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Large Vacancy Clusters in Aluminum Single Crystals with a Low Dislocation Density

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Large vacancy clusters in an aluminum single crystal with a low dislocation density were observed by X-ray Lang camera after slow cooling from high temperature. The clustering process of vacancy was simulated by using a model which takes into account the association and the dissociation of vacancy and the growth to larger clusters. Comparing the simulated results with the experimental one, it is confirmed that impurities or complexes composed of impurities are necessary for the formation of large vacancy clusters as a nucleus. In order to make certain, large vacancy clusters have been examined with a electron microscope.

§1. Introduction

Many investigations have been made on the excess vacancies in a crystals. However, most of the investigations have dealt with quenched or irradiated crystals, in which supersaturation of vacancy has been very high. There are a few investigations on the excess vacancies under a low supersaturation of vacancy.[1] On the other hand, by development in techniques on a crystal growth, dislocation free crystal or single crystal with a low dislocation density have been made in many materials, such as semiconductors or metals. For the nearly perfect crystals, excess vacancies are frozen in after very slow cooling from the high temperature in spite of very low supersaturation. Such frozen-in vacancies convert into a small vacancy clusters or dislocation loops by the following thermal treatments. And excess vacancies and the clusters play an important role in the fabrication of semiconductor devices.

Recently, we have reported that most of the excess vacancies in a nearly prefect aluminum crystal after slow cooling have formed the very small vacancy clusters, undetected by X-ray Lang topography, containing impurity atom and number density of large vacancy cluster, observed by Lang camera, had been very low.[2] In this paper, formation process of large cluster observed by Lang camera is simulated by using a clustering model which takes into account the association and the dissociation of a vacancy and their growth to large culsters. And such a large vacancy cluster in a nearly perfect alminum crystal is observed by electron microscope.

§2. Experimental Procedures and Results

Specimen used in the present experiment was an aluminum single crystals with a low dislocation density wich was grown from zone-refined polycrystalline aluminum. Dislocation density of this specimen was 5×10^2 cm^{-2}. The specimen was mounted in an electric furnace which was set up on the goniometer-head of X-ray Lang camera.

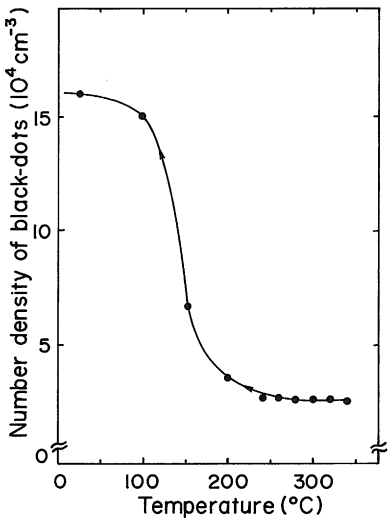

Fig. 1. Change of number density of black-dots during the cooling process. Most of these dots are large vacancy clusters.

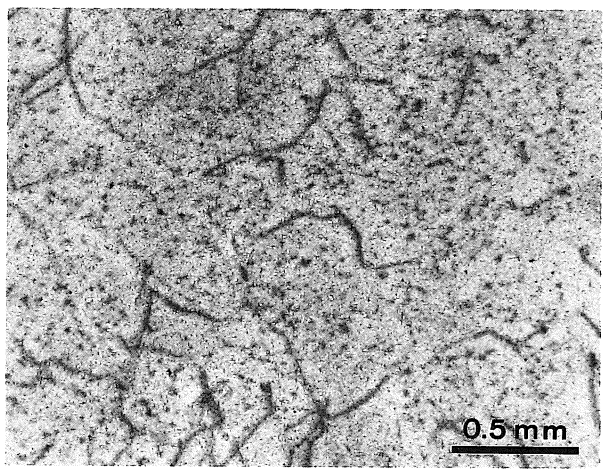

Fig. 2. Topograph of aluminum single crystal showing the large vacancy clusters. The mean diameter and number density of them are about 10 μm and 1.5×10^5 cm^{-3}, respectively.

X-ray topographs were taken at constant temperature during the cooling process. Details of the experimental procedures and the experimental results were published elsewhere.[2-4] Change of number density of black-dots observed by X-ray Lang camera during the cooling process in shown in Fig. 1. Most of these dots are large vacancy clusters unsolved by X-ray topography. Photograph of large vacancy clusters taken at 100°C is shown in Fig. 2. The mean diameter of vacancy cluster in Fig. 2 is about 10 μm and number density of them is $1.5\times10^{-5}\,\mathrm{cm}^{-3}$. Net diameter of the cluster is less than 10 μm because X-ray topograph detects the strain field near the lattice defects. Previously, we have reported that excess vacancy concentration in this specimen at 100°C had been 6.4×10^{-8} from the numerical calculation using a solution of diffusion equation.[2]

