

# The Crystallisation of Thin Amorphous Tantalum Oxide Films Heated in Air or Vacuo, and the Structure of the Crystalline Oxide

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The effect of heat on thin films of amorphous tantalum oxide is investigated by electron diffraction. Appreciable mobility of the oxide molecules, leading to crystallization of the film, occurred only above about 700 °C. The film initially crystallized to tantalum oxide with a hexagonal structure having  $a = 6.17 \text{ \AA}$  and  $c/a = 1.90$ . Further heating led to an orthorhombic structure with

$$a = 6.20, b = 69.6, c = 3.90 \text{ \AA}.$$

## 1. Introduction

A thin protective oxide film forms on many metals when they are exposed to air and, if the temperature is not unduly high, the size of crystals in this layer is often very small and sometimes the film is nearly amorphous. Since an increase in crystal size may affect the rate of oxidation it is important to know the lowest temperature at which the oxide molecules have sufficient mobility to cause appreciable crystal growth. The present experiments were carried out with thin films of amorphous tantalum oxide, free from the metal surface, for comparison with results obtained (Harvey, 1959) when Ta metal was oxidized.

Previous work on the crystallization of amorphous tantalum oxide appears to be limited to that of Vermilyea (1953) who anodized thin tantalum sheet to give amorphous oxide films approximately 4500 Å thick and heated these foils in a vacuum of 0.01 μ pressure. The X-ray diffraction examination of specimens heated for 4 hr. at 500 °C. showed that no crystallization of the amorphous oxide had occurred. After 1 hr. at 800 °C., however, sharp diffraction rings due to Ta<sub>2</sub>O<sub>5</sub> were observed and Vermilyea concluded that the crystallization temperature of amorphous tantalum oxide lies between 500 and 800 °C.

## 2. Experimental procedures

Young (1957) found that anodic films formed on chemically polished tantalum were not strongly adherent to the metal surface. Use was made of this fact to prepare thin films of amorphous oxide for the present work. Tantalum sheet obtained from Messrs. Murex Ltd. (Analysis: 0.1% Nb, 0.01% C, traces only of other elements) was chemically polished in a solution (Vermilyea, 1953) of 40% HF, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> in the proportions 2:2:5 by volume respectively. The foil was then anodized to about 25 V. at a constant

current density of 1 mA.cm.<sup>-2</sup> in 2% (by vol.) HNO<sub>3</sub>. Taking the rate of formation as about 16 ÅV<sup>-1</sup>. (Vermilyea, 1953) its thickness is about 400 Å. The electrical contacts to the cell were then reversed and the previously anodized electrode made the cathode. 1 mA.cm.<sup>-2</sup> constant current was passed through this cell for ½ hr., when inspection of the anodic film showed the presence of colourless patches. These evidently occurred where the hydrogen evolved had pushed the oxide film away from the metal, so that the interference colours usually exhibited by the adherent film were not visible. This electrode was then removed from the electrolyte and the pieces of non-adherent film carefully washed into a beaker, by a weak jet of distilled water. The film was left to wash in the distilled water for about 1 hr. before a small piece was removed on Pt gauze.

Thin films were also prepared in dilute H<sub>2</sub>SO<sub>4</sub> and supported on Ni gauze.

These specimens were examined by electron diffraction in a Finch-type camera (Finch & Wilman, 1937) operated at an accelerating voltage in the range 50–60 kV. and a camera length of 48 cm.

## 3. Results

(a) *Electron diffraction examination of tantalum oxide formed anodically in HNO<sub>3</sub> and supported on Pt gauze*

The diffuse halo pattern obtained, Fig. 1(a), from the specimen is characteristic of an amorphous material. By reference to a standard graphite pattern ( $d_{110} = 1.23 \text{ \AA}$ ) obtained at the same voltage as Fig. 1(a) the values of  $\sin \theta/\lambda$  ( $\theta =$  Bragg angle) corresponding to the haloes, were found to be 0.143, 0.195, 0.285, 0.435, 0.575 Å<sup>-1</sup>. The pattern Fig. 1(b), obtained after the specimen had been heated in air for ½ hr. at 650 °C., shows a slight sharpening of the halo pattern, indicating only a very small increase in crystal size. After heating a further ½ hr. at 715 °C. most areas of the film were crystalline and gave a sharp ring pattern,

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Fig. 1(c), but small regions remained amorphous. The film was not completely crystallized until it had been heated a further  $\frac{1}{2}$  hr. at 715 °C. and  $2\frac{1}{4}$  hr. at 710 °C. It was therefore concluded that the molecules composing the film exhibited appreciable mobility only above about 700 °C., leading to fairly rapid growth in crystal size.

