Conf-900623--8

EFFECTS OF INTERNAL HYDROGEN ON THE VACANCY LOOP FORMATION PROBABILITY IN Al*

Tho X. Bui, E. Sirois, I. M. Robertson and M. A. Kirk**
Dept. of Materials Science and Eng.
University of Illinois
Urbana, IL 61801

**Materials Science Division
Argonne National Laboratory
Argonne, IL 60439

CONF-900623--8

DE90 011114

April 1990

Submitted to the 15th Symposium on "Effects of Radiation on Materials", June 17-21, 1990, Nashville, Tennessee.

*Work supported by the DOE through BES-Materials Science Contracts AC02-76-ER01198 (U of I) and W-31-109-Eng-38 (ANL).

EFFECTS OF INTERNAL HYDROGEN ON THE VACANCY LOOP FORMATION PROBABILITY IN Al

Tho X. Bui, E. Sirois, I.M. Robertson and M.A. Kirk*
Dept. of Materials Science and Engineering
University of Illinois, 1304 W. Green St.,
Urbana, IL 61801.
*Argonne National Laboratory, 9700 South Cass Ave., Argonne Il 60439

The effect of internal hydrogen on the formation of vacancy dislocation loops from heavy-ion generated displacement cascades in Al has been investigated. Samples of high-purity aluminum and aluminum containing 900 and 1300 appm of hydrogen were irradiated at room temperature with 50 keV Kr+ ions. The ion dose rate was typically 2 x 10^{10} ions cm^{-2} sec^{-1} and the ion dose was between 10^{11} and 10^{13} ion cm^{-2}. Under these irradiation conditions, dislocation loops were observed in all compositions, although the formation probability was relatively low (less than 10 percent of the displacement cascades produced a vacancy loop). The loop formation probability was further reduced by the presence of hydrogen. No difference in the geometry or the size of the loops created in the hydrogen free and hydrogen charged samples was found.

These results are difficult to interpret, and the explanation may lie in the distribution and form of the hydrogen. To account for the large hydrogen concentrations and from calculations of the energy associated with hydrogen entry into aluminum, it has been suggested that the hydrogen enters the aluminum lattice with an accompanying vacancy. This will create hydrogen-vacancy complexes in the material; two dimensional complexes have been detected in the hydrogen-charged, but unirradiated, samples by the small-angle x-ray scattering technique. The possibility of these complexes trapping the vacancies produced by the cascade process exists thus lowering the formation probability. However, such a mechanism must occur within the lifetime of the cascade. Alternatively, if a displacement cascade overlaps with the hydrogen-vacancy complexes, the lower atomic density of the region will result in an increase in the cascade volume (decrease in the local vacancy concentration) which will also reduce the loop formation probability.

This work was supported by the Department of Energy through contracts AC02-76-ER01198 (U of I) and W-31-109-Eng-38 (ANL).

15 th Symposium on Radiation Effects.

Authors Names :

Tho X. Bui[1], E. Sirois[1], I.M. Robertson[2] and M.A. Kirk[3]

Title of Paper :

Effects of Internal Hydrogen on the Vacancy Loop Formation Probability in Al.

AUTHORS AFFILIATIONS :
[1] Tho X. Bui and E. Sirois are graduate students in the Dept. of Materials Science and Eng., University of Illinois, 1304 W. Green St.,Urbana, IL 61801.
[2] I.M.Robertson, Associate Professor, Dept. of Materials Science and Eng., University of Illinois, 1304 W. Green St.,Urbana, IL 61801.
[3] M.A.Kirk, Metallurgist, Materials Science Division, Argonne National Laboratory, Argonne Il 60439.

ABSTRACT : The effect of internal hydrogen on the formation of vacancy dislocation loops from heavy-ion generated displacement cascades in Al has been investigated by using transmission electron microscopy. Samples of high-purity aluminum and aluminum containing 900 and 1300 appm of hydrogen were irradiated at room temperature with 50 keV Kr^+ ions. Under these irradiation conditions, dislocation loops were observed in all compositions, although the formation probability was relatively low (less than 10 percent of the displacement cascades created a vacancy loop). The loop formation probability was further reduced by the presence of hydrogen. No difference in the geometry or the size of the loops created in the hydrogen free and hydrogen charged samples was found.

KEY WORDS : radiation effects, aluminum, hydrogen, electron microscopy.

