

## Construction of Filament Surfaces\*

R. P. JOHNSON

*Research Laboratory, General Electric Co., Schenectady, N. Y.*

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An incandescent tungsten filament gradually loses its die marks and comes to display a surface whose structure depends on whether the lamp was evacuated or gas-filled, and on whether it was run on a.c. or on d.c. Filaments heated in vacuum with a.c. remain smooth and nearly round. In neutral gas, with a.c., the filament tends to expose smooth concave (100) faces. The d.c. vacuum structure is steplike, is polarized with respect to the current, and seems to be due to a drift of W ions in the field along the filament. Surface migration of Th adsorbed on W, during d.c. heating, has been demonstrated in a simple electron-

optical tube. Structure identical in form with the d.c. structure appears on a.c. filaments where a temperature gradient exists, and is attributable directly to surface diffusion in the temperature gradient. On d.c. gas filaments the d.c. structure and the gas structure are concurrent. No small-scale structure is found microscopically; probably the only substructure is atomic in scale. Preliminary study of Ta, Mo, Pt, Fe and Ni filaments in vacuum indicates that these metals also develop a roughened surface on d.c. heating, but remain smooth on a.c.

### INTRODUCTION

THIS study was undertaken in the hope of finding answers to two questions. Imagine some simple solid, such as a sphere, cut out of a single crystal of metal at 0°K, with its surface as nearly smooth as the atomic nature of the lattice will allow. If this sample is heated so that atoms evaporate from it irreversibly, how will its shape change, and what sort of structure will the surface, originally smooth, come to display? If the sample is held in equilibrium with the vapor for a long time, what shape and what surface structure will result?

These questions, aside from their intrinsic interest, are of importance in the study of thermionic emission, adsorption and surface reactions, pyrometry, and lighting. A cylindrical filament of tungsten, heated by electric current, is, for well-known reasons, the metal sample most commonly used in experiments in all these fields. The tungsten filament is also a most convenient test object for studying the surface effects of drastic heating. Burned-out incandescent lamps afford a plentiful supply of specimens which have been held at high temperatures for about 1000 hours. Much of this investigation, then, has been a microscopic study of filaments from several hundred burned-out incandescent lamps, of various sizes and from various manufacturers.

\* This investigation began at the Massachusetts Institute of Technology in 1936. The results were reported in part at the Washington Meeting of the American Physical Society in April, 1938.

### RECRYSTALLIZATION OF TUNGSTEN WIRE; GAS IN LAMPS

The fibrous crystals in raw drawn tungsten wire have a [110] axis preferentially along the wire direction,<sup>1</sup> with this preference more marked near the axis.<sup>2</sup> When a straight wire recrystallizes on heating, the resulting equiaxed crystals have the same degree of alignment locally as the original fiber structure if they are so small that a cross section of the wire comprises many of them. If the final crystals are so large that they extend through the wire, they have the same degree of alignment as the original fibers near the outside. Apparently the large crystals grow from nuclei near the surface; this view is consistent with the idea that the material near the surface is most highly strained in the process of drawing.

The size of the final crystals depends chiefly on the impurity content. Wires containing 1 to 2 percent of thoria usually grow only small crystals; the "218" wire generally used in lamps is so doped that it grows overlapping crystals many wire diameters long; very pure tungsten, like other pure metals, grows crystals one or two wire diameters long, with boundaries nearly transverse to the wire. Helical lamp filaments of 218 wire often contain crystals 20 to 30 turns long; the helix is as if it were hewn from a single-crystal block.

<sup>1</sup> M. Ettisch, M. Polanyi and K. Weissenberg, *Zeits. f. physik. Chemie* **99**, 332 (1921).

<sup>2</sup> This, and succeeding statements in this paragraph, are based on unpublished x-ray studies by Mr. R. B. Nelson and the writer.

