Lawrence Berkeley National Laboratory

Recent Work

Title

DEFECTS FORMED FROM EXCESS VACANCIES IN ALUMINUM

Permalink

<https://escholarship.org/uc/item/74x0g1pr>

Authors

Das, G.
Washburn, J.

Publication Date

1964-09-01

University of California

Ernest O. Lawrence Radiation Laboratory

EFFECTS FORMED FROM EXCESS VACANCIES IN ALUMINUM

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545*

Berkeley, California

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

UCRL-11574

UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Berkeley, California
AEC Contract No. W-7405-eng-48

DEFECTS FORMED FROM EXCESS VACANCIES IN ALUMINUM

G. Das and J. Washburn

September 1964

DEFECTS FORMED FROM EXCESS VACANCIES IN ALUMINUM

G. Das^{**} and J. Washburn^{*}

Inorganic Materials Research Division, Lawrence Radiation Laboratory
and Department of Mineral Technology, College of Engineering
University of California, Berkeley, California

Introduction

Vacancy defects in metals become visible by electron microscopy only after they contain more than 10^2 to 10^3 individual vacancies. In quenched and aged aluminum three different defects have been observed. The original experiments of Hirsch et al. (1958) showed predominantly $\frac{a}{2} \langle 110 \rangle$ dislocation loops. Recently quenching experiments suggest that either $\frac{a}{2} \langle 110 \rangle$ perfect loops or $\frac{a}{3} \langle 111 \rangle$ stacking fault loops can be made to predominate. For example, increasing the purity of the aluminum has been found to increase the ratio of stacking fault to perfect loops (Cotterill and Segall, 1963). In zone refined material almost exclusively stacking fault loops were reported.

However, extreme purity does not appear to be necessary to obtain faulted loops. Quenching experiments in this laboratory on ordinary high purity (99.999) aluminum have frequently resulted in specimens containing very nearly 100% faulted loops (Strudel et al., 1963). Experiments on Al containing 3.5% magnesium show that even in an alloy it is possible to obtain faulted loops (Westmacott et al.). The third kind of defect that has been reported is an octahedral void bounded by $\{111\}$ surfaces. Kiritani (1964) observed this defect in zone refined aluminum for a wide variety of quenching and aging conditions.

* Also Research Professor - Miller Institute for Basic Research in Science

** Now at Case Institute of Technology, Department of Metallurgy, Cleveland, Ohio

Further investigation of the exact conditions under which each of these large defects is formed is of interest because results may be useful to supplement other information about the early stages of clustering where the defects are too small for direct observation. Defects containing less than 10^2 individual vacancies can only be studied by electrical resistivity (Federighi, 1959), x-ray small angle scattering (Chik et al., 1962) and mechanical property measurements (Galligan and Washburn, 1963). Application of all of these techniques combined with electron microscopy observation of the final result of the coarsening process will probably have to be applied to the same specimens before all stages of vacancy precipitation are understood.

The observed growth of all three types of defect in aluminum to a size large enough for electron microscope observation shows that transitions from one type to another are associated with high enough activation energies to make transition improbable. Saada has considered these transitions in detail (Saada, 1963). In aluminum the defect having the lowest energy for the range of sizes observable by transmission electron microscopy is the perfect $\frac{a}{2} \langle 110 \rangle$ loop. However, large stacking fault loops do not transform to perfect loops even at 175°C. The type of defect that is eventually seen is apparently determined at an early stage when only a few vacancies are involved. The choice between the three defects could depend on factors such as (i) maximum vacancy supersaturation that is achieved, (ii) maximum concentration of divacancies or trivacancies that are produced during the quench, (iii) ratio of vacancy concentration to impurity atom concentration and (iv) internal stresses.

The purpose of the present experiments was to investigate the effect of factors other than purity on the kind of defects that are formed in

quenched 99.999 aluminum. In particular an attempt was made to separate the effect of quenching stress and quenching rate on the kind of large defects that are eventually formed.

Experimental

One of the difficulties with quenching experiments is the virtual impossibility of controlling independently all of the variables that are expected to affect the results. Some of these are: (1) temperature from which the specimen is quenched, (2) dislocation density prior to quenching, (3) concentrations of various impurities in the specimen, (4) shape of the cooling curve and subsequent thermal history and (5) motion and multiplication of dislocations during quenching. For example, changing (1) might be expected to change (4) and (5) and perhaps even (2) and (3). In the experiments reported here we have tried to keep (1), (2) and (3) constant changing the quenching conditions so as to vary only the rate of cooling and the amount of dislocation motion during cooling. Even for these two variables alone it is difficult to vary one without possibly changing the other. Specimens of two different orientations were used: (i) rolled recrystallized polycrystalline sheet which always gave {100} parallel to the surface and (ii) single crystal sheets grown from the melt with {112} parallel to the surface.

