The electron microscope has been used to observe the behavior of He gas bubbles in neutron irradiated Al-Li alloys. In the case of high He concentration, the gas bubbles were observed as small white or black dots in specimens as irradiated. The bubbles initiated appreciable growth upon heating to 400°C. They precipitated preferentially along the subgrain boundaries and dislocations, as well as along the grain boundaries. The size of the bubbles, observed in a specimen heated to 550°C, ranged from about 10 Å to 1 μ.

The shape of the bubbles in the specimen heated to 400°C was hexagonal or octagonal in the two-dimensional projection and a polyhedral image of the larger bubbles was clearly observed. The number of planes that bound the polyhedral bubble increased with increasing temperature of heating. Spherical bubbles were also observed.

I. INTRODUCTION

The behavior of inert gases in metals is of considerable importance in reactor technology. The radiation-induced gases produce gross swelling or serious embrittlement in fuels and certain other reactor materials. Since Barnes, et al. observed small gas bubbles due to the precipitation of He in α-particle bombarded Cu, much experimental work has been done on the behavior of inert gases in metals under various conditions. In spite of these efforts, the behavior is not yet completely understood.

The object of the present study is to observe with an electron microscope the behavior of He gas bubbles in neutron irradiated Al-Li alloys.

Similar work has been done in the past on various gas bubbles in metals. Leteurtre, et al. observed bubbles of polyhedral shape formed by Kr or He introduced by hollow cathode discharge in Ag and U. The shape and size of gas bubbles in metals has been discussed from the standpoint of thermal equilibrium by Nelson, et al. It has been shown by Barnes and Mazey that He injected into Cu formed bubbles by nucleating upon the clusters of point defects which had been produced by α-particle bombardment. They has also discussed the migration and coalescence of inert gas bubbles in metals, on the basis of their observation of the behavior of He in Cu. Barnes has shown that, in irradiated Be, He atoms interacted with clusters of displaced atoms and vacancies, and precipitated in the form of small gas bubbles, which grew if further vacancies were available.

With irradiated Al-Li alloys, Levy, et al. observed that He bubbles precipitated heterogeneously along the grain boundaries when heated to relatively low temperatures, whereas at higher temperatures the bubbles were observed along the dislocations and homogeneously within the grains; in the case of high gas concentrations, they precipitated homogeneously within the grains even at low heating temperatures. Similar investigations were also made with UO₂. Williamson and Cornell followed the movement of Kr bubbles in UO₂ by pulse heating within an electron microscope and concluded that the process is one involving surface diffusion as its principal mechanism. It has been suggested by Barnes and Mazey from the results of their observation that the growth of He bubbles in UO₂ resulted from their collision and coalescence similarly to the case of Cu.

II. EXPERIMENTAL

Al-Li alloys, containing 0.4 and 2.7% Li, in

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the form of foil about 0.1 mm thick were annealed for 4 hr at 350°C in Ar, and then irradiated in the reactor JRR-2 to a total thermal neutron dose of either 2.9 \times 10^{19} or 2.3 \times 10^{20} n/cm^2 in ambient-water position. Helium is generated by the reaction
\[ ^{6}Li + ^{10}n \rightarrow ^{3}H + ^{4}He. \]

After suitable heat treatment at various temperatures and holding times, the irradiated foils were electrolytically thinned in an 80% ethylalcohol - 20% perchloric acid bath and were examined under a JEM-6A electron microscope operating at 100 kV.

### III. RESULTS

The gas bubbles in specimens as irradiated were observed to be small white or black dots in the Al-2.7%Li specimen irradiated to 2.3 \times 10^{20} n/cm^2 (Photo. 1), while in the specimen of lower He concentrations, the bubbles appeared only along the grain boundaries (Photo. 2). When the specimens had been heated to temperatures above 400°C, the bubbles were seen to have initiated appreciable growth, and had precipitated preferentially along the subgrain boundaries and dislocations. Photographs 3 and 4 show examples of the preferentially precipitated bubbles in Al-2.7%Li specimen irradiated to 2.3 \times 10^{20} n/cm^2 and then heated for 30 min at 550°C. In the photograph are also seen rather homogeneously precipitated bubbles within the grain.