INTRODUCTION

In pure aluminum, the efficiency with which vacancy loops form from displacement cascades has been shown to be dependent on the incident ion's mass and energy, and the ion flux and fluence [1][2][3][4][5]. From these investigations it can be concluded that projectiles with mass $\leq$ Al and energy <100 keV do not produce vacancy loops from spatially isolated displacement cascades. Within this ion mass range, dislocation loops and cavities/bubbles have been formed at high ion doses where significant spatial overlap of the displacement cascades occurs [6][7]. Ions with mass greater than Cu produce vacancy loops from isolated cascades, and the associated defect yield increases with increasing ion mass. For room temperature irradiations with gold ions, it was found that the density of defects increased with increasing ion dose and ion energy [4]. From the available literature, it appears that the formation of visible defects is dependent on the ion flux, the critical flux being dependent on the projectile mass [3,5]. Kitagawa et al [3] and Hayashi et al [5] observed no visible damage following room temperature irradiation with 40 keV Cu^+ or 40 keV Ar^+ ions, unless the ion flux was greater than 2×10^{12} ion.cm^{-2}.sec^{-1}. For an ion fluence of 5×10^{13} Ar^+ and Cu^+ ions cm^{-2}, the defect production rate increased linearly for ion fluxes between 2×10^{12} and 4×10^{13} ions cm^{-2} sec^{-1}. Above a flux of 4×10^{13} ions cm^{-2} sec^{-1}, the defect production rate was constant. This flux dependence was attributed to the vacancies from a single isolated displacement cascade not being able to form a stable loop nucleus at room temperature. A stable vacancy loop nucleus may be formed when the vacancies from multiple displacement cascades aggregate. This flux dependence was not observed for ion irradiations performed at 193 K. Beevers and Nelson[2] also found a flux dependence for 85 keV He^+ ion irradiations. Gomez-Giraldez et al [4] observed damage after room temperature irradiations with 40 keV Au^+ ions to an ion dose of 1 x 10^{11} ions cm^{-2}; the ion flux in these experiments was 1 x 10^9 ions cm^{-2} sec^{-1}.

Kitagawa et al [3] also showed that for a constant ion flux, the defect production rate is constant at the lower ion doses, but then it decreases at higher ion doses. For room temperature irradiations with either 40 keV Cu^+ or Ar^+ ions, the decrease in defect production rate occurred at an ion dose of approximately 1 x 10^{14} ions cm^{-2}.

Studies of the effect of hydrogen and helium on the radiation response of a material has been primarily confined to investigations of void swelling where the need for the impurity to stabilize the three dimensional void from collapse to a vacancy loop has been well established. Relatively little work has been performed on the effects of hydrogen on the development of the damage structure at low doses. Linderoth et al [8] showed by using the positron annihilation technique that the hydrogen is associated with the vacancies produced by 7 MeV proton irradiations of Al single crystals. Two additional vacancy recovery stages were detected. The first at 280 K was attributed to single hydrogen-vacancy complexes and the other at 400 K to multiple hydrogen occupancy of single vacancies. Wolfenden [9] observed a 10 percent decrease in the electron threshold damage voltage in aluminum pre-injected with 10 appm. of helium. Bond et al [10] found a decrease of about 50 percent in the threshold voltage in aluminum containing 600 and 1900 appm. of hydrogen. This large decrease in electron threshold voltage was explained by a two-stage energy transfer mechanism. The incident electron first transfers energy to the hydrogen atom which in turn then collides with and displaces an aluminum atom.

In this paper we compare the TEM observations of the damage structure produced, by 50 keV Kr^+ ion irradiations at room temperature, in high purity Al to that in Al containing a supersaturation of hydrogen. Preliminary results from small-angle x-ray scattering studies on the distribution of the hydrogen in the unirradiated state are also presented.

EXPERIMENTAL PROCEDURES

Sample preparation.

High purity aluminum ingots (99.9999 % pure) were rolled into thin sheets of approximately 300 micron thickness and then charged with hydrogen. To introduce the hydrogen the aluminum sheet was immersed in a solution of NaOH and deionized water with a 10 pH. With this charging technique, the aqueous solution causes a corrosion reaction at the metal surface, breaking down the normally hydrogen-impermeable oxide layer, and allows the high fugacity of the solution to drive the hydrogen into the metal (for further details on the charging technique, see reference [11]). The charging was performed for 48 and 100 hrs, resulting in hydrogen concentrations of 900 and 1300 appm, respectively. These hydrogen concentrations were determined by using the gas chromatograph technique. The uncharged specimen showed a hydrogen concentration of about 100 appm which is within the measurement error associated with this technique. These hydrogen concentrations are orders of magnitude greater than the room temperature solubility which has been estimated from elevated temperature data to be between 10^{-6} and 10^{-8} appm for hydrogen in equilibrium with 1 atmosphere of hydrogen [11]. From energy considerations, Zeides [11] has shown that it is more favorable for the hydrogen to enter the sample associated with a vacancy rather than as a single hydrogen. It is thought that it is the introduction of these hydrogen-vacancy pairs that allows these high hydrogen supersaturations to be attained.

TEM discs were punched from the pure (uncharged) aluminum and the hydrogen charged materials and electropolished to perforation via the jet method. An electrolyte of 4:1 methanol-nitric acid solution at -15 °C was used, with a potential of 20 volts. The samples were irradiated in the as-thinned condition after having been examined to ensure that the surfaces were free from artifacts that could be mistaken for irradiation induced damage.

