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X-RAY DIFFRACTION ANALYSIS OF ELECTRODEPOSITED BETA-TANTALUM

JOHN F. THOMPSON
MARK D. MILLER

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DEVELOPMENT AND ENGINEERING CENTER
CLOSE COMBAT ARMAMENTS CENTER
BENÉT LABORATORIES
WATERVLIET, N.Y. 12189-4050**



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An adherent coating of beta-tantalum (β -tantalum) has been electrodeposited on copper from a FLINAK molten salt electrolyte. Electrolyte temperatures ranged from 700 to 800°C using pulse current electrolysis at current densities higher than 100 mA/cm². The β -tantalum was deposited to a thickness of over 3 mils. The x-ray diffraction pattern of the electrodeposited β -tantalum was indexed using a Hull-Davey chart. The coatings were found to have a highly preferred orientation, and the tetragonal structure was found to have the lattice parameters of a = 6.419 Å and c = 3.051 Å.

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TABLE OF CONTENTS

INTRODUCTION	1
EXPERIMENTAL PROCEDURE	1
RESULTS AND DISCUSSION	2
CONCLUSION	4
REFERENCES	5

Tables

1. Powder Diffraction File Data of BCC-Tantalum	7
2. Powder Diffraction File Data of β -Tantalum	8
3. Part of the X-Ray Pattern of β -Tantalum Electrodeposited From Molten Salts	9

List of Illustrations

1. Schematic diagram of a high temperature plating cell used for the electrodeposition of β -tantalum from molten salts	10
2. X-ray crystallographic unit with counter diffractometer and electronic control panel with recorder	11
3. Cross-sectional analysis of BCC-tantalum and β -tantalum	12
4. X-ray diffraction pattern of electrodeposited BCC-tantalum	13
5. A coating cross section showing pure electrodeposited β -tantalum	14
6. X-ray diffraction pattern of electrodeposited β -tantalum	15
7. Sample Hull-Davey chart and log scale strip of d-values	16
8. The topography of electrodeposited β -tantalum	17
9. The topography of electrodeposited BCC-tantalum	17

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INTRODUCTION

Tantalum is known to have two crystalline phases: body-centered-cubic (BCC-tantalum) and tetragonal or beta (β -tantalum) (refs 1-3). BCC-tantalum can easily be electrodeposited from a molten salt electrolyte (refs 4-7), but only two reports have been published in which β -tantalum has been electrodeposited in thick adherent coatings from a molten salt bath (refs 8,9). The principal deposition methods for β -tantalum are sputtering and vapor deposition (refs 1,2,10-16).

β -tantalum is mainly used in the fabrication of tantalum capacitors and resistors (ref 10). Many theories exist as to how β -tantalum is formed (refs 1,2,10,13). The most widely accepted theory was introduced by Westwood and Livermore (ref 1) who found that β -tantalum is an impurity-stabilized phase in which the deposition relies on the impurities in the deposition/sputtering system. Many x-ray studies have shown that the tetragonal structure of tantalum usually deposits with a highly preferred orientation (ref 3). A powder study was conducted by Moseley and Seabrook (ref 8), and β -tantalum was indexed and the tetragonal lattice parameters (a and c) were found to be $a = 10.194 \text{ \AA}$ and $c = 5.313 \text{ \AA}$. Earlier, Read and Altman (ref 17) indexed the β -tantalum powder pattern and found that $a = 5.34 \text{ \AA}$ and $c = 9.94 \text{ \AA}$. Additionally, Das (ref 18) found β -tantalum to have $a = 10.29 \text{ \AA}$ and $c = 9.2 \text{ \AA}$. Finally, Burbank (ref 3) studied a highly preferred sample of β -tantalum and found $a = 2.831 \text{ \AA}$ and $c = 5.337 \text{ \AA}$. One of the authors has published a technical report which stated the c and a values for β -tantalum deposited from molten salts (ref 9), but the study presented herein gives a more accurate measure of the lattice parameters and the hkl index of β -tantalum deposited from molten salts. The variety of results obtained for a and c show the difficulty involved with properly indexing β -tantalum.

In this project, β -tantalum was electrodeposited on copper from a FLINAK (LiF-NaF-KF) molten salt electrolyte. The coatings were deposited using pulse current electrolysis at current densities higher than 100 mA/cm^2 and an electrolyte temperature ranging from 700 to 800°C . The x-ray diffraction patterns were indexed using a Hull-Davey chart, and the lattice parameters were $a = 6.419 \text{ \AA}$ and $c = 3.051 \text{ \AA}$.