§3. Calculation of clustering process of vacancy

The progress of clustering of vacancy is calculated in order to compere the experimental results obtained from X-ray Lang topograph with it. We consider a clustering model which takes into account the association and the dissociation of small vacancy clusters containing less than seven, and their growth to large cluster.[1] The reacting vacancy is only mono-vacancy but the annihilating vacancies to pre-existing sinks, i.e. dislocations are mono- and di-vacancy. Figure 3 shows schematical diagrams

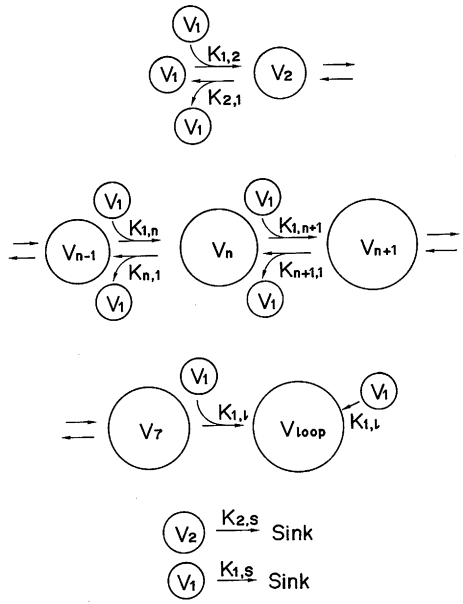

Fig. 3. Schematic diagram of association and dissociation processes of vacancy clusters. V_n is a cluster of n vacancies, V_1 and V_2 are mono- and di-vacancy, respectively, and $K_{i,j}$'s are the rate constants. Here V_{loop} is assumed to be a dislocation loop as described in the text.

of the association and the dissociation process of vacancy clusters and of the growth of a octa-vacancies as a dislocation loop. The notation of V_n is a cluster which consists of n mono-vacancies and V_1 and V_2 are mono- and di-vacancies, respectively. The notation $K_{1,n}$ is the rate constants for the association reaction $V_1+V_{n-1}\rightarrow V_n$, while $K_{n,1}$ refers to the dissociation of $V_n\rightarrow V_1+V_{n-1}$. Practically, it is difficult to take into account the processes of the association to and the dissociation from large vacancy cluster in the numerical calculation. Therefore, V_8 is assumed to grow into large cluters by absorbing mono-vacancy without dissociation. In this work, for the simplification of calculation, the clusters composed of vacancy more than 8 are regarded as the dislocation loop on (111) plane, shown in Fig. 3 as V_{loop}. The notation $K_{1,l}$ in Fig. 3 is the rate constant for the absorbing mono-vacancy to the dislocation loops. The assiociation and the dissociation processes on vacancy, shown in Fig. 3, can be expressed by differential equation in dC_n/dt, where C_n is the concentration of cluster V_n and given by N_n/N_0. Here, N_n and N_0 are the number of V_n per unit volume and that of lattice sites, respecitively. The kinetic equations were as follows,

$$\frac{dC_1}{dt}=2K_{2,1}C_2+K_{3,1}C_3+K_{4,1}C_4+K_{5,1}C_5+K_{6,1}C_6+K_{7,1}C_7-(2K_{1,2}C_1{}^2+K_{1,3}C_1C_2+K_{1,4}C_1C_3+K_{1,5}C_1C_4+K_{1,6}C_1C_5+K_{1,7}C_1C_6+K_{1,l}C_1C_l+K_{1,s}C_1,$$

$$\frac{dC_2}{dt}=K_{1,2}C_1^2+K_{3,1}C_3-K_{2,1}C_2-K_{1,3}C_1C_2-K_{2,s}C_2,$$

$$\frac{dC_n}{dt}=K_{1,n}C_1C_{n-1}+K_{n+1,1}C_{n+1}-K_{n,1}C_n-K_{1,n+1}C_1C_n \quad \text{for } 3\leqq n\leqq 7,$$

$$\frac{dC_n}{dt}=K_{1,l}C_1C_l \quad \text{for } n>7.$$

where α is estimated from the dislocation density N by the relation:[5]

$$\alpha=-2\pi N[\ln(\sqrt{\pi N}\,b)+\frac{3}{5}]^{-1}.$$

were b is the magnitude of Burgers vector. The rate constants for the association, the

Table 1. Rate constants of vacanciers for association to and dissociation from vacancy clusters.

