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A. Eikum* and G. Thomas

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

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ABSTRACT

During annealing experiments in the electron microscope, prismatic dislocation loops and helices have been observed to grow in thin foils prepared from quenched and aged samples of supersaturated aluminum-magnesium alloys. Growth in pure aluminum or dilute aluminum-magnesium alloys has not been reported. It has been suggested recently that the excess vacancies required for growth are residual quenched-in vacancies which were not able to sink at external surfaces due to the presence of an impervious oxide film.

The oxide mechanism fails to account for the fact that growth has not been observed in pure aluminum and dilute aluminum alloys. This point and others concerning the life time of vacancies in thin crystals are discussed.

* Boeing Scientific Research Laboratories, Seattle, Washington

Harris and Masters (1966a) have proposed an oxide-film mechanism to explain the observation (Eikum and Thomas 1963) that helices and prismatic loops can grow in thin foils of aluminum-5 wt. % magnesium during annealing in the electron microscope. Briefly stated, their mechanism supposes that the excess vacancies required for growth are residual quenched-in vacancies which were not able to sink at external surfaces due to the presence of an impervious oxide film. Since the paper by Harris and Masters depends primarily upon the work of other investigators, including our own, it is appropriate to point out some of the inconsistencies in their approach and in their review of the literature. The available literature does not lend adequate support to a unified theory of vacancy retention by an oxide barrier, although a need for additional experiments to elucidate the mechanisms of dislocation climb in thin foils has been appreciated for some time.

The term "unified" is used above to call attention to the suggestion that an oxide film can account for the observed growth of loops in zinc and magnesium (Harris and Masters 1966a,b), in addition to the previously mentioned results on aluminum-magnesium alloys. However, in this discussion, it should be sufficient to emphasize the available information concerning aluminum and its alloys. Specifically, the following five points which represent an appreciable contribution, i.e. apparent support, to the H.M.-oxide mechanism should be clarified; (1) growth of loops and helices in an aluminum-magnesium alloy (Eikum and Thomas 1963), (2) distribution of loops

in pure aluminum quenched from the liquid state (Thomas and Willens 1964, 1966, (3) vacancy life time in thin foils, (4) the vacancy supersaturation available for loop growth, and (5) the slow reaction observed during aging of aluminum alloys (Turnbull and Cormia 1960; Turnbull et al. 1960), and the kinetics of recovery of quenched magnesium (Beevers 1963).

Before proceeding, it may be worthwhile to recall some general features which are pertinent to concentrated, not "dilute", aluminum-magnesium alloys. Upon quenching from a temperature near the melting point to room temperature (or lower), binary aluminum alloys containing more than approximately 2% magnesium are supersaturated with respect to both vacancies and solute atoms. Thus, clustering of solute atoms is to be expected during low temperature aging. In fact, resistivity experiments indicate that the clusters are relatively stable and do contain vacancies (Panseri et al. 1963). Whereas, pure aluminum has a recovery stage at a mean temperature below 0°C, aluminum containing approximately 5% magnesium exhibits what appears to be two stages, centered at ∿50°C and ∿130°C respectively. Panseri et al. conclude that excess vacancies are retained in the form of vacancy-solute atom clusters which are stable up to approximately 100°C, in agreement with the earlier work of Perryman (1955, 1966). The above considerations are important and cannot be ignored when discussing either the mechanisms of dislocation climb, or the observed dependence upon solute atom concentration.

If the presence of an oxide film represents a necessary condition for loops to grow in aluminum-5% magnesium, then it should be reasonable to expect the same condition to hold for other aluminum-magnesium alloys, and perhaps even for pure aluminum. However, loops were never observed to grow during in-microscope annealing of thin aluminum foils (Silcox and Whelan 1960, Kannan and Thomas 1966, or in aluminum-1% magnesium alloy foils (Kannan and Thomas 1966). The observation, by Silcox and Whelan, that some loops appear to shrink at a faster rate than others is used by Harris and Masters as possible evidence for an oxide film giving rise to localized perturbations of the vacancy supersaturation. The latter is only conjecture, since local conditions could equally well be influenced by, for example, the distance between loops and the foil surface or other dislocations. In addition, no loop growth is observed in freshly quenched aluminum-magnesium alloys when magnesium is not in supersaturation (Eikum and Thomas 1964, Kannan and Thomas 1966, Eikum et al. 1966).

