Presented at Third International Conference on High Voltage Electron Microscopy, Oxford, 27-30 August 1973. To be published in Proceedings.

Conf-730831--1

EFFECTS OF IMPURITY LEVEL ON ELECTRON RADIATION DAMAGE IN ALUMINUM AT ELEVATED TEMPERATURES*

J. O. Stiegler and K. Farrell
Metals and Ceramics Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830 USA

ABSTRACT

An increase in the general level of impurities affects the formation of loops and the evolution of dislocation structure in Al and Ni during bombardment with 650 kV electrons at elevated temperatures in a HVEM. In Al at 220°C, decreasing purity increases the concentration of loops, reduces their growth rates, increases the time to reach a steady-state dislocation structure, and reduces the cut-off temperatures for loop formation, indicating that impurities enhance the nucleation of loops and suppress their growth. Annealing and reirradiation experiments just below the cut-off temperature suggest that some loops may be reinitiated at their original sites implying nucleation at impurities or submicroscopic defects. The development of large, multiply-faulted loops occurs in the higher purity materials in the near surface regions after prolonged irradiation and considerable dislocation movement.

*Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

EFFECTS OF IMPURITY LEVEL ON ELECTRON RADIATION DAMAGE IN ALUMINUM AT ELEVATED TEMPERATURES*

J. O. Stiegler and K. Farrell
Metals and Ceramics Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830 USA

The formation of voids in neutron irradiated metals is strongly influenced by impurities. Void formation is also related to dislocation structure which is believed to provide biased sinks for removal of self interstitial point defects. It is not clear whether impurities affect voids directly or through their influence on dislocation structure, or both. If impurities alter the evolution of dislocation structure their effects should be observable during electron irradiation in a HVEM.

Most of our observations were made on several grades of aluminum but we have also done a little work on two grades of nickel. Chemical analyses of the materials are given in Table 1. The aluminum materials were not analyzed for interstitial type impurities because the unavoidable presence of hydrated oxide films masks some of the analyses. Specimens were 3 mm diam by 0.5 mm thick and were annealed in air for 1 hr at 500°C (Al) or in vacuum for 30 min at 800°C (Ni). After electrothinning from two sides they were electron bombarded and simultaneously examined in a Hitachi HU 650B microscope operating at 650 kV. The area under bombardment was about 4 μm diam. Current densities were measured with a Faraday cup located below the viewing chamber. Irradiation temperatures were achieved with an electrically heated specimen stage accurate to only ±20°C but with

*Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

good reproducibility. Regions near the surfaces of the foils were frequently denuded of visible damage, so all loop concentrations were based on measurements of the thickness of the damaged regions from stereo pairs. These thicknesses are difficult to define with small loops and therefore the quoted concentrations may be true to only ±50%.

Upper Cut-Off Temperature for Loop Formation

In order to study the creation of loops and their development into dislocation structure in reasonable times it was necessary to perform the irradiations at elevated temperatures. This introduced us to a hitherto unexplored limitation, the upper cut-off temperature, which is associated with annealing of the loops. We arbitrarily define it as that temperature at which, on turning off the beam, the loops disappear in a time comparable with that required to form them originally at that temperature, in our cases within ~5 min. The cut-off temperature depends on electron flux and foil thickness. The flux dependence is weak over the range of fluxes available to us and causes no more than a 5 or 10°C shift. Our foil thicknesses were usually about 1 μm. At about 10°C above the cut-off temperature we could not nucleate loops in the thickest regions of the foil that the beam could penetrate.

The measured cut-off temperatures are shown in Table 2. Although there may be some inaccuracy in the specific values, the relative values are believed to be good; they were reproducible to within 0.01 amps of heating current, that is, within 10°C. It is clear that impurities considerably reduce the cut-off temperature. The impure materials have lower cut-off temperatures because loops anneal faster in them than in the pure materials. For example, in 49 Al at 240°C the loops were well developed within 2 to 3 min and were eliminated by a 6-min anneal. In 69 Al at 240°C the loops grew to the size of those in the 49 Al within about 1 min, but an anneal of about 15 min was required to dispel them.

Care must be exercised in working near the cut-off temperature. If the temperature of the heating stage has not stabilized, the temperature may rise above the cut-off temperature. Also, we have observed, particularly in the high purity materials, a lowering of the cut-off temperature during irradiation due to aging or to contamination of the bombarded area. These factors result in a reduction or cessation in loop nucleation. On reducing the temperature below the new cut-off point loops are again nucleated. In an extreme case of such aging or contamination, we found we could not produce damage at any temperature above ambient in a nickel foil that had sat at room temperature for two years before irradiation.