EXPERIMENTAL PROCEDURE

A high temperature electrodeposition cell (Figure 1) was used to electrodeposit the β -tantalum coatings. A ternary electrolyte mixture of LiF, NaF, and KF (FLINAK) was prepared from reagent grade (99.9 percent) fluoride salts. Additionally, 10 percent TaF₅ and less than 0.5 percent NbF₅ were added to the ternary mixture. The electrolyte was melted in the nickel crucible under vacuum at 463°C . The electrodeposition was carried out at temperatures ranging from 700 to 800°C and pulse current densities higher than 100 mA/cm^2 . Metallurgical grade copper and tantalum were used as electrodes during electrodeposition.

X-ray diffraction scans were made using a Phillips-Norelco diffractometer as shown in Figure 2. The radiation source was molybdenum K-alpha ($\text{Mo K}\alpha$) with a wavelength of 0.7107 \AA . A silicon detector was wired to an Ortec ratemeter and amplifier that measured the counts per second intensity. An Omega strip-chart recorder was used to plot the intensity versus two-theta (2θ) patterns. The scans were run over a 2θ range of 14 to 60 degrees, and the maximum intensity was set at either 1000 or 5000 counts per second. The high magnification topography photographs were produced using a JOEL scanning electron microscope operating at 20 kV that produced magnifications ranging from 100 to $10,000\times$. The microhardness was performed on a Leitz metallograph. Photographs of the grain structure and cross section were taken by an optical lens at magnifications ranging from 300 to $500\times$.

RESULTS AND DISCUSSION

As stated earlier, the electrodeposition of BCC-tantalum from a molten FLINAK salt bath has been widely established (refs 4-7), but the deposition tetragonal tantalum from the same bath has resulted in a wide variety of deposits, many unreproducible. The hardness and the amount of β -tantalum deposited with BCC-tantalum over the cross section were also observed to be unaffected by current density, pulse cycle, and electrodeposition temperature. Figure 3 shows specimens that contain both BCC- and β -tantalum. β -tantalum was almost ten times harder than BCC-tantalum, and therefore can be easily distinguished by the smaller microhardness indentations and lighter coating color shown in Figure 3.

The powder diffraction data for BCC-tantalum, given in Table 1, has been well established. The x-ray diffraction pattern of BCC-tantalum deposited from molten salts (Figure 4) can be seen to contain the precise plane direction parameters (hkl) at the indexed 2θ values. The relative intensities of the electrodeposited BCC-tantalum hkl values were different from the intensities of the powder pattern, because electrodeposited BCC-tantalum coatings are deposited with highly preferred orientations (refs 5,19). The x-ray pattern, shown in Figure 4, has a preferred orientation around the {111} family of planes. Likewise, β -tantalum was deposited with a similar preferred orientation (ref 9).

A coating of pure β -tantalum was found (Figure 5) and verified by cross-sectional photographs and microhardness tests. The x-ray diffraction pattern of molten salt electrodeposited β -tantalum is shown in Figure 6. The 2θ values for the peaks were measured and are shown in Table 3. The maximum intensity was set for 1000 counts per second. The relative normalized intensities were found by comparing them to the strongest reflection and are also shown in Table 3. The observed d-spacing for each 2θ value was calculated using Bragg's Law (Eq. (1)), (see sample calculation below).

$$\begin{aligned}\lambda &= 2d \sin(\theta) \\ \text{for } 14.9^\circ \quad d &= \frac{\lambda}{2 \sin(\theta)} \\ d &= \frac{0.7107 \text{ \AA}}{2 \sin(7.45^\circ)} \\ d &= 2.741 \text{ \AA} \quad (\text{observed})\end{aligned}\tag{1}$$

The powder diffraction data for sputtered β -tantalum, given in Table 2, is also well established. The experimentally-observed d values in Table 3 can be seen to match, within error, at least six powder diffraction d values in Table 2. This should confirm that the material being studied is β -tantalum.

A Hull-Davey chart was used to index the intensity peaks of the electrodeposited β -tantalum. A Hull-Davey chart is used to index crystalline materials and calculate their lattice parameters (refs 20,21). When using a Hull-Davey chart, the observed d values are plotted using the log scale from the chart on a strip of paper. The log scale strip was compared to Hull-Davey chart planar lines, as seen in Figure 7. The experimental data is given in Table 3. The Hull-Davey chart also gives the c/a value of the tetragonal structure; electrodeposited β -tantalum was found to have a c/a value of 0.49.

From the indexed intensity peaks, the hkl values also allowed the calculation of c and a values. In tetragonal lattices, the base lengths are defined as 'a', while the height is defined as 'c' (ref 20). An equation for the d-spacing of a tetragonal lattice with respect to c and a is seen in Eq. (2) (refs 20,21).

$$\frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2} \quad (2)$$

By choosing the hkl indexes from the d-value log scale strip such as 220, 400, and 410, and using the observed d-spacing, the a value was calculated (see sample calculation below).

$$\text{for (220)} \quad \frac{1}{(2.23)^2} = \frac{2^2+2^2}{a^2} + \frac{0^2}{c^2}$$

$$a^2 = 39.78 \text{ \AA}^2$$

$$a = 6.31 \text{ \AA}$$

The a values were then averaged and the standard deviation was evaluated with $a = 6.419 \pm 0.303 \text{ \AA}$.

