

The Identification of Second Phases Within Bubbles in Annealed Doped Tungsten Wire

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Elemental potassium was detected within bubbles formed in annealed, commercially doped tungsten wire by transmission electron microscopy and selected area diffraction. The bubbles in specimens which had been annealed in hydrogen contained liquid potassium, solid potassium, and small quantities of potassium hydride. Only solid potassium was observed within bubbles when specimens were annealed in $< 10^{-5}$ mm Hg vacuum. The potassium solidified epitaxially on the tungsten bubble surface and had virtually the same lattice orientation. The potassium hydride usually displayed a specific orientation relationship with the solid potassium and the tungsten.

SEVERAL investigations of heavily-worked doped tungsten have demonstrated that its highly creep-resistant, recrystallized structure is due to the presence of rows of a dispersed second phase aligned parallel to the direction of deformation.¹⁻⁴ Convincing evidence has been presented that these rows are composed of bubbles, formed and stabilized by a volatile material within them.²⁻⁶ The observation of moving liquid within such bubbles at near-ambient temperatures strongly suggests that this material is potassium.⁷ This deduction is supported by the observation of discrete areas of potassium on fracture surfaces of recrystallized doped tungsten rod by secondary-ion mass spectroscopy.⁸ The present investigation provides further confirmation that potassium is responsible for the formation of the bubble rows in annealed doped tungsten wire, utilizing selected area electron diffraction from thin foils. Some preliminary results of this study have been previously reported.⁹

EXPERIMENTAL PROCEDURE

Two sizes of commercially doped tungsten wire (General Electric Type 218), 2.1 and 0.18 mm diam.,

Table I. Chemical Analysis of Cleaned, As-Worked Commercially Doped Tungsten Wire

Element	Wt ppm	At ppm
K	82 ± 2	386
Al	5 ± 5	34
Si	4 ± 2	26
Mo	48 ± 2	92
Fe	8 ± 1	26
Ni	<2	<6
Cu	<2	<6
Ca	<2	<9
Sr	3 ± 1	6
Mn	<2	<7
Sn	<2	<3
Co	<2	<6
Ti	9 ± 1	35
O	9 ± 5	98
N	1 ± 1	13
C	<10	<153
H	1 ± 1	184

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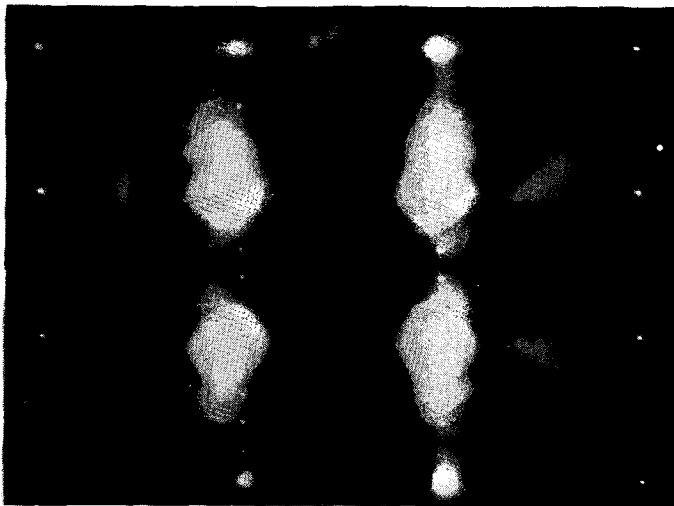
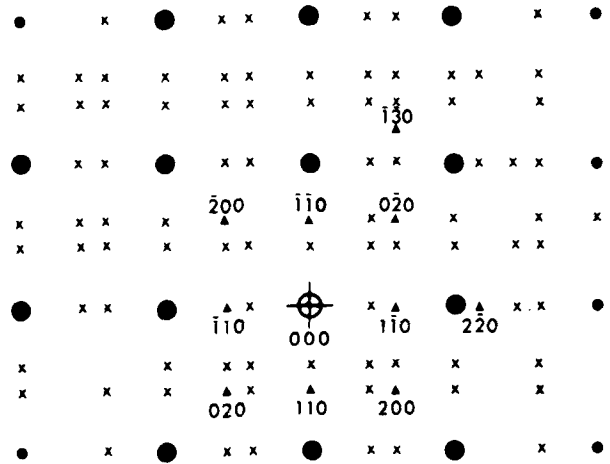
were utilized for this investigation. This wire had been processed from ingots sintered in hydrogen at approximately 3000°C by standard manufacturing procedures.¹⁰ Short lengths of both wire sizes were annealed by self-resistance heating at 3020°C for 6 min. in dry hydrogen. Other specimens of the 0.18 mm wire were furnace annealed at 2250°C for one h in a vacuum of $< 10^{-5}$ mm Hg. A chemical analysis characteristic of both as-worked wires is given by Table I. Thin foils were prepared from longitudinal sections of the annealed specimens by electropolishing at 20°C in an aqueous solution of sodium hydroxide and glycerine.¹¹ Bright field transmission electron micrographs were taken at 650 and 100 KV; dark field and selected area



