larger degree of complication in the structure of small-angle boundaries in bcc matrices.[11]

1. H. B. Aaron and H. I. Aaronson: *Met. Trans.*, 1971, vol. 2, p. 23.
2. H. I. Aaronson: *The Mechanism of Phase Transformations in Metals*, p. 47, The Institute of Metals, London, 1956.
3. P. N. T. Unwin and R. B. Nicholson: *Acta Met.*, 1969, vol. 17, p. 1379.
4. G. Thomas: *Phil. Mag.*, 1959, vol. 4. p. 606.
5. G. Thomas and J. Nutting: *J. Inst. Metals*, 1959-60, vol. 88, p. 81.
6. A. H. Geisler. *Trans. ASM*, 1952, vol. 44A, p. 269.
7. S. Toney and H. I. Aaronson: *Trans. TMS-AIME*, 1961, vol. 221, p. 909.
8. E. Hornbogen. *Acta Met.*, 1962, vol. 10, p. 525.
9. K Yagisawa, M. Okamoto, and H. Yoshida: *Trans. Nat. Res. Inst. of Metals*, 1966, vol. 8, p. 31.
10. J. A. Whitman: Univ. of Sheffield, private communication, 1969.
11. C. S. Barrett and T. B. Massalski: *Structure of Metals*, 3rd ed., p. 404, McGraw-Hill, New York, 1966.

Dopant Observations in Thin Foils of Annealed Tungsten Wire

D. B. SNOW

TUNGSTEN intended for lamp filament applications is often doped with compounds of aluminum, potassium, and silicon prior to sintering in order to obtain wire which possesses a creep-resistant recrystallized grain structure.[1] Several recent studies of doped tungsten wire have shown that fine rows of bubbles appear after annealing at temperatures greater than $0.5T_m$.[2-4] They are presumably produced by the volatization of dopants which have been previously aligned parallel to the wire axis by drawing.[3] Characterization of the chemical and physical state of the dope associated with this porosity has remained elusive.[1,4,5] Some recent data pertaining to this problem are presented here.

Doped tungsten wire drawn to 0.178 mm diam at temperatures of 750° to 1175°C was annealed by self-resistance for 6 min at 3020°C in hydrogen (post-anneal sag resistance rating was 5 to 7 mm). Atomic absorption and spectrographic analyses showed that it contained 82 wt ppm potassium, 12 wt ppm aluminum, and 4 wt ppm silicon. Short lengths of wire were ground flat on two sides, cut into 2.3 mm lengths, and thinned electrolytically.[6] The thin foils thus prepared were placed in copper sandwich grids to facilitate handling, and were examined with an AEI EM6G electron microscope equipped with a goniometer stage and an anti-contamination device.

Thin foil specimens prepared from annealed wire contained rows of enclosed bubbles which varied in size from 50 to 1200Å in diameter, Fig. 1. The most striking characteristic displayed by most, but not all, of the bubbles was that they contained a small quantity of rapidly moving liquid. This phenomenon was best observed when the foil was tilted so that a relatively intense reflection (110 or 200) was operating in the area of interest. Under such conditions the material in the bubbles behaved in a manner similar to that of a confined, heated liquid. Lowering the beam current usually caused the motion of the liquid to cease, although it could still be identified as a discrete region within the bubble, Fig. 2. When in motion, the liquid oscillated rapidly in a localized area, as if it were held there by surface tension. Occasionally, the entire volume of liquid would jump to another side of the bubble and continue to oscillate there, Fig. 3. When a particular region of the foil was continually observed, in some instances the amplitude of oscillation began to decrease after about 5 min, and ceased completely after about 15 min. This "deactivation"

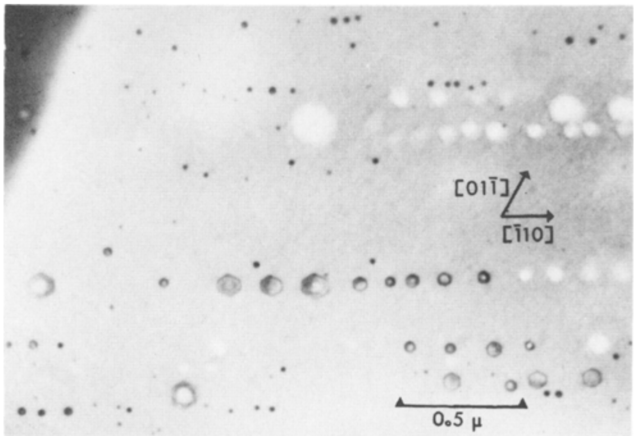

Fig. 1—Rows of bubbles formed in doped tungsten wire by annealing in hydrogen for 6 min at 3020°C. Porosity which exhibits dark contrast contains liquid. Light circular features are depressions electropolished in the foil surfaces.