Ion irradiations

The irradiations were performed in either the tandem accelerator/high voltage electron microscope facility at Argonne National Laboratory (ANL) or the accelerator facility at the Coordinated Science Laboratory, CSL, at the University of Illinois in Urbana. For the ANL irradiations, specimens were placed in a TEM sample holder and irradiated one at a time. The CSL irradiations were performed by placing samples from each of the three hydrogen concentrations in a multiple-sample holder, the ion beam was then rastered over this holder, insuring that all samples were irradiated to the same ion dose. All the irradiations were performed at room temperature with 50 keV Kr^+ ions. The ion flux was approximately 2×10^{10} ions $cm^{-2}sec^{-1}$ at both facilities and the ion dose varied from 2×10^{11} to 6.0×10^{12} ions cm^{-2}.

Electron microscopy

The damage structure created in the aluminum specimens was examined in a

Philips 420 TEM, operating at 120 keV. Although previous studies[10] demonstrated in Al-H samples dislocations loops can be produced with an 80 keV electron beam, no additional defects (dislocation loops or voids) were observed during the present experiments. The reason for the difference between these observations and those of Bond et al [10] is that they used a high electron flux, having removed the second condenser aperture and focussed the electron beam onto the specimen. Under normal imaging conditions they found damage only after prolonged (10^3 seconds) exposure to the electron beam.

The damage structure as observed in the transmission electron microscope was characterized in terms of the defect density, defect image size and Burgers vector in grains having an orientation close to [110]. The defect yield which is defined as the number of visible defects created per incident ion was determined from images taken with a <200> type diffraction condition. This diffraction condition was selected as all Frank loops (Burgers vector b = a/2<111>) and two-thirds of the perfect loops (b = a/2<110>) are imaged. The loop size was determined from dark-field micrographs taken under two beam conditions by measuring the length of interface between the black and white lobe in black-white defects and as the maximum dimension of black dot type images. It has been demonstrated that this image dimension approximates the actual defect size [12]. The Burgers vector of the defects was determined by using a combination of the invisibility condition and by matching the changes in the image symmetry as a function of the diffraction vector with computer simulated images [12].

SAXS Experiments

The distribution of the hydrogen in unirradiated charged and uncharged aluminum was investigated by using the small angle x-ray Scattering (SAXS) technique. Single crystals with <110> orientations of 99.999% pure aluminum were prepared as reference and as hydrogen charged samples. The reference samples were mechanically thinned to 90 microns, punched into 3 millimeter disks and annealed at 773K under a vacuum of 10^{-5} Pa. The charged samples were mechanically thinned to 150 microns, annealed, and then immersed in an aqueous NaOH solution of pH 10. Hydrogen charging occurred during free corrosion, which also thinned the sample to 90 microns. The quality and in plane orientation of the crystals were determined using the Laue Transmission and Back Reflection methods. The SAXS experiments were conducted using a beam of copper K_α radiation which was collimated and focused to 1 mm^2. The transmitted beams were detected by a 20 x 20 cm area detector at a distance of 5 m from the specimen having a resolution of 6.25×10^{-4} radians.

RESULTS

Damage structure as determined by TEM

The dark-field micrographs shown in Figure 1 compare the defect density produced in the uncharged and the hydrogen charged samples after a room temperature irradiation with 50 keV Kr^+ ions to a nominal ion dose of 3.5×10^{12} ions cm^{-2}. (These samples were irradiated in the same batch in the accelerator facility at CSL and therefore were exposed to the same irradiation condition). Only a small fraction of the displacement cascades created by the incident ions form defects and the number of defects produced can be seen to decrease with increasing hydrogen content. The trend of decreasing density with increasing hydrogen concentration is quantified in terms of the defect yield, the values of which are reported in Table 1 for the different irradiation doses. The change in defect yield as a function of hydrogen concentration is shown graphically in Figure 2. Clearly, irrespective of the irradiation facility and the ion dose, the presence of hydrogen decreases the loop formation probability. The decrease is of the order of 30 % for the highest hydrogen content. Observation of loops at the lowest ion dose indicates that dislocation loops can be produced from isolated displacement cascades created by 50 keV Kr^+ ions at room temperature. Comparison of the ion irradiations from the ANL Facility reveal that the defect yield remains approximately constant for each material as the ion dose is increased.

The size distribution of the defects produced by the irradiation in the CSL Facility to a nominal ion dose of 3.5×10^{12} ions cm^{-2} is shown in Figure 3 for the hydrogen charged and uncharged material. No discernible differences in the size distributions was established. The mean defect size was about 3.0 nm and the distribution median is approximately 2.8 nm for all compositions.

In addition to the statistical compilation of defect yield, a Burger's vector analysis was performed on the defects. Both Frank ($\underline{b}$ = a/3 <111>) and perfect ($\underline{b}$ = a/2 <110>) dislocation loops were present in equal numbers, regardless of the hydrogen concentration.