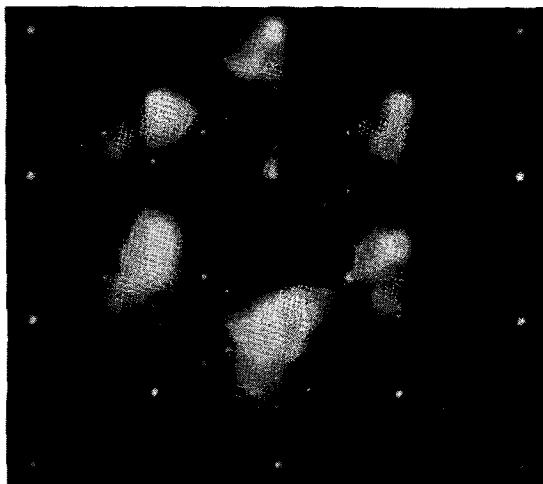
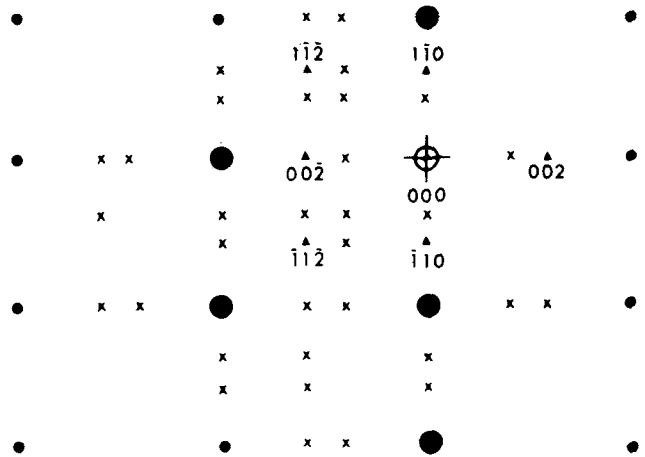
Fig. 1—Rows of bubbles containing moving liquid potassium in 2.1 mm diam. doped tungsten wire annealed at 3020°C for six min. in hydrogen. 650 KV.



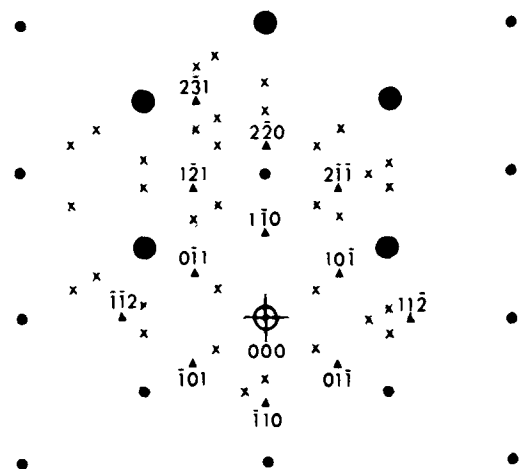
(100)



(110)



(111)



- TUNGSTEN
- ▲ POTASSIUM
- x POTASSIUM, DOUBLE DIFFRACTION

Fig. 2—Superimposed tungsten and potassium diffraction patterns from bubbles in annealed doped tungsten wire taken at 100 KV. Only the potassium spots which are not produced by double diffraction are indexed.