The second point to be discussed deals with the reported concentration of vacancies in pure aluminum which was "splat-quenched" from the liquid state (Thomas and Willens 1964). In order to calculate a vacancy concentration from the observed density and sizes of dislocation loops, these authors applied a volume correction to account for the loop free zones adjacent to the thin foil surfaces. Jackson (1965) subsequently criticized the method of correction and took the point of view, that due to the presence of a coherent surface oxide

film, external surfaces were not acting as efficient sinks for vacancies. It is not the purpose of this note to enter into any discussion between the above set of authors, but only to point out that Thomas and Willens (1966) have conclusively shown by contrast experiments that thin areas of foils are free from loops and that there are loop free zones adjacent to external surfaces. Thus, the external surfaces of "splat-quenched" pure aluminum appear to represent reasonably efficient sinks for vacancies, in spite of the fact that an oxide film must be present.

The observation of growing loops in thin foils raises two points which should be considered; (a) the source of vacancies, and (b) the maintenance of a supersaturation over the time period required for growth. Initially, the growth of loops in aluminum-5% magnesium was contrasted to shrinking loops in pure aluminum, and the difference in behavior was interpreted on the basis of excess vacancies being bound up with magnesium atoms in some form of complex cluster. (For details see Eikum and Thomas 1963). This still appears to be a reasonable explanation for the source of vacancies, i.e. a residual quenched-in supersaturation. At this point, we should reiterate that specimens used for loop annealing experiments were of the order of 10^{-2} cm (0.005 in.) thick when quenched, and were stored at room temperature for about 24 hr, or annealed at higher temperatures, prior to thinning. Therefore, trapping-in of vacancies by an oxide film is hardly credible considering that only very few vacancies are influenced by external surfaces, and those regions most

affected are subsequently destroyed during electro-polishing.

The feasibility of maintaining a supersaturation requires information concerning the life time of vacancies under conditions comparable to in-microscope annealing experiments. Exact calculations would be difficult considering the complicated boundary conditions involved, but the following estimations may serve to illustrate a point. We will consider the number of jumps, n_j, made by a vacancy during its life time, τ, as being approximately,

$$n_j = \tau \upsilon \exp \{-E/kT\} \qquad (1)$$

where $\upsilon(=10^{13})$ is the vibrational frequency, kT the Boltzman factor, and E the activation energy for the jumping process (e.g. see Lomer and Cottrell 1955). For a simple case, assuming diffusion controlled climb, $n_j \simeq 8 \times 10^6$ if the parameters in equation 1 are defined as those obtained from growing loops, viz. $\tau = 30$ sec., $E_G = 0.95$ eV for loop growth and $T \approx 365°C$ (Eikum and Thomas 1963). This is the same example, and equation, used by Harris and Masters to calculate a value for the vacancy-magnesium atom binding energy. The above relationship does not take into account the entropy factor, or the rather complicated correlation effects due to vacancy-solute atom interactions.

In using equation (1), Harris and Masters have assumed n_j equal to one which defines τ as the average time to dissociate a vacancy-magnesium atom pair. However, the initial model was clearly

stated as involving a complex cluster of magnesium atoms and vacancies, and relationship (1) should actually be improved to include the total number of vacancy jumps which are in part involved with breaking-up clusters in addition to migration through the lattice. This refinement is probably not reasonable for concentrated alloys.

It is now necessary to determine if 10^6 to 10^7 jumps is within reason for a foil of the order of 4000Å thick. This is done in the following using a diffusion model (e.g. see Damask and Dienes 1963). The mean number of jumps to distruction can be given by,

$$n_j = z(\alpha\gamma a_o^2)^{-1} \qquad (2)$$

where z (=12) is the coordination number, $\gamma = 1$ for cubic lattices, a_o(≈4Å) is the lattice parameter and α is a geometrical constant. For a thin plate where one of the dimensions, 2L, is much smaller than the others, $\alpha = (2L)^{-2}$. Taking 2L = 4000Å, we obtain $n_j \simeq 10^7$ jumps. Or, if we take one-half of the foil thickness, $n_j \simeq 3 \times 10^6$ jumps. This model presumes that vacancies are annihilated at the surface of a small volume as defined, and is independent of the temperature but strongly dependent upon the type of sink (through γ). A similar result can be obtained using random walk theory and assuming a reasonable density of surface sinks. Equation 2 is based upon random diffusion of vacancies in a pure metal. It is therefore only an approximation in the present case since the effects of correlation due to solute atoms and of a vacancy gradient have been neglected. The calculations simply illustrate that equation 1 yields a result

which appears to be more consistent with the specimen geometry, when one assumes the surface is the primary sink, than setting $n_j = 1$ as Harris and Masters have done.