SAXS Results

An isointensity contour plot of the small-angle scattered x-ray intensity from a vacuum annealed, hydrogen-free, specimen is presented in Figure 4. The contour pattern was constructed such that each successive isointensity level is a factor of two greater than the adjacent intensity level with the highest intensity at the origin. The scattering profile of the reference specimen shows relatively minor isotropic scattering which is associated with defects on the crystal surface. In contrast, Figure 5 shows the contour plots of a hydrogen charged specimen which exhibits significantly more scattering at much larger reciprocal lattice vectors, and is sharply anisotropic with rel-rods protruding along <111> directions. From these plots it is surmised that the defect responsible for this distortion is a thin platelet whose minor axis is approximately 2.0 nm. One possible defect that would give rise to such a distortion would be a platelet lying on the {111} plane with a low electron density relative the aluminum matrix. These platelets have, as yet, remained undetected in TEM examination of the samples. However, it is suspected that the SAXS results are showing the existence of platelets lying close to the hydrogen entry surface, but not smaller hydrogen vacancy complexes that might exist in the sample interior. If the density of these near-surface platelets is low, it is perhaps not surprising that they have eluded detection in the TEM

DISCUSSION

Room temperature heavy-ion irradiations of hydrogen charged and pure (uncharged) aluminum with 50 keV Kr^{+} ions using an ion flux of about 2×10^{10} ions cm^{-2} sec^{-1} resulted in the formation of defects from isolated individual displacement cascades. The probability of forming a defect from a displacement cascade was very low in pur ncharged aluminum and was further decreased by the presence of hydrogen. The magnitude of the decrease increased with increasing hydrogen concentration. Gomez-Giraldez et al[4] reported a defect yield of 0.15 following a room temperature irradiation with 40 keV gold ions to an ion dose of 1.7 x 10^{11} ions cm^{-2}; an ion flux of 1 x 10^9 ions cm^{-2} sec^{-1} was used. Kitagawa et al [3] and Hayashi et al [5] reported a yield of < 0.01 in Al irradiated with either 40 keV copper or argon ions to an ion dose of about 8 x 10^{13} ions cm^{-2}, but an ion flux > 1 x 10^{12} ions cm^{-2} sec^{-1} had to be used. Despite the different ion dose rates employed, the defect yields obtained by the different research groups are, at least qualitatively, consistent with the expected effects of ion mass and energy on the displacement cascade.

These experiments have also shown that the presence of hydrogen, probably in the form of vacancy-hydrogen complexes, can decrease the probability for loop formation from displacement cascades. The mechanism by which hydrogen inhibits cascade collapse is still unclear. However, since loop formation is expected to be a prompt reaction occurring within the lifetime of the thermal spike, 10^{-11} seconds, the effect of hydrogen must occur within this time frame. It is possible that the hydrogen may affect the distribution of the interstitial atoms and thereby enhance recombination. While this might lead to a decrease in loop formation probability, a decrease in the loop size would also be expected. No loop size difference is detected between the uncharged and hydrogen charged material. Alternatively, since the hydrogen appears to be localized, regions rich in hydrogen-vacancy complexes will be less dense than the surrounding material and this will produce a more widely dispersed displacement cascade. This increase in cascade volume (i.e. decrease in local vacancy concentration) may prohibit the conditions most favorable for loop formation from being attained. It is also possible that the presence of hydrogen stabilizes the vacancies in the cascade center preventing them from forming a vacancy loop. Hydrogen stabilization of such a cluster of vacancies is known to be a precursor to void formation. No voids were detected in the present irradiations even at the highest irradiation dose.

CONCLUSIONS

The 50 keV Kr^+ irradiation of pure aluminum at room temperature shows that vacancy loops can form from the collapse of spatially isolated displacement cascades and at low ion dose rates (2×10^{10} ions cm^{-2} sec^{-1}). The loop formation probability decreases as the hydrogen concentration increases. These effects are attributed to the hydrogen causing local changes in the atomic density which then affect the cascade dimensions and hence the vacancy concentration.

ACKNOWLEDGEMENTS

This work was supported by the Department of Energy through Basic Energy Sciences contracts AC02-76-ER01198 (U of I) and W-31-109-Eng-38 (ANL). The SAXS experiments were performed at Oak Ridge National Laboratory with the assistance of Dr. S. Spooner.

FIGURE CAPTIONS

Figure 1. Dark field micrographs comparing the damage structure produced by a room temperature irradiation with 50 keV Kr^+ ions to a nominal ion dose of 3.5×10^{12} ions cm^{-2}. (The irradiations were performed in the CSL facility). The hydrogen concentrations were in (a) 100 appm (uncharged) (b) 900 appm and (c) 1300 appm.

Figure 2. Plot Defect yield versus hydrogen concentration for all irradiations.

*The high yield values obtained for this CSL irradiation are suspected to be a consequence of a dosimetry error.

Figure 3. Image size distributions for the samples irradiated in the CSL Facility to a nominal ion dose of 3.5×10^{12} ions cm^{-2}.

Figure 4 Isointensity contour plot of the small-angle x-ray scattered intensity from a vacuum annealed hydrogen-free sample of aluminum.

Figure 5. Isointensity plot of the small-angle x-ray scattered intensity from a hydrogen charged sample of aluminum.