Table II. Interplanar Spacings of Potassium (Å)

Plane	Calculated* Spacing	Measured Avg
110	3.76	3.77
002	2.66	2.66
112	2.17	2.18
220	1.88	1.89

* $a_0 = 5.32 \text{Å}$ at 20°C^{12}

diffraction at 100 KV. Diffraction patterns were recorded on glass photographic plates with the second condenser lens defocused, using 16 to 60 s exposures.

EXPERIMENTAL RESULTS

Bubbles which contained moving liquid potassium were observed in all thin foils prepared from hydrogen-annealed specimens of both the 2.1 and 0.18 mm wire (Fig. 1). The liquid motion was caused by electron beam heating, as reported previously.⁷ The contrast within such bubbles, when observed in bright field, varied rapidly from light to dark in a manner which suggested that the electron beam was being intermittently diffracted or absorbed. Selected area diffraction patterns from the material within the bubbles were obtained by centering the intermediate aperture on a particular bubble and taking exposures of up to one minute. These patterns contained reflections from one, and in some

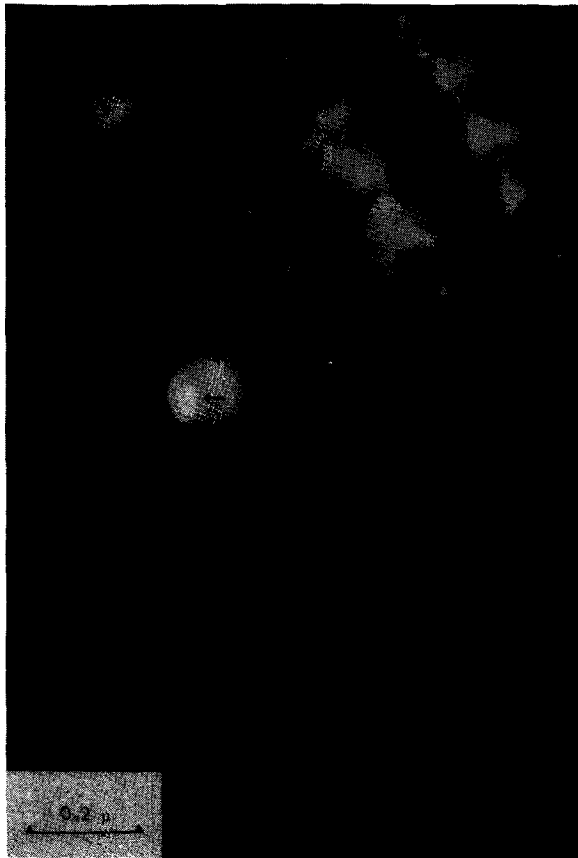


Fig. 3—Dark field image of bubble interior in 0.18 mm hydrogen-annealed doped tungsten wire. Region of immobile solid potassium shown by arrow. Operating reflection (upper right) is potassium 110, encircled by an objective aperture image.

cases two, crystalline materials which were distinct from those of tungsten.

The complex diffraction patterns produced by one of these second phases (Fig. 2) were obtained with great consistency from bubbles in both the hydrogen and vacuum-annealed specimens. The camera constant for each individual diffraction pattern was calculated from the spacing of the tungsten diffraction spots in that pattern. The lattice parameters calculated from these patterns revealed that they were produced by solid potassium (Table II). In most instances, the potassium diffraction spots were much weaker than those of the tungsten, and could be photographed only when the bubble diameter exceeded 50 nm and the foil thickness did not exceed twice the bubble diam. The intensity of the potassium spots was greatest when they came from bubbles with a diameter slightly less than the foil thickness.

