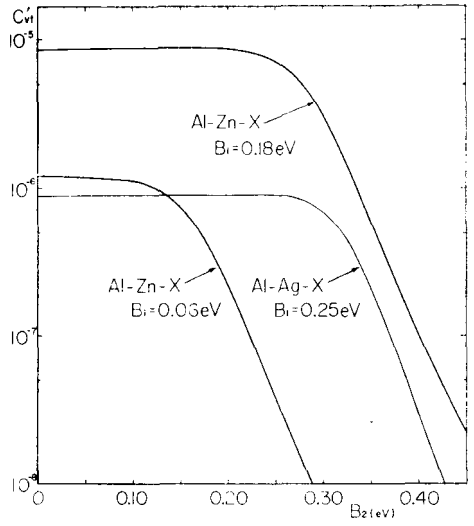

Fig. 1 Plotting of C'_{vt} for Al-Zn-X Al-Ag-X against B_2. The following values were used: T_q=613°K, T_a=273°K, B_1=0.06 or 0.18 eV, c_1=0.044, c_2=0.00064 for Al-Zn-X and T_q=593°K, T_a=273°K, B_1=0.25 eV, c_1=0.0018, c_2=0.000056 for Al-Ag-X.

In this method, the clusters formed during quenching will not have a great effect on the results obtained, if these clusters are of the same kind as those formed during aging, since the number of clusters formed quenching is small. Furthermore, it is assumed by the above mentioned method that the mechanism of diffusion was the same as those in the dilute solution despite of a little high concentration of main solute Zn atoms. However, the relation described in equation (13) may be justified since (1) the diffusion mechanisms of Zn atoms in binary and ternary alloys are considered to be the same, (2) the number and size of zones in both alloys are considered to be equal and (3) the ratio t_{Mt}/t_{Mb} is used. On the other hand, the redistribution of vacancies after quenching does not affect the results. Therefore, it is apparent that the results obtained by this method can be compared with those obtained by other methods, e.g., quenching experiments for binary alloys.

In 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 behaviours of clustering of Al-Ag binary alloys are quite similar to those of Al-Zn binary alloys. Therefore, it is considered that equation (13) can be also used in Al-Ag alloys and the binding energy between a vacancy and an Ag atom can be obtained by using equation (13), when the binding energy between a vacancy and an asom of thired element is known and fairly large.

According to DeSorbo, Treaftis and Turnbull[25] the change of electrical resistance due to clustering of Cu atoms in Al-Cu alloy is

$$\Delta R = \frac{1}{b} \log (a+bt) , \qquad (14)$$

where ΔR is the change of electrical resistance due to clustering of Cu atoms, a and b constants and t the aging time. From this equation we have

$$dt/dR = a+bt \qquad (15)$$

Thus, the reciprocal of the rate of changes in electrical resistance varies linearly with the aging time. It is known that the initial rate of aging is proportional to the initial concentration of quenched-in vacancies bound to Cu atoms and the aging temperature as well.

Therefore, comparison of the initial rates of aging between Al-Cu alloys and Al-Cu-X alloys would make it 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:

$$\frac{1}{R_0}\left(\frac{dR}{dt}\right)_{t=t_0} = \frac{1}{R_0} \cdot \frac{1}{a+bt} \qquad (16)$$

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 difficult to estimate these values from the known parameters, because of unknown contributions of Cu-vacancy, X-vacancy, X-Cu pairs and clusters to the resistance during quenching. Kimura et al.[9] 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 into 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 equation (16), R_0 and t_0 determined by these assumptions correspond to the rate at a little later stage of aging. The increase if resistance in the initial stage of aging of Al-Cu 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 both Al-Cu and Al-Cu-X alloys, it will be possible to consider that the mechanism of the increase of resistance is same for these alloys. 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 Cu atoms. The concentration of vacancies bound to Cu atoms would decrease if an atom of a third element has a fairly large binding energy with a vacancy. Kimura et al.[9] estimated the binding energy between a vacancy and a Cu atom to be 0.2 eV. Therefore, all vacancies will be bound to Cu atoms at relatively low temperatures. Therefore, it would be possible to estimate interactions between an X atom and a vacancy from the initial rates of increase of resistance in Al-Cu-X and Al-Cu alloys. Practically, since B_1 is about 0.2 eV and B_2 is larger than B_1, equation (4) can be used. Plotting C'_{vt} against B_2, curves shown in Fig. 2 are

