Electron Microscope Studies of Thoriated Tungsten*

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Many past experiments have shown that the thermionic activity of a thoriated tungsten filament is determined by the concentration of thorium on its surface. This concentration is in turn determined by the rate of arrival and rate of evaporation of thorium. Typical published values of these rates are given in Fig. 1. An electron microscope used to obtain electron images of thoriated tungsten ribbons is described. Comparison with photomicrographs shows that the active and inactive patches composing an electron image agree in size, shape and number with the exposed grains of the tungsten. The electron microscope *shows that thorium comes to the surface in "eruptions"* at a relatively small number of randomly located points. From a comparison of photomicrographs showing thoria globules and electron images of thorium eruptions, it is deduced that *all the thorium in a globule comes to the surface when an eruption occurs.* Factors such as a high temperature flash and sudden heating and cooling of the filament affect the frequency of eruptions. Thorium eruptions are the only observed manner in which thorium arrives at the filament surface. They are repeatedly observed in the early stages of thoriation. Eruptions are not observed in the later stages of thoriation where conditions are unfavorable for their observance. Electron images of a Pintsch single crystal filament reveal alternate active and inactive bands parallel to the filament axis. Thorium eruptions occur only on the active bands. With a polycrystalline ribbon the surface migration of thorium from the eruption centers is isotropic; *with a single crystal ribbon there is a strongly preferred direction of migration.* X-ray analysis shows that the surface is a (211) plane and that *the preferred direction of migration agrees with the* (111) *direction in this plane.* During the process of thoriating a filament the relative emissions from different grains change by substantial amounts; in many cases the change is so great that the relative emissions are reversed. Measurements of work function differences between grains gave values ranging up to 0.6 volt.

1. INTRODUCTION

EXTENSIVE studies have been made of the thermionic properties of thoriated tungsten and thorium on tungsten together with allied phenomena such as the reduction of thorium oxide, diffusion of thorium to the filament surface and the evaporation of thorium. In general, the thermionic activity depends on the density of thorium that can be maintained on the filament surface. This steady state thorium concentration at any given temperature is determined by the relative rates of arrival of thorium at the filament surface and evaporation therefrom.

How the steady state value of the thorium concentration varies with temperature is shown in Fig. 1 in which data published by other workers are assembled. The family of curves gives the evaporation rate as a function of temperature for various values of f.[1] This family of curves is obtained by combining results of Brattain and Becker[2] with those of Langmuir.[3] In combining the results of these two experiments the assumption has been made that at infinite temperature the evaporation rate is directly proportional to f. This assumption is relatively unimportant however in the range of temperature employed in filament work.

In addition to evaporation data, Fig. 1 contains data on the rate of arrival of thorium at the surface of thoriated tungsten as a function of temperature. Curve 1 is based on data by Langmuir[3] and curve 2 on data by Brattain and Becker.[2] Experiments by Fonda, Young and Walker[4] show that the diffusion coefficient of thorium in thoriated tungsten varies by a factor as large as 400 depending on the grain size of the filament. In the light of this, the relatively small differences in arrival rates shown by curves 1 and 2 are fully understandable.

At any given temperature the steady state value of f is obtained from the intersection of evaporation and arrival curves. In the insert in Fig. 1, curves 1*A* and 2*A*, corresponding to

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[1] The quantity f is proportional to the amount of thorium on the tungsten surface, and $f=1.0$ is defined as that surface concentration of thorium which gives the optimum thermionic emission (reference 2).

[2] Brattain and Becker, Phys. Rev. **43**, 428 (1933).

[3] Langmuir, Phys. Rev. **22**, 357 (1923).

[4] Fonda, Young and Walker, Physics **4**, 1 (1933).

curves 1 and 2, respectively, give the variation of the steady state value of f with temperature. If curve $1A$ is taken as an example, the activation and deactivation of thoriated tungsten is readily understood. At a temperature of about 1900°K, $f=1.0$ is reached which by definition of f gives the optimum thermionic activity. At 2600°K f equals 0.03 or 0.04, i.e., the thermionic activity is still slightly above that of tungsten. Such curves as $1A$ and $2A$ are reversible and one can generalize as follows: As the temperature increases, the steady state value of f decreases.

In the experiments from which the data of Fig. 1 were obtained and in other work prior to the advent of the electron microscope, studies were necessarily limited to areas larger than about 1 square millimeter. Therefore, only the average value of effects that occur during the activation and deactivation of filaments could be measured and many processes could not be studied at all. When the electron microscope was adapted to thermionic studies the processes and effects that were localized on filament areas of 0.001 mm² or less could be observed.

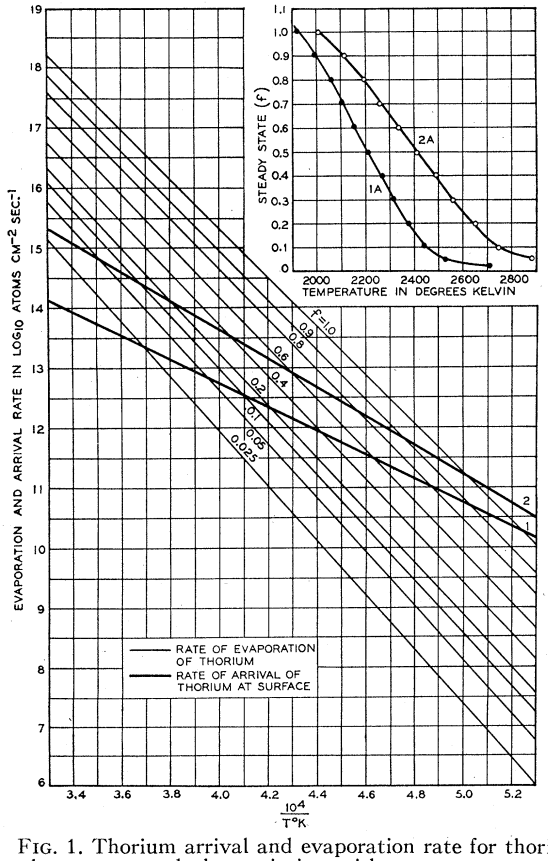

FIG. 1. Thorium arrival and evaporation rate for thoriated tungsten and the variation with temperature and amount of thorium on the surface. Curve 1, $1A$—Langmuir data. Curve 2, $2A$—Brattain and Becker data.

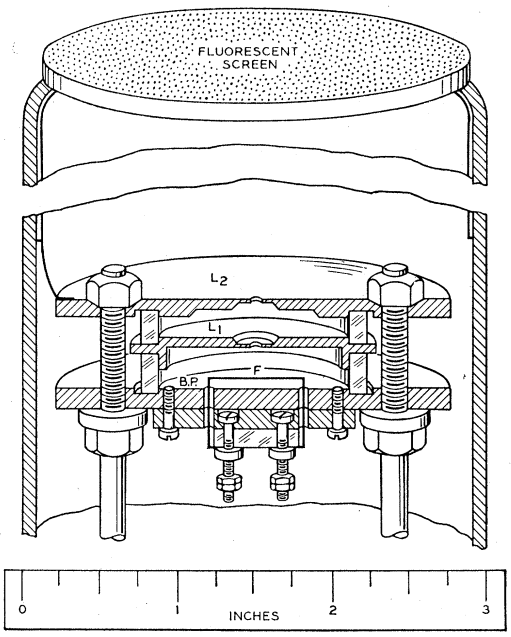

FIG. 2. Sketch of electron microscope.