Loop Formation and Development of Dislocation Structure

Nucleation of loops in the 69 Al and the 49 Al at 220°C and a flux of 4.2×10^{19} $e.cm^{-2}sec^{-1}$ was completed in the first few seconds of irradiation. In the 29 Al loop nucleation was difficult to detect in the early stages of irradiation because the loop concentration was so high; after 2 min they appeared only as a grayish haze. At 5 min individual loops could be resolved but their high concentration made counting impossible. At 15 min they had grown (and possibly coalesced) to the point where a tentative count was possible. In all three materials the loop concentrations decreased with irradiation time as dislocations were formed. The maximum concentrations of loops, i.e. those observed in the first few seconds in 69 Al and 49 Al and those after 15 min in the 29 Al, were 69 Al--9×10^{14} cm^{-3}, 49 Al--4×10^{15} cm^{-3}, 29 Al--$>>10^{17}$ cm^{-3}.

After 2 to 4 min irradiation many of the loops in the 69 Al and 49 Al began to move and interact to form a dislocation network with a resulting decrease in loop concentration. The generation rates of dislocations in these materials are shown in Fig. 1. The dislocation density was higher in the 49 Al and became saturated after about 40 min; no such trend was evident in the 69 Al but the irradiation was stopped much sooner because of the build-up of multiply-faulted loops. The development of dislocation structure in the 29 Al was relatively slow and was highly heterogeneous. The first loops to expand significantly were those at the interfaces between the matrix and inclusion particles. Such growth was noted at 5 min. At between 15 and 30 min a few loops grow into dislocations in the matrix. After 90 min the unexpanded loops in the 29 Al were smaller than those in 49 Al and very much smaller than those in 69 Al. Some of the microstructures are shown in Fig. 2.

During the formation of dislocation structure no new loops were produced until the dislocation network coarsened leaving clear areas where only a few loops formed. This depression of nucleation in a "used" region was quite marked. Loop nucleation following dislocation migration never repeated the furious nucleation at the beginning of irradiation. If the temperature was reduced by 15 to 20°C or if the beam was turned off and then on again the original burst of nucleation did not recur. Usually, rather than nucleation of new loops, the existing loops and dislocations simply continued growing. This difference in nucleation between fresh and used regions suggests a consumption of loop nuclei. Our interpretation is that some impurities are nucleating agents and are swept up by moving dislocations. When a 49 Al specimen was irradiated to produce a general dislocation structure at 220°C like that in Fig. 2(d) and was then cooled to about 50°C and the irradiation resumed at 50°C, nucleation was again prolific; but the supersaturations of point defects created at 50°C would be much higher than at 220°C and loop formation would presumably require a smaller critical nucleus and less impurities.

Effects of Preexisting Dislocations and Grain Boundaries

In a freshly prepared foil, grain boundaries and grown-in dislocations had no apparent effects on the initial nucleation of loops. However, as the loops grew larger, they interacted with the dislocations, and areas near the dislocations were the first to be swept clean of loops. In other regions loops interacted to form large dislocations which then behaved the same as the grown-in ones. In essence, areas containing grown-in dislocations were the first to clear out the loop structure and form a general dislocation network. If a foil was held at the working temperature for several hours before irradiation, preexisting dislocations climbed into regular arrays. Areas adjacent to such arrays were denuded of loops during irradiation, suggesting segregation of impurities to dislocations and inferring, again, an association of loops with dissolved impurities.

Multiply-Faulted Loops

Faults were not discerned in the initial loops that formed in aluminum during electron irradiation at temperatures in the region of 200°C. Only after extensive loop growth and dislocation motion occurred were faulted loops noted. They were large, were most prevalent in the 69 Al, and were absent in the 29 Al; many of them were multiply-faulted (up to 3 layers, possibly more) and all lay near the foil surfaces. These loops did not seem to result from general contamination of the foil surfaces because long aging times at the irradiation temperature prior to irradiation did not encourage faulted loops, and shifting the beam from a multiply-faulted region to an adjacent, previously unbombarded region resulted in nucleation of a high concentration of unfaulted loops. Rather, they required prolonged bombardment. They may be due to a low supersaturation of point defects in the surface layers or, if associated with impurities, to local contamination through the foil surfaces or to rearrangement of impurities by dislocation movement.

