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Reduction of large vacancy clusters in nearly perfect aluminum single crystals

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Large vacancy clusters in aluminum single crystals with low dislocation density, which show up as black dots in X-ray topographs, generate new dislocations and stacking faults during heat treatments. In order to obtain dislocation-free or low-dislocation-density metal single crystals, it is necessary to suppress the formation of large vacancy clusters. To this end, our starting material was either (1) ultrahigh-purity aluminum, intended to minimize the number of nucleation sites for large vacancy clusters, or (2) a dilute alloy of Zn in Al, intended to block the migration of excess vacancies by binding them with zinc atoms during slow cooling. Single crystals of the Al-Zn dilute alloy failed to improve the perfection unless a large vacancy cluster was formed. Upon cyclic annealing, however, the number density of black dots in X-ray topographs of ultrahigh-purity aluminum crystals decreased rapidly and significantly. It was thus confirmed that using a high-purity starting material was effective in suppressing the formation of large vacancy clusters.
Key words: large vacancy cluster, black dot, X-ray topography, nearly perfect single crystal, ultrahigh-purity aluminum

1. INTRODUCTION

It is well known that in metal crystals, cooling from the growth temperature often generates excess vacancies, which are absorbed by pre-existing vacancy sinks, such as dislocations and grain boundaries. In a nearly perfect crystal, the number density of vacancy sinks is very low. Thus, excess vacancies cannot be annihilated and accumulate, forming secondary lattice defects such as dislocation loops and voids. There have been many investigations on secondary defects generated from excess vacancies in metals during the past few decades [1], and it is generally accepted that the predominant secondary defects in common metal crystals are large vacancy clusters, such as dislocation loops [2]. The dislocation loops in aluminum single crystals with a low dislocation density appeared as black dots in X-ray topographs [3]. In nearly perfect crystals with a low dislocation density, large vacancy clusters act as new sources of dislocation during heat treatments. To grow low-dislocation-density or dislocation-free metal single crystals, it is necessary to suppress the formation of large vacancy clusters. In the case of aluminum, low-dislocation-density crystals were grown by the strain-annealing method. In order to prevent the formation of large vacancy clusters, we used one of two starting materials: (1) ultrahigh-purity aluminum to reduce the number of nucleation sites for large vacancy clusters or (2) an Al-Zn dilute alloy to block of migration of excess vacancies during slow cooling. Zn atoms are completely dissolved in aluminum and their binding energy with vacancies is high.

In the present paper, we describe a characterization of the defect density, in particular,

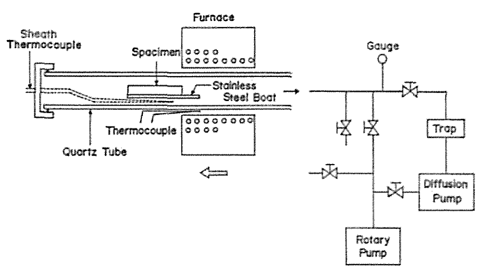

Fig.1 Schematic of the experimental setup used for growth of an ultrahigh-purity aluminum single crystal in a traveling furnace.

the number density of large vacancy clusters (black dots) in nearly perfect ultrahigh-purity aluminum and Al-Zn dilute alloy crystals.

2. EXPERIMENTAL

Ultrahigh-purity aluminum (UHP, 99.99999 at%, 7-Nine) was prepared by the zone-refining method using an induction furnace in ultrahigh vacuum. Details of the refining process have been published elsewhere [4]. A UHP aluminum block, whose residual resistance ratio R300/R4.2 was 1.0×10^5, was sliced into $0.5\times5\times50$ mm. The aluminum single crystals used in the present investigation were grown by the strain-annealing method using a travelling furnace. The experimental setup is shown in Fig. 1. The aluminum polycrystal plates were converted into single crystals in a vacuum better than 1.3×10^{-4} Pa. The maximum furnace temperature was 600 °C. The travelling speed of the furnace was 60 mm/h and the furnace was stopped when the region of maximum temperature passed the end of specimen. Subsequently, the single crystals were cooled down to 400 °C at a cooling rate of 30 °C/h, then at a rate of 7 °C/h to 150 °C, and the furnace was cooled below 150 °C.

The other nearly perfect aluminum-20 ppm zinc dilute alloy was prepared in almost the same fashion, but using a He gas flow type travelling furnace because of the high vapor pressure of zinc. The zinc concentration was found to be equal to the calculated residual concentration of excess vacancies in aluminum single crystals [5]. Figure 2 shows the gas flow type travelling furnace used for the Al-Zn alloy crystal.

These crystals were annealed cyclically six times between 250 °C and 150 °C at a heating and cooling rate of 25 °C/h (see Fig. 3) in a vacuum better than 6.7×10^{-5} Pa to further decrease the dislocation density.