The present paper describes some electron microscope studies of the details of the process of activation and deactivation of thoriated tungsten. In particular the experiments deal with the process by which the thorium arrives at the surface of the filament, the migration of thorium over the surface and the influence of the grain structure of the tungsten on these processes.

2. APPARATUS

Figure 2 is a sketch of the type of electron microscope used.[5] Four of these tubes were used in these studies. The essential parts are the filament F, the electron lenses L_1 and L_2, the backing plate $B.P.$ and the fluorescent screen. The filament consists of a flat thoriated tungsten ribbon about 3 cm long, 0.038 cm wide and 0.002 cm thick.

A voltage ratio V_{L_2}/V_{L_1} of about ten is needed to form the image on the screen of this microscope. A beam voltage V_{L_2} of two or three

[5] We are indebted to Dr. C. J. Davisson of these laboratories for the design of this electron microscope.

kilovolts is usually applied. The potential of the backing plate *B.P.* is adjusted to produce parallel equipotential planes near the filament. In the electron image shown in Fig. 9 the electrical magnification is about 100; in all other cases it is about 30.

The position of the image on the screen can readily be shifted through small displacements by the introduction of small magnetic fields. Therefore to obtain well-defined photographs of the electron image, it is necessary to avoid magnetic disturbances and to heat the filament with constant direct current.

3. The Electron Image and Grain Size of Metal

Numerous comparisons of electron images and light images of metal surfaces are to be found in the literature.[6] In general, the electron images show considerable variation in emission between adjacent regions, i.e., the image is patchy. These patches have shapes and sizes which in general agree with those of the grains appearing on photomicrographs of the metal surface.

Apparently the difference in electron emissivity on various areas of a metal surface is associated with the orientation of the various crystal grains. Measurements of work function differences between faces of single crystals[7–9] yield values up to several tenths of a volt.

Figure 3 shows a comparison of electron images[10] with photomicrographs of thoriated tungsten ribbons. Both ribbons shown here are 0.038 cm wide. Pictures *c* and *g* are photomicrographs of a portion of the thoriated tungsten ribbon having relatively large grains. Pictures[11] *b*, *d*, *f* and *h* are electron images of the same portion of this filament. The large detail on the electron images agrees almost perfectly with that shown on the light images.

Pictures *a* and *e* of Fig. 3 show respectively a photomicrograph and an electron image of a small grain thoriated tungsten filament. Here again, the two kinds of images are similar; their textures are the same and in places they agree in detail.

Thus, in general, the patches on the electron image correspond to the grains of a thoriated tungsten filament. The electron image within a given grain is not entirely free from structure, however, as shown by picture *f* in Fig. 3. A granular structure in the metal surface is invariably revealed in the electron image, but of some electron image features no counterpart is found in the optical image.

4a. Thorium Eruptions

How does the thorium arrive at the surface from the interior and how does it migrate over the surface? In the early work on thoriated tungsten it was assumed that the thorium arrived at all points of the surface at approximately equal rates. However, later studies on the activation of single crystals,[12] strongly supported the thesis that thorium diffuses to the surface only along grain boundaries.

The electron images of the polycrystalline thoriated tungsten ribbon shown in Fig. 4 reveal a different phenomenon. To obtain these, the filament was first flashed at about 2600°K; between successive pictures, all made at 1490°K short time heat treatments were given at temperatures between 1500 and 1800°K. In picture "*a*" most of the filament is very inactive; nearly all of the emission comes from a few small bright spots. The succeeding pictures trace the life history of such active spots. The one at the extreme right is a good one to follow. Between *a*, *b* and *c* it has increased both in size and in brightness; in *d*, *e* and *f* it has increased in size and decreased slightly in brightness; in *g* and *h* the spot has increased still more in size so that it is quite diffuse while the brightness has decreased greatly. The life history of other spots may be similarly traced. As a result of the development of these spots, picture *h* reveals an electron image which is more uniform and more active than that shown in picture *a*.

These spots which initially appeared as pinpoints, are places where thorium is arriving at

[6] See Brüche and Scherzer, *Geometrische Elektronenoptik* (J. Springer, Berlin 1934).
[7] Rose, Phys. Rev. **44**, 585 (1933).
[8] Farnsworth, Phys. Rev. **51**, 378 (1937).
[9] Mendenhall, and DeVoe, Phys. Rev. **51**, 346 (1937).
[10] The electron images vary in width depending on the exact value of the backing plate potential used.
[11] The differences between *b*, *d*, *f* and *h* are due to different degrees of thoriation and will be discussed later.
[12] Clausing, Physica **7**, 193 (1927).

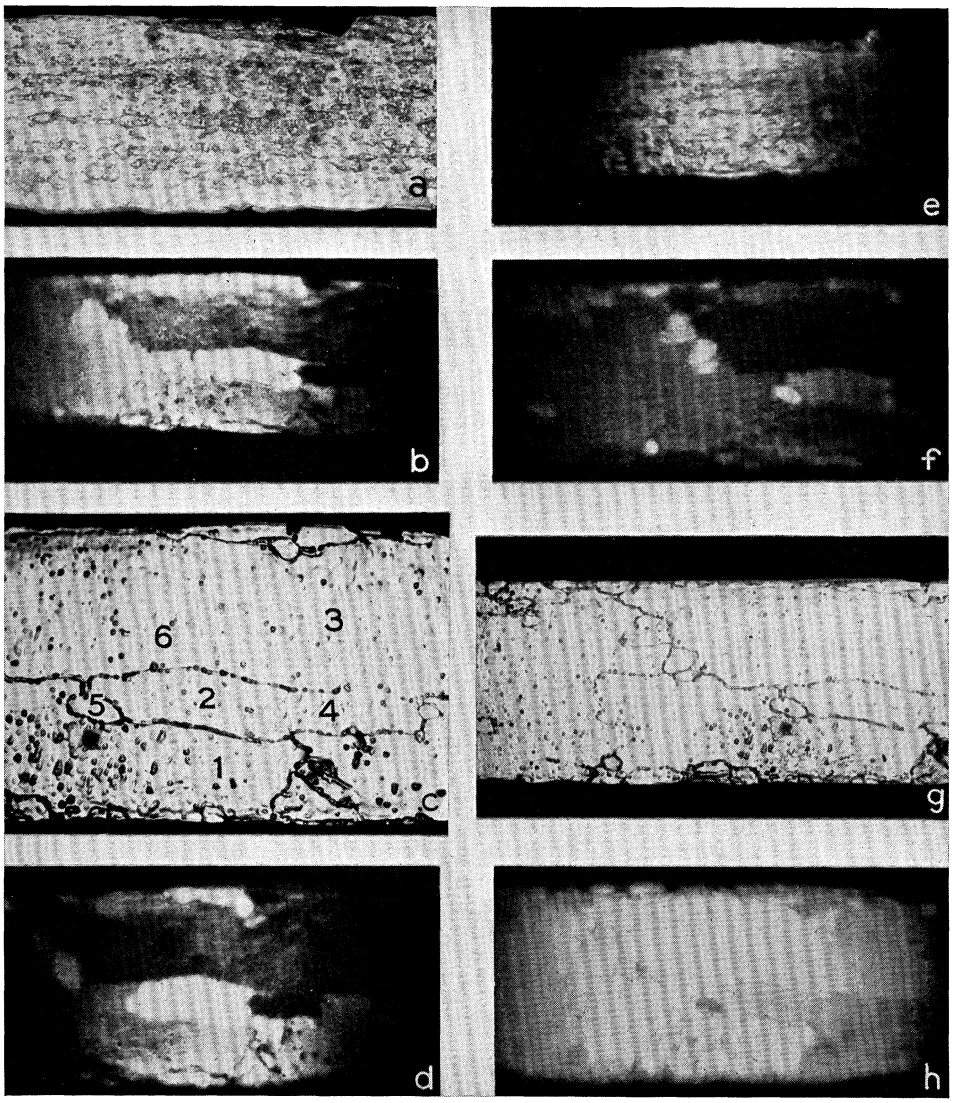

FIG. 3. Comparison of electron images and light images of thoriated tungsten (small grain and large grain ribbons). The average degree of thoriation f and photographing temperature for the electron images are given. *a*, Light (×68); *b*, electron 0.25 1460°K; *c*, light (×100); *d*, electron 0.13 1570°K; *e*, electron 0.80 1250°K; *f*, electron 0.11 1620°K; *g*, light (×71); *h*, electron 0.54 1405°K.