These combined diffraction patterns of tungsten and potassium possessed a number of unusual features. With rare exceptions, the crystallographic orientation of the potassium lattice was the same as that of the tungsten (both have BCC structure). Infrequently, the potassium lattice orientation deviated from that of the tungsten by several degrees (100 pattern, Fig. 2; Fig. 3). Ring patterns indicative of many different potassium lattice orientations within the same bubble were never observed. The complexity of the potassium diffraction patterns arose from the diffraction of the incident electron beam by the tungsten lattice above the potassium-containing bubble, so that each of the tung-

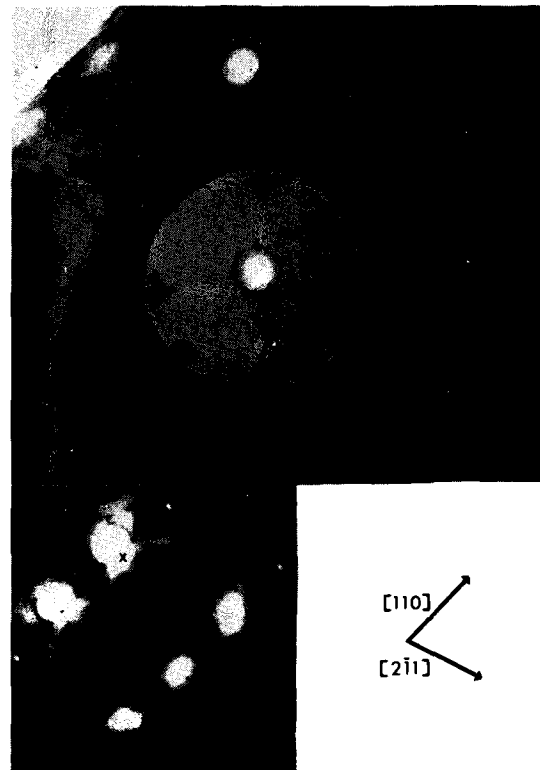


Fig. 4—Potassium-containing bubbles in 0.18 mm doped tungsten wire, annealed in vacuum for one h at 2250°C . The SAD aperture image is in the position used to obtain the $(\bar{1}13)$ diffraction pattern, with the incident beam marked "X." The pairs of weak spots are 110 and $\bar{1}\bar{1}0$ of potassium, as illustrated by Fig. 2. The higher order potassium spots are too weak to be visible here.