In order to obtain large defects that would be easily recognizable as stacking fault loops or perfect loops or voids a relatively low quenching temperature (540°C) was used for all experiments. A range of cooling rates was achieved by quenching specimens of dimension 2.5x2.5x0.0125 cm from this temperature in three ways: (i) water, (ii) oil, (iii) liquid nitrogen. After quenching all specimens were aged at 40°C. To vary the amount of

strips along one side only, to produce a thick layer of aluminum oxide. Water quenching of this type of specimen caused bending to take place during cooling. In a second series, specimens of different thickness were water quenched. Changing the thickness of the specimen was expected to cause changes both in cooling rate and dislocation motion. The thinnest specimens used were .0025 cm in thickness and the thickest were .04 cm. Because the electron microscope specimen was always taken from the center of the quenched specimen, cooling rate should decrease with increasing thickness. Deformation during the quenching might be expected to be great for some areas of the thinnest specimens because it was difficult to avoid bending during entrance into the water bath. Dislocation motion should be uniformly greatest for the thick specimens because of the temperature differential between center and surface during the quench.

Results and Discussion

Substructures produced by the three different cooling rates are shown as Figs. 1a, b, 2, 3, and 4a, b. For water and oil quenches stacking fault loops predominated; for the slowest cooling rate only octahedral voids were observed. Figure 3 shows a number of these voids at A. Their size was much greater than any of those reported by Kiritani. Their octahedral shape is clearly established by the fringes of equal thickness that can be seen at high magnification. Fig. 4a, and b shows the largest void found for 200 and 240 diffraction conditions. The diagonal of this octahedral void was approximately $2800\text{\AA}$ in length. Those in Fig 3 appear to be considerably smaller. In this same specimen many dislocation segments with both ends emerging at the same surface were observed (See Fig.3). These could have resulted from an average loop size that was greater than the transparency thickness of the foil. Therefore it is not certain that

no loops were nucleated. From the results of the two faster quenching rates it can be seen that decreasing the cooling rate decreases the number of loops and increases their average size. Average defect size, and maximum number of defects within the field of view at a magnification of 8000X (approximately $6 \times 10^{-7} \text{ cm}^2$) are summarized in Table I.

For all three cooling rates the total concentration of excess vacancies that were accounted for by the observed defects were of the same order of magnitude as the expected equilibrium concentration of vacancies at 540°C . Therefore even for the slowest cooling rate there was no evidence that a large fraction of the vacancies were being lost at other sinks. However, particularly in the case of voids the sizes and densities were only very rough estimates. For the oil quenched specimen the loops tended to be grouped into colonies. The numbers reported refer to the centers of the colonies.

The results differ from those reported by Kiritani (1964) in that in these experiments cooling rate was found to have a marked effect on defect size and density whereas he found almost no effect. This further emphasizes the difficulty of separating the effects of different variables. For example, whether or not quenching rate effects density and size of defects might be determined by impurity concentrations. Our results agree with those of Kiritani in that the formation of voids was favored by slow quenching rate. One specimen quenched from a higher temperature (658°C) into liquid nitrogen was found to contain both a high density of loops and very small defects that could only be observed in the thinnest regions of the foil. These small defects were tentatively identified as voids. See Fig. 5a, b.

Figures 6a, b shows the effect of deliberately causing motion of dislocations during quenching. It should be compared with Fig. 1b which

represents an identical history except for no intentional plastic bending during cooling. Motion of dislocations during the quench or the presence of residual stresses during aging apparently lead to the formation of a much greater fraction of perfect $\frac{a}{2} \langle 110 \rangle$ loops.

A combination of the effects due to cooling rate and quenching deformation are shown by the series of specimens having different thickness at the time of quenching. Figs 7, 1b, and 8 had identical treatment except that the thicknesses at the time of quenching were 25, 125, and 400 μ respectively. Average loop size increased with increasing quenching thickness and loop density decreased. Also the greatest fraction of perfect $\frac{a}{2} \langle 110 \rangle$ loops occurred for the thickest specimens. Regions that contained many perfect loops often were also regions of high dislocation density. See Fig. 9. Irregular loops where two or more had grown together and helical dislocations were also observed. The results for very thin specimens were variable. Some areas contained exclusively stacking fault loops whereas in others there were many perfect loops usually associated with dislocations. There were no significant differences between specimens of $\{100\}$ and $\{112\}$ orientation. Average loop size and loop density for specimens of different quenching thickness are summarized in Table II. The changes due to increasing the specimen thickness corresponded to those expected from a decrease in quenching rate and an increase in the amount of quenching deformation.