the surface of the filament.[13, 14] Thorium suddenly boils up from the interior at a point on the filament surface. This is followed by the building up of a film of thorium around this point and a migration of thorium over the surface, as revealed by the increase in brightness and size of the spots. After the arrival of thorium at the surface ceases, the surface density of thorium decreases due to the continued migration of thorium over the surface. This is shown by the decrease in brightness of the spot as it increases further in size.

Since this phenomenon of thorium spots resembles volcanic eruptions they are called "thorium eruptions." *Thousands of these eruptions have been observed with several different filaments in wire form as well as in ribbon form.*

[13] Brüche and Mahl, Zeits. f. Tech. Physik, No. 12, p. 623 (1935); No. 8, p. 262 (1936).
[14] Johnson and Shockley, Phys. Rev. **49**, 436 (1936).

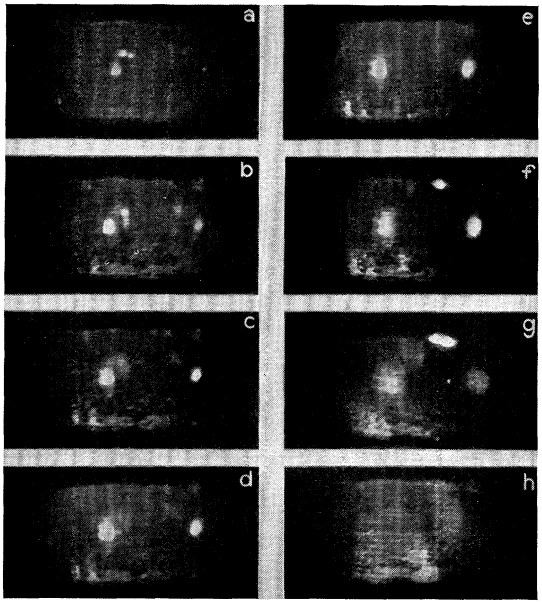

FIG. 4. Thorium eruptions on small grain thoriated tungsten ribbon. Photographing temperature 1490°K. Temperature and time of heat treatment, average degree of thoriation f and exposure time are given in order. *a*, 2550°K, 30 sec. 0.03, 60 sec.; *b*, 1530°K, 1 min. 0.06, 60 sec.; *c*, 1570°K, 1 min. 0.06, 60 sec.; *d*, 1600°K, 1 min. 0.06, 60 sec.; *e*, 1680°K, 1 min. 0.10, 40 sec.; *f*, 1720°K, 1 min. 0.10, 60 sec.; *g*, 1755°K, 1 min. 0.11, 30 sec.; *h*, 1830°K, 2 min. 0.11, 30 sec.

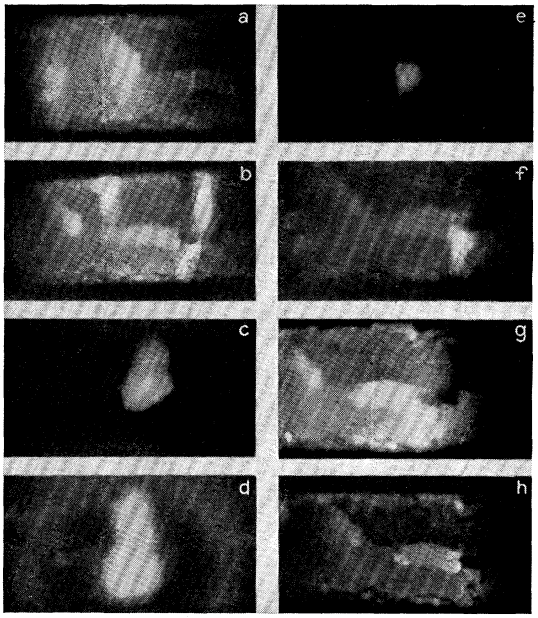

FIG. 5. Thorium eruptions on large grain thoriated tungsten ribbon. Exposure time—*a*, *b*, *c*, *d*, *f*, *g*, *h*, 60 sec., *e*, 120 sec. Temperature and time of heat treatment preceding image, average degree of thoriation f and photographing temperature are given in order. *a*, 2450°K, 7 min. 0.05, 1740°K; *b*, 2520°K, 5 min. 0.05, 1740°K; *c*, (2440°K 9 min., 1930°K 2 sec.) 0.10, 1390°K; *d*, none, 0.20, 1660°K; *e*, 1890°K, 2 sec. 0.05, 1500°K; *f*, none, 0.10, 1605°K; *g*, none, 0.10, 1710°K; *h*, 1620°K, 1 min. 0.10, 1605°K.

They appear to be the most important if not the only means whereby thorium comes to the surface.

4b. Where do Eruptions Occur?

Figure 5 shows some typical eruptions occurring on grain boundaries of a rather large grain filament. In picture *e* the growth of an eruption was arrested quite early in its life by suddenly cooling the filament. Comparison of the negatives for *e* and *f* (taken after more migration on the filament had occurred) shows very distinctly that the dark irregular lines through the spot in *e* correspond with grain boundaries in *f*. Counts of eruptions occurring on large grain filaments such as shown in Fig. 5 show that about $\frac{1}{3}$ of the eruptions occur on grain boundaries and the remaining $\frac{2}{3}$ definitely occur off grain boundaries. In general, eruptions do not repeatedly occur in the same place. Other studies have shown that eruptions do not occur with the same frequency on all grains. On some grains eruptions were never observed.

The electron emission pattern of a Pintsch single crystal thoriated tungsten filament (in an electron projection tube after the fashion of Johnson and Shockley[14]) consisted of about six active bands parallel to the filament axis alternated with inactive bands. These bands are probably related to the faces of the single crystal filament. Eruptions occurred exclusively on the active bands. This indicates that thorium diffuses in certain directions inside the tungsten crystal much more readily than in other directions.

4c. Factors That Influence the Occurrence of Thorium Eruptions

Eruptions occur at temperatures as low as 1500°K. Fig. 4 shows some that appeared after treatments at slightly higher temperatures. In general, the frequency of eruptions increases with the temperature.

A high temperature flash temporarily increases the frequency of eruptions at a lower tempera-

ture. A wire filament was flashed at about 2900°K for about a minute; then the number of eruptions per minute at 1920°K was counted. The results, plotted in Fig. 6, show that this number decreased rapidly with time soon reaching a constant value of about one-ninth of the initial value. If the filament is then suddenly cooled and reheated, the eruption frequency is temporarily increased.