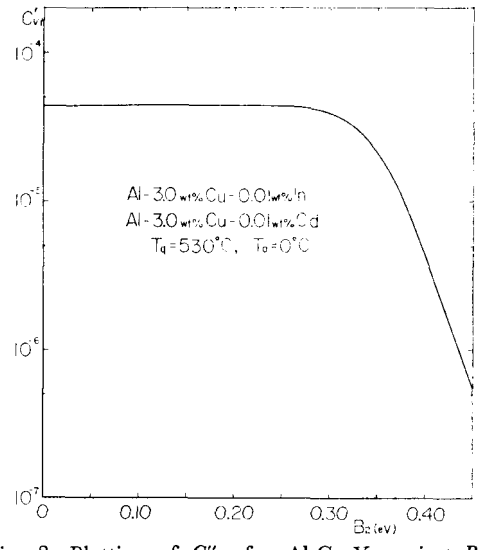

Fig. 2 Plotting of C''_{vt} for Al-Cu-X against B_2. The following values were used: $T_q = 803$°K, $T_a = 273$°K, $B_1 = 0.20$ eV, $c_1 = 0.013$, $c_2 = 0.000024$.

obtained. Binding energy between a vacancy and an X atom is determined from the point in this curve which is equivalent to the ratio of initial rate of Al-Cu-X ternary alloy to that of Al-Cu-binary alloy.

§ 3. Experimental Procedure

All alloys were made from 99.996% Al, 99.999%Zn, 99.99%Ag, 99.999%Cu and high purity elements. They were melt in a high alumina crucible altogether. The nominal weight compositions of alloys are shown in Table 1.

Ingots of 15mm in diameter were forged at about 400°C to 5mm thick sheets, and then cold rolled to the thickness of 0.4mm. The shape and size of the specimens were the same as those reported before[7].

The method of measurements were also the same as those reported before[26,27]. After measurements, the specimens were cut off from lead wire parts, and the length, thickness and weight of the specimens were measured. From these measurements, the electrical resisttvity was calcutated; the values were in fairly good agreement with those obtained by other authors.

Table 1. Nominal weight compositions of alloys used.

Alloys	Second Element (%)	Third Element (%)
Al-Zn-Cu	10	0.12
Al-Zn-Ag	10	0.13
Al-Zn-Au	10	0.008
Al-Zn-Be	10	0.0055
Al-Zn-Mg	10	0.13 or 0.3
Al-Zn-Ca	10	0.09
Al-Zn-Cd	10	0.01
Al-Zn-In	10	0.01
A-Zn-Si	10	0.1
Al-Zn-Ti	10	0.01
Al-Zn-Ge	10	0.12
Al-Zn-Zr	10	0.01
Al-Zn-Sn	10	0.01
Al-Zn-Pb	10	0.005
Al-Zn-Mn	10	0.3
Al-Ag-Cd	3	0.01
Al-Ag-In	3	0.01
Al-Ag-Ge	3	0.1
Al-Ag-Sn	3	0.01
Al-Ag-Ti	0.72	0.01
Al-Cu-Cd	3	0.01
Al-Cu-In	3	0.01

§ 4. Results

4. 1 Al-Zn base alloys

As mentioned in section **2**, in order to obtain the binding energy between an atom of a third element and a vacancy, it is essential that there should be no interaction between an atom of a third element and a main solute atom (Zn atom). There are no precise methods to decide the presence of the interaction. For convenience, it is assumed that there is no interaction when the shape of the isothermal aging curve and the increment of resistivity at the maximum point under the same condition of heat treatment are the same as those for the binary alloy. Since the shape or increment will be different if there is the interaction, this assumption might be reasonable.

Among fifteen kinds of the alloys, fourteen showed similar isothermal aging curves, and the increments in electrical resistivity equal to those for binary Al-10wt%Zn alloy. Fig. 3 and Fig. 4 show isothermal aging curves for alloys quenched from 340°C. All curves are concave upward in the initial stage, and the increment in electrical resistivity at the maximum point is nearly equal. From these and other (not shown here) results, the binding energies were estimated by the method mentioned above. That is, the binding energies between a vacancy and a Cu, Ag, Au, Be, Ca, Cd, In, Si, Ti, Ge, Zr, Sn, Pb or Mn atom were estimated to be <0.23, <0.23, >0.35, 0.28, 0.27, 0.32, 0.39, 0.28, 0.30, 0.33, 0.33, 0.43, >0.38 or 0.23($\pm$0.05) eV, respectively.