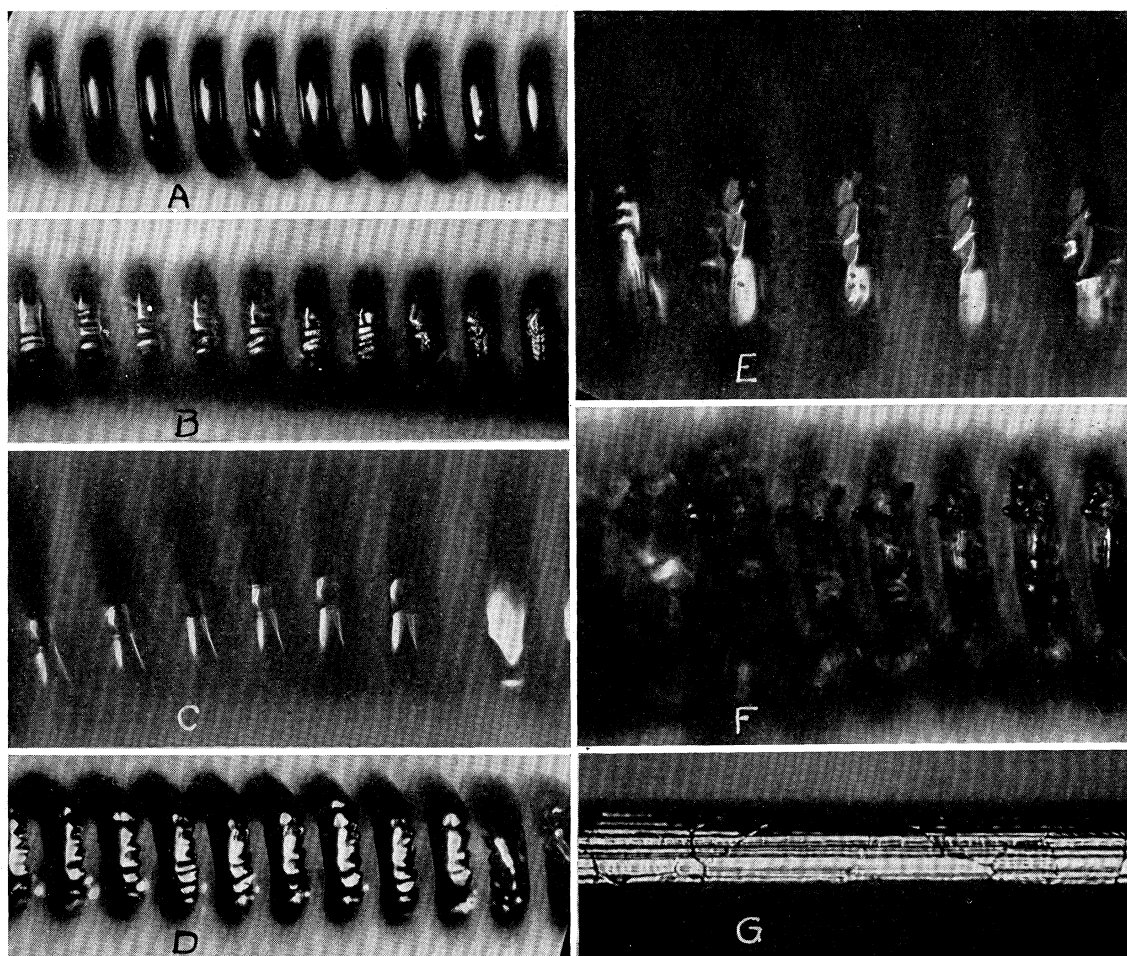


FIG. 1. *A*, Typical a.c. vacuum helix, with wire round and smooth except for grain boundaries. *B*, Hook-region structure on an a.c. vacuum helix. *C*, Structure on a small (50 w) helix heated with a.c. in lamp gas. *D*, Helix heated in vacuum with d.c., top of turns negative. *E*, Stile structure on a helix heated with a.c. in pure argon. *F*, Spine growth near a burnout in lamp gas. *G*, Residual die marks on pure tungsten heated with a.c. in vacuum.

Mazda lamps of 40 watt size and larger are currently filled with 86 percent A + 14 percent  $N_2$  ("lamp gas") at 60 cm cold pressure. Lamps of smaller size are evacuated.

#### THE FOUR TYPES OF SURFACE STRUCTURE

Judged solely by surface appearance, helical filaments from used incandescent lamps fall unambiguously into four classes. Surface structure is correlated with voltage supply and gas filling as follows:

##### (1) Alternating current in vacuum

To the naked eye, these filaments over most of their length look uniformly gray. Micro-

scopically they are smooth and round, showing no irregularities except occasional grain boundaries with rounded edges (Fig. 1(*A*)). However, at the ends of the wire and at each support hook, for about 8 turns there is a characteristic step-like structure (Fig. 1(*B*)). This structure is repetitive, except for prominence, on all the turns in a single crystal, and hence is related to the lattice arrangement.

##### (2) Alternating current in gas

The glint of these filaments under a light indicates reflecting surfaces unrelated to the original cylinder surface. Under the microscope there appears a regular structure of smoothed

curved faces with linear dimensions of the order of magnitude of the wire diameter (Fig. 1(C)). The structure is repetitive on all turns of a single crystal and therefore is oriented with respect to the lattice. The structure increases in complexity with increasing wire size. It is quite unlike the step surface on a.c. vacuum wires at hooks and ends. At hooks and ends of a.c. gas wires the characteristic step structure appears, seemingly superposed on the typical a.c. gas structure.

### (3) Direct current in vacuum

To the naked eye, the filaments look like the a.c. gas filaments. Microscopically, the structures are entirely different. The d.c. vacuum structure is apparently identical with the hook-region etching on a.c. wires. The original surface is approximated by a series of steps, smooth and nearly plane, somewhat smaller in scale than the wire diameter, and alike for all the turns in a single crystal (Fig. 1(D)).