An important conclusion to be drawn from these experiments is that what may appear to be quite minor variations in quenching procedure such as changing by a factor of only 4 the thickness of the specimen that is quenched can result in marked changes in the final loop substructure.

It is of interest to speculate as to why deformation during quenching increases the fraction of loops that are perfect. Passage of a moving dislocation near a stacking fault loop or contact interaction between the two always results in conversion to a perfect loop if it is above critical size (Strudel and Washburn, 1964). This mechanism can produce some perfect loops. Handling of the specimen while thinning or mounting in the microscope certainly moves dislocations. If in the specimens that have significant quenching deformation the dislocation density is higher than relatively more perfect loops will be created in this way in these specimens. Also, great care must be taken to observe foils with low beam current. An example of the kind of changes that can take place even in the microscope is given by Fig. 10. Stacking fault loops have become perfect loops at A, B, and C; at D a perfect loop has rotated by slip on its glide cylinder; at E two loops have combined to form one of irregular shape; at F a stacking fault loop has been converted to perfect and disappeared by slipping out of the foil on its glide cylinder. Fig. 2a, b shows, at 'A' the formation of concentric loops by the gliding together of two perfect loops having overlapping glide cylinders; both originated from stacking fault loops in which the fault was destroyed by stress aided nucleation of a Shockley Partial. Loops that are converted to $\frac{a}{2} \langle 110 \rangle$ after growth has stopped can be distinguished from those that have grown significantly after becoming perfect. The former still retain the hexagonal shape characteristic of stacking fault loops whereas the latter tend to assume rhombus shape. An $\frac{a}{3} \langle 111 \rangle$ loop tends to grow in hexagonal shape probably because it is most difficult to form new jogs along segments that lie parallel to the close packed $\langle 110 \rangle$ directions. The same reasoning leads to the expectation of four straight sides for an $\frac{a}{2} \langle 110 \rangle$ loop. It is probably most difficult to

form new jogs during growth on segments that lie in one of the two {111} planes that contain the Burgers vector. Therefore, these loops tend to assume rhombus shape. (Thomas and Washburn, 1963), (Eikum and Thomas 1963). Perfect loops of both types can be seen in Fig. 8.

The fact that most $\frac{a}{2} \langle 110 \rangle$ loops have well developed rhombus shape shows that they have been perfect during growth. It is not possible to tell whether they were nucleated as perfect loops or were converted from stacking fault loops soon after they later reached critical size ($\sim 50\text{\AA}$ diameter, Saada, 1963). However the habit planes for rhombus loops were always between {100} and {110}, (Das and Washburn, 1964). This suggests that the former may not have originally been stacking fault loops. Very thin specimens gave evidence for nucleation of loops by moving dislocations. Fig. 7a, b shows numerous examples of small loops arranged along a line and also a number of elongated perfect loops. A moving dislocation can leave behind numerous vacancy clusters or small prismatic loops all having the same Burgers vector as the moving dislocation by a mechanism suggested by Washburn, (1963). The elongated loops in Fig. 7 are probably examples. Small prismatic loops left by moving dislocations could act as vacancy sinks eventually growing into rhombus shape. If a sufficient number of these sinks are formed then the probability of nucleating $\frac{a}{2} \langle 111 \rangle$ loops would be reduced. Further support for this explanation comes from the fact that often all the rhombus loops in a given area had the same Burgers vector as in Fig. 8.

Loops arranged in a line were not always perfect Fig. 6b. Individual vacancies or slightly larger aggregates as well as larger vacancy loops can be left behind by the same mechanism. In this way the local vacancy concentration can be increased along a line. Therefore, the probability

for $\frac{a}{3} \langle 111 \rangle$ loop nucleation could also be enhanced along a line.

We believe that the results are consistent with the assumption that in regions of otherwise perfect crystal vacancy clustering in the material used for these experiments always produces stacking fault loops or octahedral voids when a specimen is quenched from 540°C. The perfect loops that are observed come from growth of small prismatic loops left by dislocations that move during the quench or from stacking fault loops that are converted after reaching critical size by the stress field of a nearby dislocation line.

Acknowledgements

The authors are pleased to acknowledge the support of this work by the United States Atomic Energy Commission through the Inorganic Materials Research Division of the Lawrence Radiation Laboratory and by the Miller Institute for Basic Research in Science through aware of a fellowship to one of us (J.W.).