The single crystals prepared were examined before and after cyclic annealing by Lang's X-ray diffraction topography technique [6], using MoKα_1

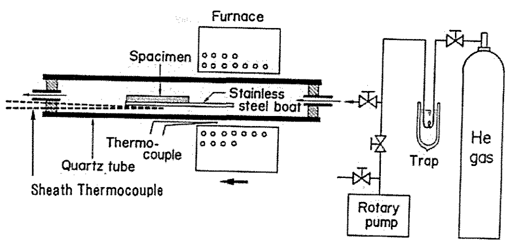

Fig.2 Schematic of the experimental setup used for growth of an Al-20 ppm Zn single crystal in a He gas flow type traveling furnace.

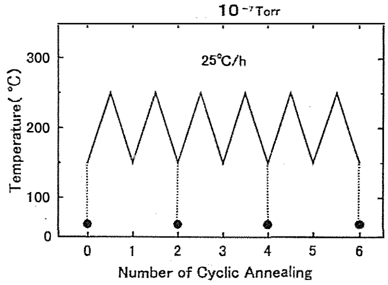

Fig.3 Temperature-time curve for cyclic annealing. X-ray topographs were taken at the filled circles in the graph.

radiation from a microfocus X-ray generator with a rotary target (RIGAKU RU-200BH). Topographs were taken in 111 reflections to determine the dislocation density. The exposure time was about 1 h. In addition, white-beam Laue topographs of the specimens were taken by the high-speed X-ray topographic camera (BL-15B1) of the Photon Factory, High Energy Accelerator Research Organization (KEK) in Tsukuba, Japan. The exposure time was 2.0 s. All topographs were recorded on Ilford L-4 nuclear plates with a 25- or 50-μm-thick emulsion.

3. RESULTS AND DISCUSSION

Figure 4 shows the X-ray topograph of an Al-20ppm Zn dilute alloy single crystal after slow cooling. Many sub-grain boundaries were observed in this topograph, as indicated by the arrow. The average number density of dislocations in this sub-grain was about 8×10^3 cm^{-2}. The specimen showed low perfection. The crystal surface was covered with a thin oxide layer, as suggested by the interference color observed. The crystal surface was oxidized by the water vapor contained in the flowing He gas. The oxide film hindered the

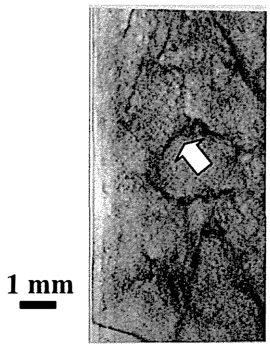

Fig.4 Topographs of the Al-20 ppm Zn dilute alloy single crystal taken after slow cooling. Many tangled lines and sub-grain boundaries are observed. The white arrow shows the sub-grain boundary.

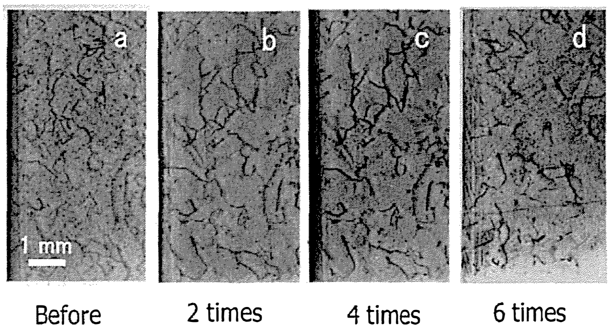

Fig.5 A series of X-ray topographs in a UHP aluminum single crystal taken (a) before and after (b) two, (c)four and (d) six annealing cycles. A rapid and significant decrease was observed in the number density of black dots upon cyclic annealing.

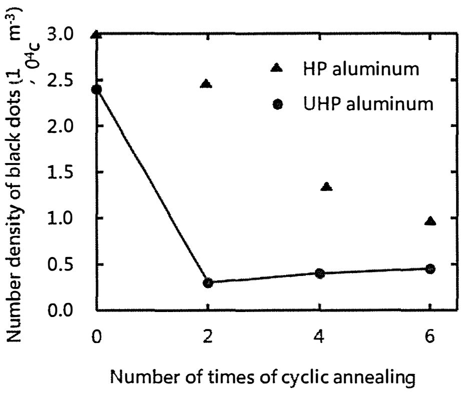

Fig.6 Change in black dot density during cyclic annealing.

annihilation of excess vacancies during cooling, and thus the nucleation and growth of dislocations occurred. Eventually, the dislocations became entangled and hence were transformed into sub-boundaries. The single crystal of Al-Zn dilute alloy failed to improve the perfection, and a large vacancy clusters were formed.

