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Binding Energies between a Vacancy and an Atom of Lead or Gold in Al-10wt%Zn Alloys

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Binding energies between a vacancy and an atom of lead or gold were measured with the same method as those previously reported. The solid solubility of lead or gold in aluminium is very small, and the small quantity of precipitates are found along grain boundaries in this experiment. Therefore, it was not possible to determine the value of binding energy, but the lower limit of binding energy was estimated. The values of lower limit for Pb-Vacancy and Au-Vacancy binding energy were 0.38 eV and 0.35 eV, respectively.

§ 1. Introduction

Binding energy between an atom of impurity element and a vacancy is of fundamental importance in order to understand the many phenomena in alloys, e. g. recovery of quenched material, aging, and diffusion etc. They can be estimated with several methods. Increment of resistivity by quenching is most frequently used for this purpose, and the several interesting results were obtained by this method[1]. However, this method have some difficulty. Redistribution of vacanies between states binding to impurity atoms and free states will occur during quenching and possible time intervals before specimens is imerged into liquid nitrogen or other cooling medium. Takamura[1] showed that this difficulty can be removed by an annealing for short time which make nearly all free vacancies to bind to impurity atoms, but this method might contain errors not so small in the process of calculation.

Beaman, Balluffi and Simmons[2,3] measured the concentration of vacancies in equilibrium state in a few alloys, and estimated the binding energy. Results obtained by them seem quite correct, but the contribution of entropy terms and divacancies might be large at higher temperatures, and it is very difficult to estimate these contributions.

There is also an approximate method to estimate the binding energy. Kimura and Hasiguti[4] studied an alloy of Al-Cu containing small amount of tin and estimated the tin-vacancy binding energy as 0.4 eV. They considered that the rate of clustering of copper atoms is determined by the concentration of vacancies bound to copper atoms, and it is decreased by the addition of tin atoms. Such decrease of rate of clustering can be occured in other age hardening alloys.

Ohta and Hashimoto[5] found that the ratio of time required to reach the maximum resistivity in aging curves of Al-10wt%Zn and Al-10wt%Zn base ternary alloys is inversely proportional to the ratio of concentration of vacancies bound to atoms of second element immediately after quenching. They could estimate the binding energies for about ten elments in Al-10wt%Zn alloy by this method, furthermore showed experimentally that the results obtained correspond to the binding energy in Al-X binary alloys[6].

In the present paper, results obtained Al-10wt%Zn-0.005wt%Pb and Al-10wt%Zn-0.008wt%Au are reported.

§ 2. Experimentals

Alloys used were made in high alumina crucible melting the constituent elements at the same time, and the nominal weight compositions were Al-10wt%Zn-0.005wt%Pb and Al-10wt%Zn-0.008wt%Au. Ingots were forged at 450~250°C to sheets 5mm thick, and these sheets were cold rolled with appropriate annealing at 350°C. The size and shape of specimens were the same as those previously roported[7].

Quenching and annealing were also the same as those reported[7]. Electrical resistivity were measured with usual potentiometric method.

Isothermal aging curves obtained are shown in Fig. 1, Fig. 2 and Fig. 3. It is seen that the shape of curves and increments of resistivity are quite

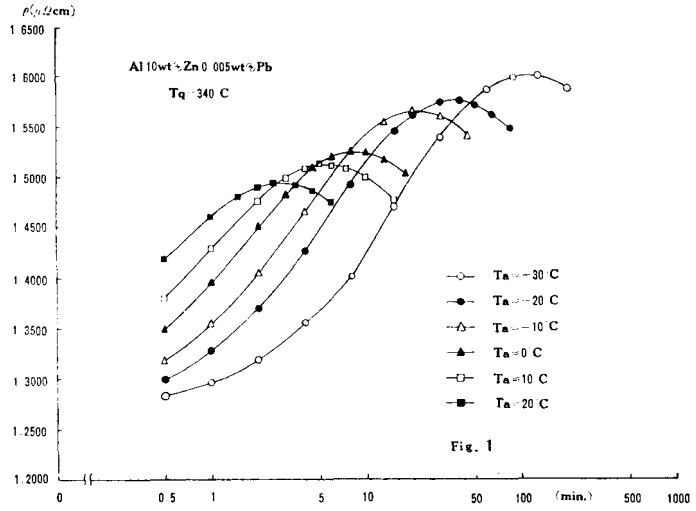


Fig. 1 Isothermal aging curves of Al-10wt%Zn-0.005wt%Pb ternary alloy at several temperatures after quenching from 340°C.

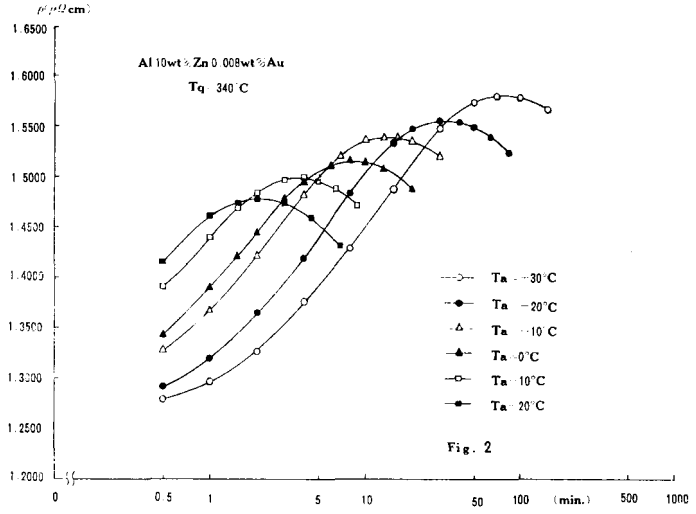


Fig. 2 Isothermal aging curves of Al-10wt%Zn-0.008wt%Au ternary alloy at several temperatures after quenching from 340°C.