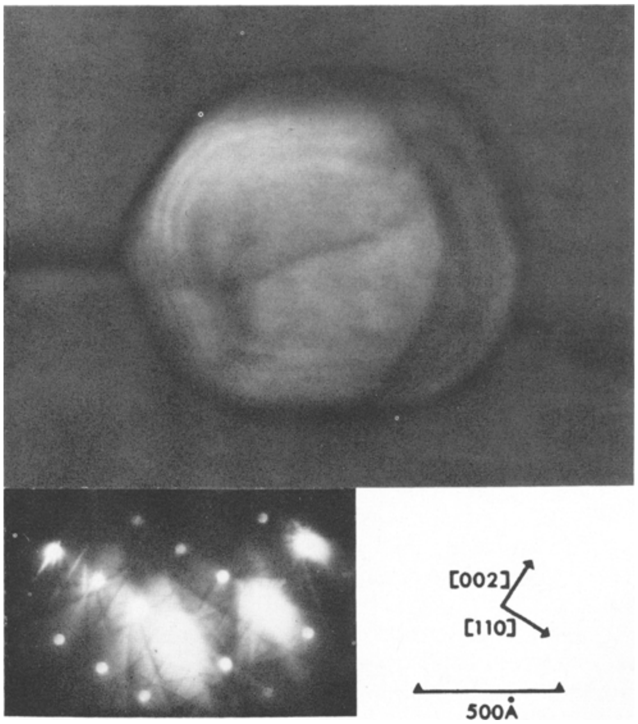

Fig. 2—Bubble formed in annealed doped tungsten wire which contains liquid at right. Note the difference in thickness fringe spacing within the bubble due to the presence of the liquid. The diffraction pattern was obtained with a $25\mu m$ aperture centered on the bubble. The linear feature external to the bubble is a dislocation.

D. B. SNOW is Research Metallurgist, Refractory Metals Laboratory, Lamp Division, General Electric Co., Cleveland, Ohio 44117.

Manuscript submitted February 14, 1972.

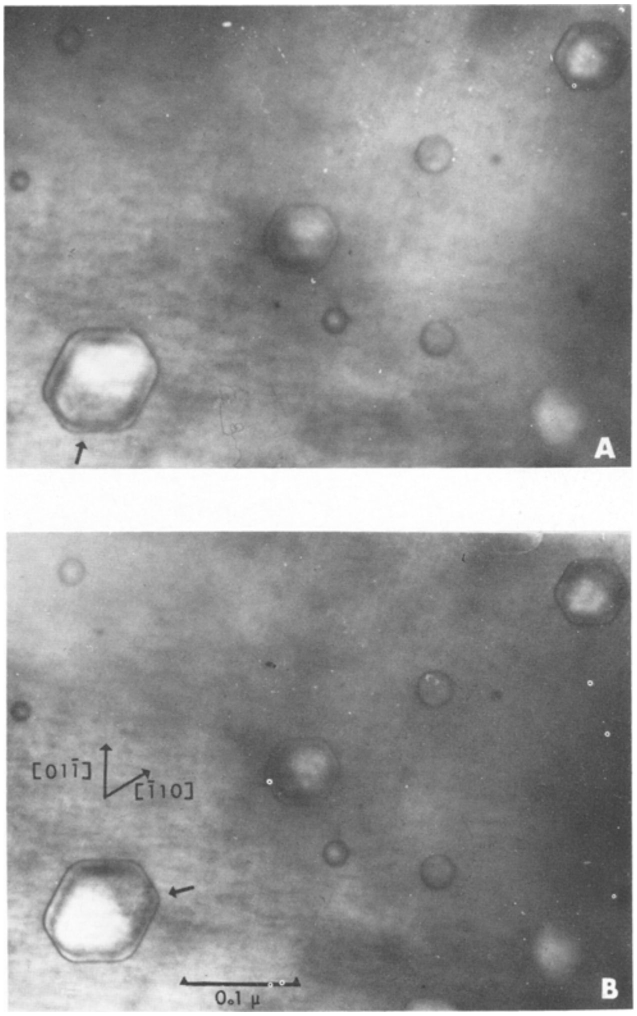

Fig. 3—Bubbles formed in annealed doped tungsten wire. Dark contrast visible within the larger bubbles is due to rapidly oscillating liquid. The liquid in the lower left bubble has jumped from its general location in Fig. 3(*a*) to that shown in Fig. 3(*b*) (arrows).

of the moving liquid during observation has thus far proved to be permanent. Oscillating liquid has been observed within bubbles irrespective of their size and shape.