Similarly, the c value was calculated using Eq. (2), the average a value, the hkl index, and the observed d-spacing (see sample calculation below).

$$\frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2}$$

$$\text{for (221)} \quad \frac{1}{(1.87)^2} = \frac{2^2+2^2}{(6.419)^2} + \frac{1}{c^2}$$

$$\frac{1}{c^2} = 0.0918 \frac{1}{\text{\AA}^2}$$

$$c^2 = 10.8921 \text{ \AA}^2$$

$$c = 3.30 \text{ \AA}$$

The c values were averaged and the standard deviation was evaluated with $c = 3.051 \pm 0.149 \text{ \AA}$. Finally, using the average c and a values and the indexed hkl values, the d-spacing was recalculated and given in Table 3 as "Calc. d". The highest error found between the observed and calculated d-spacings was evaluated at less than five percent.

The indexed hkl values found in this project differed quite substantially from the powder diffraction pattern data of β -tantalum. Equally, none of the other published x-ray studies agreed with the powder file data (refs 3,8,17,18). Each published x-ray study of β -tantalum found different c and a values as well as different hkl indexes. The data in this project most closely duplicated the data published by Moseley and Seabrook (ref 8). Although the c and a values differed by over twenty percent, many of the indexed hkl intensity peaks matched. One reason for this may be that Moseley and Seabrook used β -tantalum deposited from molten salt in their x-ray study, while all others used β -tantalum produced by vapor deposition methods. Another reason for the difference in the data can be found in Figures 8 and 9, which show scanning electron microscope topography photographs of β -tantalum and BCC-tantalum deposited from molten salts, respectively. The topography, shown in Figures 8 and 9, illustrates the

differing refinement of the crystallites. The refinement of the crystallites and the crystal facets of the β -tantalum illustrates that the growth pattern of the β -tantalum was "aged" during the growth of the coating. This is probably due to the production of dendrites (abnormal preferential crystal growth) during electrodeposition (ref 5). This difference in crystallite refinement could have affected the x-ray diffraction pattern causing the experimental error seen between this project and the work by Moseley and Seabrook (ref 21).

CONCLUSION

In summary, β -tantalum was electrodeposited from a molten salt electrolyte. The x-ray diffraction pattern was indexed with hkl planar values using a Hull-Davey chart. The tetragonal crystal structure was found to have $c = 3.051 \text{ \AA}$ and $a = 6.419 \text{ \AA}$. The index of the x-ray diffraction pattern agreed somewhat with the work by Moseley and Seabrook. The primary experimental error was found due to the change in crystallite refinement caused by dendritic growth.

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Table 1. Powder Diffraction File Data of BCC-Tantalum

BCC-tantalum
Powder Index Number [4-788]

hkl	I/I _{max}	d space (Å)	2-θ
110	100	2.3380	17.49
200	21	1.6530	24.83
211	38	1.3500	30.52
220	13	1.1687	35.40
310	19	1.0453	39.75
222	7	0.9543	43.73
321	29	0.8835	47.43
400	4	0.8265	50.93

Table 2. Powder Diffraction File Data of β -Tantalum

β -Tantalum
Powder Index Number [25-1280]

hkl	I/I _{max}	d space (Å)	2- θ
002	40	2.658	15.37
410	80	2.474	16.52
330	55	2.403	17.01
202	55	2.354	17.37
212	80	2.294	17.82
411	100	2.241	18.25
331	65	2.190	18.68
312	18	2.054	19.93
631	30	1.462	28.14
413	45	1.444	28.49
720	30	1.401	29.39
513	25	1.326	31.09
820	20	1.237	33.32

Table 3. Part of the X-Ray Pattern of β -Tantalum Electrodeposited From Molten Salts

2θ ($^\circ$)	Normalized Intensity (%) [*]	Observed $d(\text{Å})$	hkl	Calc. $d(\text{Å})$
14.9	5.7	2.74	101	2.75
16.5	43.2	2.47	111	2.53
18.3	100.0	2.23	220	2.26
20.0	9.1	2.05	211	2.09
21.9	6.8	1.87	221	1.82
25.7	7.9	1.60	400	1.60
26.7	12.5	1.54	410	1.55
28.7	39.8	1.43	330	1.51
30.3	15.9	1.36	411	1.38
33.3	16.5	1.24	430	1.28
34.3	10.6	1.21	501 (431)	1.18
35.2	15.9	1.17	530	1.10
36.0	19.3	1.15	600	1.07
37.6	11.4	1.10	601	1.01
40.9	10.2	1.02	611	0.997
43.2	15.0	0.965	621	0.965
46.0	13.6	0.909	720	0.881