Photograph 5 reveals that the size and distribution of the bubbles are different from one grain to another in the Al-2.7% Li specimen irradiated to 2.3 \times 10^{20} n/cm^2 and heated for 7 hr at 550°C. This may be due to the uneven thickness of the specimen. As evidence, Photo. 6 shows that the smaller bubbles are concentrated in the thinner parts of a specimen of Al-2.7% Li irradiated to 2.3 \times 10^{20} n/cm^2 and heated for 30 min at 550°C. The size of the bubbles seen in this photograph ranges from about 10 Å to 1 μ.

The shapes of the bubbles in an Al-2.7%Li specimen irradiated to 2.3 \times 10^{20} n/cm^2 were crystallographic polyhedra as shown in Photos. 7 and 8. These photographs give as indication of their shapes in the three dimensions. The number of planes bounding the polyhedral bubbles in the specimen heated for 30 min at 550°C (Photo. 8) is larger than in the case of the specimen heated for 30 min at 400°C (Photo. 7). The number seems to depend on the heating temperature, and not on the size of bubbles; the number increasing with heating temperature. When heated only to 400°C, even for 13 hr, the bubbles in an Al-2.7% Li specimen irradiated to 2.3 \times 10^{20} n/cm^2 were still very small — of the order of 10 Å, although very large bubbles also were occasionally observed. The shape of all these bubbles is hexagonal or octagonal in the two-dimensional projection. An example is given in Photo. 9, which shows a number of small hexagonal bubbles as well as a large hexagonal bubble having complex contrasts.

Photograph 10 shows the changing image of bubbles observed on altering the reflecting conditions. In Photo. 10(a), the bubbles and dislocations appear along an almost <110> direction in the Al-2.7% Li specimen irradiated to 2.3 \times 10^{20} n/cm^2 and heated for 30 min at 550°C. The images of the bubbles and dislocations were changed by tilting the specimen by 2°~3° as shown Photo. 10(b). A similar effect is seen also in Photo. 3, where the contrast and distribution of the bubbles and dislocations differ between the two sides of the subgrain boundary containing large bubbles.

### IV. DISCUSSION

The inert gas atom He is extremely insoluble in Al even at temperatures close to melting point. The atomic solubility of He in Al is considered much lower than that of He in Al which is of the order of 10^-8 or below(11). Helium concentrations in the specimens used in the experiment are estimated to be 3.3 \times 10^{-5}~1.5 \times 10^{-3}. The He atoms, generated by nuclear reaction in the specimen, supersaturate during the irradiation and precipitate to form embryo gas bubbles on suitable nuclei. Before the precipitated gas atoms can behave as a gas bubble, their separation must be increased by the removal of surrounding matrix atoms(12). This process occurs when vacancies can flow into the embryo bubbles.

The gas bubbles cannot be observed within the grain in the specimen as irradiated, unless
He concentration is as high as $10^{-3}$. This indicates that most of the He atoms remain in the state of embryo gas bubbles and/or He atom clusters at the irradiated state, because most of radiation-induced vacancies would immediately disappear, and the number of vacancies available for forming gas bubbles is much smaller than required. The behavior of the small embryo gas bubbles can be clearly observed by means of $^3$H autoradiography, which has revealed precipitation of the embryo gas bubbles within the grains in specimens as irradiated, even in specimens containing concentrations of He and $^3$H atoms lower than in this experiment\(^{(10)}\).

When the specimen is heated above the temperature where equilibrium number of vacancies increases steeply, the embryos absorb the vacancies and grow into gas bubbles of observable size. In the experiment, the bubbles began to grow appreciably upon heating to 400°C almost regardless of He concentration. Under a condition where high concentration of He is produced, radiation-induced vacancies flow into already formed embryo bubbles, which grow into observable gas bubbles during the irradiation (Photo. 1).