For three ternary alloys of Al-Zn-Cu, Al-Zn-Ag and Al-Zn-Mn, the shape of isothermal aging curves is quite similar to that for the Al-Zn binary alloy.

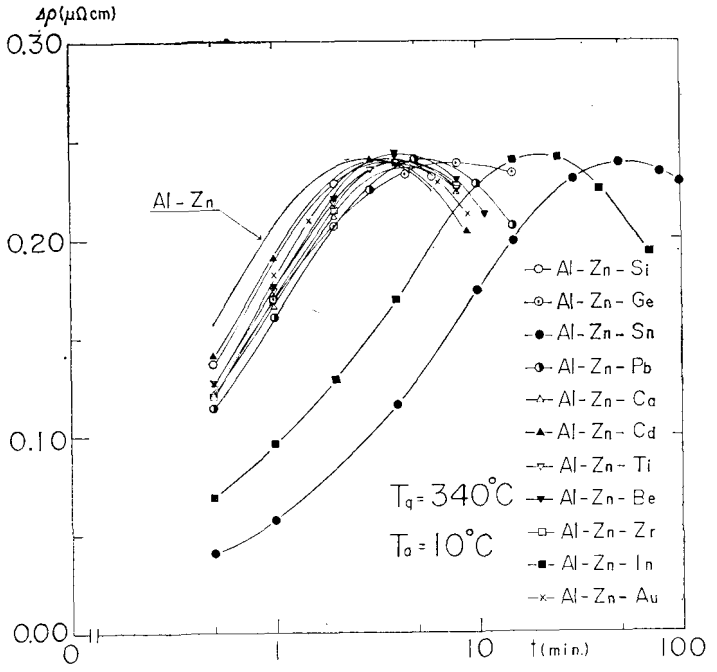

Fig. 3 Isothermal aging curves at 10°C after quenching from 340°C.

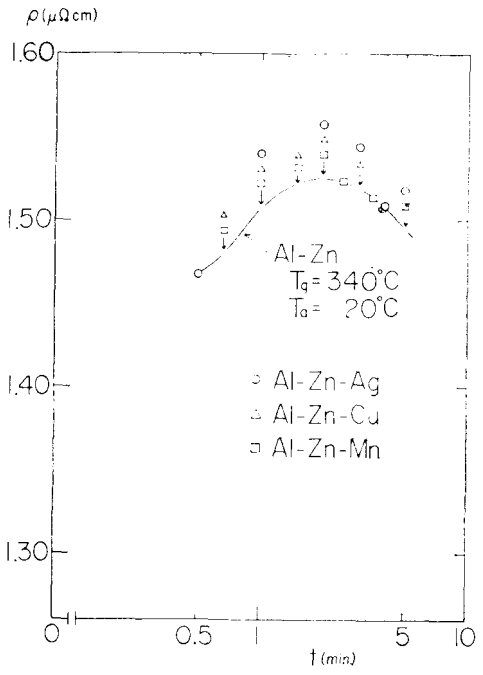

Fig. 4 Isothermal aging curves at 20°C after quenching from 340°C.

The increment in resistivity at the maximum point is equal to that for the binary alloy. However, t_{Mt} for these alloys is not changed by the addition of a third element, and $t_{Mt}/t_{Mb} = 1$. Therefore, it is impossible to estimate the value of B_2 when it is smaller than (B-0.05 eV). It is probable that the binding energy between a vacancy and an atom of Cu, Ag or Mn is about 0.23 eV or smaller that it.

For tow ternary alloys of Al-Zn-Au and Al-Zn-Pb, the shape of curves and increments of resistivity are quite similar to those of Al-Zn binary alloy, and we can conclude that there is no interaction between Zn atoms and atoms of third element. However, soild solubility of Pb or Au in Al is very small, and it was not sure that all amount of third element could be soluble in these alloys. Therefore, specimens quenched from the same temperature as those of resistivity measurements were polished electrolytically and examined by optical microscope. As the results, it was clear that small amount of third elements precipitated along grain boundaries. Therefore, the value of binding energy obtained must be errorful, since the concentration of third element was assumed to be nominal one. However, precipitates in the crystals could not be observed, and the shape of aging curves were quite the same as those of binary alloys. Then, it might be possible to assume that true concentration of third element in solid solution was decreased and other changes were not occur. And it is considered that the obtained values of binding energies correspond to alloys containing smaller amount of third elements. The true values of binding energy must be larger than those obtained.