Eruptions were observed to occur only at values of f below about 0.4. There are reasons for believing that it should be very difficult to observe eruptions at high values of f. The contrast in brightness between the eruption point and its immediate surroundings would be much smaller at high activities. The migration and evaporation of thorium from an eruption point would be faster at high activities. Hence, it would be difficult if not impossible to observe eruptions at high activities.

4d. Comparison of Thorium Eruptions and Thoria Globules

The amount of thorium coming to the filament surface when an eruption occurs was estimated in the following ways. For photographs of electron images like those in Fig. 4 showing the life history of thorium eruptions, the assumption was made that at its maximum brightness the eruption spot was covered with one monatomic layer of thorium. From the magnification, the spot diameter at which this maximum brightness persisted and the number of thorium atoms in a monatomic layer (7.1×10^{14} atoms/cm^2) the number of thorium atoms emitted during an eruption was calculated. These range from 1×10^9 to 52×10^9 atoms per eruption for the fine grained ribbon of Fig. 4 and from 110×10^9 to 540×10^9 atoms per eruption for the large grained ribbon of Fig. 5.

The second method of calculation can be outlined with the aid of Fig. 4. From the measured temperature and emission current density,[15] the average f was found[2] to be 0.11 in picture h. This corresponds to 8×10^{13} atoms per cm^2 and to 1.2×10^{11} atoms in the field of view. In the picture sequence a to h, about 15 eruptions appear. The assumption is made that these eruptions contributed all of the thorium that is on the surface in picture h. The average amount emitted by one eruption is $1.2\times10^{11}/15$ or 8×10^9 atoms of thorium. The two methods give concordant results.

From the known value of N, the number of thorium atoms per eruption, the mass of the corresponding N molecules of thorium oxide was calculated. From this mass and the density of thorium oxide (9.7 g/cm^3) the volume of the thorium oxide was determined. From this the equivalent sphere diameter was calculated. Curve 1 of Fig. 8 gives the distribution curve of such sphere diameters. On the large grain ribbon the necessary data and photographs for these calculations were taken for only a few eruptions. These individual values are indicated by triangles on the diameter axis of Fig. 8. Thus Fig. 8, curve 1, gives the percentage of eruptions, whose equivalent sphere diameters lie in the interval d to $d+10^{-5}$, as a function of their diameter d.

On neither the large nor on the small grain filament did eruptions occur in the same place

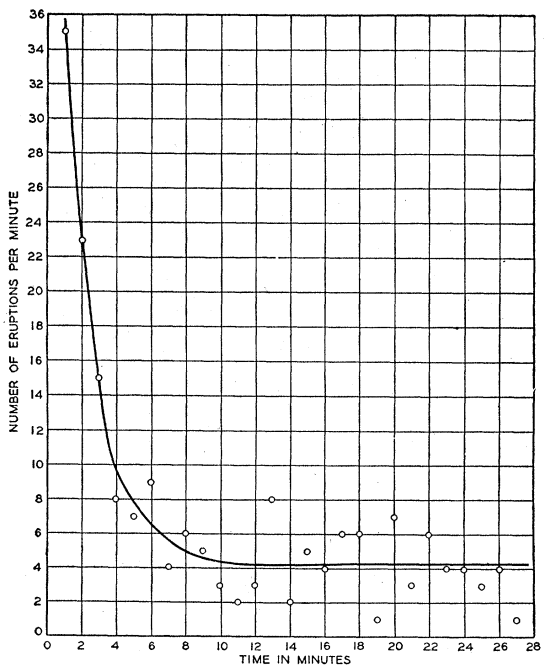

Fig. 6. Variation of eruption frequency with time after flashing thoriated tungsten wire.

[15] For the small grain ribbon, the current density was calculated from the emission and the area of the entire ribbon. For the large grain ribbon, it was calculated from the emission coming from the area of the filament in the field of view.

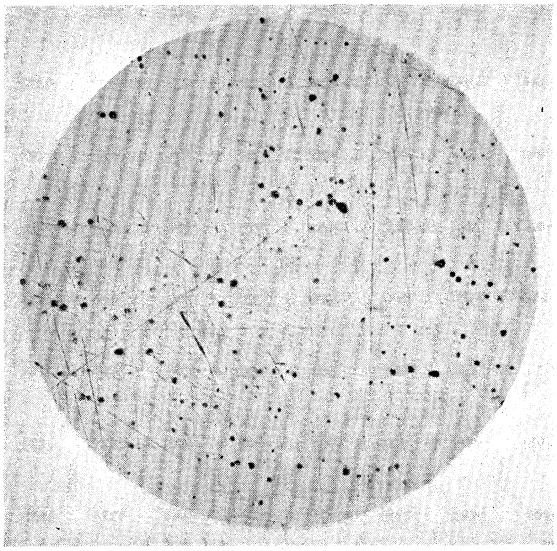

FIG. 7. Photomicrograph of interior section of fine grain thoriated tungsten ribbon (×1000).

repeatedly. Furthermore, the eruptions on the large grain filament were in general much larger than those on the fine grained one. Now it is well known that the globules of thorium oxide increase with the grain size of the tungsten. To explain these facts, the following hypothesis was made; when an eruption occurs, a globule of thorium oxide decomposes and all of the thorium in the globule comes to the surface.

This hypothesis was tested by an independent determination of the size of the thorium oxide globules as follows. The photomicrographs of the ribbons shown in Fig. 3 made after the electron image studies were concluded, reveal a large number of small black spots. The following facts indicated that these spots are related to the thorium oxide in the tungsten.

1. Tests with an optical microscope with different types of illumination show that the spots are depressions or holes whose shapes were roughly parts of spheres. Now in thoriated tungsten which has been heat treated, the thorium oxide is dispersed in little globules.

2. On the large grain filament these spots are larger than on the fine grain one. As stated earlier, the thoria globules increase in size as the grain size of the tungsten increases.

3. More of these spots occur on grain boundaries than within the grains. The thoria globules also occur more frequently on grain boundaries[16] than within the grains.

[16] Jeffries, Proc. Inst. Met. Div. (A.I.M.E.), (1927), p. 395.

These related facts suggest that the spots or holes are former sites of thoria globules at or near the surface and that the size of the globules can be calculated from the size of these holes. The diameters thus calculated were about twice the value deduced from eruption data. Since evaporation of tungsten would tend to enlarge the holes on the surface, it seemed preferable to examine the interior of the ribbon. Therefore, the ribbons were ground down and the new surfaces were polished. Fig. 7 is a photomicrograph of this interior section of the fine grain ribbon at a magnification of 1000. Black spots, i.e., holes again appear. On the large grain ribbon (not shown) they are larger in size and smaller in number than on the fine grain ribbon.

To test further the assumption that the circular spots on these polished surfaces are sections through thorium oxide globules the total volume corresponding to the spots was calculated.[17] This volume ranged from 1 to 3 percent of the tungsten volume for various regions of the ribbon. Chemical analysis of large samples of these ribbons showed that the thorium oxide content was about 2 percent by volume. This confirms the assumption that these spots are sections through thoria globules.

We want to obtain the diameter distribution of the thorium oxide globules that appear in Fig. 7. Unfortunately this photomicrograph does not give a direct measure of these globule diameters. Due to the grinding and polishing of the ribbon the resulting sections of globules of a given diameter d appear as spots whose diameters range from zero to d. Curve 3 of Fig. 8 which is for the region shown in Fig. 7 gives the distribution of the section diameters of the globules.