It is not clear in the experiment whether dislocations act as effective nuclei for small bubbles during the irradiation; whereas grain boundaries have definitely shown themselves to be effective nuclei (Photo. 2). Vacancy clusters and dislocations may become the nuclei for embryo bubbles within the grains, but these nuclei cannot act as vacancy sources for gas bubbles\(^{(14)}\). On the other hand, grain boundaries do serve as vacancy source and moreover movement of He atoms is easier along the boundaries than that within the grain, so gas bubbles always precipitate preferentially along the grain boundaries.

It is indubitable that growth of the bubbles is due to their migration and collision process; Barnes and Mazey\(^{(6)}\), and Williamson and Cornell\(^{(9)}\) have shown direct evidence of the coalescence process. There have been published a number of papers discussing the migration and growth of inert gas bubbles in metals under various conditions\(^{(12)} (15) \rightarrow (18)\). According to the theories and experiments by these authors, the bubbles migrate by a surface diffusion process, and consequently the smaller bubbles should migrate faster than the larger, and the bubbles should grow fairly uniformly whilst decreasing their number. In the present experiment however, the bubbles did not always grow uniformly within the grain at heating temperatures above 400°C; their radius still ranged from 10 Å to 1 μ even upon heating at 550°C for an extended period.

The re-solution mechanism\(^{(9)} (19) \rightarrow (21)\) does not offer a suitable for the explanation for this coexistence of smaller bubbles with larger ones. The solubility of inert gas atoms in metals is very low and permeation of inert gases through metals has been scarcely detected\(^{(22)}\). The process of inert gas re-solution in metal is very similar to that of the permeation of inert gas through metal. Re-solution of $^3$H atoms can occur at high temperatures, and re-solved atoms diffuse out from the free surface\(^{(12)} (22)\) or precipitate on adjacent larger bubbles. However, this is not sufficient to explain the existence of small bubbles at high temperatures, because the small bubbles should migrate and coalesce with the other bubbles.

It is thought that He clusters which have not yet grown into gas bubbles may remain even at rather high temperatures if the concentration of He is high. The clusters become small gas bubbles by absorbing vacancies when the specimen is heated to yet higher temperatures. Some of the He atoms leave the clusters and precipitate on the dislocations or gas bubbles. The bubbles can become larger in areas where the vacancies are supplied more easily. The neighborhood of grain boundaries is such a case. Photograph 11 shows an example where the bubbles seen in the vicinity of the grain boundary are larger than interior of the grain.

The larger bubbles are often observed to precipitate on the dislocations, as shown in Photo. 4, but the circumstances are rather complicated in this case. A dislocation line is not the only vacancy conductor, but it drags bubbles with it and induces the bubbles to migrate if it is stressed\(^{(23)}\). Dislocation pipe diffusion\(^{(24)}\) may not also be neglected, although it does not play an important role in the swelling of fissile materials.
Photo. 1  Small Bubbles in Al-2.7 % Li Specimen Irradiated to $2.3 \times 10^{20}$ n/cm$^2$ and Unheated

Photo. 2  Bubbles along the Grain boundary in Al-0.4 % Li Specimen Irradiated to $2.9 \times 10^{19}$ n/cm$^2$ and Unheated

Photo. 3  Larger Bubbles Precipitated along the Subgrain Boundary in Al-2.7 % Li Specimen Irradiated to $2.3 \times 10^{20}$ n/cm$^2$ and Heated for 30 min at 550°C

Photo. 4  Larger Bubbles Precipitated on the Dislocations in Al-2.7 % Li Specimen Irradiated to $2.3 \times 10^{20}$ n/cm$^2$ and Heated for 30 min at 550°C
(Note the image of the larger bubbles.)

Photo. 5  Bubbles in Al-2.7 % Li Specimen Irradiated to $2.3 \times 10^{20}$ n/cm$^2$ and Heated for 7 hr at 550°C
(Note difference in bubble size in different grain.)

