Growth and Surface Properties of Tantalum Crystals*

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A method consisting of a moving temperature gradient for producing centimeter-long crystals in commercial tantalum wire is described. Based on one run, the method was less successful on commercial molybdenum wire. Thermionic projection tube patterns from the resulting crystals were qualitatively the same as that from tungsten. Plateau-like structure similar to that of tungsten was observed on both the tantalum and molybdenum crystals.

THE three most refractory metals are tungsten, tantalum, and molybdenum. Since these three all form body-centered cubic crystals, they might be expected to display similar crystallization, surface-structure, and electron-emission properties. Of these three metals, only the properties of tungsten have been investigated extensively.

I. CRYSTAL GROWTH TECHNIQUE FOR TANTALUM

In order to study the thermionic properties of crystals, it is most convenient to use crystals the order of a centimeter in length in fine wires.[1] In the case of tungsten wires, which are widely used for incandescent lamp filaments, additives have been developed which promote large grain growth[2] so that only a simple heating schedule of the raw wire is necessary to produce crystals centimeters long occupying the entire wire cross section.[3] In the cases of tantalum and molybdenum, there has been no development similar to that of tungsten and only "commercially pure" wire is available. The tantalum wire used was obtained from the Fansteel Metallurgical Corporation and was designated T71-Q25014A-No. R8130-8 dated March 13, 1951. It is well known that the crystal growth properties depend on the purity of the metal and on the mechanical strain in the wire.[3,4] The writer has been informed that the Fansteel wire "conforms with our specifications for purity which designate limits; namely, iron 0.03 percent max, carbon 0.03 percent max, and tantalum 99.9 percent min." "Variations between lots may be expected to be small" and "no detailed analysis of the specific lot is available."[5] Mrowca[4] has reported that in the case of tantalum ribbon, a cold stretch resulting in about 2 percent elongation produced the largest crystals.

All the wires were 0.005 inch in diameter and were polished to remove the die marks.[6] With the exception of one run on tantalum in which helium was used as a filler gas, all runs were made in tubes continuously pumped by mercury vapor pumps with no stopcocks on the high-vacuum side. After baking at 500°C, a vapor trap between the tube and the pumps was refrigerated by liquid nitrogen during the runs. The Langmuir-Malter temperature scale was used.[7] All heating was done on ac to avoid dc etching.[8]

As a preliminary test, a tantalum wire 30 cm long was first given a cold stretch of 2 percent and then mounted in an electron projection tube as indicated in Fig. 1(a).[9] A heating schedule similar to that described by Robinson[3] was used consisting of 21 hours at 2100°K, 26 hours at 2300°, 7 hours at 2500°, 15½ hours at 2600°, and ¾ hour at 2700°. The electron projection tube showed only very small crystals and optical microscope examination showed that some crystals were several wire diameters long and occupied the entire cross-section of the wire. These results suggested that a moving temperature gradient similar to that used by the writer on tungsten might extend such crystals to greater length.[10]

For this purpose, an arrangement sketched in Fig. 2 was used.[11] The weight was a piece of tungsten rod 0.060 inch in diameter and ¾ inch long. The mercury was distilled in. The adjustable leak was a Hoke

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[1] See, for example, G. F. Smith, preceding paper [Phys. Rev. **93**, 295 (1954)], and references thereto.

[2] C. J. Smithells, *Tungsten* (D. Van Nostrand Company, Inc., New York, 1936), second edition.

[3] C. S. Robinson, J. Appl. Phys. **13**, 647 (1942).

[4] B. A. Mrowca, J. Appl. Phys. **14**, 684 (1943).

[5] By private correspondence with Dr. L. F. Yntema of the Fansteel Corporation.

[6] Johnson, White, and Nelson, Rev. Sci. Instr. **9**, 253 (1938).

[7] L. Malter and D. B. Langmuir, Phys. Rev. **55**, 743 (1939). See also D. B. Langmuir and L. Malter, Phys. Rev. **55**, 748 (1939).

[8] R. P. Johnson, Phys. Rev. **54**, 459 (1938).