### (4) Direct current in gas

On these wires, the gas structure found on a.c. filaments and the d.c. structure found on vacuum filaments are apparently concurrent.

Straight filaments and coiled-coils also fit uniformly into these four groupings.

On samples of all these various surface types, etching on a smaller scale has been sought with a Leitz Ultropak illuminator and magnification up to 2500. No trace of regular structure appears. If substructure exists, its linear dimensions cannot exceed a few thousand atom diameters.

## MECHANISM AND DETAIL OF THE GAS ETCHING

Since the gas structure and the d.c. structure are superposable, they can be attributed to independent mechanisms. We consider first the difference between the smooth a.c. vacuum wires and the strikingly "etched" a.c. gas wires, and overlook for the moment the hook-region structure which is common to both.

The wires in gas have not suffered more net evaporation: weighing of several thousand counted turns showed that the wires burned out in vacuum had lost about 17 percent of their weight, while the wires burned out in gas had

lost only about 5 percent.<sup>3</sup> Etching in HF+HNO<sub>3</sub> showed that the crystals in both groups have the same average size. The deep gas structure obviously could not be formed by gouging tungsten from a new wire, without losing at least 20 percent of the material. Clearly, tungsten must have been transported from one part of the wire to another. The stationary gas jacket, through which evaporated tungsten atoms diffuse, with high probability of returning to the wire and recondensing,<sup>4</sup> obviously provides a mechanism for moving tungsten from surfaces with high evaporation rate to surfaces with low evaporation rate. The observation that the gas structure is less prominently developed on the inside of helices and coiled-coils, where the wire surface is slightly hotter and the gas is more tenuous, is consistent with this view.

The gas structure, then, seems to merit attention as an intermediate stage between the original helical filament and the form that would develop if the wire attained equilibrium with the vapor. Helical single crystals, exposing every possible crystallographic surface twice in each turn, are particularly apt for study. The 40-watt filaments have the gas structure in its simplest form. The feature most readily identified is a small projecting face, about  $\frac{1}{3}$  the wire diameter in size, approximately plane, generally rhombic, and quite often hollowed out in the center with an elliptical dimple. From each corner of the rhombus a ridge runs away, and from each edge a long concave smooth surface extends to an edge of the next such dimpled flat. The complicated structure on larger wires is actually of the same sort: The single dimples are replaced by groups of dimples, 10 or 12 in a group on 200-watt wires. The ridges running from corners, and the long concave smooth surfaces, occur on the larger wires as on the smaller. Goniometric study of 50 long crystals in wires of different sizes, checked by Laue pictures, has led to the following crystallographic assignment: the dimpled flat faces and the ridges are both approximately normal to the dodecahedral [110] axes, and the large concave smooth surfaces are approximately normal to [100] axes.

<sup>3</sup> See G. R. Fonda, *G. E. Rev.* **32**, 206 (1929) for similar results on weight loss from straight wires.

<sup>4</sup> I. Langmuir, *A.I.E.E.* **32**, 1913 (1913).

## INTERPRETATION OF THE GAS ETCHING

Several considerations might deter us from taking the cube, which these helical crystals are apparently approaching, as the approximate form of a tungsten single crystal in equilibrium with the vapor. First, there is the possibility, since a.c. and d.c. produce widely different surfaces, that the electric current itself influences the surface form, and that heating in lamp gas without current would give yet another surface. That this caution is probably extreme appears when the frequency of the heating current is varied. Filaments of various sizes, straight, helical, and coiled-coil, in vacuum and in gas, were run on 60-cycle a.c., 25-cycle a.c., 500-cycle a.c., 25-megacycle a.c., and square-wave a.c. with a period of two minutes. No dependence on frequency was found. It can be concluded with fair reason that heating with a.c. is equivalent to heating without passage of current.

Second, there is the effect studied by Langmuir,<sup>5</sup> that a tungsten atom evaporating into an atmosphere containing  $N_2$  readily (probability near unity for a single gas-kinetic collision) combines with a nitrogen molecule to form the nitride  $WN_2$ . This molecule, if it reaches the bulb wall, contributes to a brown deposit. Since the lamp gas contains  $N_2$ , heating in lamp gas is not, at first glance, even approximately equivalent to heating in a Hohlraum; in the lamp gas, many tungsten atoms that return toward the surface bring with them two nitrogen atoms. It seems unlikely, however, that this difference will have any effect on the developing surface structure. It could be effective only if the  $WN_2$  molecules reached the filament without dissociating, and if the condensation coefficient for these were a different vector function from that for W atoms. The experimental fact that the gas jacket does greatly retard net evaporation indicates that the condensation coefficient must be near unity for all the surface—such small local differences as may exist are not probably decisive for the structure.