$a = 6.419 \pm 0.303 \text{ Å}$ $c = 3.051 \pm 0.149 \text{ Å}$
^{*}Normalized to strongest reflection

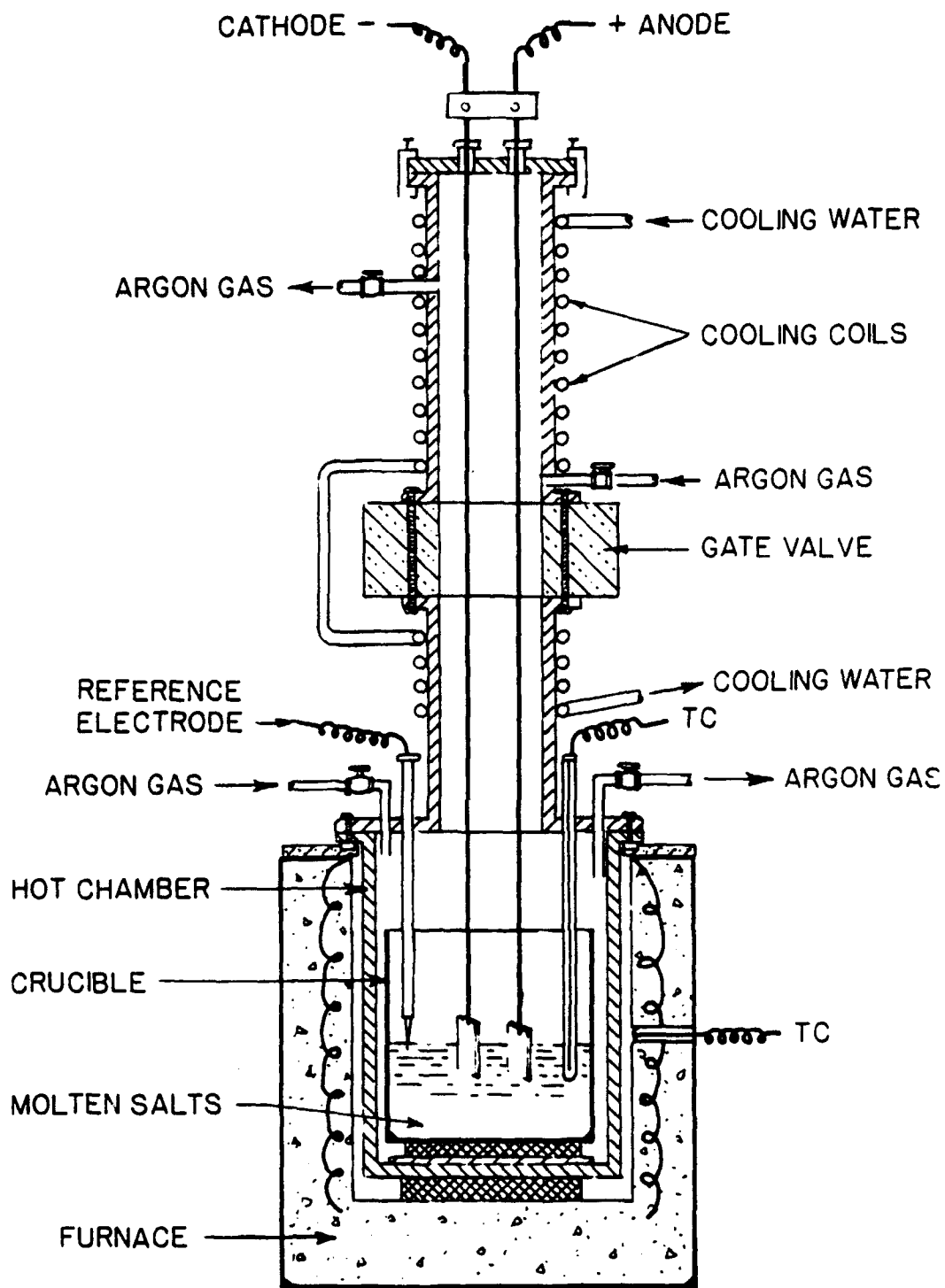


Figure 1. Schematic diagram of a high temperature plating cell used for the electrodeposition of β -tantalum from molten salts.

