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TOPICAL REPORT
STUDY OF VAPOR-DEPOSITED TUNGSTEN
AND TUNGSTEN-RHENIUM ALLOYS
FOR USE AS THERMIONIC EMITTERS

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I. PARTIAL POLE FIGURES FROM CYLINDRICAL AND PLANAR TUNGSTEN SPECIMENS

A. ABSTRACT

The spatial distribution of a single crystal-plane in a polycrystalline specimen can be explored by x-rays, and the resulting pole figure can be useful either in ranking members of a set of specimens according to their degree of preferred orientation, or in studying the dependence of the microstructure on mechanical and thermal treatment of the specimen.

Previous work by others has been extended to cover cylindrical tungsten specimens. A modification to a Philips-Norelco X-ray Diffractometer is described, which had been designed and built to hold a specimen (between 0.5 and 1 inch in diameter) in the exact position with respect to the x-ray beam, and subject it to the required motions. Results obtained from this device are presented, showing satisfactory agreement with those from a conventional Pole Figure Accessory for planar specimens.

Vapor-deposited and wrought specimens have been examined. It is found that grinding produces a randomly-oriented surface; mild heat treatments typically used in emitter preparation recrystallize this only slightly, so that the highly-oriented emitters often used may in fact have a nearly randomly-oriented surface. The heat treatment necessary to recrystallize the random layer and regenerate the underlying orientation is indicated. It is found that the removal of two mils of tungsten by electropolishing is sufficient to eliminate the random layer introduced by grinding and to expose the substrate orientation. The reproducibility of a set of cylindrical vapor-deposited samples is shown. Heat treatment is shown to alter the grain size of the material without altering its pole figure.

B. INTRODUCTION

The complete description of the preferred orientation of a given set of crystal planes in a sample is customarily presented in the form of a stereographic projection of the density of poles of the planes found in different directions in the specimen.¹ This two-dimensional projection is necessary because the pole distribution can vary independently about two axes. However, it is found that material prepared by chemical vapor deposition can usually be described in a simpler way. Experience indicates that most vapor deposits consist of columnar grains growing perpendicular to the substrate and tending more or less strongly to have a particular crystal direction parallel to the growth direction.² (In cubic materials only, it follows that a corresponding crystal plane will have a similar tendency to be parallel to the gross specimen surface.) However, there is generally no tendency for a particular crystal direction to be oriented preferentially in the plane of the specimen; rather, individual grains tend to be randomly oriented with respect to any direction on the specimen surface. These properties result from the nature of the CVD process. At the start of deposition, a large number of grains nucleate on the substrate surface, usually with random orientations, uninfluenced by the substrate. Each of these grows most rapidly in one particular crystallographic direction, and then tends to interfere with neighboring nuclei. The nuclei which survive and become grains in the deposit are those which the preferred growth direction does not lead into contact with other grains, but leads directly away from the substrate into the surrounding gas mixture. Thus, the resulting deposit tends to consist of grains originating at nuclei oriented so that the preferred growth direction is perpendicular to the substrate. When

the bottom or substrate side of the deposit is examined, by etching away the substrate, it is very nearly randomly oriented.

The preferred growth direction varies according to the compounds and the temperature used in deposition. For tungsten, two types of preferred orientation are common. The hexafluoride WF_6 , reduced with hydrogen in the temperature range of 500 - 800°C, gives deposits with a (100) direction perpendicular to the surface, and the hexachloride can be used at higher temperatures to give deposits with a (110) direction perpendicular to the surface.² In each case Laue back-reflection photographs confirm the generalization that the deposits are randomly oriented in their own plane, since they show uniform ring patterns.

The bounding surface of a grain of tungsten deposited from WF_6 is not the (100) plane, as might be expected from the fact that the grain has grown along the (100) direction. Rather, the grain terminates in a four-sided pyramid of (111) planes, with the apex outmost and near the center of the grain.³ The effect of this in a many-grained deposit is to give a flat, matte, unreflecting surface, which has a highlight or glint only if examined very obliquely.