Third, there is a possibility that  $N_2$  may be attacking the wire slightly, at a rate which varies markedly with lattice direction. Fonda<sup>6</sup> has

<sup>5</sup> I. Langmuir, *J. Am. Chem. Soc.* **35**, 931 (1913); *Zeits. f. anorg. allgem. Chemie* **85**, 261 (1914).

noted that lamp filaments suffer a greater average loss of weight in pure A than in lamp gas, and a greater loss in lamp gas than in pure  $N_2$ . If there is a slight direct attack by some mechanism involving  $N_2$ , at a rate which increases with temperature more rapidly than does the evaporation rate of W, the disastrous effect of thin spots in the wire will be accelerated in the presence of  $N_2$ , and the observed order of weight-loss at burnout is to be expected.

To check these last two possibilities, several lamps were exhausted and refilled, some with pure A and some with pure  $N_2$ . On 60-cycle a.c., the filaments in  $N_2$  developed the same structure as appears in lamp gas. The structure in A was different in one major particular; the small (110) faces, instead of being dimpled, were built up in a symmetrical stile-like arrangement of flat steps and short risers; the larger wires had more steps in each stile (Fig. 1(E)).

It can be concluded tentatively that the dimpling of the residual (110) faces in gas containing  $N_2$  is due to an attack on the metal, the reaction rate of which is a vector function. Conversely, the structure developed in pure A by a.c. heating can be taken as an approximation to the equilibrium structure. Recalling that the sample is not growing slowly from a nucleus, but is slowly modifying an imposed form, we may plausibly assume that if equilibrium were attained the (110) faces would have disappeared, and only the (100) surfaces would remain exposed. The (100) surfaces are concave, probably because they have a temperature gradient from the center outward—the Joule heating is more widely dispersed near a projecting edge, and the wire is not in an isothermal enclosure. Material will obviously be transported down such a temperature gradient, whether the mechanism be one of evaporation-condensation or one of surface diffusion. Concavity of true equilibrium faces need not be expected. It is to be noted that the cubic (100) surfaces, which are apparently increasing their exposure in this simple evaporation-condensation process, are not so densely populated as the dodecahedral (110) surfaces, which an elementary theory would regard as the most stable bounding planes for a body-centered cubic lattice.

The projecting spines, sometimes found on several helix turns at each side of a burnout in gas, are other evidence for anisotropy of crystal growth. These spines spring almost without exception from the raised edges of the original structure (Fig. 1(F)). The concave (100) faces remain smooth; the dimple in each (110) face remains depressed and is surrounded by a rosette of spines grown out from the neighboring flat region. The ends of spines are often flat, or pyramidal with flat faces. Occasionally the "spines" are clusters of quasi-perfect crystals. It seems necessary that atoms, after diffusing from the vapor and striking the spines, migrate on the surface to favorable permanent locations. Spine structure occurs only in gas, and is comparatively rare. More often the end at a burnout is a polished sphere which, etching shows, comprises 3 or 4 crystals.

#### MECHANISM OF THE D.C. ETCHING

We next inquire why d.c. heating in vacuum produces a step-like structure, in contrast to the smooth surface developed on a.c. Alternating current at any frequency greater than about 1 cycle/min. produces the typical smooth a.c. surface. Half-wave 60-cycle rectified current produces the typical rough d.c. surface. Intermittent heating with an on-off period of about 1 sec., on either d.c. or 60-cycle a.c. produces the same sort of surface as continuous heating from the same sort of voltage supply. From this evidence it is clear that the frequency, form, and amplitude of the temperature oscillations are not concerned. Whether the a.c. or the d.c. structure develops depends only on whether the current is unidirectional or alternates in direction. The d.c. structure occurs with equal average prominence on all sides of a helical wire, inside as well as outside. This observation rules out any significant action of the magnetic field or of the electric field on evaporating ions or atoms. Any mechanism primarily involving tungsten ions in the vapor is ruled out by the rarity of ion evaporation: a rough estimate gives  $10^{-7}$  as the probability that a tungsten atom in evaporating shall leave a valence electron with the metal.

The d.c. structure is apparently due to a migration, over the surface, of positive tungsten

atom-cores, driven by the longitudinal electric field. If we assume that the rate of drift depends on the type of underlying surface, and is different for different directions on a surface of given type, obviously the development of steps on a surface which is continually changing in character in the direction of the field (a helix, for example) can be qualitatively explained. This assumption is inherently reasonable, and is supported by two pieces of evidence on the analogous process of diffusion. One of these is the spine growth mentioned above; the other is the observation, by electron-optical methods, that activating material diffusing from a source spot out over a heated single-crystal surface of metal, spreads symmetrically but not circularly, with the contours of equal concentration oriented with respect to the lattice.<sup>6</sup> Once steps have started, cooling from the edges and dispersion of the Joule heating will both act to accelerate their growth.