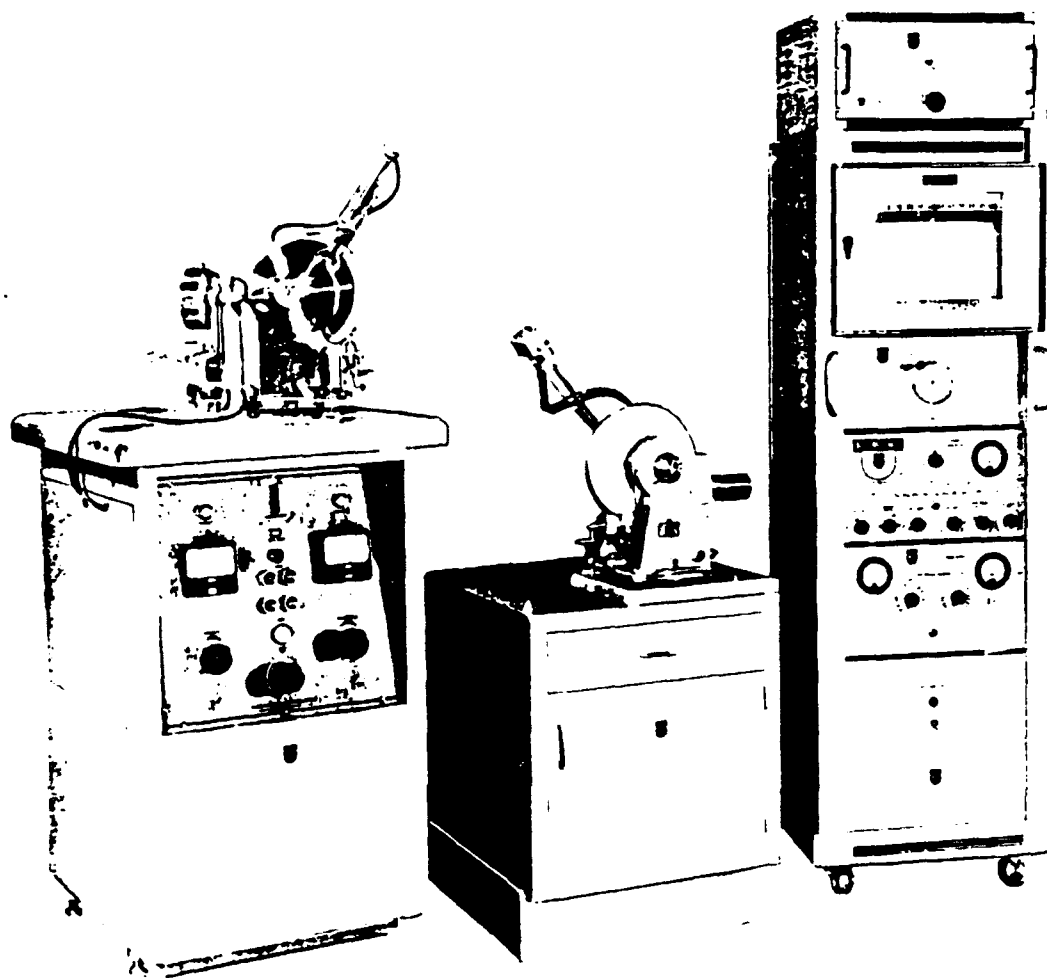
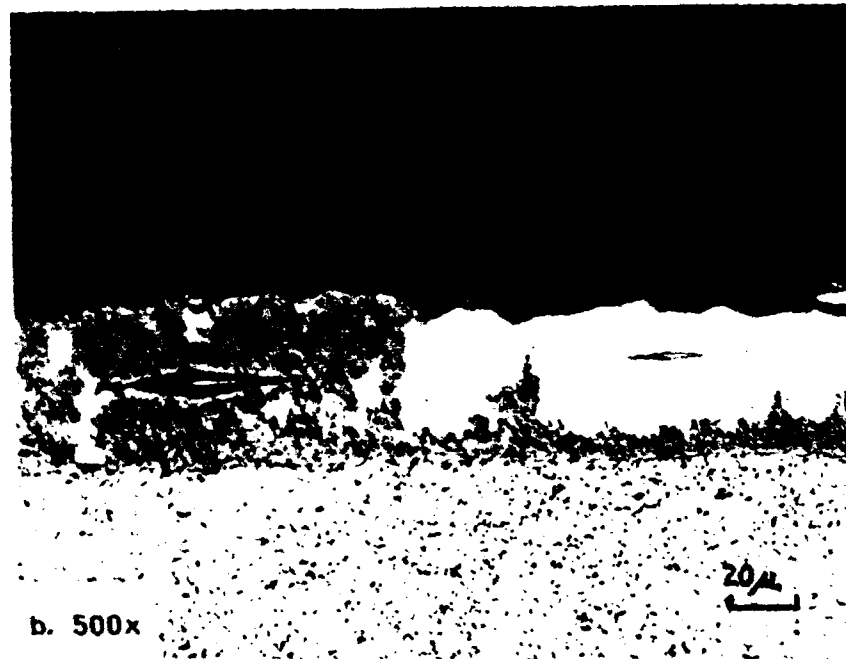


Figure 2. X-ray crystallographic unit with counter diffractometer and electronic control panel with recorder.



a. 300x

50 μ



b. 500x

20 μ

Figure 3. Cross-sectional analysis of BCC-tantalum and β -tantalum.