Figure 5(a) shows the X-ray topograph of a UHP aluminum single crystal after slow cooling. The number density of black dots and dislocations were 2.5×10^4cm^{-3} and 3×10^3cm^{-2}, respectively [5]. These values in high-purity (HP) aluminum single crystals (R300/R4.2 = 2.0×10^4) were 3.0×10^4cm^{-3} and 3×10^3cm^{-2}, respectively [5] [7]. The values in UHP and HP aluminum single crystals just after growth were almost the same. Next, the crystal was annealed cyclically six times between 250 °C and 150 °C. Figure 5 shows a series of topographs of UHP aluminumcrystal taken (a) before and after (b) two, (c) four and (d) six annealing cycles. The change in black dot density as a result of cyclic annealing is shown in Fig. 6. A rapid and significant decrease was observed in the number density of black dots upon cyclic annealing.

Furthermore, number density of residual dislocation was found to be the same as that reported in the literature [5]. In order to characterize the nature of the black dots in the specimens, we first determined the stress field of a dot through topography, by finding the reflection at which the dot becomes invisible.

Figure 7 shows synchrotron radiation topographs obtained using white beam X-rays, with the same area irradiated under different diffraction planes. In order to take topographs with different diffraction plane, Laue topography is very useful and uncomplicated technique because many diffraction spots were taken at one shot by white-beam X-ray. The black dot, indicated by the white arrow, is visible in Fig.7 (a), (d) and (e). However, the black dot indicated by the black arrow in Fig. 7 was observed in all topographs regardless of different diffraction plane. We could not determine the stress field of black dot by finding the reflections for which the dot image became invisible. Our results also indicate that black dots have complex stress fields. In order to confirm the real identity of black dot, we carried out the electron microscopic observation. Figure 8 shows the electron

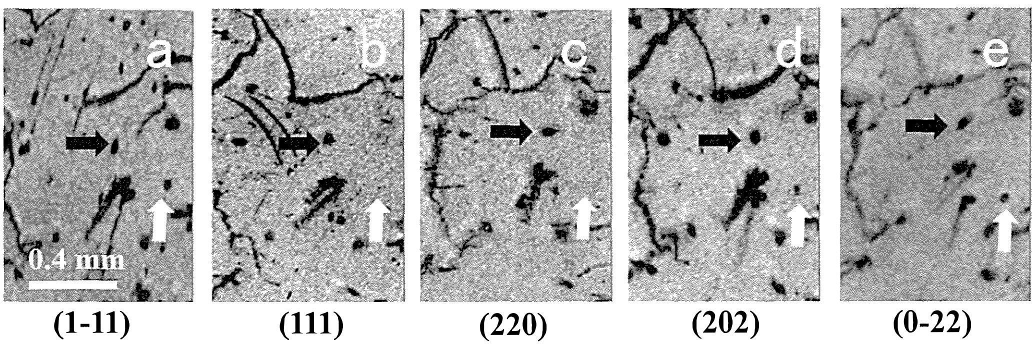

Fig.7 Laue topographs with different diffraction planes taken by white-beam X-ray. The diffraction planes used in (a), (b), (c), (d), and (e) were (1-11), (111), (220), (202), and (0-22).

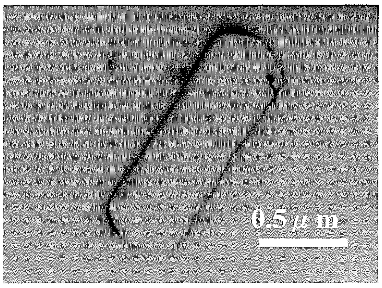

Fig.8 Electron micrograph of black dot in a UHP aluminum single crystal with low dislocation density. A large dislocation loop with other defects, such as impurity clusters, was observed.

micrograph of black dots in a UHP aluminum single crystal with low dislocation density. A large dislocation loop of other defects, such as impurities or impurity clusters, was observed in the micrograph.

Due to the rapid rise in temperature during cyclic annealing, a large vacancy deficiency occurs with respect to the thermal equilibrium concentration. To compensate for that, vacancies must be supplied rapidly into the lattice. If vacancies were supplied only from pre-existing dislocations and the specimen surface, it would take a long time for vacancies to achieve thermal equilibrium over the whole volume of the specimen because the concentration of these sources is very low in nearly perfect crystals. In the case of UHP aluminum, many large vacancy clusters shrank so as to supply vacancies, emitting vacancies and disappearing. The vacancies emitted were, in turn, absorbed by other vacancy sinks or remained as very small vacancy clusters, undetected by topography. Thus, the number density of black dots was reduced upon cyclic annealing.

In this paper, we described an approach to reducing large vacancy clusters (black dots) in nearly perfect aluminum single crystals. In order to minimize the nucleation sites for large vacancy clusters, we used ultrahigh-purity (UHP) aluminum as a starting material. However, the black dot density decreased dramatically upon thermal cyclic annealing. Thus, the use of high-purity materials proved very effective in decreasing the number density and size of large vacancy clusters.

ACKNOWLEDGMENT

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