Suppose we now calculate the distribution of sections to be expected if the true globule diameters are given by curve 1, Fig. 8. Consider a sphere cut by a large number of parallel equally spaced planes. The resulting section diameters will increase rapidly from zero as the intersecting planes go from the pole to the equator. Thus it is evident that a plane, cut through a volume containing a number of spheres

[17] In making this calculation section diameters were converted to true sphere diameters as explained in subsequent paragraphs.

of equal diameter d, will reveal many sections whose diameters are nearly equal to d and relatively few that are nearly zero. The distribution function for the section diameters is

$$f(x) = x/(d^2 - x^2)^{\frac{1}{2}}, \qquad (1)$$

where the section diameter x ranges in value from zero to the sphere diameter d.

By means of Eq. (1) it is possible to derive the distribution of section diameters that would be expected from the distribution of globule diameters given by curve 1 of Fig. 8. Curve 2 gives this section distribution derived from eruption data. Curve 3 gives the section distribution observed in an optical microscope. The agreement between curves 2 and 3 is probably better than would be expected. These curves are for the fine grain ribbon.

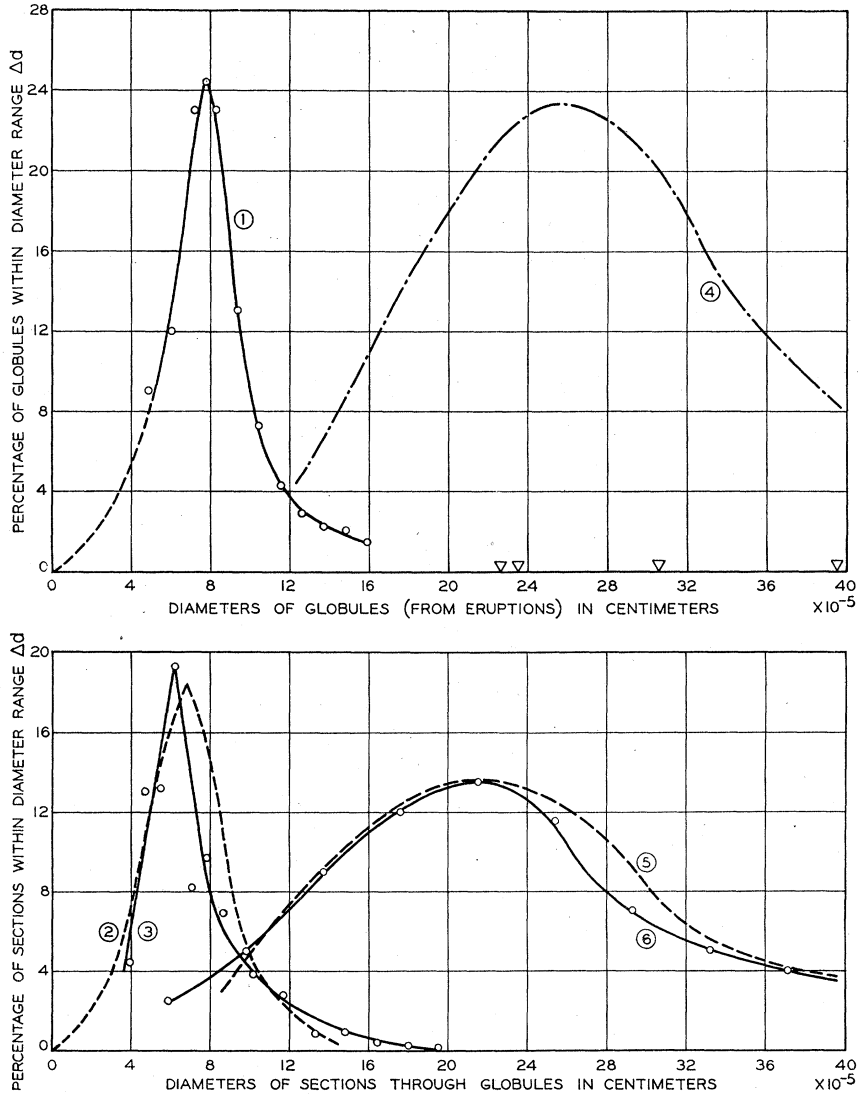

FIG. 8. Distribution of thorium oxide globule diameters. Fine grain ribbon ($\Delta d = 1 \times 10^{-5}$ cm). Curve 1, calculated from electron images of thorium eruptions. Curve 2, distribution on a section expected from curve 1. Curve 3, distribution observed on photomicrograph of section. Large grain ribbon ($\Delta d = 5 \times 10^{-5}$ cm). ▽ calculated from electron images of thorium eruptions. Curve 4, assumed distribution. Curve 5, distribution on a section expected from curve 4. Curve 6, distribution observed on photomicrograph of section.

On photomicrographs of the coarse grain filament, the distribution of section diameters given by curve 6, Fig. 8, was observed. By trial and error, curve 4 for sphere diameters was found which gave a section diameter distribution (curve 5) that is in good agreement with the observed curve 6. As previously stated, only four values of globule diameters were obtained from eruption data. They are shown by the triangles along the diameter axis in Fig. 8. These four measured values fall within the expected range given by curve 4.

The data of Fig. 8 particularly curves 1, 2 and 3 indicate very strongly that the distribution curve obtained from the eruption data gives the actual distribution of thorium oxide globules. Now in the eruptions, the phenomenon is one in which thorium has come to the surface. This confirms the hypothesis proposed at the beginning of this section; *when an eruption occurs approximately all of the thorium in a globule of thorium oxide comes to the surface.*

On the basis of these observations and deductions, we believe that a thorium eruption occurs when a vent is opened between a thorium oxide globule and the surface of a filament. When this happens, all of the thorium oxide is reduced and the thorium diffuses to the surface, where it migrates or evaporates. This suggestion is supported by the evidence of Wartenburg and Moehl[18] that tungsten reduces thorium oxide. A thorium oxide globule embedded in a mass of tungsten represents a closed system in which the following reaction would be in equilibrium

$$\mathrm{Th\,O_2 + W \leftrightarrows WO_2 + Th.}$$

Of the four constituents, the tungsten oxide and the thorium have the higher vapor pressures. When a vent between the cavity and the tungsten surface is opened they escape more rapidly than the thorium oxide and tungsten. Thus the equilibrium is upset and the reaction proceeds from left to right until the thorium oxide is completely reduced.

The particular part played by the tungsten oxide in this process is not yet clear. It may evaporate much more readily than thorium; or tungsten oxide on tungsten may not greatly alter the emission properties of thorium on tungsten. There is some evidence that a thoriated filament gives off oxygen,[19, 20] or an oxide, which deactivates another tungsten filament in the same tube.

[18] Wartenburg and Moehl, Zeits. f. physik. Chemie **128**, 439 (1927).

5. Migration of Thorium on Tungsten

Migration of thorium occurs at the lowest temperature at which eruptions occur, i.e., about 1500°K. Fig. 4 shows this migration from the eruption centers over the surface of the tungsten. During their growth the spots remain approximately circular in shape. This shows that on the fine grained filament, the thorium migrates with equal ease in all directions.

In contrast to this isotropic migration of thorium on the polycrystalline ribbon, Fig. 9 shows the migration phenomenon after an initially small grained filament had been grown into a single crystal.[21] Here the thorium migrates in a preferred direction over the surface of the tungsten crystal. This preferred direction of migration makes an angle of from zero to 12° with the cross direction of the ribbon, the most probable angle being about 7°.