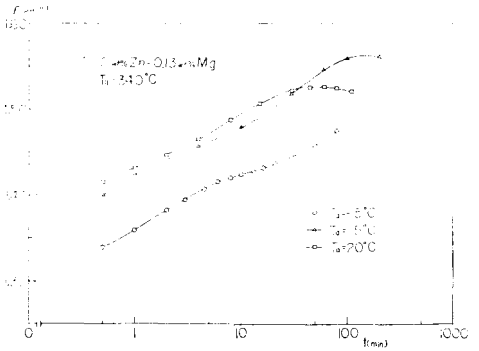

Fig. 5 Isothermal aging curves after quenching from 340°C.

Fig. 5 shows an example of isothermal aging curves of Al-Zn-Mg alloys. It is seen that the shape of isothermal aging curves and the increment in electrical resistivity are both different from those for Al-Zn binary alloys. As the details have already been published[3,4], several important facts will be described here. As the Mg content is increased, t_{Mt} is increased, and the increment in resistivity is also increased. On the other hand, the small convex part in the isothermal aging curve occurring before the principal maximum becomes clear as the aging temperature lowered. It may be concluded from these results that G. P. zones which are different from those in the binary alloy are formed in these ternary alloys and have a binding energy to vacancies. It was impossible to obtain the value of binding energy between an Mg atom and a vacancy. However, the effect of Mg on the rate of aging in the initial stage is very large.

4.2 Al-Ag and Al-Cu base alloys

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 an Ag atom, B_1, can be obtained by using equation (13), when the binding energy between a vacancy and an atom of third element is known and fairly large. As shown in Fig. 6, the

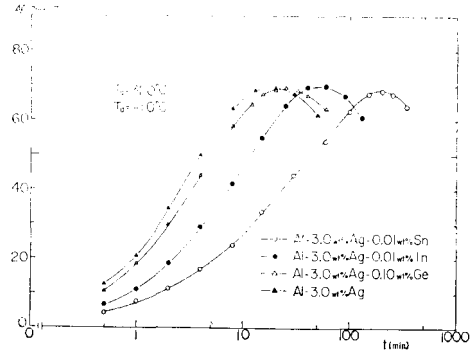

Fig. 6 Isothermal aging curves of Al-Ag, Al-Ag-Ge, Al-Ag-In and Al-Ag-Sn alloys at −10°C after quenching from 320°C.

forms of curves for Al-3.0wt%Ag-0.10wt%Ge, Al-3.0wt%Ag-0.01wt%In and Al-3.0wt%Ag-0.01wt%Sn ternary alloys are quite similar to those of Al-3.0 wt% 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 Ag atom and atoms of third element. Therefore, the binding energy between a vacancy and an Ag atom can be obtained using equation (13), since the binding energy between a vacancy and a Ge, In or Sn stom are known as 0.33, 0.39 or 0.43 eV, respectively. From these results, the binding energy between a vacancy and an Ag atom was estimated to be 0.25±0.05 eV.

Next conversely, if 0.25 eV was used as the binding energy between a vacancy and an Ag atom, the binding energy between a vacancy and an X atom can be estimated. As shown in Fig. 7 and Fig. 8, the forms of curves for Al-3.0wt%Ag-0.01wt%Cd and Al-0.72wt%Ag-0.01wt%Ti ternary alloys are quite similar to those of Al-3.0wt%Ag and Al-0.72wt%Ag binary alloys, respectively. Therefore, it may be considered that an Ag atom does not appreciably interact with a Cd or Ti atom. As the results, the binding energy between a vacancy and a Cd or Ti atom in Al-Ag alloys

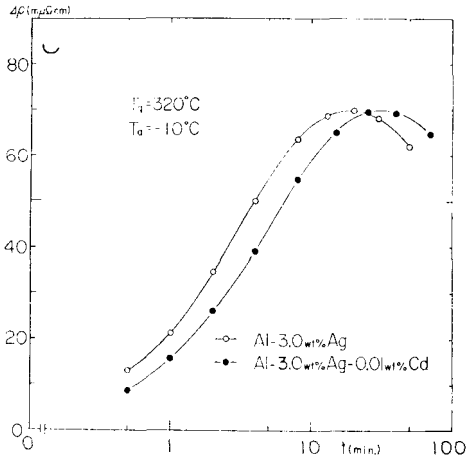

Fig. 7 Isothermal aging curves of Al-Ag and Al-Ag-Cd alloys at −10°C after quenching from 320°C.