Photo. 6  Bubbles in Al-2.7 % Li Specimen Irradiated to $2.3 \times 10^{20}$ n/cm$^2$ and Heated for 30 min at 550°C
(Note distribution of bubble size.)
Photo. 7 Polyhedral Bubbles in Al-2.7 % Li Specimen Irradiated to $2.3 \times 10^{20}$ n/cm$^2$ and Heated for 30 min at 400°C
(Note the image of the bubbles.)

Photo. 8 Polyhedral Bubbles in Al-2.7 % Li Specimen Irradiated to $2.3 \times 10^{20}$ n/cm$^2$ and Heated for 30 min at 550°C

Photo. 9 Polyhedral Bubbles in Al-2.7 % Li Specimen Irradiated to $2.3 \times 10^{20}$ n/cm$^2$ and Heated for 13 hr at 400°C

Photo. 10 Changing Image of Bubbles in Al-2.7 % Li Specimen Irradiated to $2.3 \times 10^{20}$ n/cm$^2$ and Heated for 30 min at 550°C

(a) Specimen viewed along an almost <110> direction

(b) Specimen tilted 2°~3° from (a)

Photo. 11 Larger Bubbles in the Vicinity of Grain Boundary in Al-2.7 % Li Specimen Irradiated to $2.3 \times 10^{20}$ n/cm$^2$ and Heated for 13 hr at 400°C
The shapes of gas bubbles shown in Photos. 7 and 8 are thought to be in thermal equilibrium, judging from the stress fields around the bubbles. The bubbles in specimens heated to 400°C take hexagonal or octagonal forms in the two-dimensional projection, although the precise shape of very small bubbles could not be determined in the present experiment. The larger bubbles in Photo. 7 offer indication that the three-dimensional shape would be polyhedral, bounded by eight \( \{111\} \) and six \( \{100\} \) faces, as discussed by Nelson, et al.\(^4\). The fact that the shape of the bubbles does not depend on their size (Photo. 9) supports the idea of Nelson, et al. that the polyhedral shape of the bubbles is caused by the orientation dependence of surface energy.

It has been reported by Nelson, et al.\(^4\) that the equilibrium shape of He bubbles in Al cooled from 550°C consists of \( \{110\} \), \( \{100\} \) and \( \{110\} \) planes. In this experiment, the shape of the bubbles in the specimen cooled from 400°C is very similar to the results by these authors. On the other hand, the polyhedral bubble in the specimen cooled from 550°C has higher index planes as well as those mentioned above. This may be explained by presuming that the difference of surface energy due to the difference in orientation may be less in Al-Li alloys than in pure Al, and further that in the alloy it diminishes with increasing the temperature. The shape of the bubbles precipitated along the grain boundary is very different from that precipitated within the grain (Photo. 2). The shape of the equilibrium bubbles in the alloy will be discussed in more detail on another occasion.

V. CONCLUSION

Helium gas bubbles in specimens as irradiated were observed to be small white or black dots. In the case of low He concentration, the bubbles were not present within the grain due to insufficiency of vacancies to form gas bubbles, and instead were observed along the grain boundaries. Larger bubbles precipitated along the subgrain boundaries and dislocations, sometimes also in the vicinity of the grain boundaries, where vacancies are supplied more easily. The bubbles did not grow uniformly within the grain: Their radius ranged from 10 Å to 1 μ even when heated at 550°C for an extended period. This may suggest that not all the radiation-induced He atoms precipitate as gas bubbles and migrate to grow, but remain in the form of He clusters at least in the case of high He concentration.

The shape of bubbles heated at 400°C was hexagonal or octagonal in the two-dimensional projection and a polyhedral image of the larger bubbles was clearly observed, in agreement with the forms discussed by Nelson, et al.\(^4\). The number of planes that bound the polyhedral shape of the bubble increased with heating temperature. This may be explained by the temperature dependence of surface energy. Bubbles of spherical form were also observed. The shape of the bubbles precipitated along the grain boundary is very different from that of bubbles precipitated within the grain.

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--- REFERENCES ---

(5) Barnes, R.S., Mazey, D.J.: ibid., 5, 1247 (1960).