#### DETAIL AND POLARIZATION OF THE D.C. STRUCTURE

Study of a large number of d.c. helical crystals (chiefly from small size gas-filled lamps, with the simpler gas structure as an orienting background) has shown that the flat steps are approximately (100) planes. The d.c. structure on helices has a definite polarization, easily recognizable. In silhouette, the etching shows sawteeth of greater or less pitch, which point always toward the negative end of the wire.

On straight wires, the d.c. structure consists of steps which run diagonally across the wire, giving a herringbone effect. These herringbone stripes first begin to come out on sides of the single-crystal cylinder where (110) planes are most nearly coincident with the surface, while other sides of the wire are still smooth. Where the etch on straight wires is well developed, it is polarized with the sawteeth pointing toward the negative end. It will be noted that the hypothesis advanced above for the d.c. structure will not account for steps running diagonally across a straight cylindrical crystal. No fully satisfactory way of avoiding the symmetry con-

<sup>6</sup> A. J. Ahearn and J. A. Becker, Phys. Rev. **54**, 448 (1938). I am indebted to Dr. Ahearn for a discussion of this point.

sideration, that all points on an element of a single-crystal cylinder are equivalent, has yet appeared. Some phenomenon of "rhythmic precipitation" is seemingly involved. Only a few straight large-crystal wires have thus far been studied.

It has been remarked that current reversal once a minute results in the typical smooth a.c. surface. When the current is reversed every 24 hours, the d.c. steps develop noticeably. Some lamps were run for 100 hours on d.c., then for an additional 415 hours with reversed polarity. The d.c. structure appeared with full prominence, and the polarization appropriate to the original polarity of current was preserved. In these tests, involving some 40 lamps, no marked difference was found among filaments of different sizes and therefore of different operating temperatures, nor among helices, straight wires, and coiled-coils, nor between gas-filled and evacuated lamps. It appears that a lamp filament in a few minutes of d.c. heating at normal temperature can develop enough structure to be barely "remembered" during a like interval of heating with reversed current.

#### SURFACE DRIFT OF Th ON W<sup>7</sup>

It seemed worth determining whether Th atoms adsorbed on a W filament migrate toward the negative terminal. A simple electron-optical tube was used for the test. A loop of 1-mil thoriated wire 6 mm long was mounted on 30 mil leads at the center of a spherical bulb 3 inches in diameter coated inside with willemite. The final anode, a wire ring near the neck of the bulb, was made a few thousand volts positive to the filament, and the emitted electrons formed on the screen a magnified orthogonal image of the loop. A 10-mil Ni wire, welded to one filament lead and projecting between the ends of the loop, cast an electrical shadow on the pattern which permitted distinguishing the emission from the two ends, and also prevented evaporation of Th from one end across to the other.

With no voltage on the anode the filament was first flashed and then was heated, from a 2 v

supply, for 20 or 30 minutes at a low activating temperature. The electron image, observed briefly at a low temperature where the Th is immobile, was then brightest opposite the negative end of the loop, with a sharp cut-off toward the lead and a gradual decrease toward the center. The positive side of the screen was dark. With 60-cycle a.c. heating the activation was always symmetrical about the center of the wire. The processes involved in activation of a short filament are obviously complicated, but the net result, that Th accumulates preferentially at the negative end, strongly suggests a drift of ions in the electric field. Ionization in the space is ruled out by the low voltage of the heating supply, the shadow-caster stops evaporation from one end to the other, and thermionic emission from one end to the other is at the worst limited by space charge to a value too low to give appreciable cooling.

#### ETCHING AT HOOKS AND ENDS

The step-like etching at hooks and ends of a.c. wires, in vacuum and in gas, might be due to a rectifying effect of the temperature gradient on the drift in the electric field, or it might arise directly from diffusion in the temperature gradient. On wires heated with 25 megacycle current (reversal every  $2 \times 10^{-8}$  sec.) the hook region etch is identical in prominence with that on 60-cycle wires. Ten lengths of 1-mil wire about 1 mm long, between heavy leads, were heated on d.c. in vacuum for several hours to burnout. The etch structure was polarized with sawteeth pointing toward the cool ends of the wire, in the direction of the conventional current on one-half of the wire, but against it on the other. The conclusion from these two observations is that the structure developed in a temperature gradient is due primarily to diffusion of atoms toward cooler regions. That it is identical in form with the d.c. structure means that the surfaces and directions which are favorable for drift in an electric field are also favorable for migration down a temperature gradient—a plausible analog to the well-known universal relation between mobility and diffusion coefficient for ions in gases.

<sup>7</sup>This experiment has been reported: Phys. Rev. 53, 766L (1938).

