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Excess Vacancies in Nearly Perfect Crystals of Aluminum after Slow Cooling

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Excess vacancies in nearly perfect aluminum single crystals after slow cooling were investigated by high-temperature X-ray Lang camera. A series of topographs was taken 10°C, 20°C and 50°C intervals during the cooling process in the temperature range between 310°C and 100°C. A lot of black dots formed by excess vacancies were observed at 100°C. However, most of excess vacancies were contained in the form of small vacancy cluster undetected by X-ray Lang camera. And the cluster nucleated at impurity atom.

§1. Introduction

When crystals are cooled from high temperature, excess vacancies are generated. However, all of excess vacancies are absorbed by dislocations because the dislocation density of such a crystal is more than 10^8 cm^{-2}. So, few excess vacancies are contained in the crystal.

On the other hand, most of excess vacancies are frozen in a single crystal with a low dislocation density or dislocation free crystal in spite of very slow cooling. In a semiconductor crystal, such a frozen-in point defects convert into a so-called swirl defects during the thermal treatment and their presence generally is detrimental to the fabrication of devices.

There is little investigation concerning the frozen-in excess vacancies in the nearly perfect crystals. The present work was planned for the purpose of making clear the state of existence of excess vacancies. A series of *X*-ray Lang topographs was taken at elevated temperature during a cooling process on an aluminum single crystal with a low dislocation density, because the fundamental properties of vacancy and the other defets are well known in aluminum.

§2. Experimental procedures

Specimen used in the present work is an aluminum single crystal with a low dislocation density which was grown from zone-refined polycrystalline aluminum. This single crystal was prepared in the following way: Zone-refined aluminum of which residual resistance ratio was 1.1×10^4 without size correction was rolled down to 0.5 mm in thickness and shaped into 5 mm in width. After pre-annealing at 250°C

for 60 minutes in air, these plates were strained 3.6% by extension and cut out about 50 mm in length. Then the plates were electro-polished to remove the oxide layer on the surface, and were converted into single crystal under vacuum by a travelling furnace. The travelling speed of the furnace was 60 mm/h and the maximum temperature was 600°C. After single crystals were grown, the furnace was stopped and the crystals were cooled down to room temperature for about 50 hours. Furthermore, single crystals were annealed cyclically six times between 250°C and 150°C at the heating and cooling rates of 25°C/h in vacuum.

The specimen was mounted in an electric furnace which was set up on the goniometer-head of *X*-ray Lang camera. Details of the apparatus was published elsewhere.[1] A characteristic X-ray used in this experiment was $AgK\alpha_1$ radiation. The topographs were exposed on Ilford L-4 nuclear plate with emulsion thickness 50 μm and the exposure time was about 30 hours. The topographs were taken in [200] reflection.

A series of topographs was taken at constant temperatures; 310°C, 300°C and 20°C or 50°C intervals below 300°C in cooling process. The cooling rate was 7°C/h above 200°C and 100°C/h below 200°C. The heating process was similar to the cooling one. Details of the experimental procedure and experimental results concering the dislocations were published previously.[2]

§ 3. Experimental Results

Several topographs in an aluminum single crystal during the cooling process are shown in Fig. 1. Figure 1(a), (b), (c) and (d) are traverse topographs taken at 310°C, 260°C, 200°C and 100°C, respectively. The dislocation density and the number density of black dots were estimated from the topographs. The dislocation density at 310°C and 100°C were 500 cm^{-2} and 800 cm^{-2}, respectively. So, increase of dislocation density is a small. On the other hand, many black dots were observed at 200°C

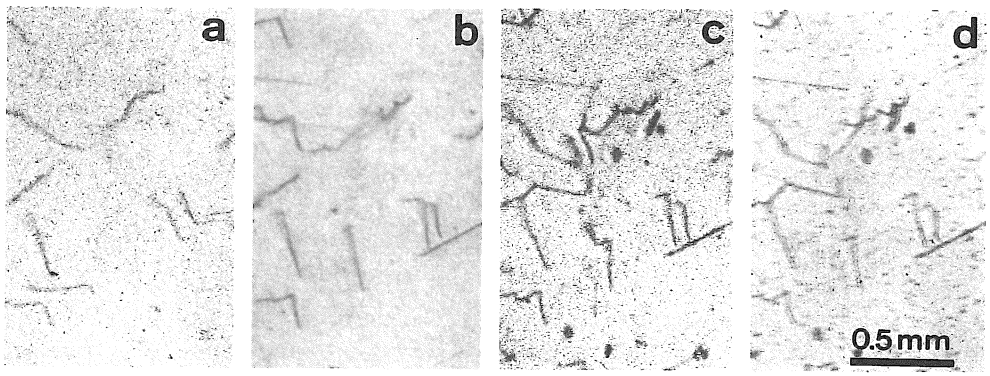

Fig. 1. A series of topographs of aluminum single crystal showing the generation of black dots due to the slow cooling; (a) at 310°C, (b) at 260°C, (c) at 200°C and (d) at 100°C.

for the first time. Change of number density of black dots during the cooling process are shown in Fig. 2. The number density of black dots, which was about 2×10^4 cm^{-3} around 300°C, increased gradually below 250°C, and rapidly increased below 150°C and the final density was 1.6×10^5 cm^{-3}. Almost of these dots are vacancy type dislocation loops unresolved by X-ray Lang camera and the mean radius of them was about 10 μm. If we consider that all black dots are consist of vacancies, total concentration of excess vacancy contained in the crystal at 100°C in the form of vacancy loops observed by X-ray Lang camera is 1.1×10^{-8}. And this excess vacancy concentration is correspond to the thermal equilibrium one in aluminum at 150°C.