[9] Tantalum wire does not have as much tensile strength as tungsten wire so that tungsten spiral springs, which are used extensively with tungsten filaments, are not suitable for tantalum. Worthing (see reference 12) gives data on the thermal expansion of tantalum from which the cold extension of a spring can be calculated so as to let the wire go slack at any desired temperature. However, no data on the tensile strength of tantalum as a function of temperature are available. Flat molybdenum springs in zigzag shape were used and after several tries, the dimensions in Fig. 1(b) were found to give sufficiently weak springs to avoid breaking the wire. The width of the spring was 0.15 cm and the thickness of the molybdenum sheet was 0.003 inch. After forming, the springs were heated in hydrogen to approximately 1200°C for several hours. Springs four cycles in length were used for wires 30 cm long.

[10] M. H. Nichols, Phys. Rev. **59**, 297 (1940).

[11] A nickel wire guide ring, indicated schematically at *A*, was necessary because, without it, surface tension effects in the mercury pushed the weight over to the side of the tube. The position of the guide was such that the surface tension effects applied only between the thin tantalum wire and the guide.

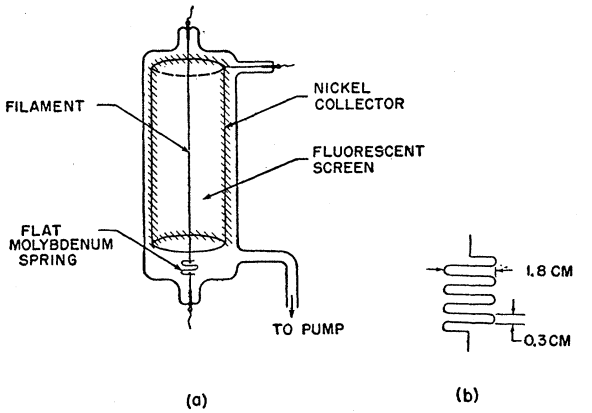

FIG. 1. (a) Schematic diagram of electron projection tube used for observing thermionic emission patterns. (b) Schematic diagram for the zigzag spring.

"OK" needle valve. With this apparatus, four runs were made with cold stretch of 1.2 percent, 2 percent, $2\frac{1}{2}$ percent, and 4 percent. Temperatures from 2200°K to 2600°K were used during the lowering of the mercury. Mercury lowering rates ranged from 4 cm to 0.12 cm per hour. In the case of each wire, the effect of growing "seed" crystals prior to the lowering of the mercury was tried. This was done by a "static" heating schedule, similar to that of the first test run, with the mercury stationary. At the completion of the schedule, the mercury was first raised to overlap the seed crystal, formed just above the mercury during the heating, and then lowered at the desired rate. It was found that seed crystals were not necessary inasmuch as about as many of the longer crystals appeared to be started during the lowering as from seed crystals. From these runs, one crystal 1.5 cm long, one 1.2 cm long, and numerous crystals ranging up to 8 mm in length were obtained. The best results were obtained with a cold stretch of 2 percent, temperature 2400–2500°K, and lowering rate about 0.3 cm/hr. The 1.2 percent stretch produced only very small crystals and the 4 percent stretch appeared to be less effective than the 2 percent in producing larger crystals. This is in agreement with Mrowca's results.[4] Figure 3 is a photograph of a projection tube showing one crystal 1.5 cm long just below level No. 1 and one 1.2-cm crystal just below level No. 4 grown at 2400°K and lowering rate 0.35 cm/hr and 2500°K and lowering rate 0.3 cm/hr, respectively. The 1.2-cm crystal was more perfect than the 1.5-cm crystal.

One run was tried with helium at a pressure of 4.5 cm Hg as a filler gas in order to increase the temperature gradient at the surface of the mercury. The wire was raised to a temperature estimated by the color to be between 2500 and 2600°K and the mercury lowered at a rate of 0.2 cm/hr. After the mercury had gone down approximately 1.2 cm, the wire burned out. Subsequent electron projection tube examination showed no crystals over millimeter length.

The foregoing experiments should not be considered as a complete investigation of the crystal growth properties of tantalum, but rather as a background for further experiments.