Table 1 Comparison of the defect yields for the hydrogen charged and uncharged materials irradiated to different ion doses with 50 keV Kr^{+} ions in the ANL and CSL irradiation Facility. The error in these values is $^{+}\ ^{<}$ 10%.

ION DOSE X 10^{12}	0.2	1	2	3.5	3.5*	6
ions cm^{-2}	ANL	CSL	ANL	ANL	CSL	ANL
PURE Al	0.075	0.059	–	0.058	0.082	0.046
Al–900 appm H	0.045	0.047	0.037	0.042	0.073	0.039
Al–1300 appm H	0.038	0.038	0.027	–	0.056	0.023

* ion dosimetry error expected.

REFERENCES

1. Ruault, M.O., Jouffrey, B., Joyes, P., "Etude de Defauts Crees dans une Matrice d'Aluminium par Bombardement d'Ions Al^+," Phil. Mag., vol. 25, 1971, pp.833-853.

2. Beevers, C.J., and Nelson,R.S., "The Formation of Defect Clusters in Aluminium by Ion Bombardment" Phil. Mag., vol. 8, 1963, pp. 1189-1202.

3. Kitagawa,K., Yamakawa,K., Fukushima,H., Yoshie,T., Hayashi, Y.,Yoshida,H., Shimomura,Y. and Kiritani, M., "Ion-Irradiation Experiment for the Fundamental Studies of Damage Evolution of Fusion Materials," J. Nuclear Mats., vol. 133 & 134, 1985, pp. 395-399.

4. Gomez-Giraldez, C., Hertel, B., Ruhle, M., and Wilkens M., "Transmission Electron Microscope Studies of Defect Clusters in Aluminium Irradiated with Gold Ions," Applications of Ion Beams to Metals, S.T. Picraux, E. P. EerNisse, F.L. Vook., Eds., 1973, pp.469-480.

5. Hayashi, Y., Yoshida, H., Kitagawa, K., and Shimomura,Y., "Cascade Damages in Metals and Alloys Induced by Self-Ion Irradiation," Proc. 8th Symp on ISIAT, '84, Tokyo 1984.

6. Howe, L.M., McGurn,gw.F., and Gilbert, R.W., "Direct Observation of Radiation Damage Produced in Copper, Gold, and Aluminum During Ion Bombardments at Low Temperatures in the Electron Microscope," Acta Metallurgica, Vol. 14, 1966, pp. 801-820.

7. Furuno, S., Isui, K., Ono, K., and Kino, T., "Effects of Ion Species on the Evolution of Structural Damage in Ion Irradiated High-Purity Aluminium," Journal of Nuclear Materials, Vol. 133 & 134, 1985, pp. 400-404.

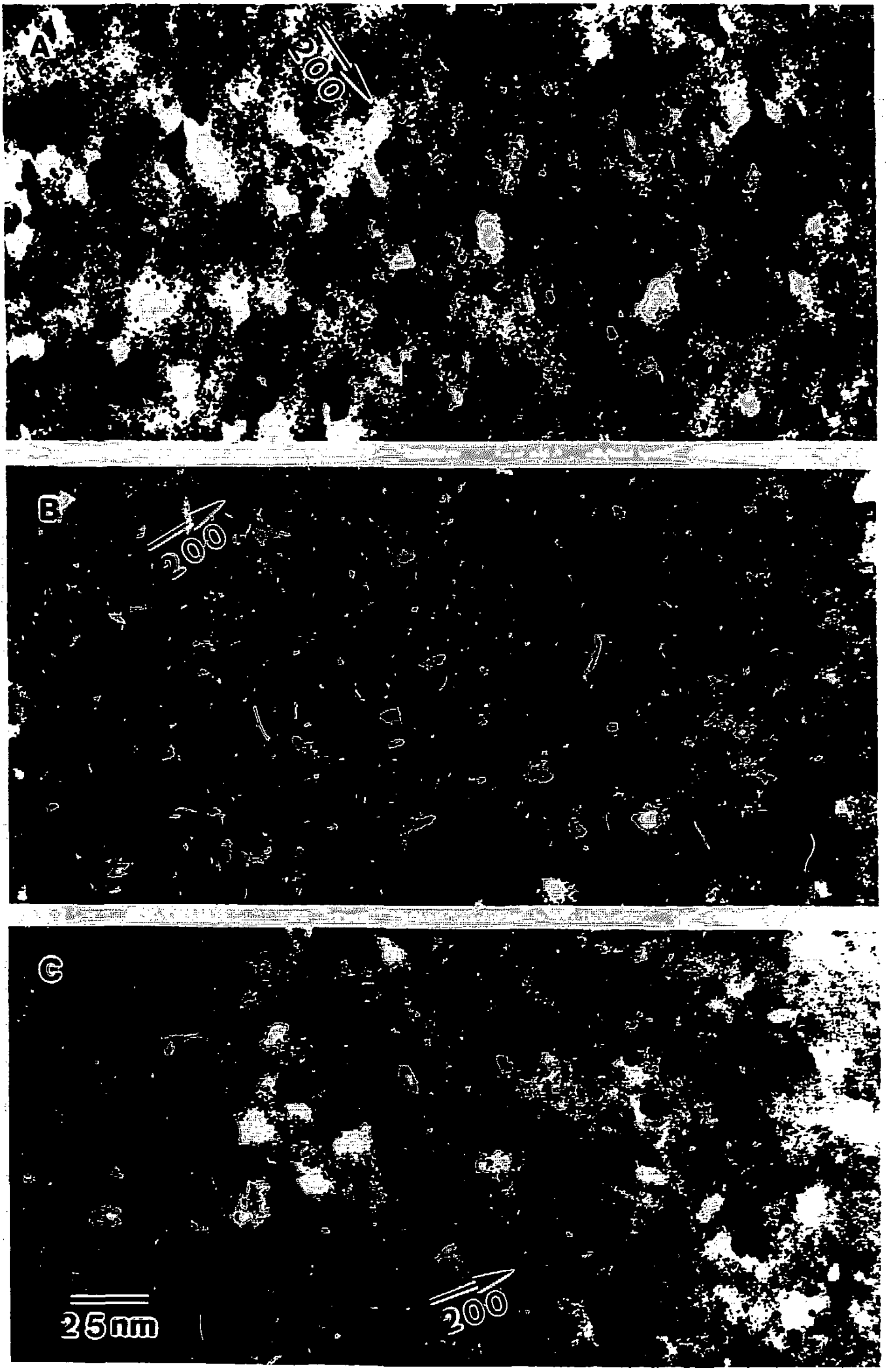
8. Linderoth, S. Rajainmaki, H., and Nieminen, R.M., "Defect Recovery in Aluminum Irradiated with Protons at 20 K," Physical Review B., Vol. 35, 1987, pp. 5524-5527.