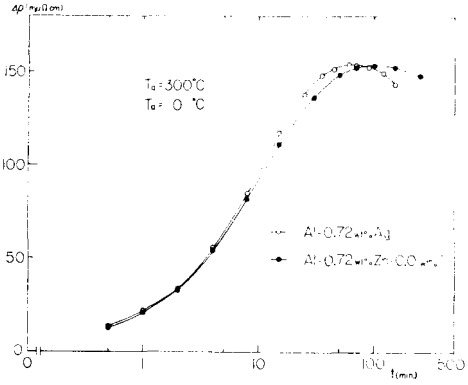

Fig. 8 Isothermal aging curves of Al-Ag and Al-Ag-Ti alloys at 0°C after quenching from 300°C.

was obtained as 0.34±0.05 or 0.31±0.05 eV, respectively. The values of the binding energy between a vacancy and a Cd or Ti atom estimated from Al-Zn and Al-Ag base alloys agree with each other within the experimental accuracy.

Fig. 9, Fig. 10 and Fig. 11 show the examples

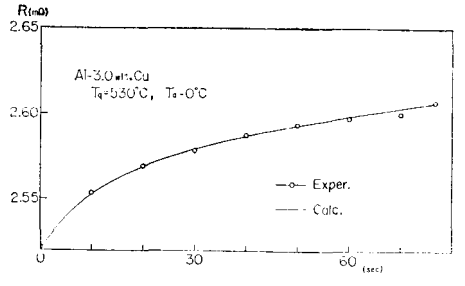

Fig. 9 Isothermal aging curve of Al-Cu alloy at 0°C after quenching from 530°C.

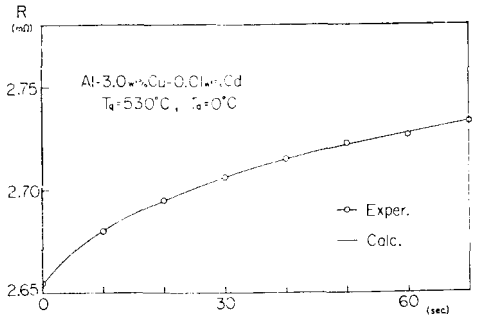

Fig. 10 Isothermal aging curve of Al-Cu-Cd alloy at 0°C after quenching from 530°C.

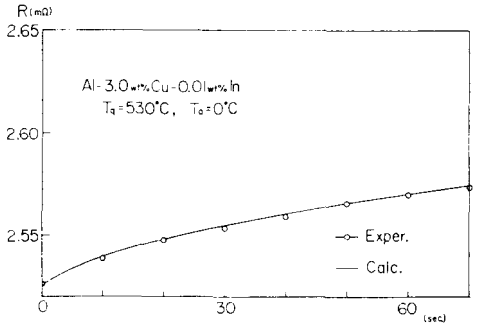

Fig. 11 Isothermal aging curve of Al-Cu-In alloy at 0°C after quenching from 530°C.

of the isothermal aging curves of Al Cu, Al-Cu-Cd and Al-Cu-In alloys. The shapes of isothermal aging curves for the Al-Cu, Al-Cu-Cd and Al-Cu-In alloys were expressed with the experimental formula obtained by De-Sorbo et al[25]. Therefore, it may be considered that a Cu atom does not appreciably interact with an atom of the third element. The ratios of the initial rates of clustering for the Al-Cu-Cd and Al-Cu-In alloys to that for the binary alloy were 0.66 and 0.45, respectively, at 0°C (Fig. 12). As the results, the binding energy between a vacancy and a Cd or In atom in Al-Cu alloys was obtained as 0.33 ± 0.05 or 0.36 ± 0.05 eV, respectively. The values of the binding energy between a vacancy and a Cd or In atom estimated from Al-Zn and Al-Cu base alloys agree with each other within the experimental accuracy.