II. CRYSTAL GROWTH IN MOLYBDENUM

One run was made on molybdenum wire using the apparatus of Fig. 2. The wire was Fansteel MOLY-G spec. 1.100–17 percent No. R8130-9 dated March 13, 1950. The writer has been informed[5] that the wire "conforms to our specifications which designate limits; namely, iron 0.05 percent max, carbon 0.03 percent max, and molybdenum 99.9 percent min." The data of Worthing[12] on the emissivity and resistivity of molybdenum were used in comparison with the same quantities relative to tungsten[13] to obtain an approximate temperature scale. The mercury was lowered at rates ranging from 0.3 to 1.1 cm per hour at temperatures between 2000 and 2050°K. Figure 4 is a photograph of the thermionic projection tube containing this wire. Because the wire above No. 3 was thinned by evaporation, only the emission above this level shows in the photograph. Approximately $\frac{2}{3}$ of the way from level 1 to level 3, several crystals jointly occupied the cross section of the wire but they extended several centimeters along the wire. The seed crystal technique was tried several times in this run but yielded no positive results.

III. THERMIONIC PROJECTION TUBE PATTERNS

The thermionic projection tube patterns of tantalum and molybdenum appeared to be qualitatively identical to that of tungsten.[1] The crystals are oriented with a

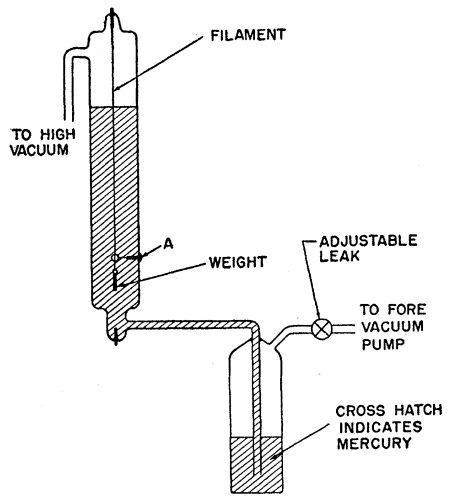

FIG. 2. Schematic of apparatus for producing moving temperature gradient.

[12] A. G. Worthington, Phys. Rev. **28**, 190 (1926).
[13] H. A. Jones and I. Langmuir, Gen. Elec. Rev. **30**, 310, 354, 408 (1927).

(110) crystal axis aligned with the wire axis. This results from slippage of the crystal planes during the drawing process.[2] Thermionic and field emission patterns of tungsten are qualitatively identical.[14–17] No field emission projection tube patterns for tantalum have been published. Benjamin and Jenkins[17] have published a photograph of field emission from molybdenum. If the "lacy" pattern surrounding the (001) direction is assumed to be the result of impurities, than the pattern agrees with that of tungsten. As best could be determined from the molybdenum crystals of Fig. 4, the thermionic and field emission patterns for molybdenum are also identical. To explain the identical field emission and thermionic emission patterns on the basis of internal effects alone—i.e., on the basis of forbidden electronic energy bands—it would be necessary to have gaps in the allowed bands both at the Fermi level and at the surface barrier level for the (110), (112), and (001) directions.[18] That such should occur for the three different metals (still must be checked for the field emission from tantalum) all in the same way is, of itself, very unlikely. The other explanation of anisotropy of emission is variation in the dipole moments of the surface double layers on the various crystal surfaces.[18] Since the three metals all form body-centered cubic crystals, presumably having similar electronic structure, it would be expected that the double layers would be of similar nature. Thus, based on these experimental results alone, it is reasonable to conclude that the anisotropy in the field and thermionic emission patterns of these metals is due mainly to differences in the moments of the double layers rather than to gaps in the allowed energy bands.

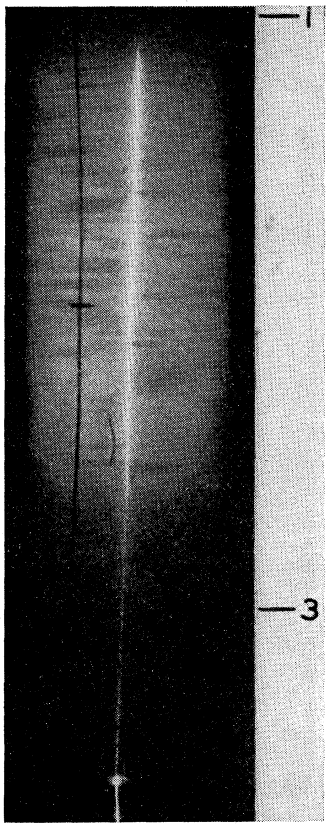

FIG. 4. Photograph of electron projection tube containing the molybdenum wire.