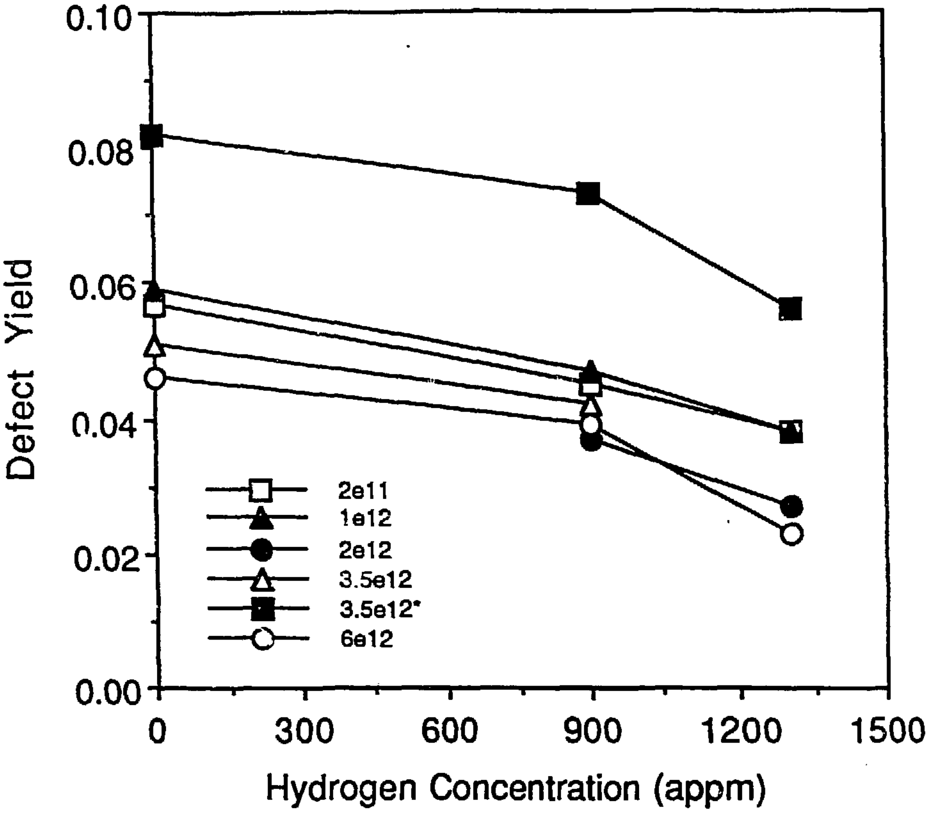
9. Wolfenden, A., "Electron Radiation Damage Near the Threshold Energy in Aluminum," Radiation effects, vol. 14, 1972, pp.225-229.