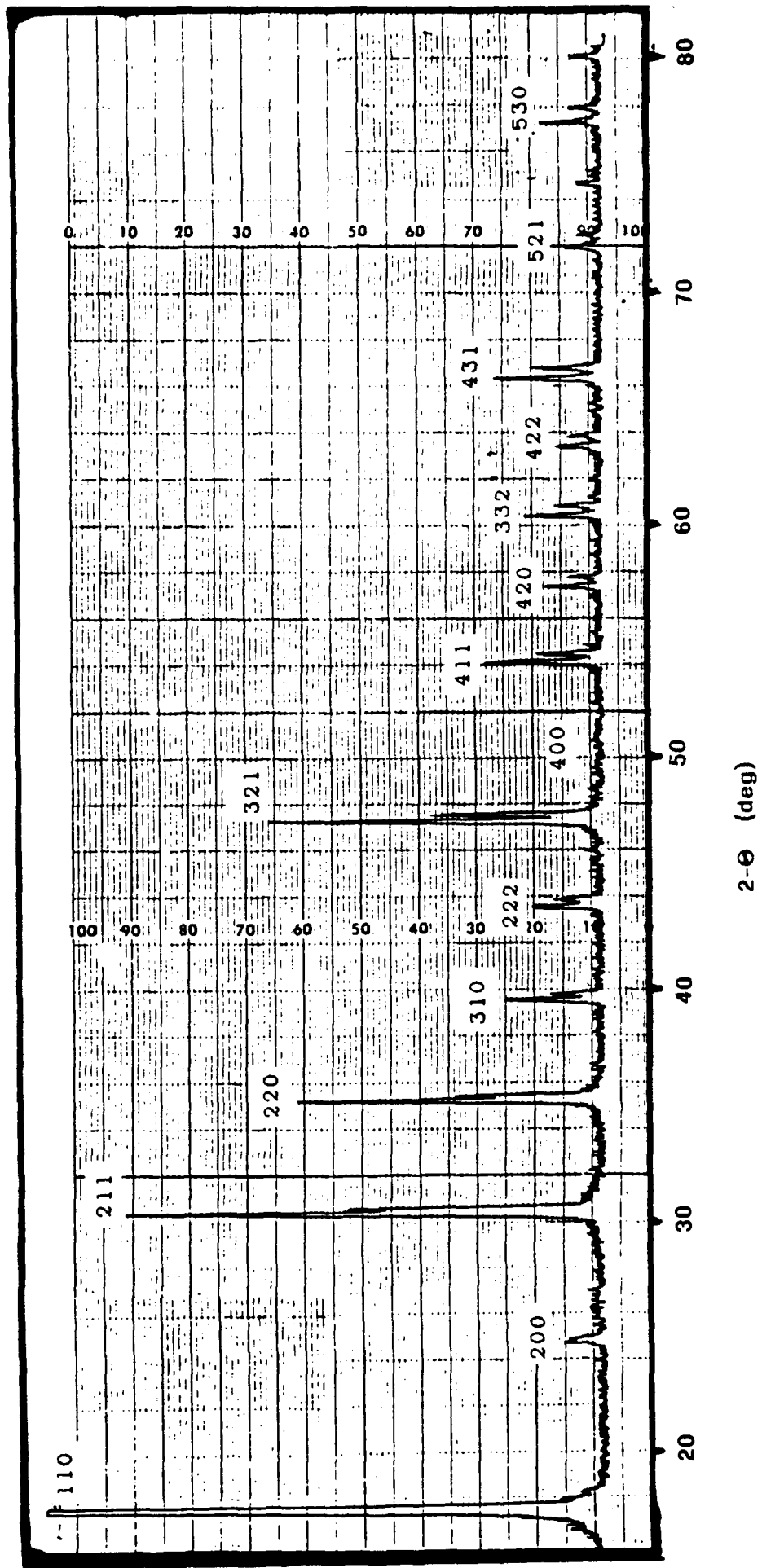


Figure 4. X-ray diffraction pattern of electrodeposited BCC-tantalum.