After the microscope was dismantled, this filament was examined by x-rays.[22] An 11 mm section of the filament containing the field of view consists of one single crystal with the exception of some small crystals on the two edges. The orientation of this (body-centered cubic) single crystal is as follows. The surface of the ribbon is a (211) plane with a (110) normal at an angle of 8° with the rolling direction (the length of the ribbon) and a (111) normal making an angle of 8° with the cross direction. The direction of most probable migration (about 7°) is in excellent agreement with this (111) direction. These two facts show that *on the (211) plane of a tungsten crystal, thorium prefers to migrate in the (111) direction.* In this plane, this is the direction in which the separation between rows of atoms is greatest. This probably means that in this direction the migrating atom encounters the lowest potential hills.

[19] Nottingham, Phys. Rev. **49**, 78 (1936).
[20] Coomes, Phys. Rev. **53**, 936 (1938).
[21] The circular spot near the center is due to light from the filament.
[22] We are grateful to Mr. F. E. Haworth of these laboratories for this analysis.

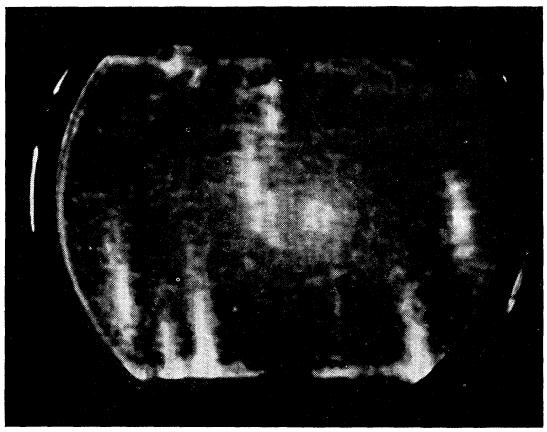

FIG. 9. Thorium eruptions and the migration of thorium in a preferred direction over the surface of a single crystal of thoriated tungsten.

At one stage in the growth of this single crystal, the field of view as shown diagrammatically in Fig. 10 consisted of an island of polycrystalline tungsten surrounded by the single crystal. When an eruption occurred in position 1, the thorium migrated in the preferred direction shown by the arrows, corresponding to the preferred direction of Fig. 9. When one occurred in position 2, the thorium migrated equally in all directions until it reached the edge of the polycrystalline island. Then the thorium migrated in the preferred direction over the single crystal. Conversely when an eruption occurred in position 3, the migration took place in the preferred direction until the thorium reached the polycrystalline island; then it migrated fanwise over this island.

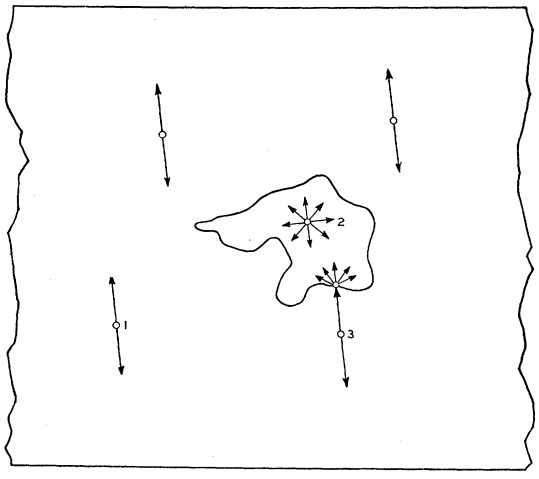

FIG. 10. Directional migration of thorium. Polycrystalline surface *vs.* single crystal surface thoriated tungsten ribbon.

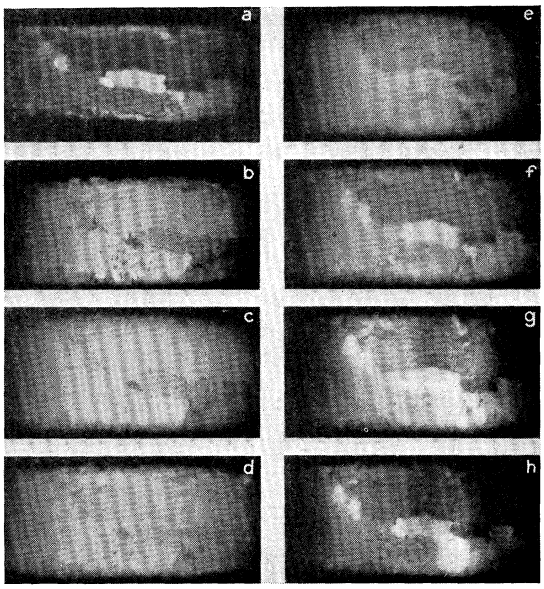

FIG. 11. Reversal of electron image pattern with change in degree of thoriation. Exposure time—*b*, *c*, *d*, *e*, *f*, *g*, *h*, 5 sec., *a*, 60 sec. Temperature and time of heat treatment preceding image, average degree of thoriation *f* and photographing temperature are given in order. *a*, 0.11, 1620°K; *b*, 0.54, 1405°K. Further activation treatments raised *f* to 0.70. *c*, 1970°K, 10 min. 0.56, 1440°K; *d*, 2100°K, 1 min. 0.42, 1515°K; *e*, 2140°K, 1 min. 0.32, 1580°K; *f*, 2180°K, 5 min. 0.22, 1675°K; *g*, 2220°K, 6 min. 0.13, 1755°K; *h*, 2340°K, 5 min. 0.07, 1840°K.

Some of the photographs in Fig. 5 also show a preferred direction of migration. The direction of migration on one ribbon which contained only 3 or 4 large grains varied as much as 90° for different grains.

6. Reversal of Pattern with Degree of Thoriation

How do the relative electron emissivities of different crystal grains vary as the average amount of thorium on the filament surface is varied? The series of photographs in Fig. 11 shows the changes in the electron image as the degree of thoriation was varied from about 0.11 to about 0.70 and then down again to about 0.07. A comparison of pictures *a* and *b* shows that the relative emissivity of nearly every grain with respect to its neighbors is markedly

changed. Moreover, in most of these cases, this change is so great that the relative emissivities are reversed. The degree of this reversal, however, varies considerably from grain to grain.

During the dethoriation process, as shown by the picture sequence *c* to *h*, the image reverses back to the original pattern shown in *a*. At $f=0.4$ approximately, the electron image is quite uniform and lacking in contrast.

One factor which probably contributes to the reversal is the different rates of accumulation of thorium on different grains. The rate of accumulation on any one grain is probably determined by the surface forces associated with the particular exposed face of the grain or single crystal. It is probably conditioned also by the abundance of thorium oxide globules within the grain or in its neighborhood. Furthermore, the phenomenon of migration in a particular direction characteristic of the face of the grain may be a factor influencing the rate of accumulation.

Another factor which contributes to the reversal phenomenon is suggested by the probable fact that of two surfaces the one having the higher work function when clean will have the lower work function when covered with the optimum amount of adsorbed electropositive material. If this is true, the emission from two grains of tungsten having different work functions would vary as shown schematically in Fig. 12 as thorium is deposited thereon. The electron images of grains *A* and *B* of Fig. 12 would become "reversed" beyond $f=0.3$.