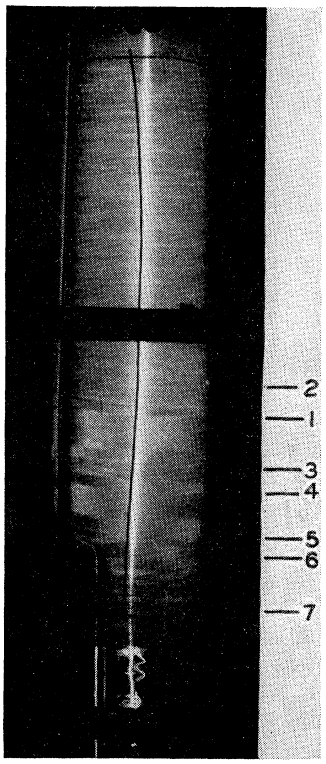

FIG. 3. Photograph of electron projection tube showing thermionic emission pattern from single crystals of tantalum. A mechanical support blocks the view of the tube at about the middle. The nickel wire for collecting the secondary electrons from the fluorescent screen casts a dark shadow; the vertical collector wire is almost coincident with the hot filament.

IV. SURFACE STRUCTURE OF TANTALUM CRYSTALS

The surface structure of the tantalum crystals produced by the techniques described in Sec. I was examined and photographed by the methods described in the accompanying paper.[1] The surface structure of tantalum crystals is similar to that of tungsten in that plateaus are formed normal to certain crystal directions and usually display a shingle-like structure.[1] Figure 5(a) is a photograph of the surface normal to the (110) direction of the lower of the two large crystals appearing in Fig. 3. This was taken after the heating given the wire during the crystal growth procedure, namely $3\frac{1}{2}$ hours at 2500°K and 20 minutes at 2600°K. Careful examination of the other surfaces showed in some places a very faint plateau structure normal to the (001) direction but it was too faint to photograph. According to the

[14] E. W. Müller, Z. Physik **120**, 261, 270 (1943).
[15] R. O. Jenkins, Repts. Progr. Phys. **9**, 177 (1943).
[16] R. Haefer, Z. Physik **116**, 604 (1940).
[17] M. Benjamin and R. O. Jenkins, Proc. Roy. Soc. (London) **A176**, 262 (1940).
[18] C. Herring and M. H. Nichols, Revs. Modern Phys. **21**, 185 (1949), especially pages 203 and 247.