$K_{1,2}=84\nu_1\exp(-E_m^1/kT)$	$K_{2,1}=14\nu_1\exp[E_m^1+B_2)/kT]$
$K_{1,3}=114\nu_1\exp(-E_m^1/kT)$	$K_{3,1}=15\nu_1\exp[E_m^1+B_3-B_2)/kT]$
$K_{1,4}=78\nu_1\exp(-E_m^1/kT)$	$K_{4,1}=16\nu_1\exp[E_m^1+B_4-B_3)/kT]$
$K_{1,5}=86\nu_1\exp(-E_m^1/kT)$	$K_{5,1}=17\nu_1\exp[E_m^1+B_5-B_4)/kT]$
$K_{1,6}=94\nu_1\exp(-E_m^1/kT)$	$K_{6,1}=18\nu_1\exp[E_m^1+B_6-B_5)/kT]$
$K_{1,7}=102\nu_1\exp(-E_m^1/kT)$	$K_{7,1}=18\nu_1\exp[E_m^1+B_7-B_6)/kT]$
$K_{1,l}=\beta\nu_1\exp(-E_m^1/kT)$	
$K_{1,s}=\alpha a^2\nu_1\exp(-E_m^1/kT)$	$K_{2,s}=\frac{1}{6}\alpha a^2\nu_2\exp(E_m^2/kT)$

Table 2. Total binding energy B_n of vacancy cluster V_n.

B_2=0.176 eV
B_3=0.353 eV
B_4=0.553 eV
B_5=0.763 eV
B_6=0.982 eV
B_7=1.209 eV

dissociation and the annihilation are given in Table I. In this table, k is the Boltzman constant, T is the temperature and β is the number of the capture sites from which mono-vacancy is able to associate to the loop by a jump.[1] The binding energy of vacancy cluster B_n are assumed as tabled in Table II.[6] The calculation was performed by using FACOM M-140 at Computer Center, Shimane University.

§4. Calculated results and discussions

The clustering process of vacancy was calculated using the model shown in previous section. In this calculation, initial concentration of vacancy was 6.4×10^{-8} and the other parameters were E_m^1=0.65 ev, E_m^2=0.50 ev, N=500 cm^{-2}, a=4.05 Å, b=2.86 Å, $\nu_1=1\times10^{13}$ Hz and $\nu_2=5\times10^{12}$ Hz. Figure 4 shows the number density of vacancy

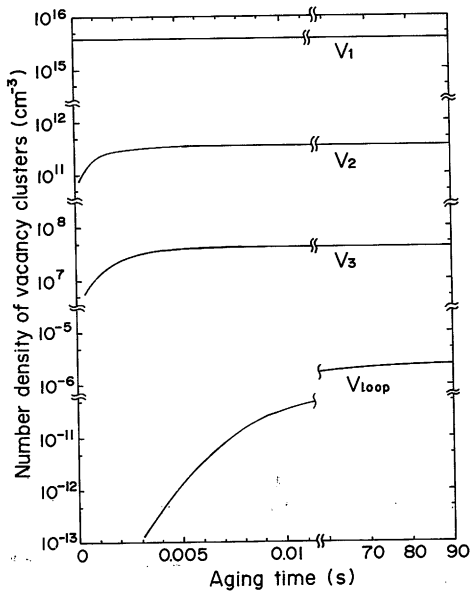

Fig. 4. The variation of number density of vacancy clusters during aging at 100°C, which was calculated by using the model shown in Fig. 3.

clusters plotted against the aging time. The number densities of V_4 to V_7 are omitted from Fig. 4 because the number density covers the wide range. In this result, the number density of small vacancy clusters, such as V_2 and V_3, reaches constant value in early stage of the aging but that of large cluster regarded as dislocation loop attains to $2.6\times10^{-6}\,\mathrm{cm}^{-3}$ after several tens of seconds. Therefore, according to this simulation, few large vacancy clusters have been formed at 100°C. However, many vacancy clusters were observed in the topograph taken at 100°C. The experimental result is not explained by this model which take into account the reaction of only vacancies. So, it is necessary to take into account the association and the dissociation process of not only vacancies but impurities which have large binding energy between vacancies. Impurity concentration in the specimen is about 1 ppm, so it seems that the large vacancy clusters nucleate at the impurity atom or the complex composed of impurity.

On the other hand, in order to confirm the above conclusion, we observed the large vacancy cluster by electron microscope. A electron micrograph of them in the similar specimen is shown in Fig. 5. As seen in this figure, a black dot is observed near the center of dislocation loop. It looks like the nucleus of dislocation loop, but its details are unknown for the present.

In conclusion, impurities or its comprexes are necessary for the formation of large vacancy clusters, observed by X-ray Lang camera under the low supersaturation of vacancy, as a nucleus for the growth.

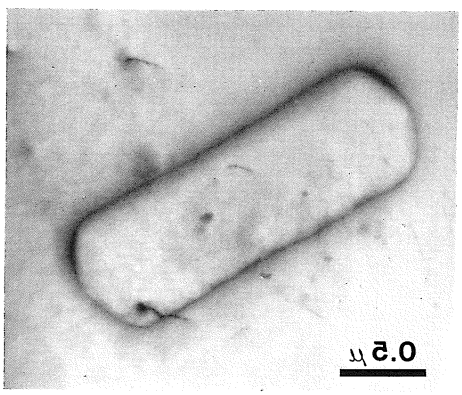

Fig. 5. Dislocation loop in aluminum single crystal with a low dislocation density after slow cooling.

Ackowlegement

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