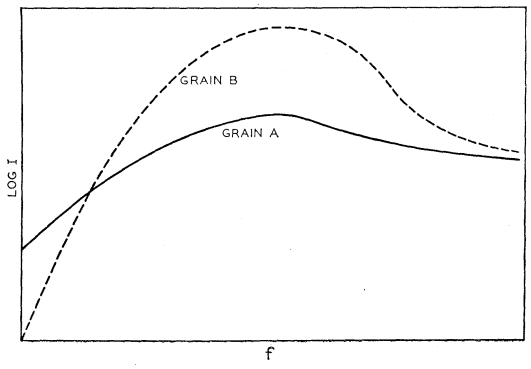

FIG. 12. Activation curves for different grains of thoriated tungsten suggested by reversal of pattern of electron image.

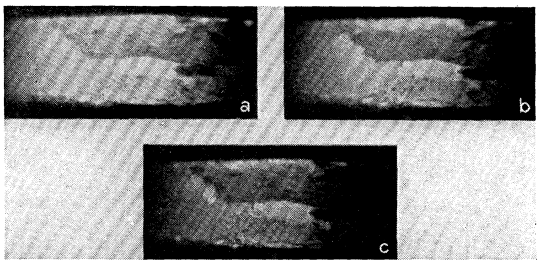

FIG. 13. Work function differences between grains of thoriated tungsten. Filament temperature 1460°K. Degree of thoriation *f* 0.25. Exposure times, *a*, 120 sec.; *b*, 60 sec.; *c*, 30 sec.

7. Work Function Differences

The electron microscope is readily adapted to a quantitative measure of work function differences between grains of filaments. The method consists in taking photographs of the electron image, keeping all conditions such as temperature, applied voltages, etc., constant but varying the time of exposure. To determine work function differences between a pair of grains from such a series of photographs one selects the shortest time exposure of the more active grain and determines the exposure on which another grain shows the same degree of blackening. To a first approximation one may then conclude that the inverse ratio of the two exposure times gives the ratio of their electron emissivities and from this ratio, by means of the equation

$$i=120T^2\epsilon^{-\phi e/kT} \qquad (2)$$

one can calculate the difference in work function for pairs of grains.

Figure 13 contains 3 photographs in which only the exposure time is varied. These show the grains numbered in Fig. 3. Matching densities of grains 2 and 1, 1 and 6, 6 and 3, 3 and 4 showed that the electron emissivity of grain No. 2 is about one hundred twenty-eight times as great as that of No. 4. Eq. (2) then gives a work function difference between grain No. 4 and 2 of about 0.6 of a volt. The electron images of Fig. 13 where $f=0.25$ reveal work function differences between grains ranging from 0 to 0.6 volts. The electron images of Fig. 11 show that this work function range depends upon *f*.

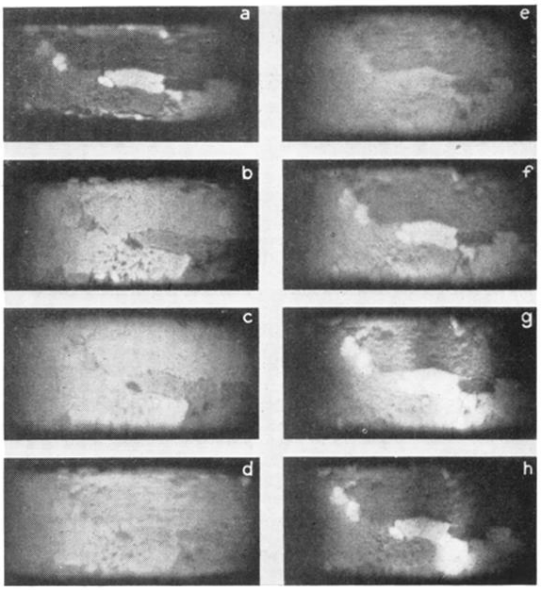

FIG. 11. Reversal of electron image pattern with change in degree of thoriation. Exposure time—*b*, *c*, *d*, *e*, *f*, *g*, *h*, 5 sec., *a*, 60 sec. Temperature and time of heat treatment preceding image, average degree of thoriation *f* and photographing temperature are given in order. *a*, 0.11, 1620°K; *b*, 0.54, 1405°K. Further activation treatments raised *f* to 0.70. *c*, 1970°K, 10 min. 0.56, 1440°K; *d*, 2100°K, 1 min. 0.42, 1515°K; *e*, 2140°K, 1 min. 0.32, 1580°K; *f*, 2180°K, 5 min. 0.22, 1675°K; *g*, 2220°K, 6 min. 0.13, 1755°K; *h*, 2340°K, 5 min. 0.07, 1840°K.

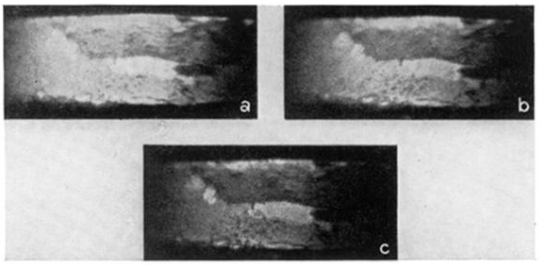

FIG. 13. Work function differences between grains of thoriated tungsten. Filament temperature 1460°K. Degree of thoriation f 0.25. Exposure times, *a*, 120 sec.; *b*, 60 sec.; *c*, 30 sec.