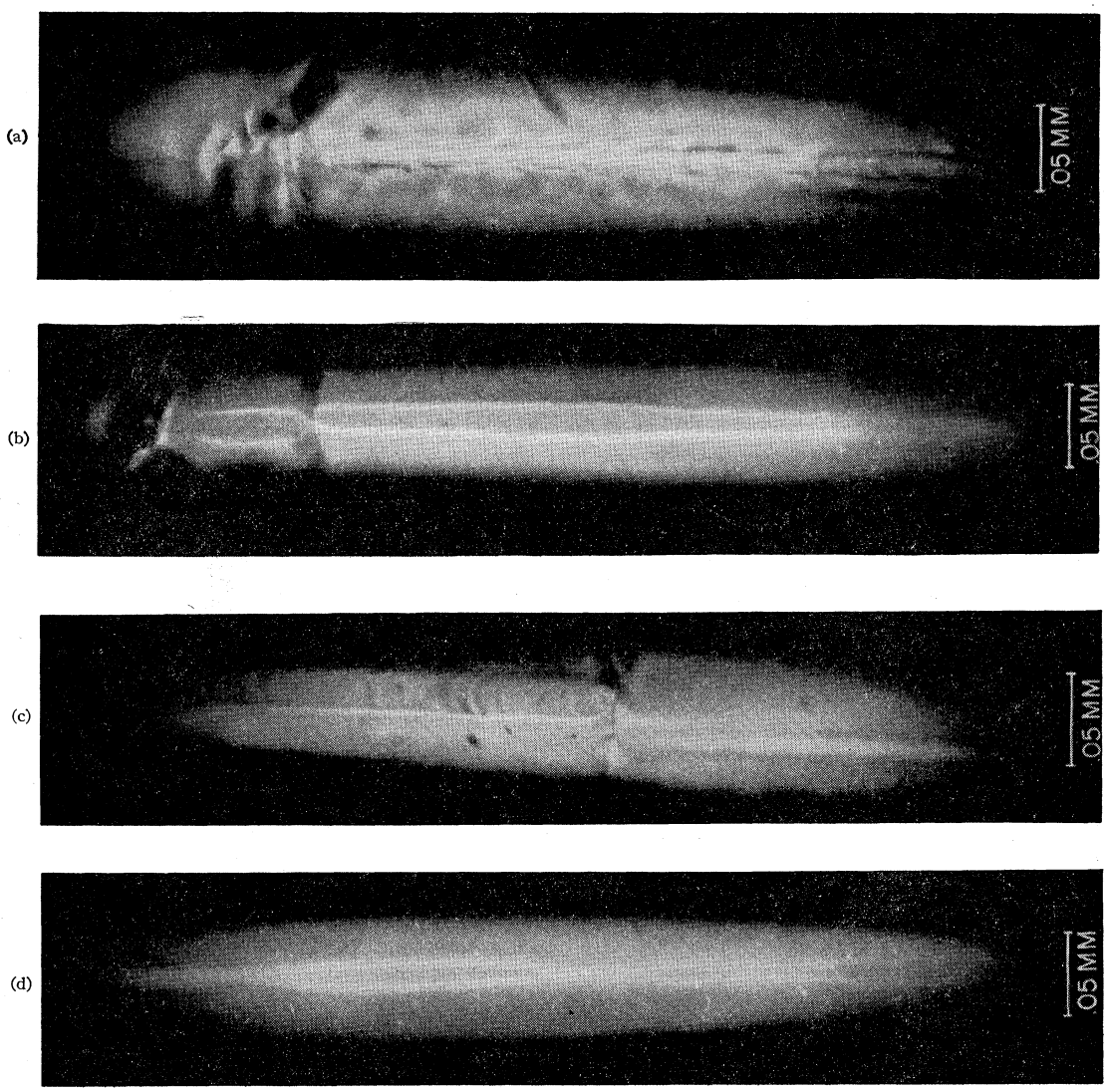

FIG. 5. Photomicrographs of tantalum crystal. (a) Photomicrograph taken along a (110) crystal direction after $3\frac{1}{2}$ hours at 2500°K and 20 minutes at 2600°K. (b) Photomicrograph along (110) direction of same crystal as (a) after evaporating away approximately 5 percent of the wire diameter. (c) Photomicrograph of a grain boundary showing two plateaus. The larger plateau is normal to a (110) direction and the smaller is normal to a (001) direction. (d) Photomicrograph of portion of same crystal as in (b) taken along (110) direction. This shows variation in the plateau width.

data of Langmuir and Malter,[7] the heat treatment up to this point would produce, by evaporation, a reduction in wire radius of 10^{-5} cm.

The section of the wire including the two large crystals of Fig. 3 was mounted in a Pyrex tube containing a barium-aluminum getter bulb. This tube was evacuated, baked, gettered, and sealed off with the usual precautions. Although no ionization gauge was used, a leak test using a mercury cutoff and the system McLeod gauge indicated a tight tube. The wire was then heated according to the schedule of Table I. The temperatures in this table were calculated from the original wire diameter corrected for evaporation using the data of Langmuir and Malter[7] and are only approximate. After approximately 5 percent of the wire diameter was evaporated, the wire burned out. The wire was removed from the tube and the photomicrographs of Figs. 5(b), (c), and (d) were taken.

Figure 5(b), according to the writer's notes, is a photograph of the same section of the wire as shown in Fig. 5(a). It is hard to explain the change in apparent grain boundaries, etc., in Fig. 5(b), but it is certain that both figures are photographs along a (110) direction. Structure could be found normal only to the (110) and (001) directions; the rest of the surface was smooth to within the resolution of the microscope except for the grain boundaries. The (110) plateau of Fig. 5(a) is approximately 0.01 mm wide. In Fig. 5(b), the (110)

plateau has grown to twice this width and the (001) plateau in Fig. 5(c) is approximately 0.01 mm wide. Since the diameter of the wire was 0.12 mm, a width of 0.01 mm subtends an angle of about 10° at the center of the wire. Figure 5(c) shows a crystal boundary and (110) and (001) plateaus for comparison. The wider plateau is the (110).