The bulk properties of the deposit, but not the surface properties, may be investigated by x-ray diffraction, and any preferred orientation may be characterized and perhaps quantified. The standard method for doing this on planar vapor deposits has been developed by Yang,⁴ and is also used by the present author. This method entails detecting the x-rays diffracted from the one particular class of crystal planes supposed to be found parallel to the surface, and examining the intensity of this diffracted beam when the specimen is tilted so as to bring planes which are not parallel to the surface into a position to

diffract. Figure 1 shows this schematically. In 1A, grain G_1 is oriented so that its (100) planes produce the diffracted beam D_1 . G_2 has no correctly aligned planes, and does not contribute to the diffracted intensity. However, when the specimen is rotated about the point on its surface where the x-rays strike, through an angle equal to the angle α between (100) planes in G_1 and G_2 , then G_2 produces the diffracted beam D_2 .

For a suitably fine-grained sample, a representative curve of I versus α can be obtained while the specimen is rotated through a range of $\pm 20^\circ$ or 30° of α . In practice, the rotation axis is such that the surface normal moves out of the plane of the x-ray beams. This eliminates the need for absorption corrections, but Figure 1 illustrates a case which is simpler to depict. It is customary to reduce the x-ray data by taking readings of I at a number of values of α , correcting them for the background at large α , and calculating a normalized cumulative sum of the intensities, which is then plotted to give a "Partial Pole Figure" (PPF) approximating $\int_0^\alpha I d\alpha$, running from zero at $\alpha = 0$ to unity at some α , depending on the specimen.⁴ A randomly-oriented sample has I independent of α , and so the PPF obtained from it is a straight line, reaching 1 at an arbitrary value of α . An oriented sample has an upward convex partial pole figure; downward convex curves have been found in wrought material, indicating that the planes under investigation occurred less frequently than in a random sample.

Cylindrical specimens cannot be manipulated in the conventional Norelco Pole Figure Accessory, and so a modified accessory for these had been built for use with a Norelco X-ray Diffractometer.⁵

(A)

(B)

Figure 1. Diagram of Relation between X-ray Beams and Correctly Spaced Planes in Two Grains of Sample. (In each picture, only one grain contributes to the diffracted beam.)

The specimen was supported in a holder which was hung from a rod passing through the axis of the diffractometer. The specimen cylinder axis was parallel to the diffractometer axis, and was also arranged so that:

1. The point under examination on the upper surface of the specimen was on the diffractometer axis, regardless of specimen diameter.
2. The specimen surface normal could be adjusted to bisect the incident and diffracted beams, by moving it in their plane, to satisfy the Bragg condition for a chosen class of crystal planes. This adjustment was made with the 2θ control of the diffractometer.
3. The specimen surface normal could be rotated, in a plane perpendicular to that described in 2 above, so that it moved out of the plane of the x-ray beams. This tilt was measured by the angle α through which the surface normal moved. The center for this rotation was a point on the diffractometer axis, and therefore on the specimen surface, at which the axis of the incident beam collimator intersected that of the detector. This was the point under examination.
4. The specimen rotated about its own axis. This motion was provided so that a band around the specimen was sampled by the x-rays.
5. Different areas of the specimen could be examined and specimens of different lengths could be accommodated.

A schematic diagram of the α and θ motions is shown in Figure 2, and pictures of the apparatus are shown in Figures 3 and 4. Further details of its construction are given in Reference 5. Data were obtained using CuK α radiation from a tube operating at 35 KV, 15 mA, a scintillation counter and a single channel pulse height analyzer.

C. RESULTS

It should be realized that this device does not give all the information necessary to plot a complete pole figure on a stereographic projection. However, it is capable of characterizing samples of vapor-deposited material, in terms of the distribution of one set of planes. It does not give information on the relative intensity of different preferred orientations that can be obtained from a study of intensity versus 2θ for different specimens. However, checks on representative samples have confirmed that the planes for which the $\int I d\alpha$ PPF's are convex upwards are also the planes which have peaks in the I versus 2θ plots much higher than the corresponding peaks in the I versus 2θ plots from random samples. The PPF's presented here are quantitative representations of the tendency of a particular plane to be oriented parallel to the specimen surface. They cannot be summarized in terms of one parameter, so comparisons between them have to be made visually.