Anneal-Reirradiation Experiments

At temperatures near the cut-off temperature we found that when we irradiated, annealed, and then quickly reirradiated a specimen of 49 Al, the concentration of loops never changed significantly from cycle to cycle, at least for nine anneal-reirradiate cycles. Moreover, after the first cycle about 20% of the loops seemed to reappear at their original sites. This was determined by overlaying transparancies oriented with respect to reference points. When random overlays were attempted no more than 10% coincidences were found. Photographs taken after the anneal showed clearly that the loops, or at least a contrast effect from the loops, disappeared. The coincidence of loops was reduced to the 10% level with more than one anneal-reirradiation cycle. If a long anneal (2 to 3 min longer than to anneal all visible damage) was made after the first irradiation there was no significant coincidence of loop positions. There was no enhancement of this phenomenon in the commercial purity 29 Al.

If these experiments can be taken to indicate renucleation of loops at previous sites, there must be something acting to retard the rate of shrinkage of some of the original loops. Perhaps impurities stabilize the loops against complete shrinkage. The small fraction of coincidences and the elimination of coincidence by longer annealing would indicate that any point defect-impurity complexes that may form are unstable and eventually dissolve.

Conclusions

An increase in the general level of impurities affects the formation of loops and the evolution of dislocation structure in Al and Ni during bombardment with 650 kV electrons at elevated temperatures in a HVEM. In Al, decreasing purity increases the concentration of loops, reduces their growth rates, increases the time to reach a steady-state dislocation structure, and reduces the cut-off temperatures for loop formation, indicating that impurities enhance the nucleation of loops and suppress their growth. Annealing and reirradiation experiments just below the cut-off temperature suggest that some loops may be reinitiated at their original sites implying nucleation at impurities or submicroscopic defects. The development of large, multiply-faulted loops occurs in the higher purity materials in the near surface regions after prolonged irradiation and considerable dislocation movement.

TABLE AND FIGURE TITLES

Table 1. Chemical Analyses of Materials (wt ppm).

Table 2. Upper Cut-off Temperatures for Loop Formation.

Figure 1. Build-up of Dislocation Structure in Aluminum during Electron Bombardment.

Figure 2. Microstructures of Aluminum Specimens Irradiated at 220°C at 4.2×10^{19} $e.cm^{-2}sec^{-1}$.

(a)(b)(c) 69 Al irradiated 0+ min, 8 min and 140 min, respectively.

(d) 49 Al irradiated 120 min.

(e)(f)(g)(h) 29 Al irradiated 0+ min, 15 min, 30 min, and 90 min, respectively. Note small size of loops in 29 Al, and dislocation growth at inclusions in (f).

Table 1. Chemical Analyses of Materials (wt ppm)

Nominal Composition	Identification	H	N	O	C	Al	Co	Cr	Cu	Fe	K	Mg	Mn	Mo	Ni	Si	Ta	Zn	Zr
99.9999 % Al	69 Al	-	-	-	-	bal	-	<50	1	60	-	10	5	<10	<10	5	-	< 50	<10
99.99% Al	49 Al	-	-	-	-	bal	-	<50	10	80	-	20	10	<10	<10	50	-	< 50	<10
99+% Al[a]	29 Al	-	-	-	-	bal	-	<50	200	1800	-	10	20	<10	<10	200	-	50	<10
Zone refined Ni	EB Ni	3	<1	2	<10	15	-	10	20	10	7	<4	1	-	bal	-	3	< 1	-
Commercial Ni	270 Ni	6	2	74	20	≤10	<10	<10	<10	15	<10	1	<3	< 5	bal	≤10	-	<200	<30

[a]Commonly known as 1100 grade aluminum.

Table 2.

Upper Cut-Off Temperatures for Loop Formation

69 Al	290°C (0.60 T_m)	EB Ni	575°C (0.49 T_m)
49 Al	240°C (0.55 T_m)	270 Ni	475°C (0.43 T_m)
29 Al	220°C (0.53 T_m)		

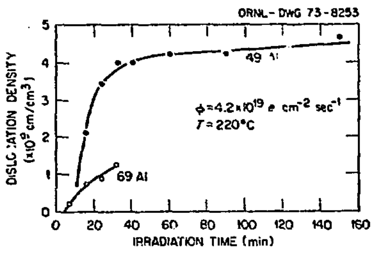


Figure 1. Build-up of Dislocation Structure in Aluminum during Electron Bombardment.