Figure 5(d) shows a (110) plateau of varying width. To a lesser extent, the width of the (110) plateau of Fig. 5(b) also varies. It is interesting to note that the shingle effect is not discernible in the region of narrowing width but is usually observed in the constant-width plateaus, as in Fig. 5(c), for example. This might imply that the region of narrowing plateaus is one of approach to an ideal crystal plane so that the plateau growth is inhibited.[1] A slight kink in the wire, changing wire diameter, or a slight bending of the crystal could bring this condition about.

In general, the features observed and discussed relative to tungsten in the accompanying paper[1] are also applicable to tantalum. There are two features which appear to be different, however. One is that no plateau was discernible normal to the (112) directions in tantalum. The other is that the heat treatment between the taking of Fig. 5(a) and Figs. 5(b), (c), (d) approximately doubled the width of the (110) and (001) plateaus, whereas in tungsten such heat treatment did not appreciably change the plateau widths. Also, no interferometer measurements were made of wire diameter so that the effect in Fig. 3 of the accompanying paper[1] was not observed.

TABLE I.

Temperature °K	Time at temperature in hours
2260	44
2300	46
2350	48.5
2400	50
2430	46.5
2460	194.5
2400	97.5
2360	48.5
2330	44.3
2360	11

It should be mentioned that a cursory examination of the molybdenum crystals of Fig. 4 also revealed plateau and shingle structure.

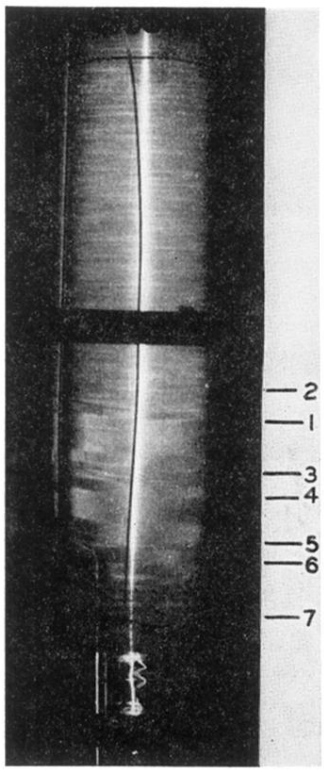

FIG. 3. Photograph of electron projection tube showing thermionic emission pattern from single crystals of tantalum. A mechanical support blocks the view of the tube at about the middle. The nickel wire for collecting the secondary electrons from the fluorescent screen casts a dark shadow; the vertical collector wire is almost coincident with the hot filament.

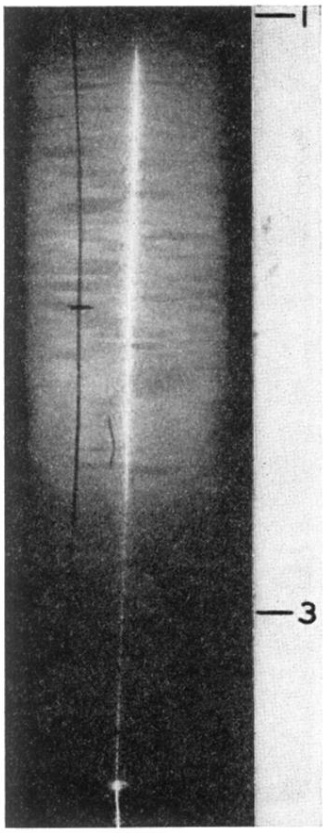

FIG. 4. Photograph of electron projection tube containing the molybdenum wire.