1. Random Samples

Powders of tungsten and rhenium (-325 mesh) were mixed with epoxy resin and applied to recesses in cylindrical mandrels. After hardening, the epoxy/metal was machined down to the same diameter as the mandrel and examined. The diffractometer was set to detect the strongest peak from the random sample, and the I versus α plots were

found to be constant to $\pm 2\%$ from $\alpha = -20$ to $\alpha = 20^\circ$. This was taken to mean that no geometric or absorption corrections were needed, and data from other samples were corrected only for the background reading at $\alpha = 20^\circ$. A piece of 1-mil tungsten foil was examined on the Planar Pole Figure Accessory, and then wrapped on a mandrel and re-examined on the cylindrical specimen accessory. The two resulting PPF's are shown in Figure 5 and agree reasonably well. This sample, in fact, has a strong preferred orientation with (100) planes parallel to the surface.

2. Fluoride Material

As-deposited fluoride material shows a fairly strong preferred orientation of (100) planes parallel to the surface which increases somewhat with thickness, particularly in the first 0.02 inch of growth. Figure 6 shows PPF's for planar deposits of different thicknesses. Figure 7 shows the total range of PPF's for six cylindrical samples cut from a long bar of CVD material, and so gives an idea of the combined variation due to sample and instrument. Figure 8 shows the effect of heat-treating planar deposits. Considerable changes in the microstructure occurred,³ but the PPF's remain very similar.

Grinding of this material, or any other material, destroys the preferred orientation and produces a layer of randomly-oriented material. This material can be removed by electropolishing to disclose the oriented material underneath. We have found that, in tungsten, removal of two mils reveals a surface whose PPF is typical of the bulk material. It might be expected that heat treatment would recrystallize the disturbed material, and in fact it does, but very severe treatments are necessary to regain fully the orientation of the underlying material. For example, Figure 9 shows that during 100 hours of heat treatment at 1800°C , some

Figure 2. Diagram of α and θ Motions of Cylindrical Sample.

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Figure 3. Photograph of Accessory at $\alpha = +20^\circ$.

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Figure 4. Photograph of Accessory Installed on Diffractometer at $\alpha = 0$, $2\theta = 60^\circ$.

Figure 5. PPF's for 1-mil Tungsten Foil Examined in Planar and Cylindrical Form.

I-13

I-219

Figure 6. PPF's from 0.2-inch planar deposit, 0.015-inch planar deposit, 0.005-inch cylindrical deposit, and 0.055-inch cylindrical deposit.

Figure 7. Range of PPF's for Six Cylindrical Samples.

I-15

I-212

Figure 8. PPF from Specimen WF 12 as-received (A) and after 1 hour at 2000°C (B), 6 hours at 2000°C (C), and 1 hour at 2230°C (D).

Figure 9. PPF from Specimen Ground and Heat-Treated for 6, 30, and 100 hours at 1800°C.

recrystallization occurs, and the PPF begins to deviate from the straight line characteristic of the ground layer. However, the full orientation is not obtained, indicating that a surface which is ground and treated for 100 hours at 1800°C has an orientation characteristic of the treatment and not of the underlying material. Figure 10 shows a PPF for a sample ground and heated for 6.5 hours at 2600°C in which the surface has recovered most of the intrinsic preferred orientation.

3. Chloride Material

As-deposited chloride material tends to have (110) planes parallel to the surface, in contrast to fluoride material. In the sample examined, which was 0.04 in thick, the tendency is less strong than that in the thicker fluoride sample, as may be seen in Figure 11. It is well known that the grain structure of this material is much less stable than that of fluoride material. Consequently, most heat-treated samples have a grain size so large that the area examined by x-rays does not provide a representative sample of the material. The I versus α plot contains a few random peaks, and the reduced data curve consists of a few steps and does not characterize the material well.

4. Wrought Material

Samples of extruded tungsten bars were fabricated at Oak Ridge National Laboratory and examined by this method. The samples had a rather rough surface which precluded examination in the as-extruded condition. One was ground just enough to measure its diameter, which was then 0.545 to 0.546 inch (sample 1). Another was ground to remove about 0.012 inch from the surface, giving 0.520 to 0.521 inch diameter (sample 2).

The as-ground surfaces were examined for (100) reflections and were found to be completely random, as expected. Both samples were annealed in vacuum at 1750°C for 30 minutes, and re-examined. The lightly-ground sample 1 showed a mild positive (100) preferred orientation and a marked inverse (110) one, as shown in Figure 12. Sample 2 (Figure 13), from which more material had been removed, showed a practically identical mild (100) preferred orientation, and a very similar inverse (110) one. In each case the raw data were more irregular or "noisy" than is usual for vapor-deposited material, but they gave smooth curves when the data were reduced. The specimens were then re-annealed for 30 minutes at 1950°C and re-examined. Sample 1 now showed a near random partial pole figure for (100) and a definite inverse preferred orientation for (110) planes, as shown in Figure 14, as did sample 2. Further recrystallization during the higher temperature anneal had eliminated the vestiges of preferred orientation that had been present.