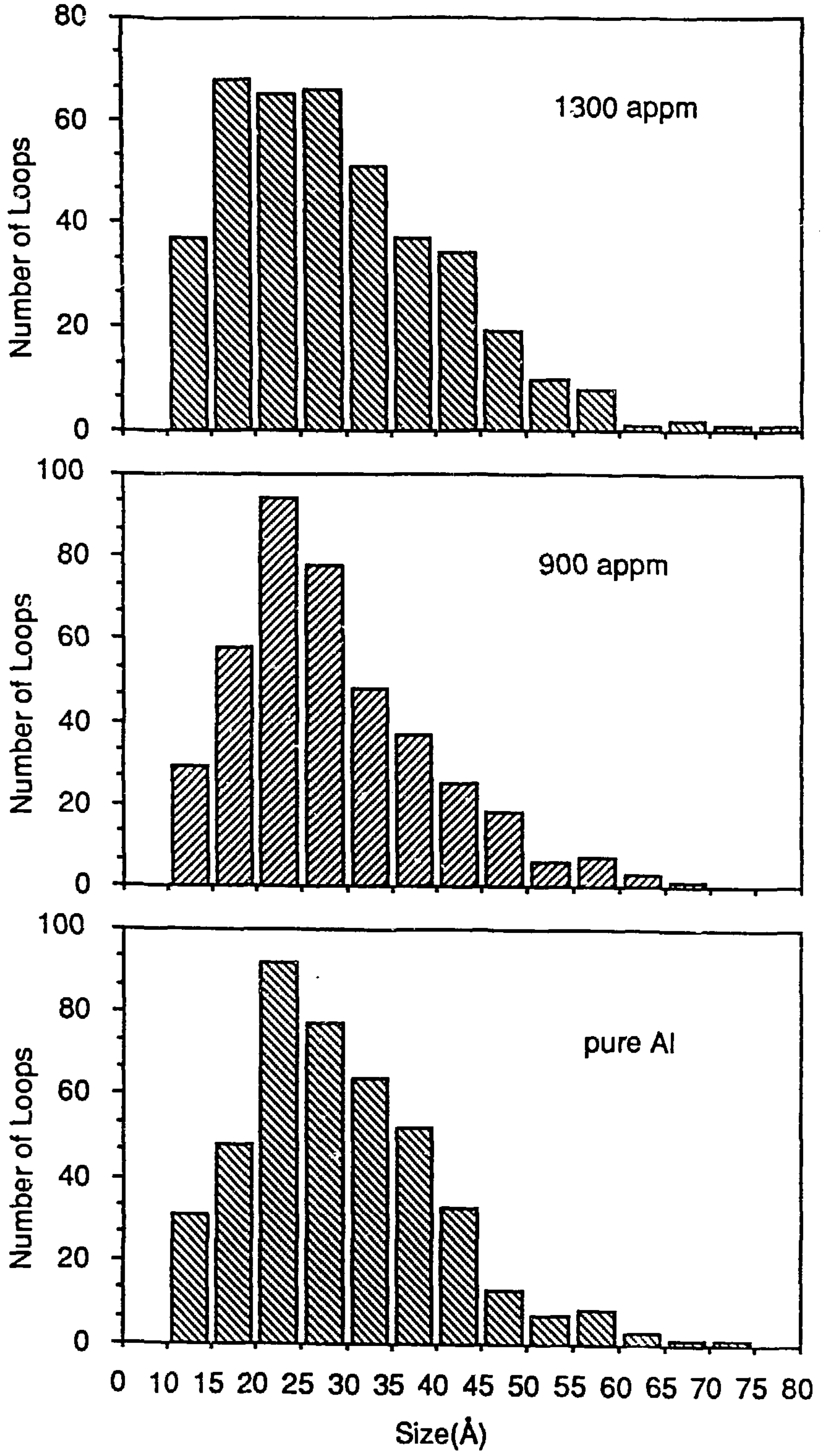
10. Bond. G.M., Robertson, I.M.,Zeides, F. and Birnbaum, H.K., "'Sub-Threshold' Electron Irradiation Damage in Hydrogen-Charged Aluminium," Phil. Mag. A, vol. 55, no. 5, 1987, pp. 669-681.

11. Zeides, F., "Effect of Hydrogen on the Mechanical properties and Fracture Behavior of High Purity Aluminum," Ph. D. Thesis, University of Illinois in Urbana, 1986.

12.Saldin,D.K., Stathopoulos, A.Y., and Whelan, M.J., "Electron Microscope Image Contrast of Small Dislocation Loops and Stacking-Fault Tetrahedra," Phil. Trans. Roy. Soc., vol. 292, 1979, pp. 523-537.