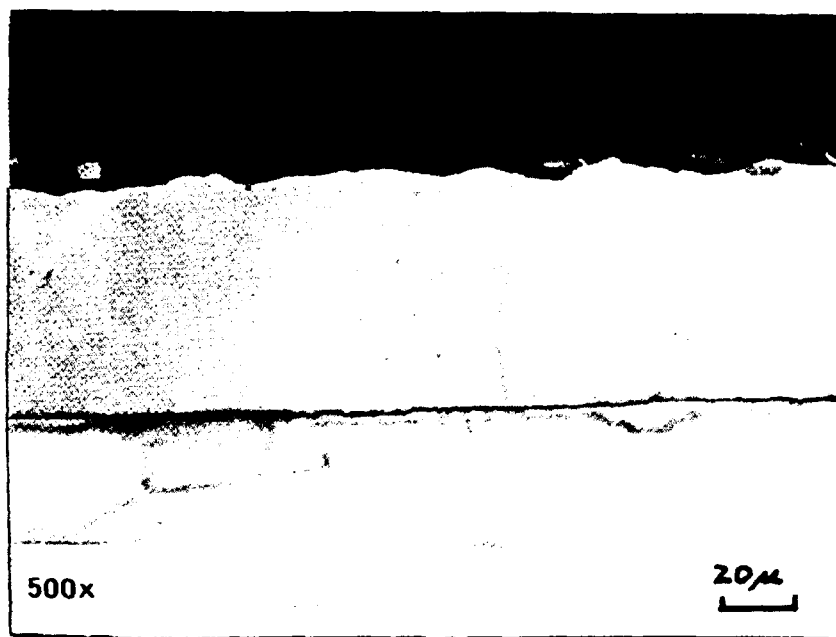


Figure 5. A coating cross section showing pure electrodeposited β -tantalum.

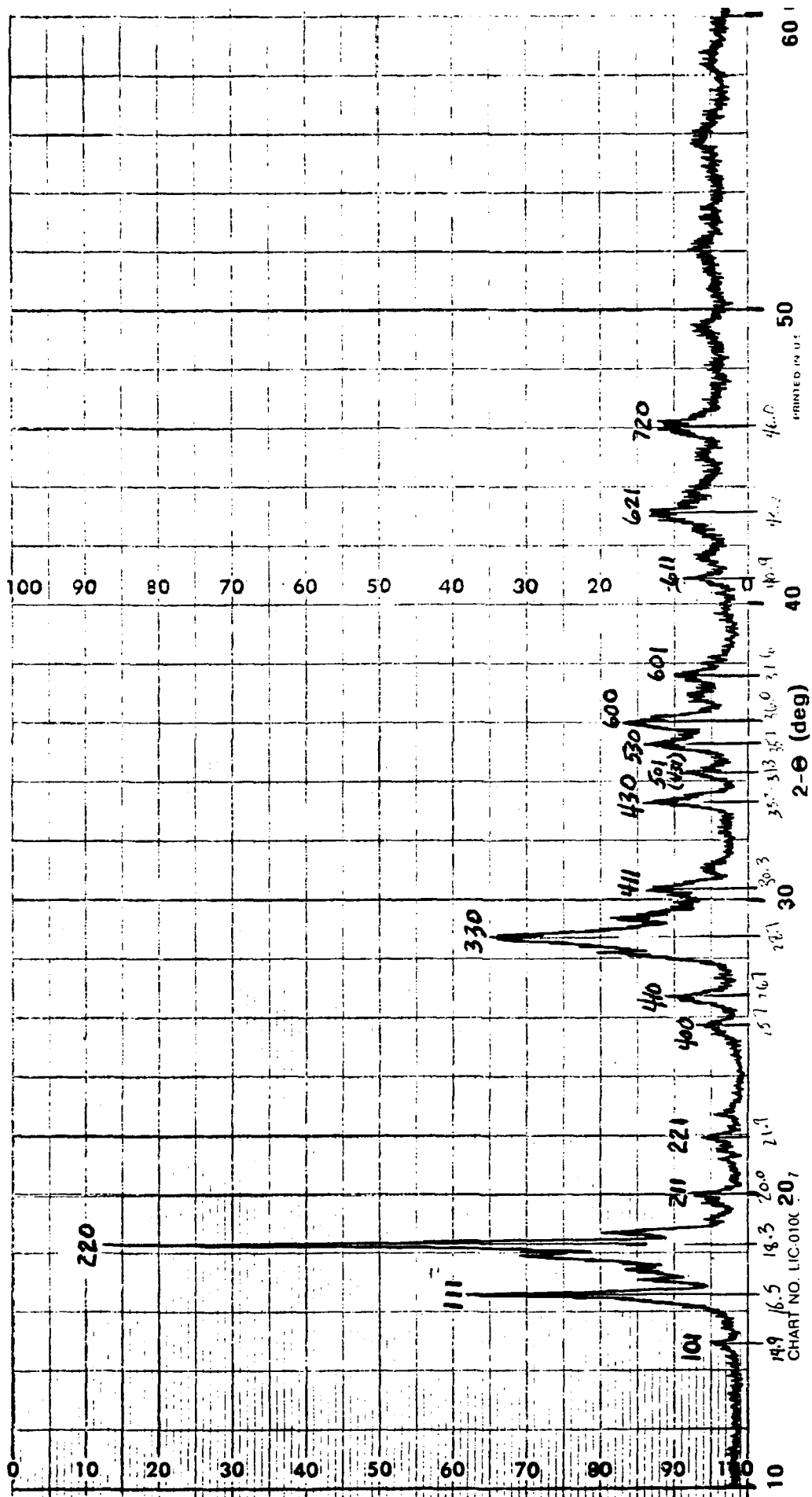


Figure 6. X-ray diffraction pattern of electrodeposited β -tantalum.