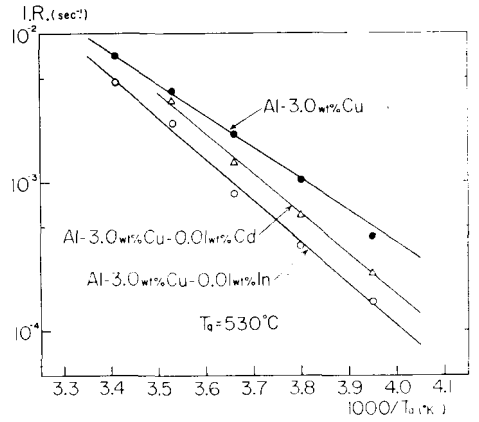

Fig. 12 Logarithmic plotting of initial rate of Al-Cu, Al-Cu-Cd and Al-Cu-In alloys after quenching from 530°C against the reciprocal of absolute aging temperature.

§ 5. Discussion

Table 2 shows the binding energies between a vacancy and a Cd, In, Ti or Sn stom in Al which were estimated by using Al-Zn, 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 Kimura and Hasiguti[23]. It may be considered that the concentrations of Zn atom in Al-10wt%Zn binary alloy or Al-10wt%Zn base ternary alloys are a little high for Lormer's formula to be adopted. But as shown in Table 2 the Cd-V, In-V and Ti-V binding energies estimated using the low concentration Al-Ag and Al-Cu base ternary alloys agree with those estimated using Al-10wt%Zn base ternary alloy within experimental accuracy with each other.

Table 2. Binding between a vacancy and a Cd, In or Sn atom estimated using Al-Zn, Al-Ag and Al-Cu base ternary alloys.

Alloys	Binding Energy (eV)		
	Cd-V	In-V	Sn-V
Al-Zn-	0.32 ± 0.05	0.39 ± 0.05	0.43 ± 0.05
Al-Ag-	0.34 ± 0.05	(0.39 ± 0.05)	(0.43 ± 0.05)
Al-Cu-	0.33 ± 0.05	0.36 ± 0.05	[0.42]

Table 3 shows the binding energies between an atom of a third element and a vacancy with the atomic radii and valency of third elements. It is seen from this table that the values thus obtained agree with those obtained by other authors (for instance, by the quenching method). For instance, the binding energy between an Si atom and a vacancy was estimated to be 0.28 eV by this method when B_1 (Zn-binding energy) was assumed to be 0.18 eV as estimated by Shimizu and Takamura[11]. The binding energy between an Si atom and

Table 3. Binding energies between an atom of a third element and a vacancy.

Element	Atomic Eadius (Å)	Valency	Binding Energy (obtained) (eV)	Binding Ennrgy (other authors) (eV)
Cu	1.276	1	<0.23	0.29)
Ag	1.442	1	0.25±0.05	0.412), 0.0813)
Au	1.439	1	0.35<	
Be	1.123	2	0.28±0.05	
Ca	1.970	2	0.27±0.05	
Cd	1.543	2	0.32±0.05	
In	1.660	3	0.39±0.05	
Si	1.316	4	0.28±0.05	0.2729)
Ti	1.467	4	0.30±0.05	
Ge	1.366	4	0.33±0.05	
Zr	1.597	4	0.33±0.05	
Sn	1.620	4	0.43±0.05	0.4228)
Pb	1.746	4	0.38<	
Mn	1.306	0	<0.23	

a vacancy was estimated to be 0.27 eV with quenching method by Okazaki and Takamura[29]. Both values are almost consistent. Furthermore, the binding energy between an Sn atom and a vacancy was 0.43 eV by the present method, and Kimura and Hasiguti[1,28] estimated this binding energy to be 0.42 eV. Again the agreement of both values is very satisfactory. Binding energy between an Ag atom and a vacancy was estimated to be 0.25 eV by this method. This value is larger than that estimated by Beaman et al.[13], but coincides with the results obtained by other authors. It is smaller than the upper limit determined by Baur and Gerold[12], and coincide with the results previously reported within experimental error[14]. Westmacott and Barnes[30] proposed a series of the binding energy in Al binary alloys to be Zn<Cu<Ag<Mg<Si from electron microscopy. On the other hand, the binding energy between a vacancy and a Zn, Cu, Mg or Si atom is estimated to be 0.18, 0.20, 0.18 or 0.28 eV, respectively, by several authors[9,11,15,29,31] and these values, except for the case of Mg-V, coincide with Wastmacott and Barnes' relation. Therefore, it may be considered that the binding energy between a vacancy and an Ag atom in aluminium obtained by present study is suitable value. This agreement seems to show that the present method for ternary alloys is essentially of the same order of accuracy as by a quenching method.