Maintaining a vacancy supersaturation appears feasible from the above discussion of n_j, but there is still a question of whether or not it is sufficiently large to account for the observed growth. Assuming the climb process to be destruction (emission) controlled, Harris and Masters estimated the required vacancy supersaturation to be $c/c_o = 1.1743$ for a loop growing at 10Å/sec at 365°C, i.e. the supersaturation must be of the order of 10 to 20 per cent. This requirement appears reasonable, and is a function primarily of the dislocation line tension.

Let the excess vacancies for growth be due to release of vacancies from complex clusters. For the case of a continuous source in a thin plate, the steady state solution for an excess free vacancy concentration, c_e, is given by Carslaw and Jaeger (1959) as,

$$c_e = \frac{A_o L^2}{2D_v} \qquad (3)$$

where A_o is the release rate for trapped vacancies, 2L the foil thickness, and D_v the diffusion coefficient for vacancies. Now, using $A_o = 9.2 \times 10^{17}$ per cm^3 per sec. 2L = 2000Å and $D_v(365°C) = 1.7 \exp\{^{-0.54}/kT\} = 1.09 \times 10^{-4}$ cm^2/sec., Harris and Masters calculated the available supersaturation,

$$c_t/c_o = \frac{c_o + c_e}{c_o} = 1 + (7.86 \times 10^{-6})$$

where c_o (365°C) = 4.2×10^{11} vacancies per cm^3. Clearly, this value is many orders of magnitude smaller than the required 17.4%. Allowing that the destruction controlled climb and continuous source models are valid, consider the importance of the various parameters.

Specifically, replace E = 0.54 eV by 0.95 eV and let the foil thickness be 4000Å, then $c_e = 3.4 \times 10^{15}$ per cm^3, and consequently,

$$c_t/c_o = 1.064 \ .$$

The estimated value for <u>available</u> supersaturation (6.4%) is now within an order of magnitude of the required 17.4% which is reasonable agreement for this type of calculation. The only difference between our calculation and that due to Harris and Masters is; (a) 2L = 4000Å is used since our foils were typically 4000 to 6000Å thick, and (b) the activation energy appropriate to equation 3 is taken as the value measured from growing loops E_G = 0.95 eV (Eikum and Thomas 1963). Therefore, the availability of an adequate supersaturation does not appear unreasonable. In any event, the criticism by Harris and Masters based upon an inadequate vacancy supersaturation no longer appears to be valid when considered in the above manner.

As previously mentioned, in order to estimate the required vacancy supersaturation, the process of growing loops was assumed to be controlled by the destruction of vacancies at the dislocation.

However, there is the possibility, recently emphasized by Siedman and Balluffi (1966), that the rate controlling process could be diffusion of vacancies through the lattice (Friedel 1964, Silcox and Whelan 1960). Diffusion controlled climb may be more realistic for loops growing under the influence of an internal vacancy source in the form of dissolving clusters, and this point deserves more attention which is beyond the scope of the present discussion.

The final point, concerning recovery experiments with quenched specimens, will now be briefly discussed. Harris and Masters have suggested that an impervious oxide film can be used to explain the apparently long vacancy life time observed during aging of quenched aluminum-alloys (Turnbull and Cormia 1960, Turnbull et al. 1960). It should be noted that the latter experiments were carried out using specimens $\sim 10^{-2}$ cm. thick which is greater than the upper limit for the mean diffusion length of vacancies, even in high purity aluminum having a very low sink density. That is to say, external surface sinks may not be too important, compared to internal sinks, in specimens of this size. The work of Beevers (1963), who studied the recovery of vacancies in quenched magnesium, was also referred to as supporting the surface oxide mechanism. Beevers used 0.05 cm. diameter wires, and gave the grain size as being 0.001 cm. Now, provided these numbers are correct and that the grain size remained relatively unchanged throughout the annealing experiments, these specimens contained about 50 grains in cross section. Therefore, in order for an oxide on the external surface

to be an effective barrier, vacancies would have to migrate past (or through) several boundaries without being annihilated. This seems to be a highly improbable postulation.

The preceding discussion does not represent a complete critique of the oxide film mechanism. However, based upon the known behaviour of aluminum alloys, the arguments presented by Harris and Masters in support of an impervious oxide mechanism appear to be inadequate, particularly since their mechanism cannot account for the consistent observations that loops do not grow in thin foils of pure aluminum or aluminum-1% magnesium. It is obvious that additional critical experiments are required.

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