## DIE MARKS

Grooves left by the diamond die are plainly visible on raw tungsten wire under a microscope; these grooves are not entirely removed from lamp filaments until after about 50 hours at normal temperature; except in a.c. vacuum lamps, they are followed immediately by the d.c. or gas structure. The treatment recommended for producing a "well-aged" tungsten filament,<sup>8</sup> which involves heating 10 minutes at 2900°K, does not remove the die marks.<sup>9</sup> Wire used in recent studies of thermionic emission<sup>10</sup> and of the properties of tungsten as functions of temperature<sup>11</sup> still show, after removal from the tubes, surfaces deeply grooved. From the fact that a brief heating which does not remove the die marks does make the surface properties constant during the course of experiments, the inference is that the die marks, long before they suffer any large-scale changes, adjust themselves to some standard condition. Probably a rearrangement, by surface migration and by differential evaporation between the sides of grooves, rapidly replaces the hodge-podge surface of the raw wire with a surface exposing only low index planes. As this adjustment proceeds simultaneously with evaporation, the die mark should move into the wire, should become smoother and less prominent, and should shift parallel to itself and change the tilt of its sides to conform with the lattice orientation. Such sidewise displacement and change in character of the residual die marks as they cross crystal boundaries can readily be observed on straight large-crystal wires that have been evaporated to an intermediate degree (Fig. 1(G)).

EFFECT OF NORMAL ELECTRIC FIELD<sup>12</sup>

Open-wound helical filaments in two commercial rectifier tubes were burned out slowly, one filament on d.c., the other on 60-cycle a.c.,

<sup>8</sup> H. A. Jones and I. Langmuir, *G. E. Rev.* **30**, 310 (1927).

<sup>9</sup> Z. Jeffries, *Trans. Am. M. and M. Eng.* **60**, 588 (1919); see photomicrographs on p. 641.

<sup>10</sup> W. B. Nottingham, *Phys. Rev.* **49**, 78 (1936).

<sup>11</sup> W. E. Forsythe and E. M. Watson, *J. O. S. A.* **24**, 114 (1934).

<sup>12</sup> Changes in the rate of evaporation from W and Mo wires when a strong field is applied have been reported: A. G. Worthing, *Phys. Rev.* **17**, 418 (1921); G. B. Estabrook, *Univ. Pittsburgh Bull.* **29**, No. 3 (Jan. 1933).

with the anodes kept at  $-10,000$  v during life ( $\sim 10^5$  v/cm at the wire surface). As controls, filaments in two similar tubes were burned out, with the anodes floating. The two a.c. filaments were alike, smooth, while both d.c. filaments showed the typical rough structure. No effect of the field on either type of surface could be found. A straight 5-mil filament in an experimental tube was run on d.c. for 350 hours with a constant average field of  $\sim 10^6$  v/cm at the surface. The filament was etched in the usual d.c. fashion, and was indistinguishable from filaments heated with d.c. in plain glass envelopes. Filaments from 100,000 v Kenotrons after 2000 hours at normal temperature on a.c. show the usual smooth surface, with the usual etching toward the cool terminals. It appears that a strong normal field has little effect on the character of the surface developing in vacuum. No large effect is to be expected, if the suggested mechanisms are correct.

## SMALL-GRAIN FILAMENTS

Some 30 or 40 thoriated filaments, in which the equiaxed crystals remain much smaller than the wire diameter, have been examined after long heating in vacuum. The a.c. crystals are smooth, and are markedly convex, because of the rounding-off of the exposed grain edges. The d.c. crystals are also smooth, but are tilted at various angles up to  $\sim 45^\circ$  away from the mean surface. Regular step-like d.c. structure rarely appears on one crystal—presumably one would-be step reaches clear across each tiny grain. Polarization of the d.c. structure appears as a preferential tilting of the exposed crystallite surfaces; in silhouette, the wire looks to be budding toward the negative terminal.

## ETCHING BY WATER VAPOR

When water vapor is present in a lamp, the wire surface tends to develop a characteristic rough structure on a smaller scale than the crystal size, which exposes flat faces with sharp edges—a surface quite similar to that brought out in an acid etch bath. The character of this structure is independent of the gas filling and the type of voltage supply. Its prominence depends on the quantity of H<sub>2</sub>O present; it may

completely obscure the typical d.c. or gas structure which would appear in a bulb thoroughly dried. The well-known water cycle,<sup>13</sup> a mechanism which transports tungsten from the hot wire to cooler surfaces in the neighborhood, is presumably responsible for this etching. The structure has not been systematically studied. Most of the observations have been on small-grain filaments in bulbs which by accident contained some H<sub>2</sub>O.

#### METALS OTHER THAN TUNGSTEN

Some rather sketchy experiments with hair-pins of Ta, Mo, Pt, Fe and Ni in vacuum have shown that these metals, like tungsten, become and remain smooth with 60-cycle a.c. heating, but develop a rough surface on d.c. On none of these metals is the d.c. structure brought to prominence with so little evaporation as on W. The character of the structure seems to differ markedly among these different metals.