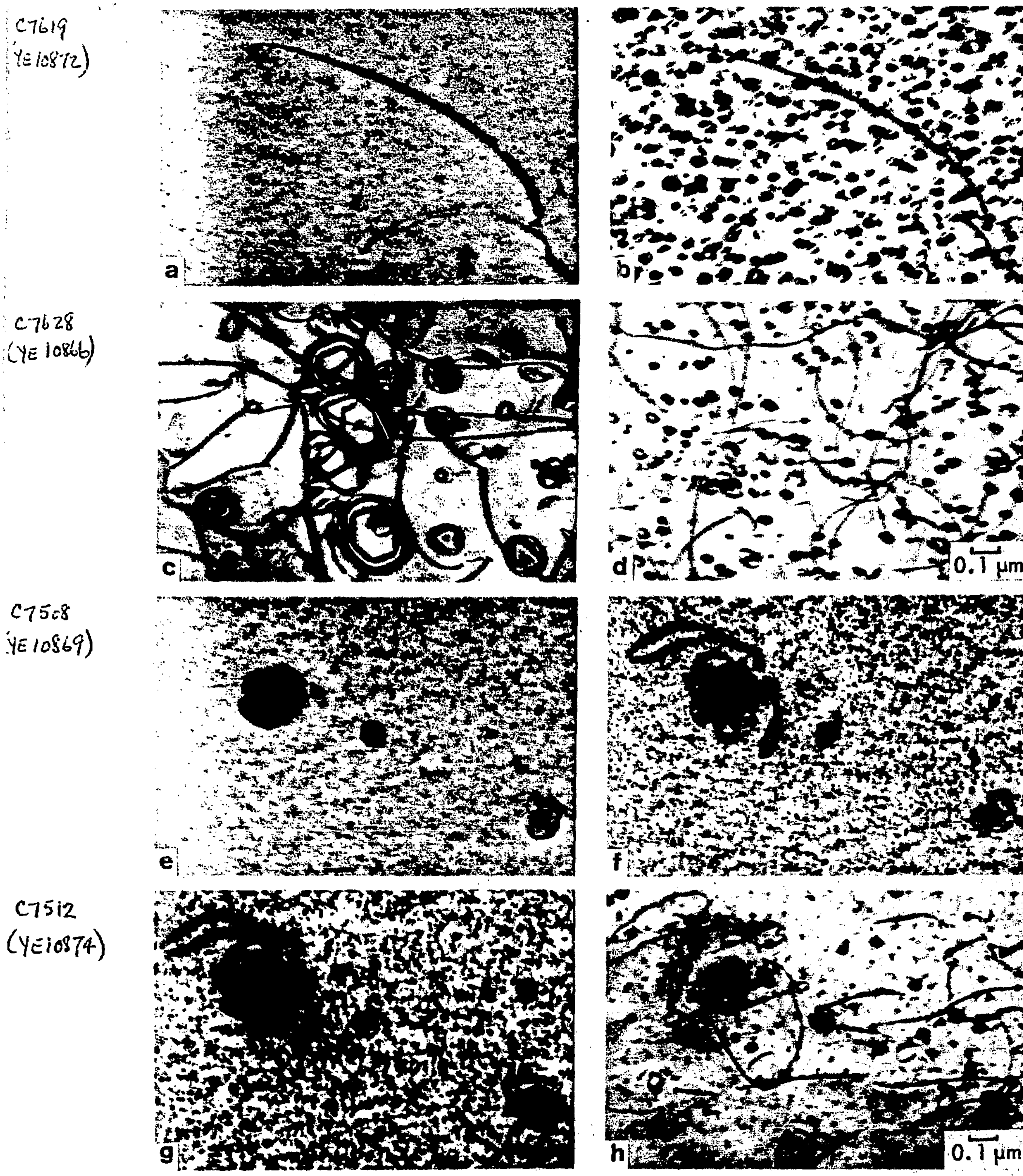
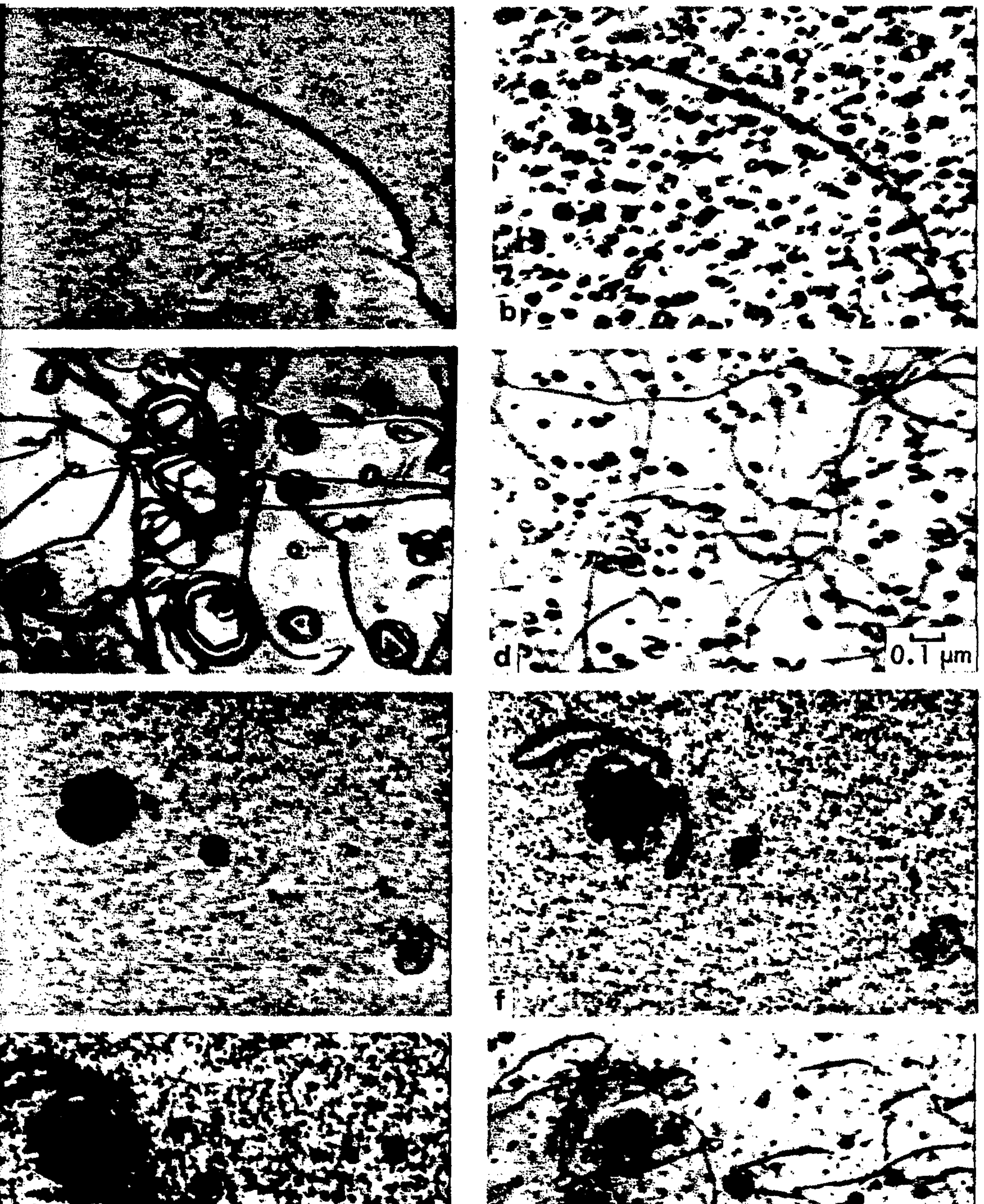


Figure 2. Microstructures of Aluminum Specimens Irradiated at 220°C at 4.2×10^{19}

(a)(b)(c) 69 Al irradiated 0+ min, 8 min and 140 min, respectively.

(d) 49 Al irradiated 120 min.

(e)(f)(g)(h) 29 Al irradiated 0+ min, 15 min, 30 min, and 90 min, respectively. Note small size of loops in 29 Al, and dislocation growth at inclusions in (f).



C7621 (YE10873)

C7396 (YE10868)

C75101 (YE10870)

C7514 (YE10871)

icrostructures of Aluminum Specimens Irradiated at 220°C at 4.2×10^{19} $e.cm^{-2}sec^{-1}$.

50,000X

(a)(b)(c) 69 Al irradiated 0+ min, 8 min and 140 min, respectively.

(d) 49 Al irradiated 120 min.

(e)(f)(g)(h) 29 Al irradiated 0+ min, 15 min, 30 min, and 90 min, respectively. Note small size of loops in 29 Al, and dislocation growth at inclusions in (f).

2