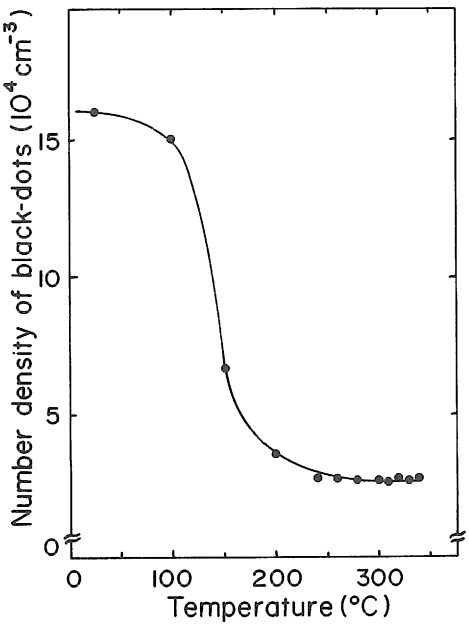

Fig. 2. Change of number density of black dots during the cooling process. Number density of them was increased gradually below 250°C and rapidly increased below 150°C.

§ 4. Discussion

We compare the excess vacancy concentration obtained from the experimental result with that calculated from the solution of diffusion equation of vacancy. Calculated excess vacancy concentration at 100°C in the specimen is necessary. In Fig. 1(a), which is the topograph at 310°C after the annealing at the same temperature for about 100 hours, all dislocations are almost straight. Therefore, it may be considered that there is no excess vacncy in the crystal just before the temperature drop from 310°C. Supposing that the excess vacancies in the specimen during the cooling are absorbed

to dislocations because the crystal surface is covered with oxide film, and that the temperature is dropped by stepwise ΔT. The excess vacancy concentration ΔC_n after the n-th temperature step is expressed in the similar way by Ham as follows,[3]

$$\Delta C_n = \sum_{j=1}^{n} \exp\left(-\frac{j\Delta t}{\tau}\right)[C_0(T_{n+1-j}) - C_0(T_{n+2-j})]$$

$$\tau = \frac{r_s^2}{2D)\,T)}\left[\ln\left(\frac{r_s}{r_0}\right) - 0.6\right]$$

$$r_s = (\pi N_d)^{-1/2},$$

where Δt is a time interval for the stepwise temperature change. $D(T)$ is the diffusivity of a vacancy at T and $C_0(T)$ is the equilibrium concentration of vacancy in aluminum, and these are expressed by

$$D(T) = D_0 \exp\left(\frac{E_m}{kT}\right)$$

$$C_0 = \exp\left(\frac{S}{k}\right)\exp\left(-\frac{E_f}{kT}\right),$$

respectively, the other notations are as follows;

T_n: temperature of the specimen after the n-th step, ie. $T_0 - n\Delta T$,
S: the formation entropy of a vacancy,
E_f: the formation energy of a vacancy,
E_m: the migration energy of a vacancy,
N_d: the dislocation densty,
r_0: the radius of dislocation core,
k: Boltzman constant.

The calculation was performed using $S = 1.52\,k$,[4] $E_f = 0.71$ eV,[4] $E_m = 0.65$ eV,[5] $D_0 = 0.176$ cm^2/s,[6] $N_d = 750$ cm^{-2} and taking 0.1°C as ΔT. The calculated excess vacancy concentration during the slow cooling from 310°C to 100°C at the mean cooling rate of 0.42°C/h is shown in Fig. 3, and final concentration of excess vacancy attains to 6.4×10^{-8}. The excess vacancy concentration at 100°C obtained from the above calculation is six times larger than that from the experimental result. Therefore, most of excess vacancy is contained in the form of small vacancy cluster undetected by the X-ray topograpy in the specimen. On the other hand, concentration of impurity in the specimen is about 1×10^{-6}.[7] It seemes that the small vacancy clusters nucleated at the impurity atom.

In conclusion, the following are shown in the present investigation; Most of excess vacancies in the nearly perfect metal crystal after slow cooling form the small vacancy clusters containing impurity atom. And the clusters are so small that they are not detected by the X-ray Lang camera.

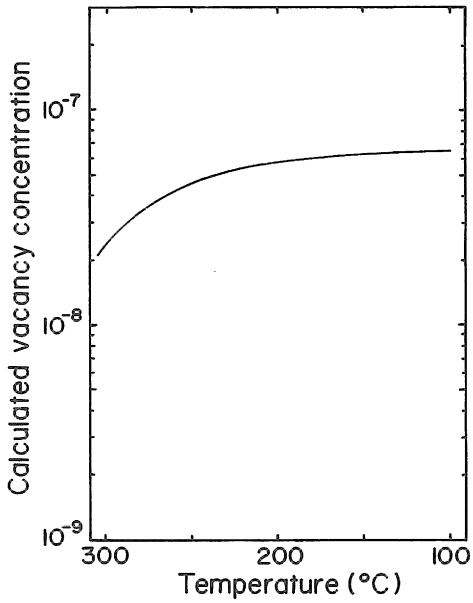

Fig. 3. The calculated vacancy concentration in a specimen plotted as a function of temperature during the cooling process with the mean rate of 0.42°C/h.

Acknowlegement

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