#### EVAPORATED SURFACES AND EQUILIBRIUM SURFACES

The first of the two questions posed in the introduction appears to be answered by the observations, if the one assumption is allowed, that heating with a.c. is equivalent to heating without passage of current. A single-crystal tungsten sample evaporating in vacuum first loses such projections as die marks, and thereafter presents a smooth convex surface, with no regular structure larger than a few thousand atom diameters. On a multicrystal sample, the edges of the grains round themselves off so that finally each crystallite is smoothly convex outward. Since the evaporation rate is a vectorial function, a single crystal originally in a simple, perfect geometrical form (a cylinder, for example) should, as evaporation proceeds, gradually become idiomorphic. Helical tungsten filaments in vacuum, however, lose up to 17 percent of their weight before this tendency toward distortion becomes noticeable under the microscope.

These are the observations. The assigned upper bound of a few thousand atom diameters for regular substructure is set by the magnification

used. There is no evidence that regular structure on a smaller scale actually exists. It seems probable that the sample after long evaporation has no surface structure larger than a few atoms in scale. If one draws a plane square array of atoms bounded on one side by a jagged line in which the steps and risers are many atoms broad, one finds, on considering energy bonds between nearest and next-nearest neighbors, that energy can be continually derived from the system by shifting atoms from corner positions into re-entrant angles, until the mean direction of the surface is approximated as closely as the atomic nature of the lattice will allow—until no step and adjacent riser are both more than one atom broad. Obviously, similar analysis applied to the three-dimensional body-centered lattice of tungsten is not likely to lead to a result precisely opposite, that a surface originally smooth can increase its stability by digging out grooves and pits in itself. Curvature of the smooth surface is not incompatible with minimum energy, since the specific surface energy is a continuous function of surface orientation.<sup>14</sup>

The second question, what surface will be displayed in equilibrium with the vapor, is not so definitely answered by the observations. If the structure developed by long heating with a.c. in argon is taken as an intermediate stage between the original helix and the equilibrium form, then in equilibrium the (100) surface will certainly predominate. It is not certain whether it will appear exclusively, or whether other faces, such as the more dense (110), will also be present; it is also uncertain whether the equilibrium faces will be flat or curved. In equilibrium, atoms from the vapor are striking the surface at random places; by the principle of statistical balance, atoms must also be leaving the surface from random places. Hence, at first glance, either the surface atoms must be in such disorder that the surface is effectively an isotropic liquid, or else all parts of the surface must be alike—the sample must expose only one kind of crystallographic plane. The former hypothesis is clearly untenable at low temperatures. The latter hypothesis cannot be readily accepted, since the edges and corners of faces

<sup>13</sup> C. J. Smithells, *Tungsten* (D. Van Nostrand, New York, 1927), p. 62.

<sup>14</sup> P. Ehrenfest, *Ann. d. Physik* **48**, 360 (1915).



patently need special consideration. For practical purposes, it is sufficient to conclude that trend of a tungsten filament toward equilibrium increases the exposure of cube-face type (100) surface. The considerations mentioned in the preceding paragraph obviously also apply to the case where some or all of the evaporated atoms are returned to the filament surface; tungsten filaments heated in an atmosphere of neutral gas, or in an isothermal enclosure with tungsten walls, presumably have no regular surface substructure larger in scale than a very few atom diameters.

#### PREVIOUS OBSERVATIONS ON TUNGSTEN FILAMENT SURFACES

Langmuir's conclusion<sup>15</sup> which has been generally used in the interpretation of thermionic and adsorption data, that a tungsten sample heated in vacuum rapidly develops a faceted surface and exposes only (110) planes, is not supported by the results of the present study. The samples studied by Langmuir had been heated in wet H<sub>2</sub>, and the water cycle is presumably responsible for the sharp etching he observed. Bien,<sup>16</sup> studying the optical reflections from filaments briefly heat treated, concluded that the surface is grooved longitudinally, and that the groove sides are predominantly (110) and (211) planes. There is good reason to believe that this grooved structure consisted of residual die marks, and was not a result primarily of the evaporation. Seemann<sup>17</sup> shows photomicrographs of a straight

filament burned out in an amplifier tube after 800 hours life, which has prominent typical d.c. herringbone structure. It is unlikely that the new wire Seemann used in his experiments, after a few minutes of heating, had any surface resemblance to this veteran. Simon<sup>18</sup> shows a longitudinal section of a single-crystal Pintsch filament after 8000 hours life, which has a pronounced sawtooth edge. This structure he attributes to a vectorial evaporation rate; presumably it is actually the result of heating with d.c. Lieb<sup>19</sup> shows pictures of helical and straight filaments, run on a.c. and on d.c., in gas and in vacuum, which agree perfectly with the present observations. Lieb erroneously supposed that in the d.c. wires, since the surface is rougher, the crystals are correspondingly smaller.

It may be mentioned incidentally that Lieb's study showed a slightly more rapid decline in luminous efficiency of lamps on d.c. than on a.c., and that a similar difference in rate of change of chromaticity has been tentatively noted by Judd.<sup>20</sup> Differences of this sort are to be expected, since the developing d.c. roughness gives the filament some black-body character and acts to nullify the favorable selective emissivity of smooth tungsten.