A piece of stock arc vacuum cast and wrought bar was ground to 0.509 ± 0.001 inch diameter and examined by the standard method, after annealing 30 minutes at 1750°C. It also gave positive (100) and inverse (110) pole figures, with a marked deficiency of (110) planes oriented close to the specimen surface as compared to a random specimen, seen in Figure 15.

Subsequently, a further sample of wrought tungsten tube was examined. This had been prepared at ORNL by vapor-depositing a tube, sheathing it in TZM molybdenum, and extruding and drawing the assembly. Then the sheath was etched away and the rough tube surface ground to allow examination. The ground surface was removed by electropolishing (1 to 0.002 inch depth) to avoid further

Figure 10. PPF from Specimen Ground and Heat-Treated for 6.5 hours at 2600°C.

Figure 11. PPF's from the (100) Planes of the Fluoride, 0.055 in thick and (110) Planes of the Chloride Material, 0.04 in thick.

Figure 12. PPF from Lightly-Ground and Annealed Wrought Tungsten Bar #1, after 30 minutes at 1750°C.

Figure 13. PPF from Similar Bar #2, with 0.012 inch Removed, after 30 minutes at 1750°C.

Figure 14. PPF from Bar #1 after another 30 minutes at 1750°C.

Figure 15. PPF from Ground AVC Bar Annealed 30 minutes at 1750°C.

alteration of the grain structure, and the sample was examined by the standard method. Here a considerably stronger positive (100) orientation was found, coupled with a curious feature. The peak of the raw I versus α curve was displaced +4 degrees from the $\alpha = 0$ position. When the sample was removed from the apparatus, turned end-for-end, and replaced, the peak shifted to -4 degrees from $\alpha = 0$. Apparently the extruding and drawing processes had systematically tilted the grains so that their axes were a few degrees off the radius of the tube. Intuitively, it seems likely that the grain axes were tilted back towards the trailing end at the outside of the tube, as might be expected from friction with the die face. However, since the leading and trailing ends of the specimen were no longer distinguished, it is not possible to confirm this. It is clear that the tube had acquired a kind of polarity, so that structurally it was not symmetrical with respect to its two ends. A metallographic examination of a longitudinal cross-section revealed that the grains were highly elongated along the tube length, as would be expected for heavily wrought material. Similar phenomena have been reported previously elsewhere.⁶

Because the peak was highly symmetrical about $\alpha \sim 4$ degrees, it was reduced and treated about $\alpha = 4$ instead of $\alpha = 0$, and so the PPF is not strictly comparable with those of other specimens reported here (Figure 16).

D. CONCLUSIONS

The random surface produced when oriented vapor-deposited material is ground is not eliminated by treatment for 100 hours at 1800°C. Either more intense heat treatment or electropolishing is

necessary to disclose the highly oriented structure characteristic of vapor-deposited material.

The grain size of heat-treated samples of chloride material seriously impairs the data which can be obtained from them. However, it appears that the samples examined had a slightly less-pronounced preferred orientation than the samples of material prepared from the fluoride.

Wrought material with cylindrical symmetry, if ground and annealed, shows a mild positive (100) preferred orientation parallel to the surface, and a corresponding inverse (110) orientation. These can be eliminated by further annealing. Preferential orientation of (110) planes parallel to the surface has not been observed in the specimens examined.

Figure 16. PPF from Extruded CVD Tungsten Bar Ground and Electropolished (see text).

II. STUDY OF VAPOR-DEPOSITED TUNGSTEN-RHENIUM ALLOYS FOR USE AS THERMIONIC EMITTERS

A. ABSTRACT

Five tungsten-rhenium alloys containing not more than 26% Re were prepared by vapor deposition onto tungsten substrates. Samples were subjected to various heat treatments and surface preparations and examined metallographically and by x-ray diffraction. Bare work function measurements failed to reveal any clear trend in the work function that could be attributed unambiguously to the effect of rhenium additions.