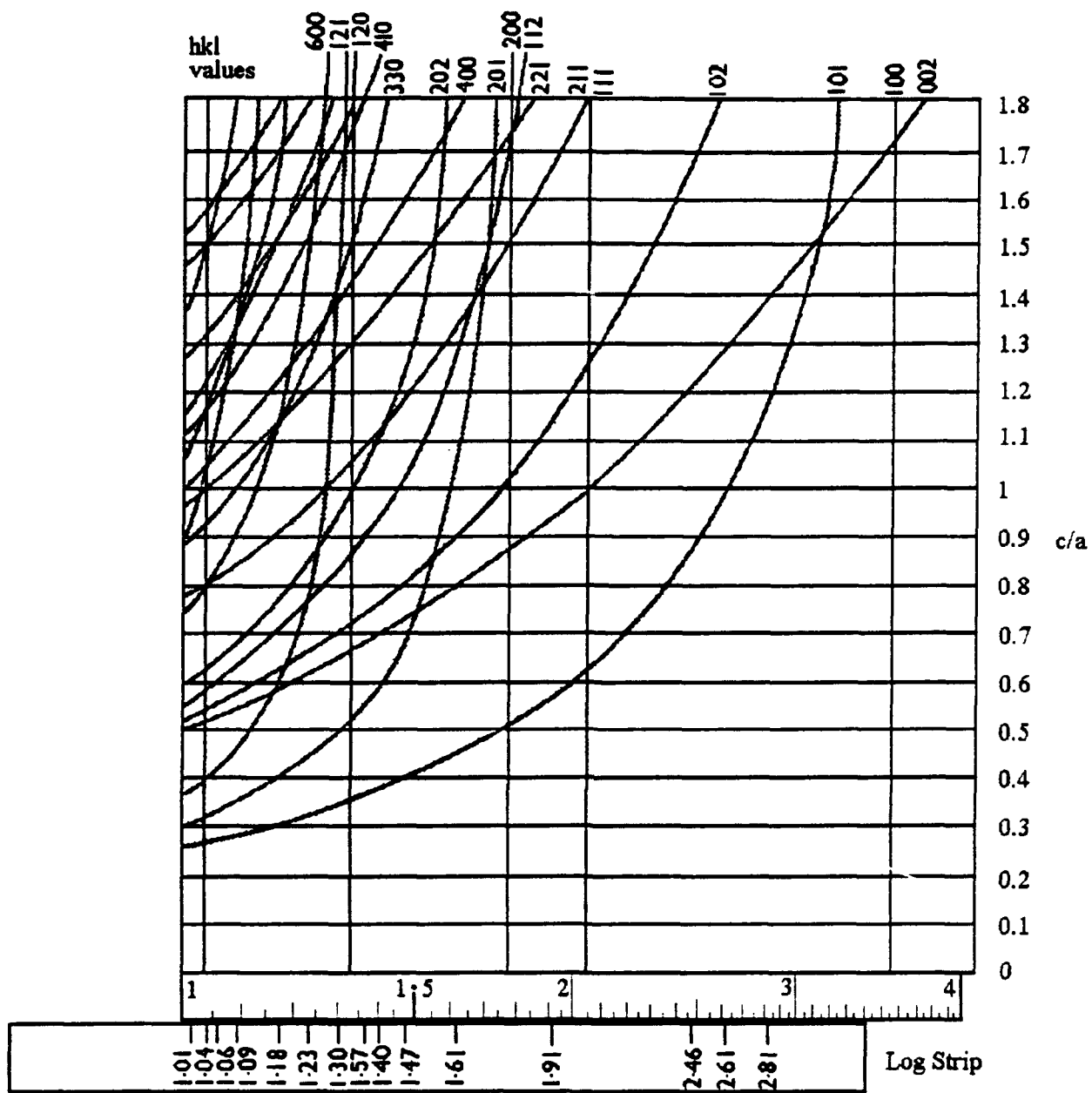


Figure 7. Sample Hull-Davey chart and log scale strip of d-values.



Figure 8. The topography of electrodeposited β -tantalum.



Figure 9. The topography of electrodeposited BCC-tantalum.