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<sup>18</sup> H. Simon, *Handbuch der Experimental Physik*, Vol. 13 (Leipzig 1928), p. 292.

<sup>19</sup> J. W. Lieb, *Trans. Ill. Eng. Soc.* **18**, 5 (1923).

<sup>20</sup> D. B. Judd, *Nat. Bur. Stand. J. Research* **17**, 679 (1936).

<sup>15</sup> I. Langmuir, *Phys. Rev.* **22**, 374 (1923).

<sup>16</sup> R. P. Bien, *Phys. Rev.* **47**, 806A (1935).

<sup>17</sup> H. Seemann, *Zeits. f. Physik* **92**, 253 (1934).

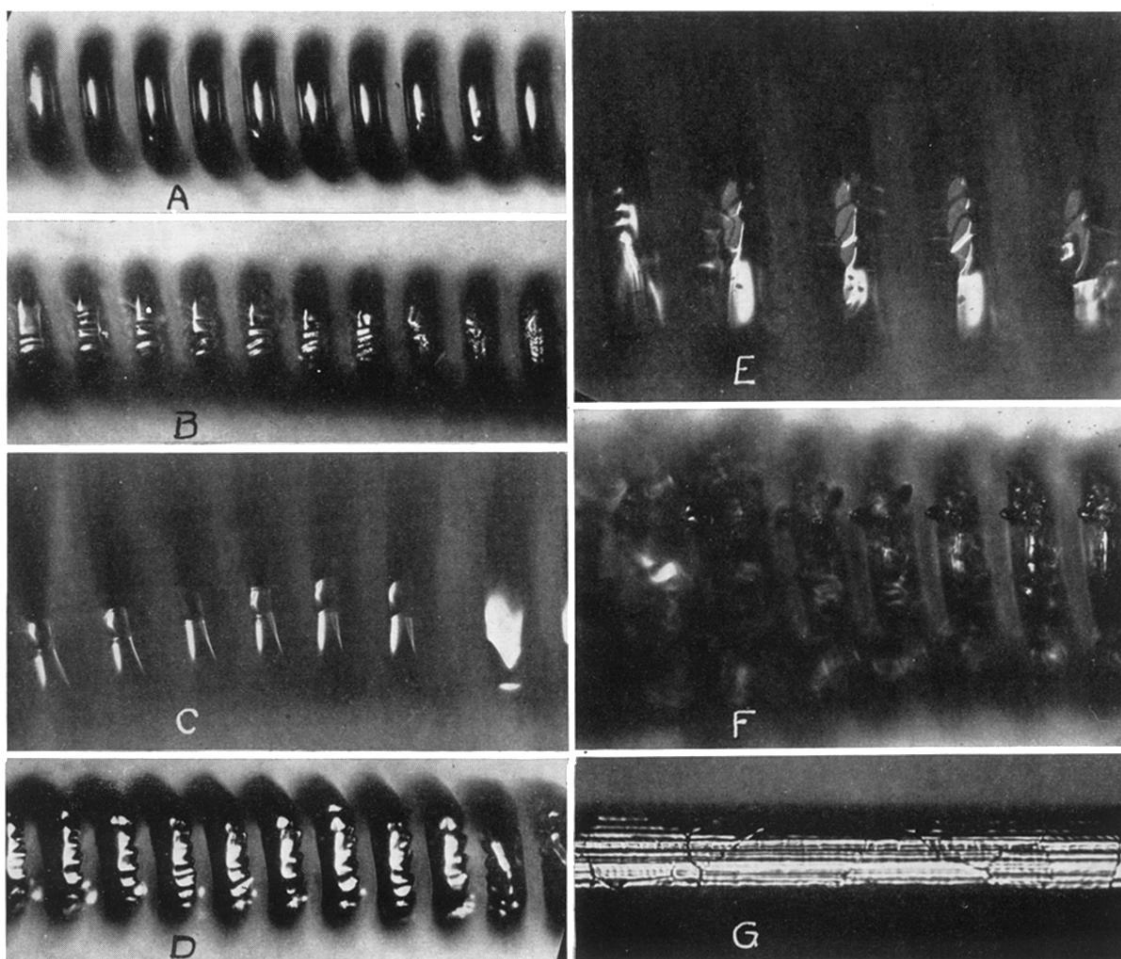


FIG. 1. *A*, Typical a.c. vacuum helix, with wire round and smooth except for grain boundaries. *B*, Hook-region structure on an a.c. vacuum helix. *C*, Structure on a small (50 w) helix heated with a.c. in lamp gas. *D*, Helix heated in vacuum with d.c., top of turns negative. *E*, Stile structure on a helix heated with a.c. in pure argon. *F*, Spine growth near a burnout in lamp gas. *G*, Residual die marks on pure tungsten heated with a.c. in vacuum.