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Comment on "Formation of Vacancy Pits on the Surface of Aluminum on Quench Annealing"

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Quench-annealing experiments on aluminum (99.995% purity) have shown that vacancy condensation pits on the surface can only be formed when the annealing temperature is 200 °C or more. In contrast to slow-cooling treatments, the pit distribution is then uniform over the whole surface; no depleted zones are observed around grain boundaries and subboundaries. There is a strong disagreement between our own results and Tariyal and Ramaswami's paper which showed pit formation by quench annealing at 20 and 50 °C. The reasons for such a disagreement are discussed.

A great number of experiments performed in our laboratory during the last fifteen years[1-6] enabled us to make precise the conditions of vacancy-pit formation at the metal-oxide interface of pure aluminum. We particularly mentioned that such pits were also observed to grow upon reheating after a quench.[5,6]

Furthermore, recent experiments[7,8] have shown that vacancy pits also could form in the *intergranular* interfaces (Figs. 1 and 2). The nucleation conditions are then more critical, i.e., the intergranular pits are never observed after a straight cooling from high temperatures.

Certain results obtained by Tariyal and Ramaswami[9] are in strong contradiction with our own observations. We can summarize our results, relative to the comparison of slow cooling with quench and annealing treatments, in the following three points:

(1) The size, shape, and number of superficial pits are different when obtained by "slow" cooling from high temperatures or by reheating after a quench: After quench and annealing treatments the vacancy-pit size is smaller, their shape often tends to be less geometric or rounded, and finally the number per unit surface is much higher (Figs. 3 and 4).

(2) After slow-cooling treatments, the superficial vacancy pits are always absent on both sides of the grain-boundary intersections (the width of the "pit-free zone" depends on the cooling conditions and on the purity of the aluminum). After quench and annealing treatments, pit-free zones were *never* observed (Figs. 5 and 6).

(3) We have found that, after quenching, the minimum annealing temperature necessary to grow vacancy pits to a size permitting observation in the optical microscope is always greater than 50 °C (a three month holding time at 25 °C after quenching has not permitted the development of detectable pits, not even by dark-field illumination). For example, in a 99.99% aluminum, more than 1-h annealing at 200 °C is necessary for the observation of surface vacancy pits.

Tariyal and Ramaswami's observations relative to quench and annealing treatments (large and geometric pits with depleted zones around the grain boundaries) have all the characteristics we found for slow cooling pits. In fact, considering the very low-heat-transfer capacity of quartz and vacuum, and the calefaction phenomenon of liquid nitrogen, we think that the so-called "quench" of a vacuum-sealed specimen into liquid nitrogen is equivalent to a *slow* cooling and could easily permit vacancy-pit formation during the quench itself.[10]

Moreover, the interpretation given by Tariyal and Ramaswami to explain that Doherty and Davis[11] have not observed any vacancy pits after quench and annealing does not seem to be valid. Our specimens are relatively thick so that slip bands are observed on the surface after rapid quenching. The observations have shown that the vacancy pits formed on reheating are far from being absent along these slip

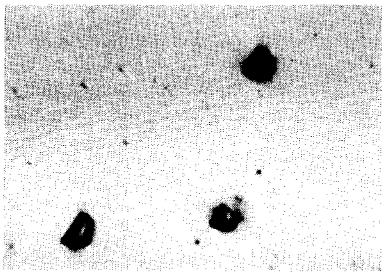

FIG. 1. Intergranular vacancy pits in a 99.99% Al specimen formed by 1-h annealing at 300 °C after an iced-water quench from 640 °C (grain boundary separated by liquid-gallium decohesion) (×1000).

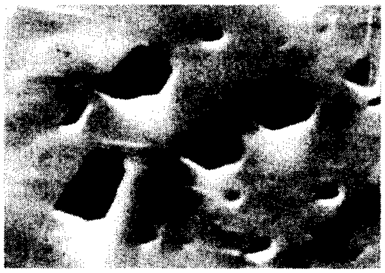

FIG. 2. Scanning electron micrograph of intergranular vacancy pits in a 99.99% Al specimen after same heat treatment as Fig. 1 (grain boundary separated by liquid-gallium decohesion) (×5000).