Chik, K., Seeger, A., and Rakle, M., Proc. 5th Internatl. Congress

Electron Microscopy, Academic Press (1962), p. J-11.

Cotterill, R. M. J., and Segall, R. L., Phil. Mag., 8, 1105 (1963).

Das, G., Washburn, J., J. Appl. Phys. Letters, to be published.

Eikum, A., Thomas, G., J. Appl. Phys., 34, 3363 (1963).

Federighi, T., Phil. Mag., 4, 502 (1959).

Galligan, J., and Washburn, J., Phil. Mag., 8, 1455 (1963).

Kiritani, M., J. Phys. Soc. Japan, 19, 618 (1964).

Saada, G., J. Phys. Soc. Japan, 18; J. Appl., 3, 41 (1963).

Strudel, J. L., Vincotte, F., and Washburn, J., Appl. Phys. Letters, 3,
148 (1963).

Strudel, J., and Washburn, J., Phil. Mag., 9, 491 (1964).

Thomas, G., and Washburn, J., Rev. Mod. Phys., 35, 992 (1963).

Washburn, J., Electron Microscopy and Strength of Crystals, Interscience
Publishers, New York, 1963, p. 301.

Westmacott, K. H., Hull, D., Smallman, R. E., Phil. Mag. 6, 929 (1961).

Table I

Quenching Medium	Average Diameter of Defect	Maximum Number in Field of View at 8000 X
Water	Loops 1400 Å	200
Oil	Loops 3000 Å ^o	80
Liquid N ₂	Voids ~ 500 Å	~ 10

Table II

Quenching Thickness	Average Loop Diameter	Maximum Number in Field of View at 8000 X	Type of Defect
25 μ	500 Å	300 +	Perfect and imperfect loops
125 μ	1400 Å	200	mostly im- perfect (stacking fault loops)
400 μ	2500 Å	50	mostly perfect

FIGURE CAPTIONS

- Fig. 1 Typical loop substructure produced by quenching a 125 μ thick foil into 40°C water (a) {112} orientation. Note sharp fringes in loops that are near foil surfaces. All four sets of $\frac{a}{3}$ {111} loops are easily distinguishable. (b) {100} foil orientation.
- Fig. 2 Two successive photographs of the same colony of large stacking fault loops produced by oil quenching from 540°C. At 'A $\rightarrow$ a' stress aided nucleation of Shockley partials and prismatic glide has converted two imperfect loops into two concentric perfect loops.
- Fig. 3 Voids 'A' and dislocation segments 'C' in foil quenched from 540°C into liquid nitrogen then aged at 40°C. Dislocation segments may be remnants of very large loops.
- Fig. 4 The largest octahedral void found in the same specimen as that of Fig. 3 shown at high magnification for two different diffraction conditions. (a) 240 single diffraction condition. (b) $\bar{2}00$ single diffraction condition.
- Fig. 5 Thick and thin areas of the same foil after quenching into liquid nitrogen from 658°C. (a) small defects visible only in very thin parts of the foil. (b) stacking fault loops visible in thicker areas.
- Fig. 6 Effect of deformation during quenching. (a) perfect loops predominate in areas near dislocations. (b) stacking fault loops were found mostly in areas having few dislocations.

- Fig. 7 Loop substructure in a specimen that was only $25\ \mu$ thick when quenched into water at 40°C from 540°C . Note strings of loops as in deformed specimen (Fig. 6).
- Fig. 8 Loop substructure in a specimen that was very thick ($400\ \mu$) when quenched into water at 40°C from 540°C . Note hexagonal perfect loops 'A' and rhombohedral perfect loops 'B'.
- Fig. 9 Region of high dislocation density in thick specimen of Fig. 8. Note helical dislocation at 'A' and string of loops that have grown together to form large elongated loop at 'B'.
- Fig. 10 Changes in loop substructure that take place during observation if beam current is not kept low enough. (a) First picture (b) Second picture of same area. At A, B, C stacking fault loops have become perfect loops. At D a perfect loop has rotated on its glide cylinder. At E two perfect loops combined to form one of irregular shape. At F a stacking fault loop has disappeared by first losing its fault then gliding to one of the foil surfaces.

ZN-4517

Fig. 1a

ZN-4518

Fig. 1b

(a)

(b)

ZN-4523

Fig. 2

ZN-4519

Fig. 3

(a)

(b)

ZN-4524

Fig. 4

(a)

(b)

ZN-4525

Fig. 5

(a)

(b)

ZN-4526

Fig. 6

ZN-4520

Fig. 7

ZN-4521

Fig. 8

ZN-4522

Fig. 9

(a)

(b)

ZN-4527

Fig. 10

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.