Effects of the addition of fifteen elements studied in Al-10wt%Zn alloy may be classified in to three groups: (1) Elements which lowers the rate of aging in such a manner that atoms of a third element absorb vacancies and the concentration of vacancies bound to Zn atoms is decreased by a large binding energy between an atom of third elements and a vacancy (Au, Be, Ca, Cd, In, Si, Ti, Ge, Zr, Sn, Pb), (2) elements which do not affect the rate of aging (Cu, Ag, Mn), and (3) Mg atoms cluster into zones different from those in the binary alloy, and the large binding energy between these zones or Zn-Mg pairs and vacancies plays the same role as that in the alloys belonging to (1).

The effects of Cu, Ag and Mn can be considered in the following way: The binding energy between an atom of these elements and a vacancy may be about 0.23 eV or smaller than it, or these atoms which form a pair with Zn atoms do not interact with vacancies and their contribution to the eletrical resistivity is nearly the same as a sum of contribution of individual atoms. As already mentioned, the binding energy between a Cu atom and a vacancy was estimated to be 0.2 eV by Kimura and Hasiguti[9]. This value agrees with the present results. The binding energy between an Ag atom and a vacancy was discussed previously. As for the binding energy between an Mn atom and a vacancy, the upper limit of the same kind was assumed to be 0.3 eV by one of the present authors from a study of the low temperature aging of Al-Cu-Mn alloys[7]. In the present case, the value of the upper limit was decreased to 0.23 eV. It is probable from these considerations that binding energies between an atom of these elements and a vacancy are not very large. However, there may be an interaction between atoms of two kinds of solute elements.

It is generally assumed that the binding energy is caused by the valence of a solute element and the difference in atomic radius between solute and solvent atoms. Several theoretical calculations for these effects, have been established, but it was not possible to estimate which factor was more effective because of the lack of the experimental results. Shimizu and Takamura[11] suggested that the effect of the valence would be more effective.

It is seen from Table 2, that the effect of the

valence of solute atoms on the binding energy is fairly remarkable. For instance, the radius of an atom of Cd, In or Sn in different from each other and larger than that of Al, and the radius of an In atom is the largest among them. However, the binding energy between a vacancy and an atom of these elements increases as the valence of these elements increases. The same tendency is also observed for Cu and Si, and in this case the radius of an atom of a third element is smaller than that of Al.

On the other hand, the difference in atomic radius of a third element may also affect the binding energy. For instance, Si, Ge and Sn all belong to the IVa group of the Periodic Table and may be considered to have an equal number of valence electrons. However, their binding energy to vacancy increases as the atomic radius increases. In this case, it is likely that the effective valence in the solid solution is different from the number of valence electrons, and the former is larger when the atomic number of the element is fairly large. It is possible that the effective valency of Sn or Ge is larger than that of Si. If so, the observed effects in these elements might also be caused by the valence effect. However, some example shows the size effect more clearly. The atomic radius of Ca is much larger than those of Al, Mg and Zn, and the position of Ca in the Periodic Table lies be tween Mg and Zn in II group. The binding energy between a vacancy and a Ca atom is much larger than that between a vacancy and a Mg atom or Zn atom, although the latter values two have been estimated by other authors[11,31]. In this case the effect of effective valency would be considerablly difficult to assume, and a fairly large binding energy between a Ca atom and a vacancy might be caused by larger radius of a Ca atom. How ever, in the case of Ca, Zn and Mg, the difference in binding energy is not very large, although the difference in atomic radius is fairly large. Furthermore, in the case of Cd, In and Sn, the effect of the atomic radius on the bindng energy could not be observed. These facts suggest that the effect of valence of the solute element is more predominant than the effect of the atomic radius of the solute element.