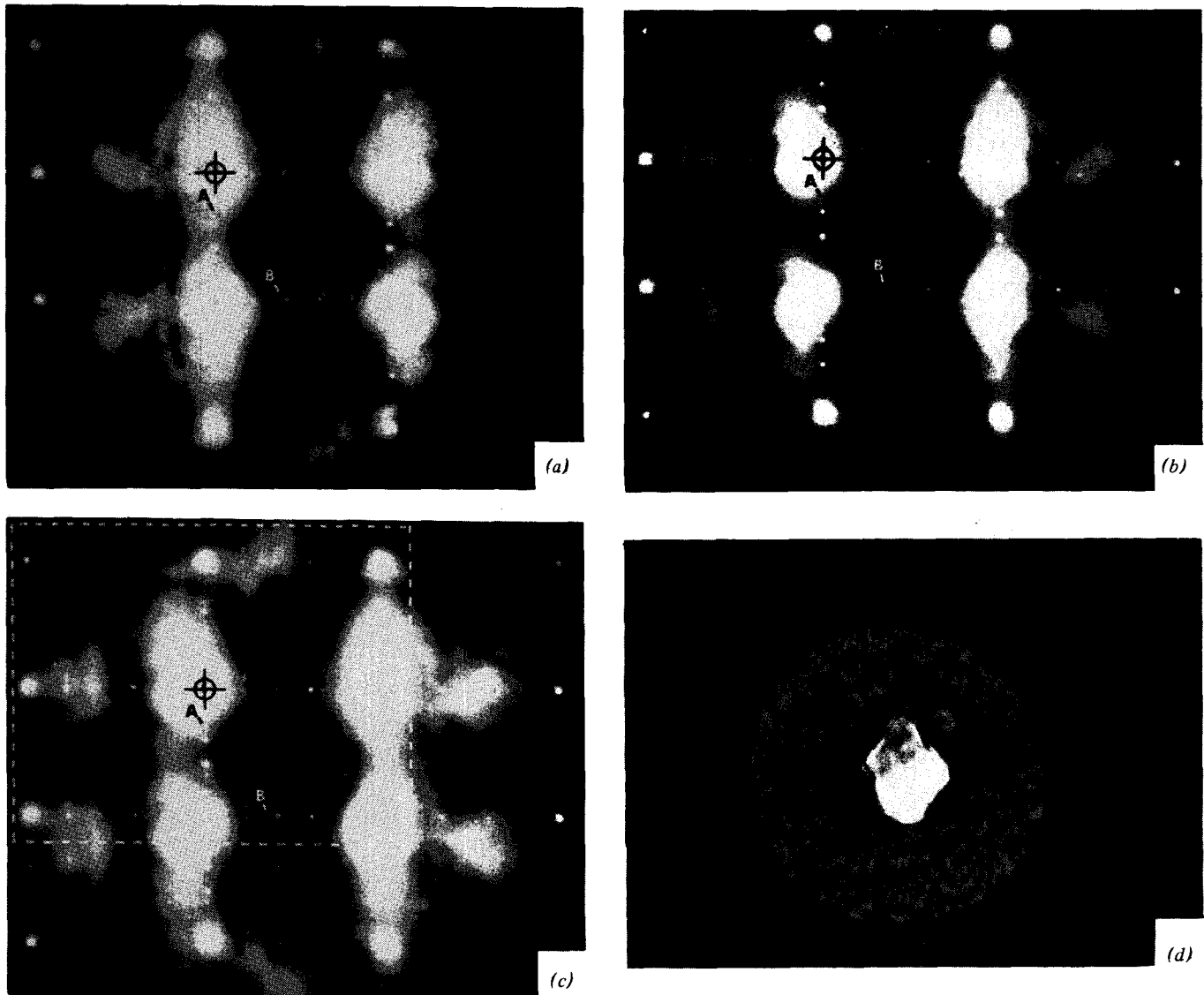


Fig. 5—Superimposed (110) diffraction patterns of tungsten and potassium taken at 100 KV which contain additional reflections from potassium hydride. (a), (b), (c) were taken consecutively with a $25\ \mu\text{m}$ SAD aperture centered on a bubble (d) so as to record the rapid changes in the potassium hydride diffraction patterns, as at the locations marked A and B. Diffraction patterns (a) and (c) were exposed for 60 s; (b) for 30 s. The area outlined by the white dashed line in (c) is described further in Fig. 6.

sten-diffracted beams was subsequently re-diffracted by the potassium. The resulting multiplicity of potassium spots can be readily indexed by considering each of the strong tungsten reflections as an incident beam with respect to the potassium.

The potassium diffraction patterns from hydrogen-annealed specimens displayed a particularly distinctive characteristic. Although the positions of the potassium reflections in reciprocal space were constant, their intensity varied in a random fashion and with the same approximate frequency as the moving liquid potassium in the bubble. Consequently, the potassium diffraction spots appeared to flicker rapidly when observed on the fluorescent screen of the microscope. Dark field photomicrographs of the regions of solid potassium within the bubbles were taken using a potassium 110 reflection. When observed on the microscope screen, the position of the diffracting potassium and the brightness of its image changed rapidly and irregularly within each bubble. Since the weak diffracted intensity from the potassium necessitated exposures of >15 seconds, the re-

sulting images were somewhat blurred. A few bubbles contained small amounts of stationary solid potassium which produced intense dark field images (Fig. 3). However, observations of the majority of the hydrogen-annealed specimens using both bright and dark field suggest that small amounts of potassium are continually solidified epitaxially and remelted on the tungsten surface of each bubble.

Selected area diffraction patterns of potassium were also obtained from within the bubbles in thin foils prepared from 0.18 mm wire annealed in vacuum at 2250°C (Fig. 4). Although these patterns were identical to those from the hydrogen-annealed specimens, no moving liquid was observed within the bubbles after annealing in 10^{-5} mm Hg vacuum. The intensity of the potassium diffraction spots were generally much weaker; so much so that attempts to form dark field images using potassium reflections were unsuccessful. The bubbles were, however, partially filled with solid material which presumably was potassium.