B. ALLOY EMITTERS

The purpose of this task is to investigate thermionic emission from tungsten-rhenium alloys, because there are reasons to believe that the bare work function of such alloys might be larger than that of pure tungsten,⁷ and because such alloys have certain mechanical properties superior to pure tungsten.⁸

Mechanical properties were not studied because other workers had established that rhenium additions confer greater ductility to tungsten in many physical forms. Thermionic properties were studied by measuring the bare work function of specimens in a specially designed apparatus.

Because the work function of a material varies with crystal orientation, it was desirable to control the crystal orientation of the alloy specimens examined so that work function differences could be attributed to alloying rather than to orientation variations. To this end,

five samples were prepared by vapor deposition. The vendor* was asked to supply samples with zero, 5, 10, 15, and 25% rhenium codeposited with the tungsten onto wrought tungsten substrates. Three-inch diameter discs were supplied with vendor's analyses of zero, 2.5, 9, 16, and 26% rhenium in them. Vapor deposition was chosen because it seemed to offer a way of varying alloy content without changing other variables. Upon receipt, the samples were cut into smaller discs and provided with radial black-body holes (L/D in the range of 8-9). A homogenization anneal of 30 minutes at 2000°C in vacuum was applied, followed in certain cases by a more intense anneal. The samples were also examined by x-ray diffraction to characterize their preferred orientation by well-established techniques.

C. METALLOGRAPHY

A leftover piece from each sample was used to study the cross section of the vapor-deposited layer from the tungsten substrate to the top of the deposit. These cross sections were finely ground through 600 grit SiC, electropolished, and electroetched in 5% NaOH, and then photographed, as shown in Figures 17c through 21c.

The marks on the borders of the photographs indicate the location of the beginning of the deposit layer. The substrate-deposit interface could easily be located on the as-received material, since prior to the annealing, the substrate displayed an elongated grain structure (typical of wrought material) which was perpendicular to the elongated grain structure of the deposit layer. In the photographs, the annealed layers appear to be thinner than the as-received layers, due to further rounding off at the edge caused by the second electropolishing and etching.

---

* San Fernando Laboratories, Pacoima, California

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Figure a. 150 x
As-received
Lightly electroetched

Figure b. 150 x
As-received
Heavily electroetched

Figure c. 150 x
Annealed 30 min at 2000° C
Heavily electroetched

Figure 17. Pure W Scrap

8849

Figure a. 150 x
As-received
Lightly electroetched

Figure b. 150 x
As-received
Heavily electroetched

Figure c. 150 x
Annealed 30 min at 2000° C
Heavily electroetched

Figure 18. W 5% Re Scrap

8845

Figure a. 150 x
As-received
Lightly electroetched

Figure b. 150 x
As-received
Heavily electroetched

Figure c. 150 x
Annealed 30 min at 2000° C
Heavily electroetched

Figure 19. W 10% Re Scrap

8843

Figure a. 150 x
As-received
Lightly electroetched

Figure b. 150 x
As-received
Heavily electroetched

Figure c. 150 x
Annealed 30 min at 2000° C
Heavily electroetched

Figure 20. W 16% Re Scrap

8844

Figure a. 560 x
As-received
Lightly electroetched

Figure b. 560 x
As-received
Heavily electroetched

Figure c. 560 x
Annealed 30 min at 2000° C
Lightly electroetched

All of the W/Re deposit layers showed distinct discontinuities in the as-received condition. Annealing for 30 minutes at 2000°C eliminated some of these discontinuities and caused a marked increase in grain size. There was no sign of the polyhedral growth front found on other samples of vapor-deposited pure tungsten. Prior to annealing, all but the W 26% Re showed an elongated and feather-like structure (Figures 17b through 20b). After annealing, most of the grains in the pure W were equiaxial (Figure 17c), whereas all of the alloys showed at least some signs of a columnar structure. In the pure W and in the W 5% Re and W 10% Re, after annealing at 2000°C, the average grain size was largest at the beginning of the deposit, and in the case of the 5 Re and 10 Re alloys, these larger grains were more nearly equiaxial than those in the rest of the deposit. By contrast, in the W 16% Re (Figure 20 c), the columnar structure began very near the bottom of the deposit, and the 2000°C annealing produced a number of huge grains in the top half of the deposit.