§ 6. Summary

The experimental results and considerations mentioned above may be smmmarized as follows:

(1) The ratio of the time required to reach the maximum electrical resistivity in isothermal aging curves of the Al-Zn-X or Al-Ag-X ternary alloy to that in the Al-Zn or Al-Ag binary alloy may be inversely proportional to the ratio of the concentration of vacancies bound to Zn or Ag atoms immediately after quenching in the ternary alloy to that in the binary alloy. And also the ratio of initial rate of clustering for Al-Cu-X ternary alloy to that in the binary alloy may be inversely proportional to the ratio of the concentration of vacancies bound to Cu atoms immediately after quenching in the ternary alloy to that in the binary alloy. It is possible to deduce the binding energy between an atom of an X element and a vacancy by using these relations.

(2) Binding energies obtained by this method agree very well with those obtained other authors who used different methods. This fact is be considered to show the reliability of the present method for obtaining the binding energy.

(3) The effect of valence of the solute element on the binding energy between an atom a third element and a vacancy is remarkable.

(4) The effect of the atomic radius of the solute element on the binding energy is also observed, but this effect is smaller than that of valence.

References

1) H. Kimura and R.R. Hashiguti: Acta Metallurgica 9 (1961), 1076.
2) C. Panseri and T. Federighi: Acta Metallurgica 11 (1963), 575.
3) M. Ohta and F. Hashimoto: J. Phys. Soc. Japan 19 (1964), 130.
4) M. Ohta and F. Hashimoto: J. Phys. Soc. Japan 19 (1964), 1337.
5) G. Bartsch: Acta Metallurgica 12 (1964), 270.
6) C. Panseri and T. Federighi: Acta Metallugica 12 (1964), 272.
7) M. Ohta: J. Japan Inst. Metals 27 (1963), 197.
8) M. Ohta: Trans. Japan Inst. Metals 2 (1965), 4.
9) H. Kimura, A. Kimura and R.R. Hashiguti: Acta Metallurgica 10 (1962), 607.
10) C. Panseri and T. Federighi: Acta Metallurgica 8 (1959), 217.
11) H. Shimizu and J. Takamura: Suiyokwai-shi 15 (1963), 95.

12) R. BAUR and V. GEROLD: Z. Metalkde. 52 (1961), 671.
13) D.R. BEAMAN, R.W. BALLUFFI and R.O. SIMMONS: Phys. Rev. 134 (1964), A532.
*) Some of the results were published in references in 14)~21).
14) M. OHTA and F. HASHIMOTO: J. Phys. Soc. Japan 19 (1964), 133.
15) F. HASHIMOTO and M. OHTA: J. Phys. Soc. Japan 19 (1964), 1331.
16) F. HASHIMOTO and M. OHTA: J. Phys. Soc. Japan 19 (1964), 1501.
17) M. OHTA and F. HASHIMOTO: J. Phys. Soc. Japan 19 (1964), 1987.
18) F. HASHIMOTO: J. Phys. Soc. Japan 20 (1965), 336.
19) M. OHTA, F. HASHIMOTO and T. TANIMOTO: J. Phys. Soc. Japan 21 (1966), 562.
20) M. OHTA, F. HASHIMOTO: J. Phys. Soc. Japan 22 (2967), 352.
21) M. OHTA, F. HASHIMOTO and T. TANIMOTO: Memo. School of Engineering, Okayama Univ. 2 (1967), 39.
22) H. HERMAN and J.B. COHEN: Nature 191 (1961), 63.
23) H. HERMAN, J.B. COHN and M.E. FINE: Acta Metallurgica 11 (1963), 43.
24) W.M. LOMER: Inst. of Metals, Monograph and Report Series No. 23 (1958) London, P.85.
25) W. DESORBO, H.N. TREAFTIS and D. TURNBULL: Acta Metallurgica 6 (1958), 401.
26) M. OHTA: J. Japan Inst. of Metals 27 (1963), 140.
27) M. OHTA: Trans. Japan Inst. of Metals 5 (1964), 171.
28) H. KIMURA and R.R. HASIGUTI: J. Phys. Soc. Japan 18 Suppl. III (1963), 73.
29) K. OKAZAKI and J. TAKAMURA: Suiyokwai-shi 15 (1963), 89.
30) K.H. WESTMACOTT and R.S. BARNES: Phil. Mag. 6 (1961), 217.
31) J. TAKAMURA, K. OKAZAKI and I.G. GREENFIELD: J. Phys. Soc. Japan 18 Suppl. III (1963), 75.