Diffraction patterns distinctly different from those of

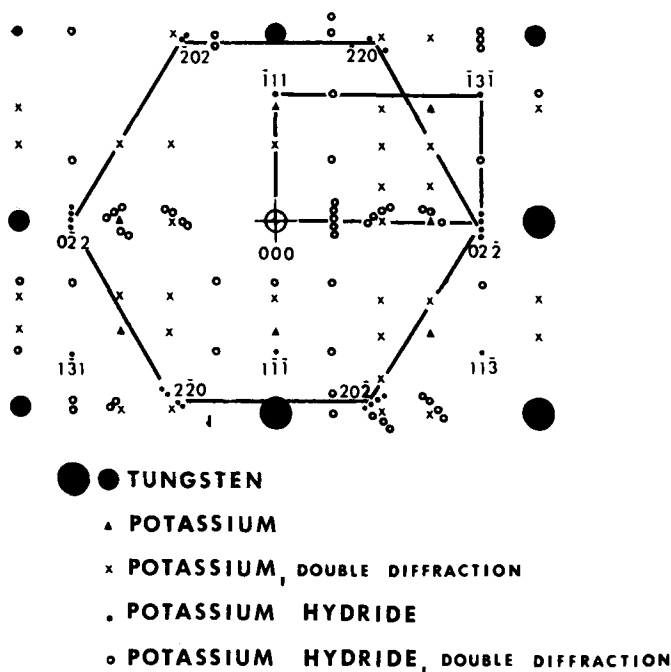


Fig. 6—(211) and (111) diffraction patterns of potassium hydride, together with (110) tungsten and (110) potassium patterns, corresponding to the area outlined in Fig. 5(c).

Table III. Interplanar Spacings of Potassium Hydride (Å)

Plane	Published ¹³ Spacing	Measured Avg
111	3.30	3.32
002	2.86	2.86
220	2.02	2.03
311	1.72	1.73

potassium which indicated the presence of very small quantities of another solid phase within the bubbles were infrequently observed only in hydrogen-annealed specimens. Both the fine structure and the overall symmetry of these patterns changed over a period of minutes, as illustrated by Fig. 5. Often, two distinct spots which were recorded on one photographic plate proved to be part of a short arc of spots at the same location seen in an exposure taken less than a minute later, as in Fig. 5(a) and 5(c). The arcs of spots, when present, were very short, and ring patterns were never observed. These diffraction patterns did not appear to vary in any systematic manner.

Only a limited number of diffraction spots and/or short arcs from this second phase were present in the majority of the patterns which were photographed. Their relative intensity was generally less than even that of the potassium spots. Several of the more complete patterns were successfully indexed, as illustrated by Fig. 6. Four distinct lattice spacings were repeatedly observed, and the phase from which they originated was identified as potassium hydride (Table III). A rationale for the existence of this compound within the bubbles in samples which had been annealed well above its reported decomposition temperature¹⁴ will be subsequently discussed.

Two additional distinctive characteristics were observed in the diffraction patterns obtained from the area of ≥ 150 nm bubbles in hydrogen-annealed specimens. First, the tungsten matrix spots in the (111) and

(110) patterns exhibited short streaks in $\langle 112 \rangle$ directions. These streaks were not present close to the center of the pattern, but became visible and increased in length with increasing order of reflection (Fig. 7). They were always centered on the tungsten spots, and never extended through the pattern for long distances. Similar streaking was present in patterns obtained from bubble sites where the bubble had been intersected by the foil surface. However, they were not observed in any diffraction pattern from bubble-free area of tungsten at distances greater than $0.15 \mu\text{m}$ from a bubble edge.