The deposit layer of W 26% Re was not nearly as thick as the other four samples. (Note that Figures 21a, b, and c were taken at 560x while all the preceding ones were taken at 150x.) Because of this apparent discrepancy, the W 26% Re was re-examined more carefully. It was first plated with copper to avoid rounding off of the top of the deposit and was then reground through 600 grit SiC. This time it was mechanically polished (with 6μ diamond) and chemically etched (with caustic Ferricyanide) instead of being electrolytically polished and etched. Figures 22a and b indicate that the previous metallography had not revealed the whole deposit layer. In Figure 22a, the mandrel is at the left and has a large crack in it; the dark portion at the right

8847

Figure a. 150 x
Annealed 30 min at 2000° C
Copper-plated
Chemically etched

Figure b. 300 x
Detail of 6a

Figure 22. W 26% Re Scrap

is the plastic mounting material and the uneven layer next to the plastic is the copper plating. The deposit layer, between the mandrel and the copper, is obviously quite heterogeneous. It is apparent that the top portion of the deposit rounded off completely in the previous examination, so that Figures 21a, b, and c show only the columnar portion (approximately the first half) of the deposit. However, even when the top portion is preserved by the copper plating, the whole deposit layer is still only about half as thick as the other four samples. The unusual degree of rounding-off suggests more rapid dissolution of the outer layer, perhaps because of compositional differences.

In addition to the metallography on "scrap" material described above, one of the discs from the W 16% Re sample and one from the W 26% Re sample were also examined. On each of the two discs a flat edge was cut, again to study the "longitudinal" cross section of the deposit layer. Both discs were annealed for 30 minutes at 2000°C and then for 3 hours at 2330°C. As in the first set of experiments, they were ground through 600 grit SiC and electrolytically polished and etched. By comparing Figure 23 with 20c, and 24 with 21c, it can be seen that the more intensive annealing further increased the grain size.

The flat surface of the samples whose work functions were measured are shown in Figures 25 to 29 at the same magnification. These emphasize the grain size difference between the low temperature and high temperature anneals. They also show the heterogeneous nature of the surface of W 26% R3C, which bears out the observations of heterogeneity on the cross section.

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Figure 23 W 16% Re, Disc 3C

150 x

Annealed 3 hrs at 2330° C

Heavily electroetched

Figure 24 W 26% Re, Disc 3C

560 x

Annealed 3 hrs at 2330° C

Heavily electroetched

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Figure 25 Surface of Sample W0R3B after
Work Function Measurement.

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Figure 26 Surface of Sample W5R3B after
Work Function Measurement.

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Figure 27 Surface of Sample W10R3B after Work Function Measurement.

Figure 28 Surface of Sample W16R3C after Work Function Measurement.

Figure 29 Surface of Sample W26R3C after Work Function Measurement.

D. X-RAY DIFFRACTION STUDY OF PREFERRED ORIENTATION

X-ray diffraction studies were made on a number of the W and W/Re discs. Some were studied in the as-received condition, some after annealing, and some after electropolishing to remove 2 to 3 mils of material. The data were obtained by impinging the x-ray beam onto the top surface of each disc and therefore served to characterize only the top few microns of any given sample. * On all but the electropolished samples, a scan of I versus 2θ was made at 2° or $4^\circ/\text{min}$ to determine the various peak positions and the relative peak heights. Then, whenever possible (see subsequent text for discussion of prohibiting factors), the degree of W (100) orientation was determined by rotating the disc about the x-ray beam, between $\alpha = 20^\circ$ and $\alpha = -20^\circ$ on either side of the normal position, as described in Reference 2. The angular resolution was not as good as in normal x-ray diffraction work because of the pole figure accessory used. The output signal at any point depended upon how much of the x-ray beam was being diffracted and therefore on how much of the specimen was in a position to diffract. The preferred orientation could then be plotted as a cumulative integral (C.I.) of intensity versus angle α running from 0 to 1. The range up to $\alpha = 20^\circ$ was explored. Thus, a random orientation would give 50% C.I. at 10° , and a preferred orientation would have a curve reaching 1 at some angle less than 20° .