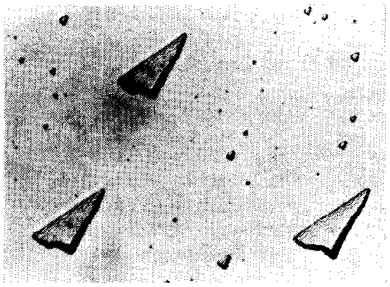

FIG. 3. Surface vacancy pits in a 99.99% Al specimen formed by slow cooling from 640 °C (×1000).

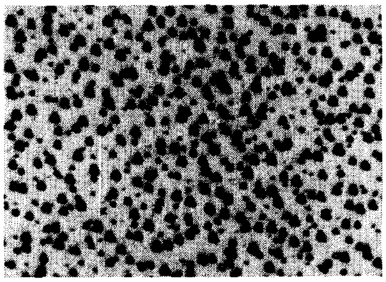

FIG. 4. Surface vacancy pits in a 99.99% Al specimen formed by 30-min annealing at 300 °C after iced-water quenching from 640 °C (×1000).

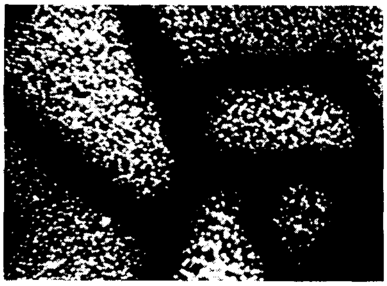

FIG. 5. Surface vacancy pits in a 99.99% Al specimen formed by slow cooling from 640 °C (dark-field illuminated) (×200).

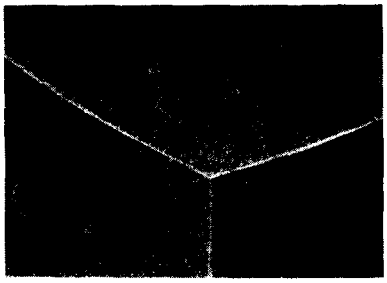

FIG. 6. Surface vacancy pits in a 99.99% Al specimen formed by 30-min annealing at 300 °C after iced-water quenching from 640 °C (dark-field illuminated) (×200).

bands, but, on the contrary, they are more numerous or larger in size. It seems, therefore, in this case that dislocations do not act as preferential vacancy sinks.[5]

In conclusion, we do not think that vacancy pits are likely to be formed after a few seconds of annealing at 50 °C following quenching; we neither agree that vacancy pits are identical in size, shape, and distribution after a quench annealing or after a straight slow cooling. It has to be particularly pointed out that the *absence* of a pit-free zone around the grain-boundary intersections on the surface is an essential feature of quench-annealing treatments. Finally, the pits observed by Tariyal and Ramaswami show all the characteristics of vacancy cavities obtained by a relatively slow cooling from high temperature.

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[1] G. Wyon, J.M. Marchin, and P. Lacombe, Rev. Met. (Paris) 53, 945 (1956).

[2] G. Wyon, J.M. Marchin, and P. Lacombe, Mem. Sci. Rev. Met. 56, 549 (1959).

[3] G. Wyon, J.M. Marchin, and P. Lacombe, Compt. Rend. 252, 1467 (1961).

[4] G. Wyon, J.M. Marchin, and P. Lacombe, Mem. Sci. Rev. Met. 60, 257 (1963).

[5] A. Marmai, G. Wyon, and M. Leroy, Compt. Rend. 264, 552 (1967).

[6] G. Wyon, thesis (Paris, 1968) (unpublished).

[7] C. Brichet, L. Peeters, C. Roques-Carmes, and G. Wyon, Compt. Rend. 271, 617 (1970).

[8] C. Roques-Carmes, L. Peeters, C. Brichet, M. Aucouturier, G. Wyon, and P. Lacombe, Metallography 4 (1971).

[9] B.K. Tariyal and Ramaswami, Appl. Phys. Letters 16, 227 (1970).

[10] The presence of tin in the aluminum used by these authors does not seem to be a determining factor, and if there is any influence, it would be an effect of stabilizing the vacancies in the matrix (strong vacancy-solute binding energy) [see Federighi, *Lattice Defects in Quenched Metals* (Academic, New York, 1965), p. 217].

[11] P.E. Doherty and R.S. Davies, Acta Met. 7, 118 (1959).