Diffraction patterns from the area of large bubbles also exhibited a fine, cross-hatched pattern as a part of the background intensity near the tungsten diffraction spots (100 pattern, Fig. 2; Fig. 5). The symmetry of this cross-hatched background pattern corresponded to that of the zone axis of the diffraction pattern: 4-fold for [100], 3-fold for [111] and 2-fold for [110]. No satisfactory explanation for the presence of these background patterns has become apparent. They appear to be associated with the presence of large polyhedral or spherical bubbles with diameters greater than 120 nm.

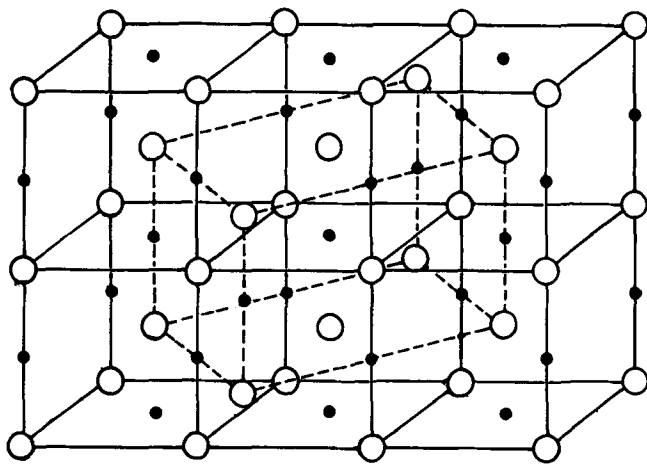
DISCUSSION

The incorporation of potassium into commercially doped tungsten wire is best explained by a mechanism similar to that proposed by Moon and Koo,⁴ in which potassium compounds are entrapped during the sintering of the pressed-powder ingot. It is probable that these compounds are reduced when hydrogen from the sintering atmosphere permeates the tungsten at approximately 3000°C , and that most of the reaction products diffuse away. The relatively large atomic size and consequent low diffusivity of potassium cause some of it to remain dispersed in discrete regions at the original sites of its entrapment. The subsequent mechanical processing of the ingot into fine wire at successively decreasing temperatures greatly elongates these potassium-rich regions, which volatilize and produce rows of bubbles when the wire is subsequently annealed.

Annealing doped tungsten in hydrogen, rather than in vacuum or an inert protective atmosphere, greatly facilitates the observation of both moving liquid potas-



Fig. 7—Increase in matrix spot streaking in $\langle 112 \rangle$ (example shown by arrow) with distance from the incident beam (X). Superimposed (111) diffraction patterns of tungsten and potassium from the area of a bubble similar to that shown in Fig. 5(d).



○ POTASSIUM ● HYDROGEN

Fig. 8—Representation of a BCC potassium lattice with one-third of the octahedral interstitial sites filled by hydrogen. Dotted lines show the face-centered tetragonal cell which closely approximates the NaCl structure of potassium hydride.

sium and solid potassium diffraction patterns from within the bubbles. Although this effect was not thoroughly investigated here, it seems probable that the high diffusivity of hydrogen in tungsten at temperatures near 3000°C^{15,16} results in the reduction of any residual potassium compounds within the bubbles. However, the failure to observe moving liquid potassium in bubbles in the vacuum-annealed specimens is not so readily explained. Evidently, the choice of annealing atmosphere has a subtle effect on the state of the potassium in the bubbles. The origin of this effect remains unexplained, since the selected area diffraction patterns give no indication of a change in the chemical state of the potassium.

The most probable first-layer structures of potassium atoms adsorbed on several low-index planes of tungsten have been previously described by Schmidt.¹⁷ In all cases, the structure of the adsorbed layer at intermediate coverages corresponded closely to that of the tungsten substrate. Further addition of potassium caused the first adsorbed layer to become more closely packed. Properties characteristic of bulk potassium appear after two to three monolayers have been formed.¹⁸ This model is consistent with the structural relationship observed in the present investigation, in which the crystallographic orientation of the solid potassium within the bubbles and that of the surrounding tungsten matrix were virtually identical in most cases. The good agreement between the observed and calculated lattice spacings of solid potassium is also consistent with the concept of the formation of a normal BCC potassium structure a few layers from the tungsten. As mentioned previously, this process appears to occur continuously when the bubbles in hydrogen-annealed specimens are observed by TEM, in that dark field observations using a potassium reflection indicate that small regions of solid potassium appear to solidify and remelt on the bubble surface as the bulk of the liquid moves about under the influence of beam heating (estimated to be < 50°C above ambient temperature).⁷