The first discs to be examined were one disc from each of the five samples in the as-received condition (Series 2A). On the pure W disc, the highest 2θ peak was from the W (200) planes and the second highest was from the W(310) planes. The same was true for the W 5% Re disc

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*It should be noted that in the case of the W 26% Re, the surface exposed to the x-ray beam is visible in Figure 22 but not in Figures 21 and 24.

but not for the other three. On all but the pure W and W 5% Re, auxiliary peaks showed up immediately before and after the W (110) peak, becoming more pronounced as the Re content increased. These peaks are probably due to Federite, the unstable W-Re phase.⁹ All the peaks attributable to W got broader and less symmetrical with increasing % Re until 26% Re was reached, at which point the W (200) and W (310) peaks were gone from the 2θ scan. The degree of W (200) preferred orientation increased in the following order: pure W, W 5% Re, W 16% Re, and W 10% Re. The W 26% Re had given no W (200) peak at all, and all of the 2θ peaks that were present showed random α orientations.

Five other discs (series 3B) were annealed for 30 minutes at 2000°C and were examined as above. There was evidence that the annealing had had some homogenizing effect. This time the auxiliary peaks, near W(110), were less pronounced and the W 10% Re joined the pure W and the W 5% Re in having W (200) as the highest peak and W (310) as the second highest. The W 16% Re now had W (200) and W (110) as the main and second peaks, as had the W 10% Re prior to annealing. The W 26% Re still had no W (200) peak at all and still showed completely random orientations at all discernible 2θ peaks. Although the W 5% Re now showed a slightly weaker (200) orientation and the other three showed slightly stronger ones, the preferred orientation increased in the same order as before: pure W, W 5% Re, W 16% Re, and W 10% Re (see Figure 31).

The W 16% Re and W 26% Re discs from series 3 were annealed more intensively, for 3 hours at 2330°C. The W 26% Re again gave no W (200) peak and showed only random orientations. The grain size of the W 16% Re was increased prohibitively by such severe annealing (as indicated in Figure 23). This disc gave a strong and abnormally narrow W(200)

peak and no others; the corresponding α scan gave several sharp peaks, each one probably caused by a single grain, and this completely unsymmetrical curve could not be reduced to give useful data.

The pure W, W 5% Re, and W 10% Re discs from series 3 were electropolished to remove 2 to 3 mils of material to examine the diffraction characteristics further down in the deposit layer. In each case the preferred orientation was less, but only in the case of the pure W was the reduction substantial.

The W 10% Re was chosen to make a study of orientation variations from one place to another within the same sample. Three discs were examined while still in the as-received condition and three after annealing for 30 minutes at 2000°C. The results, shown in Figure 30, indicate that the range of orientations present in as-received material is larger than that in annealed material, where it is negligible.

Partial pole figures obtained from the surfaces whose work functions were measured are presented in Figure 31. These indicate significant variations in orientation between specimens. The bare work functions of the specimens are also indicated. The results are discussed below.

E. WORK FUNCTION MEASUREMENT

The apparatus used is shown schematically in Figure 32. Emission from the specimen is brought to the collector by an external applied field. The guard receives the emission from the specimen support ring and part of the specimen; only the emission from the central 0.5 cm^2 passes to the collector and is measured in an external circuit. The leakage resistance between the (grounded) specimen and the collector or guard is greater than 10^7 ohms. The lower temperature limit for measurements is that at which the emission current becomes small compared to the leakage current.

Figure 30. Partial Pole Figure Range for Different Regions of Specimen W 10 R (annealed).

Figure 31. Partial Pole Figures for Different Alloy Specimens.

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Figure 32 Schematic Drawing of Bare Work Function Measurement Apparatus.

The specimen temperature is measured on a black body hole in the edge, by means of a micro-optical pyrometer sighted through a window in the vacuum system. The pyrometer and window were calibrated against a NBS-traceable lamp to 2300°C before taking data.

The current-voltage curve between emitter and collector is recorded on an x-y plotter by the use of suitable shunts (100Ω to 0.1Ω) with applied voltage up to 1225 V. From these curves Schottky plots can be made as necessary or the saturation current density can be estimated with a practiced eye. This current density J and the specimen temperature T are substituted in the Richardson equation,

$$J = AT_e^2 e^{-\phi_e/kT_e},$$

to obtain the work function ϕ , assuming a value for the constant A of 120.4. The solution is obtained by means of prepared graphs of J vs ϕ with T as a parameter. The accuracy of the resulting ϕ value varies with the J , T , and ϕ involved, but is better than 15 millivolts.