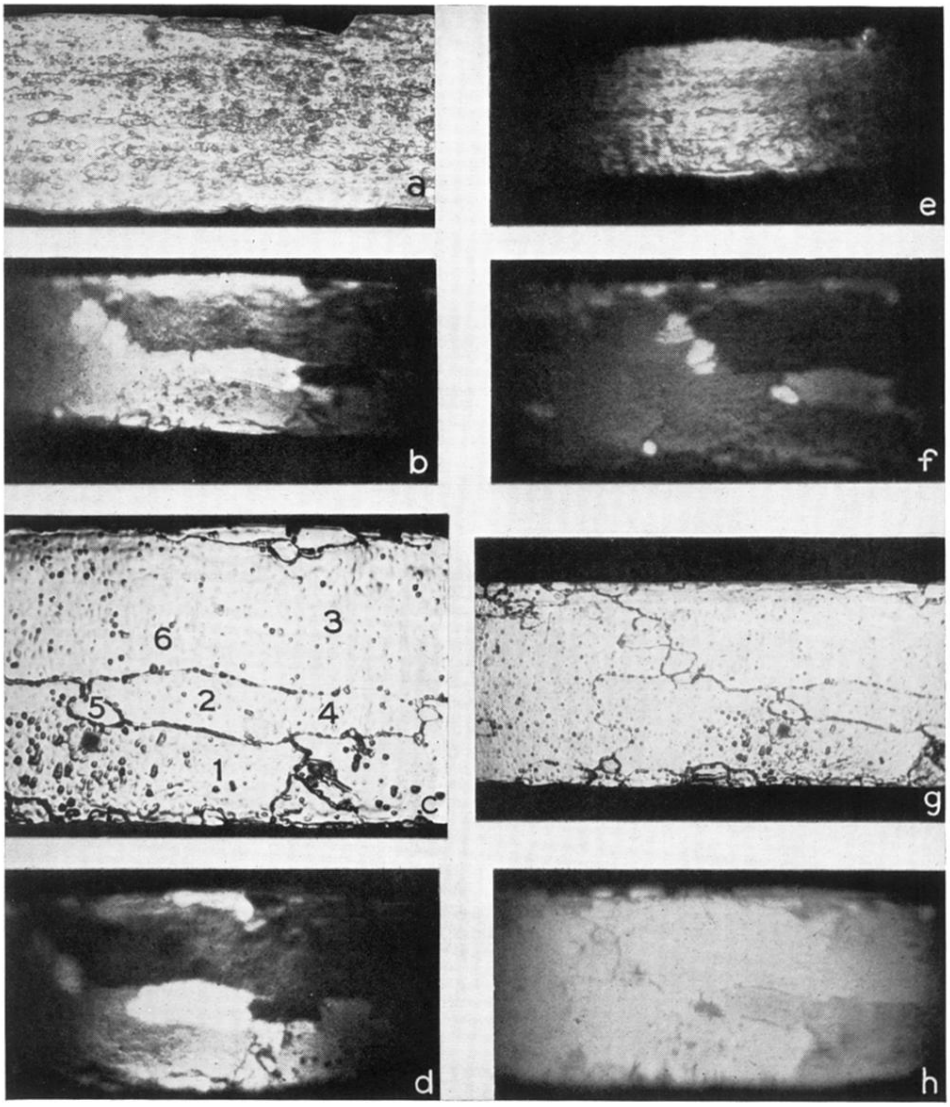

FIG. 3. Comparison of electron images and light images of thoriated tungsten (small grain and large grain ribbons). The average degree of thoriation f and photographing temperature for the electron images are given. *a*, Light (×68); *b*, electron 0.25 1460°K; *c*, light (×100); *d*, electron 0.13 1570°K; *e*, electron 0.80 1250°K; *f*, electron 0.11 1620°K; *g*, light (×71); *h*, electron 0.54 1405°K.

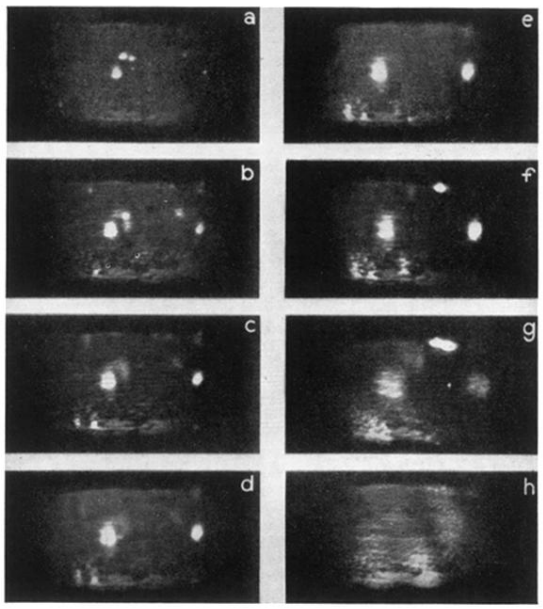

FIG. 4. Thorium eruptions on small grain thoriated tungsten ribbon. Photographing temperature 1490°K. Temperature and time of heat treatment, average degree of thoriation f and exposure time are given in order. *a*, 2550°K, 30 sec. 0.03, 60 sec.; *b*, 1530°K, 1 min. 0.06, 60 sec.; *c*, 1570°K, 1 min. 0.06, 60 sec.; *d*, 1600°K, 1 min. 0.06, 60 sec.; *e*, 1680°K, 1 min. 0.10, 40 sec.; *f*, 1720°K, 1 min. 0.10, 60 sec.; *g*, 1755°K, 1 min. 0.11, 30 sec.; *h*, 1830°K, 2 min. 0.11, 30 sec.

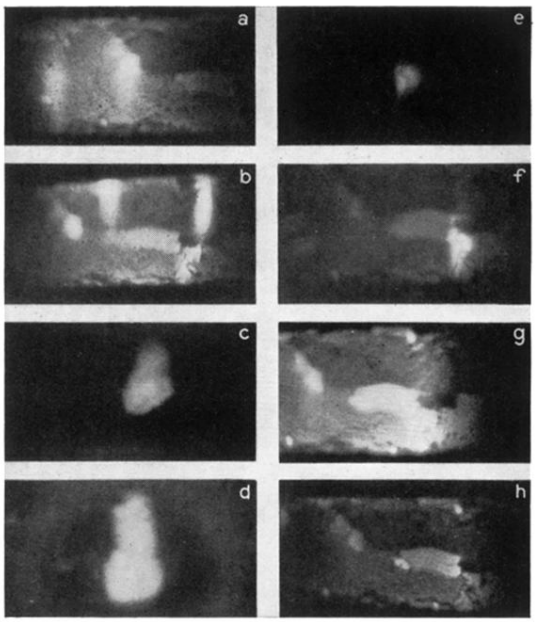

FIG. 5. Thorium eruptions on large grain thoriated tungsten ribbon. Exposure time—*a*, *b*, *c*, *d*, *f*, *g*, *h*, 60 sec., *e*, 120 sec. Temperature and time of heat treatment preceding image, average degree of thoriation *f* and photographing temperature are given in order. *a*, 2450°K, 7 min. 0.05, 1740°K; *b*, 2520°K, 5 min. 0.05, 1740°K; *c*, (2440°K 9 min., 1930°K 2 sec.) 0.10, 1390°K; *d*, none, 0.20, 1660°K; *e*, 1890°K, 2 sec. 0.05, 1500°K; *f*, none, 0.10, 1605°K; *g*, none, 0.10, 1710°K; *h*, 1620°K, 1 min. 0.10, 1605°K.

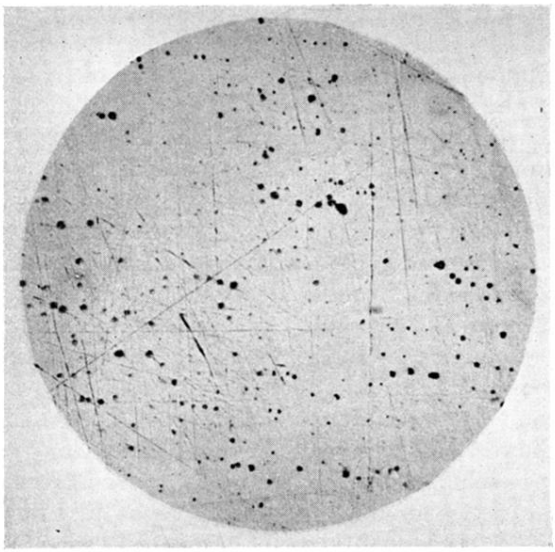

FIG. 7. Photomicrograph of interior section of fine grain thoriated tungsten ribbon (×1000).

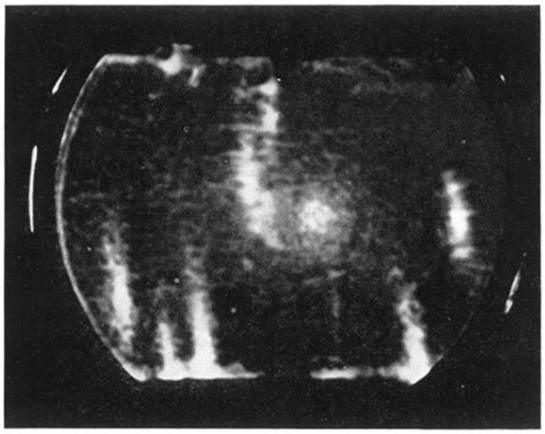

FIG. 9. Thorium eruptions and the migration of thorium in a preferred direction over the surface of a single crystal of thoriated tungsten.