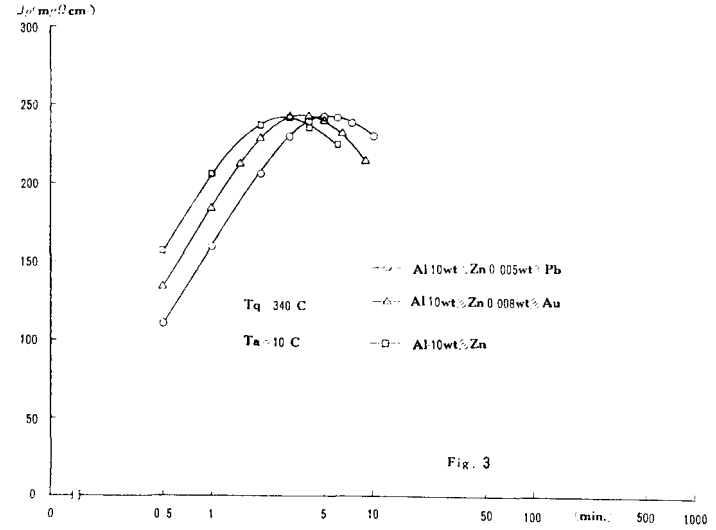
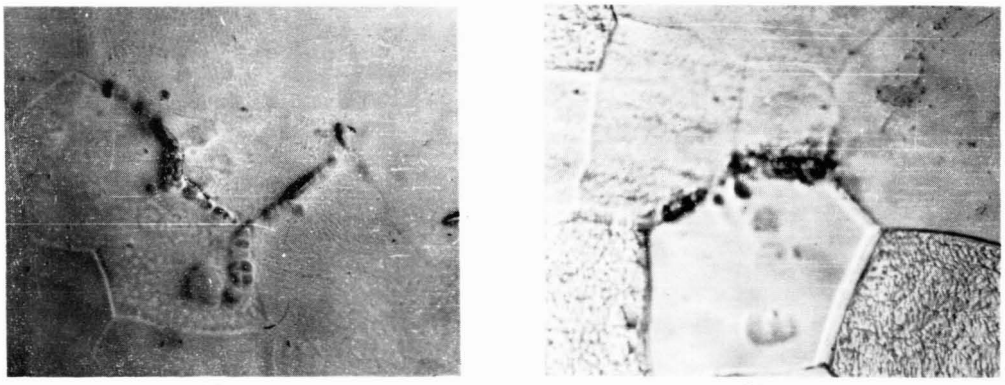


Fig. 3 Isothermal aging curves of Al-10wt%Zn binary alloy, Al-10wt%Zn-0.005wt%Pb and Al-10wt%Zn-0.008wt%Au ternary alloys at 10°C after quenehing from 340°C.



(a) (b)

Photo. 1 (a) Microstructure of Al-10wt%Zn-0.005wt%Pb ternary alloy quenched from 340°C. (×400)
(b) Microstructure of Al-10wt%Zn-0.008wt%Au ternary alloy quenched from 340°C. (×400)

similar to those of Al-Zn binary alloy, and we can conclude that there is no interation between zinc stoms and atoms of third element.

The binding energy between an atom of lead and a vacancy was estimated to be 0.38 eV or 0.35 eV, respectively from the ratio t_{Mt}/t_{Mb}. However, solid solubility of lead or gold in aluminium 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. A few examples are shown in Photo. 1. From these photographs, it is clear that small amount of third elements precipitated along grain boundaries. These amount of precipitates decreases as the quenching temperature raised.

§ 3. Discussion

As previously shown, the results obtained with the method used in the present study correspond to the binding energy obtained in Al-X binary alloys[6]. But, as mentioned above, small amount of third element precipitates along boundaries, and it is not possible to determine the amount of third element which is in the solid solution. Therefore, the value of binding energy obtained must be errorful, since the concentration of third element was assumed to be the nominal one. However, precipitates in the crystals could not be observed, and the shape of 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, that is, Pb-Vacancy binding energy is 0.38 eV and Au-Vacancy binding energy is 0.35 eV. Since solid solubility of lead or gold must be smaller than 0.005wt% or 0.008wt% at 340°C, it is very difficult to make such a dilute alloys correctly.

The value of binding energy between a lead atom and a vacancy obtained is very large. As previously reported, the binding energy between an atom of Si, Ge, or Sn are 0.28, 0.33, or 0.43 eV, respectively, and these results are explained by the atomic radii and possibly effective valence of these elements in aluminium[5]. Since lead is an element belonging to the IV B group and its atomic radius is 1.746 Å, this large value of binding energy might be reasonable.

The value of binding energy between an atom of copper and a vacancy was estimated to be 0.2 eV by Kimura, Kimura and Hasiguti[8]. And the Ag-Vacancy binding energy is 0.25 eV[9]. Atomic radius of gold is nearly equal to that of silver. Therefore, the effect of atomic radius on the binding energy might be small, and effective valence of gold in solid solution might be the main course.

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