Bubbles which were not active in this manner displayed uniformly light contrast in their interiors. When observed in stereo, such bubbles were seen to have been intercepted by the foil surface during electropolishing, and thus were no longer completely enclosed within the foil. Bubbles with diameters greater than 200Å displayed partially developed facets, which were determined by stereographic analysis to be $\{110\}$, rather than $\{100\}$ as observed in a previous investigation.[7]

There was no indication that the degree of beam heating which caused the entrapped material to melt and oscillate was greater than normal. The microscope was operated at 100 kv, using a 500 μm variable contion depending on bias setting, and a 2 μm beam diam on the foil. Previous investigations[8,9] indicate that these conditions, together with the use of a copper sandwich grid held in the cartridge by a copper cooling ring, should minimize specimen heating. Using the correlation of temperature rise with thermal conductivity suggested by Gale and Hale,[8] the temperature rise in tungsten foils used in this study is estimated to be approximately 50°C above ambient. It is possible that the temperature within the bubbles was somewhat higher if they possessed a coating of low thermal conductivity.

The presence of entrapped material within the bubbles in annealed doped tungsten wire is consistent with the doping mechanism proposed by Moon and Koo.[3] According to their model, the dopant is entrapped in the powder metallurgy ingot during sintering, is extended into thin rods or ribbons by drawing, and volatilizes during high-temperature annealing to form strings of bubbles by bulk diffusion of vacancies. The presence of discrete regions of dope in fine tungsten wire had been detected by field ion microscopy,[10] as well as by transmission[11] and replica[5] electron microscopy. The results of the present study show that dope in condensed form is present after high-temperature annealing, in support of the same conclusion made by Tufts.[5]

The extremely low melting point of the entrapped material suggests that it is potassium (MP 64°C). This hypothesis is supported by the presence of potassium in the doping chemicals, and in fine wire to the extent of 60 to 100 wt ppm.[12] The large atomic size and consequent low diffusivity of potassium in tungsten explains its presence as a discrete phase in fine wire despite many opportunities for homogenization during processing. The mechanism by which the cessation of dopant motion occurs during observation in the electron microscope is not apparent. Attempts to make more positive identification of the dopant by microprobe analysis of the largest pores have been unsuccessful. An extensive study of the effects of annealing temperature and heating rate on dope morphology and size distribution will be reported subsequently.

The author is indebted to D. D. White and N. Tall for the specimen preparation.

---

1 G. D. Rieck: *High Temperatures-High Pressures,* 1970, vol. 2, pp. 149-54.
2. G. Das: *Met. Trans.,* 1971, vol. 2, pp. 3239-41.
3. D. M. Moon and R. C. Koo: *Met. Trans.,* 1971, vol 2, pp. 2115-22.
4 C F Tufts: *Proc. 28th Annual Meeting EMSA,* C. J. Arceneaux, ed., pp. 438-39, Claitor's Publishing Div., Baton Rouge, 1970.
5 C. F. Tufts: *Proc. 29th Annual Meeting EMSA,* C. J. Arceneaux, ed., pp. 128-29, Claitor's Publishing Div., Baton Rouge, 1971.
6. W. C. Coons and A. S. Gleason: *Metal Progr.,* October, 1967, vol. 92, p 9.
7. G Das and S. V. Radcliffe: *Trans. TMS-AIME,* 1968, vol. 242, pp. 2191-98.
8. B. Gale and K. F. Hale· *Brit J. Appl. Phys.,* 1961, vol. 12, pp. 115-17.
9. M. Watanabe, T. Someya, and Y. Nagahama: *J. Phys.-D,* 1970, vol. 3, pp. 1461-68.
10. G. Meyrick: *J. Less-Common Metals,* 1967, vol. 12, pp. 242-46.
11. D. B. Snow: General Electric Company, Refractory Metals Products Dept., Refractory Metals Laboratory, 21800 Tungsten, Rd., Cleveland, Ohio 44117, unpublished research, 1971.
12. S. Friedman and J. Brett: *Trans. TMS-AIME,* 1968, vol. 242, pp. 2121-27.