The temperature dependence of the dissociation

pressure of potassium hydride is quoted by Hurd¹⁴ as $\log p_{\text{mm}} = -5850/T + 11.2$. Consequently, no potassium hydride would be expected to exist in doped tungsten wire when resistance-annealed in hydrogen at 3020°C, even at the high internal pressure within the bubbles at that temperature. However, sufficient hydrogen should be present to react with the potassium in the bubbles and form small amounts of potassium hydride at the lower temperatures which occur during the 8 to 10 s required for the wire to cool. The potassium hydride was usually discretely oriented with respect to both the potassium and the tungsten, as illustrated by Fig. 6, in which $(110)_{\text{K}}$ is parallel to $(111)_{\text{KH}}$ and $(001)_{\text{K}}$ is parallel to $(01\bar{1})_{\text{KH}}$. If a potassium BCC structure is considered in which one of the three sets of octahedral interstices is occupied by hydrogen atoms, face-centered tetragonal unit cell can be constructed which is quite similar to the NaCl structure of potassium hydride (Fig. 8), and which is oriented with respect to the potassium as described above. This crystallographic relationship is one which, under suitable circumstances, would allow potassium which was supersaturated with hydrogen to transform to cubic potassium hydride with a minimum of atomic rearrangement. In the present case, however, it is probable that the potassium hydride forms epitaxially on the tungsten at temperatures considerably above the melting point of potassium (64°C at 1 atm). The short arcs of potassium hydride diffraction spots shown in Fig. 5 appear to have originated from many small crystallites which deviate from an exact orientation with the tungsten. The changing appearance of these arcs can be accounted for by the random motion of the liquid potassium within the bubble, which absorbs the diffracted intensity from different potassium hydride crystallites at different times.

The nature of the streaked tungsten diffraction spots described previously indicates that they originate from an elastic distortion of the tungsten matrix, rather than the shape effect of some otherwise undetectable precipitate. Extensive attempts to obtain this diffraction effect from areas away from bubble sites produced negative results. It is possible that the streaking is due to the elastic relaxation of the tungsten lattice at the bubble surface (negative dilatation).^{19,20} Strain contrast at the bubble surface produced by this relaxation could not be detected in bright or dark field. In any case, such contrast would be weak and, therefore, difficult to observed since the diam of the bubbles which were studied greatly exceeded the extinction distance of the various reflections used.²⁰ Another possible explanation for this effect involves the existence of a high concentration of interstitially dissolved atoms near the bubble surface in sufficient quantity to produce detectable tungsten lattice strain. Such a concentration of interstitials could result from the diffusion of vacancy-interstitial pairs to the bubble as proposed by Anthony.²¹ Unfortunately, the tungsten spot streaking was not sufficiently pronounced to allow verification of one of these mechanisms.

CONCLUSIONS

- 1) Selected area electron diffraction data have confirmed that the bubble-forming element in commercially doped tungsten wire is potassium.
- 2) The observation of moving liquid potassium and

of solid potassium diffraction patterns by transmission electron microscopy is aided by annealing the specimens in hydrogen prior to thinning.

3) Potassium solidifies epitaxially on the inner surface of the tungsten bubbles, usually in such a way that the tungsten and potassium lattices have the same orientation.

4) Small amounts of potassium hydride are formed within the potassium-containing bubbles when doped tungsten specimens cool after being annealed in hydrogen at approximately 3000°C.

5) The most frequently observed relative orientation between the potassium hydride and potassium lattices was: $(110)_K$ parallel to $(111)_{KH}$ and $(001)_K$ parallel to $(01\bar{1})_{KH}$.

6) Selected area diffraction patterns from the vicinity of >120 nm diameter bubbles contained streaked tungsten diffraction spots, indicative of elastic tungsten lattice strains near the bubble surface. The origin of these strains was not determined.

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