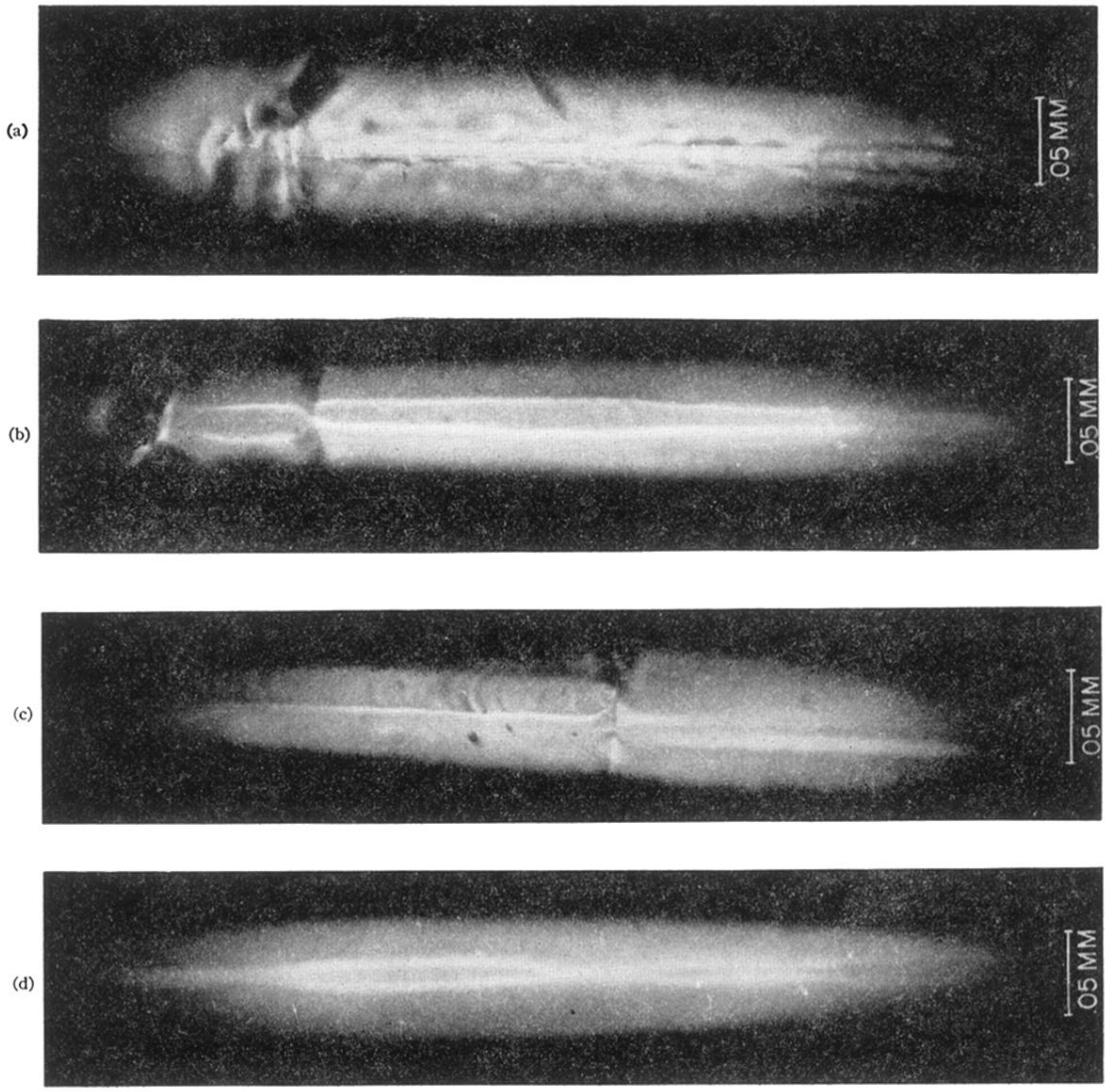

FIG. 5. Photomicrographs of tantalum crystal. (a) Photomicrograph taken along a (110) crystal direction after 3½ hours at 2500°K and 20 minutes at 2600°K. (b) Photomicrograph along (110) direction of same crystal as (a) after evaporating away approximately 5 percent of the wire diameter. (c) Photomicrograph of a grain boundary showing two plateaus. The larger plateau is normal to a (110) direction and the smaller is normal to a (001) direction. (d) Photomicrograph of portion of same crystal as in (b) taken along (110) direction. This shows variation in the plateau width.