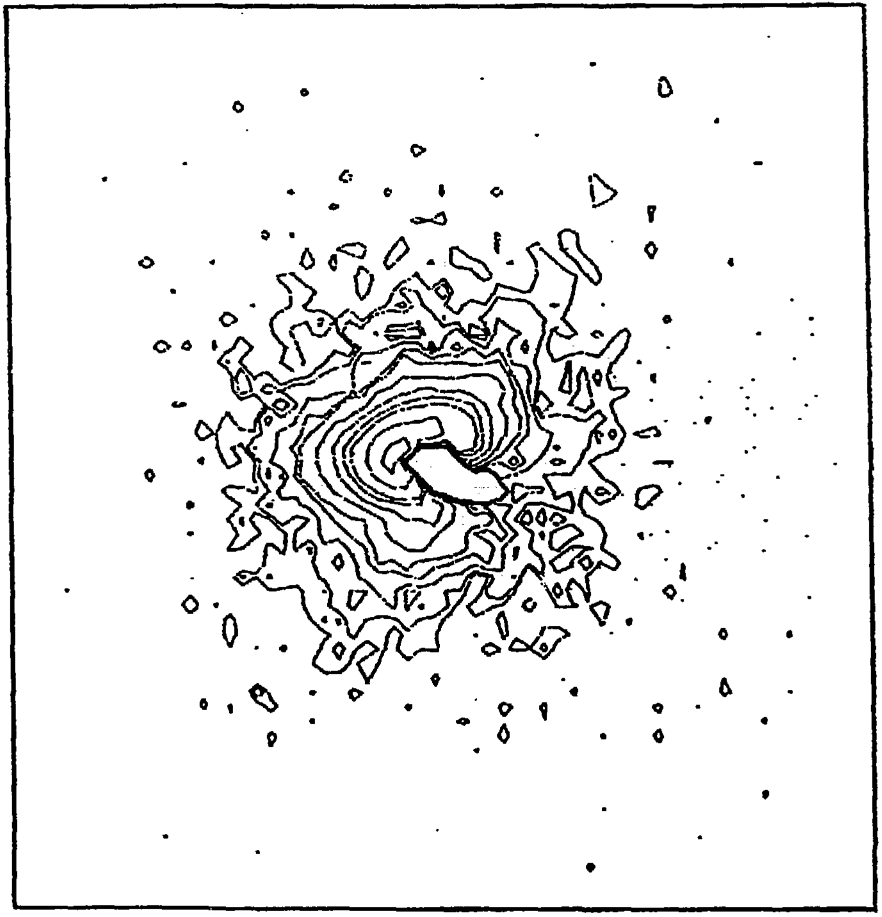

A
200
B
200
C
25nm
200

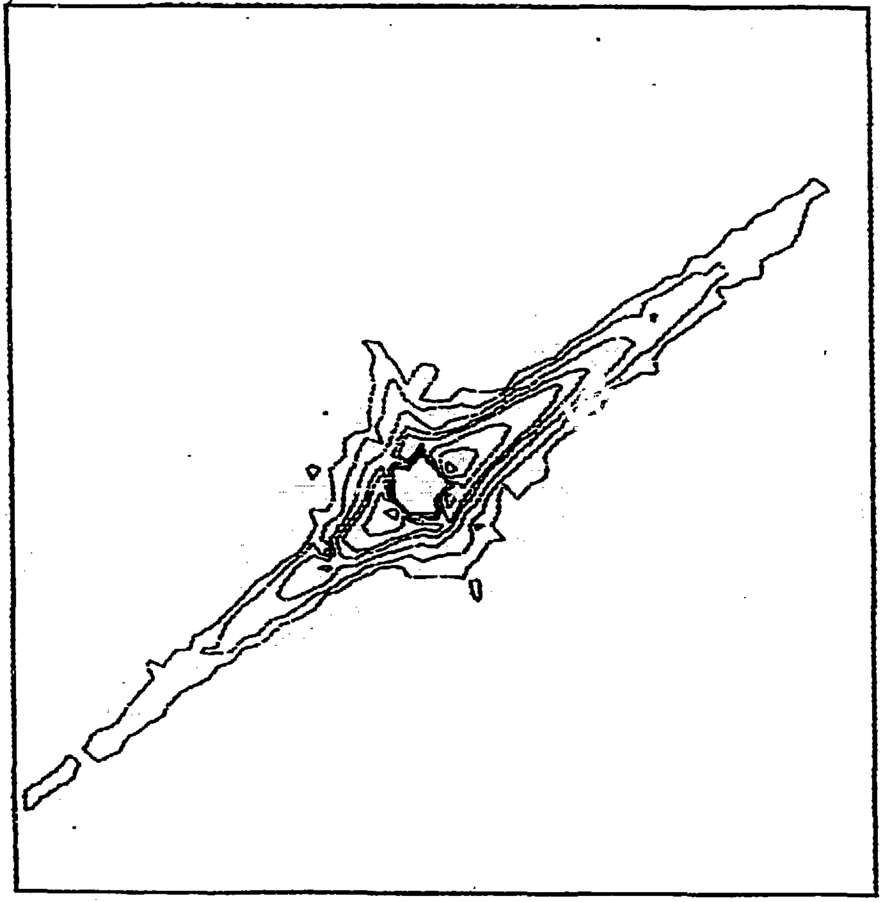

0.10
0.08
0.06
0.04
0.02
0.00
Defect Yield
0
300
600
900
1200
1500
Hydrogen Concentration (appm)
2e11
1e12
2e12
3.5e12
3.5e12*
6e12


80
60
40
20
0
Number of Loops
1300 appm
100
80
60
40
20
0
Number of Loops
900 appm
100
80
60
40
20
0
Number of Loops
pure Al
0 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80
Size(Å)

ALUMINUM VACUUM ANNEALED

SEQ. NO. 22036





ALUMINUM SC CHARGED