The vacuum system pressure is generally about 10^{-7} torr, depending somewhat upon specimen temperature and considerably upon duration of pumping. The effects of oxygen adsorption on the specimen are frequently observed at the lowest temperatures of measurement (below 2000°K). The ϕ obtained is higher than that from high temperature data. At higher temperatures the results are independent of temperature (over 500°K range of T) and time and this is taken to indicate that adsorption effects are absent. No effects due to selective evaporation of Re from alloy surfaces have been detected, despite searches for hysteresis in ϕ during temperature cycles.

The emitter-collector spacing is generally 0.5 to 1.5 mm while hot and varies slightly with temperature. It is not regarded as a significant parameter and is not measured accurately.

The collector and guard are both water-cooled and operate below 50°C usually and below 100°C even during sustained bombardment with the emitter saturation current. They are heated for outgassing by reducing the water cooling.

F. RESULTS

The work functions obtained from electropolished surfaces of annealed vapor-deposited W-Re samples are tabulated below. A representative set of raw data for one specimen is in Figure 33 and a representative J-V curve in Figure 34.

Work Function Values (A = 120, 4) for W-Re Alloy Samples
Annealed and Electropolished

<u>Number</u>	<u>% Re</u>	<u>Preparation</u>	<u>ϕ (eV)</u>
WOR3B	0	30 m 2000°C + Electropolished	4.70 ± 0.05
W5R3B	2.5		4.70 ± 0.05
W10R3B	9.0		4.63 ± 0.03
W16R3C	16.0	30 m 2000°C + 3 hrs 2330°C + Electropolished	4.67 ± 0.02
W26R3C	26.0		4.81 ± 0.03

The data for WOR3B showed a systematic and reproducible tendency to lower ϕ at higher temperatures in the range of 1855 to 2497°K with $\frac{d\phi}{dT} \sim 3 \times 10^{-4} \text{ deg C}^{-1}$. Upon removal from the apparatus,

the specimen was found to have a blister about 0.2" x 0.1" in extent and 0.01" high on its surface. Swelling of fluoride tungsten deposits during heat treatment has been widely reported elsewhere¹⁰, and is associated with high residual fluorine contents. It may be that residual fluorine in this material diffuses to the surface at high specimen temperatures and changes the work function. This hypothesis cannot be tested with the present apparatus. Other specimens examined did not show swelling or significant $\frac{d\phi}{dT}$.

Reported values for ϕ_{100} of tungsten are in the range 4.52 to 4.66 eV while those for (100) oriented vapor deposits are predominantly in the range 4.50 to 4.53 eV³. The sample WOR3B, however, does not have the columnar structure typical of fluoride vapor deposits, but is seen to have an equiax grain structure suggesting a random orientation. This may account for the ϕ value obtained, but adsorbed fluorine may also be involved.

Owing to the considerable variation in partial pole figures of the different samples (Figure 31), it is not possible to draw firm conclusions about the effect of rhenium alloying additions on the work function of tungsten. It has been found previously that there is not a clear correlation between pole figure shape and work function for various samples of pure tungsten having (100) preferred orientations.² The conclusion that can be drawn is that rhenium does not lower the work function of tungsten below that normally obtained for fluoride vapor-deposited samples. It would therefore be possible to improve the ductility of such material without loss of work function and with possible gains in work function.

	$T_{e\text{ obs}}$	$T_{e\text{ corr}}$	J Scale	Shunt	J_{sat}	ϕ
	$^{\circ}\text{C}$	$^{\circ}\text{K}$	mV/in	Ω	mA/cm ²	eV
A	1650 1653	1950	0.5	10	.135	4.85
B	1696 1701	1997	1.0	10	.37	4.80
C	1740 1738	2042	2.0	10	.66	4.81
D	1807 1807	2113	0.5	1	1.75	4.82
E	1840 1837	2138	1.0	1	3.1	4.77
F	1888 1883	2200	2.0	1	6.0	4.79
G	1940 1940	2230	2.0	1	9.0	4.79
H	2005 2000	2298	5.0	1	20.0	4.78
I	2040 2040	2338	10.0	1	34.0	4.77
					Mean	4.79 eV

Figure 33. Table of Measured and Derived Data
for Work Function Measurement on
One Specimen

(2.5% Re. Anneal 30 m 2000°C and electropolish 3 March 1969 W5R3B)

II-24

I-366

Figure 34. Representative J-V Curve for One Entry in Figure 33.

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