(b) *Electron diffraction examination of tantalum oxide prepared anodically in H<sub>2</sub>SO<sub>4</sub> and supported on Ni gauze*

When net-plane spacings (see Table 1) corresponding to the sharp ring pattern, e.g. Figs. 1(c) & 4 from crystallized films, were compared with previous X-ray

Table 1. *Comparison of net-plane spacings from a crystallized tantalum oxide film (see Fig. 4) with the net-plane spacings of an orthorhombic cell having:*

$a = 6.2, b = 69.6, c = 3.90 \text{ \AA}$

<i>I</i> *	<i>R</i> (cm.)	<i>d</i> † (Å)	<i>hkl</i>	<i>d<sub>c</sub></i> (Å)
<i>w</i>	0.4165	5.72	150	5.66
<i>mw</i>	0.4508	5.20	170	5.19
<i>w</i>	0.4960	4.81	190	4.84
<i>m</i>	0.6135	3.89	001	3.89
<i>mw</i>	0.6930	3.44	1,17,0	3.42
<i>vs</i>	0.7645	3.12	{ 1,19,0 200	{ 3.15 3.10
<i>w</i>	0.8220	2.90	1,21,0	2.92
<i>w</i>	0.8700	2.74	2,12,0	2.73
<i>v</i>	0.9175	2.60	2,14,0	2.63
<i>s</i>	0.9810	2.43	{ 1,19,1 201	{ 2.45 2.42
<i>vw</i>	1.0625	2.24	1,23,1	2.23
<i>m</i>	1.1265	2.12	{ 2,24,0 1,31,0	{ 2.12 2.11
<i>m</i>	1.175	2.03	{ 350 2,26,0	{ 2.06 2.03
<i>vw</i>	1.1204	1.98	{ 370 1,33,0	{ 2.02 2.00
<i>ms</i>	1.282	1.86	{ 3,15,0 0,12,2 3,17,0 156	{ 1.89 1.85 1.84 1.84
<i>ms</i>	1.325	1.80	{ 176 0,14,2 3,19,0 3,21,0	{ 1.829 1.815 1.800 1.754
<i>vs</i>	1.4505	1.64	{ 1,19,2 202 222	{ 1.659 1.651 1.649
<i>mw</i>	1.5125	1.575	{ 3,19,1 2,38,0	{ 1.634 1.578
<i>mw</i>	1.5715	1.515	{ 1,43,0 3,31,0	{ 1.566 1.526
<i>m</i>	1.6325	1.460	{ 2,40,0 1,45,0 4,14,0	{ 1.517 1.501 1.480
<i>vw</i>	1.659	1.435	{ 3,33,0 401	{ 1.476 1.440
<i>m</i>	1.7015	1.400	{ — 2,26,2	{ — 1.405
<i>s</i>	1.800	1.323	{ 1,33,2 0,38,2 3,19,2	{ 1.395 1.335 1.323

\* *s* = strong, *m* = medium, *w* = weak, *v* = very.

† Relative to graphite  $d_{110} = 1.230 \text{ \AA}$ .

data for Ta<sub>2</sub>O<sub>5</sub> (Hahn, 1951; Vermilyea, 1953; Zaslavskii *et al.*, 1955) it was found that, although the strongest rings agreed well, many of the weaker rings did not fit with any of the X-ray patterns. The possibility of the presence of impurities was therefore considered. Holtzberg *et al.* (1957) found that the temperature at which the amorphous-crystalline transition occurred for Nb<sub>2</sub>O<sub>5</sub> was very sensitive to the presence of impurities (0.5% NH<sub>4</sub>Cl lowered the transition temperature by 200 °C.) and it was thought that the transition from amorphous to crystalline Ta<sub>2</sub>O<sub>5</sub> would similarly be impurity-sensitive.

An anodic film was therefore formed to 30 V. at 2 mA.cm.<sup>-2</sup> in 1% (by vol.) H<sub>2</sub>SO<sub>4</sub>. The film was stripped from the metal and supported on Ni gauze. This specimen was heated in air for periods of  $\frac{1}{2}$  hr. and the transition to crystalline oxide was again found to occur in the range  $715 \pm 10$  °C. for a heating time of  $\frac{1}{2}$  hr., and the diffraction pattern from the crystalline film was similar in all respects to the pattern, Fig. 1(c), from the film prepared in dil. HNO<sub>3</sub> and heated on Pt gauze. Similar patterns were obtained when the films, supported on either Ni or Pt gauze were heated in a vacuum of  $10^{-5}$  mm. Hg. It was therefore concluded that any impurity present was not due to the electrolyte in which the films were formed, nor to the nature of the supporting wire gauze.

Stripped anodic films were therefore examined in a Siemens 'Elmiskop I' electron microscope to attempt to obtain single-crystal diffraction patterns from small areas of the film, and hence to index the additional weak rings in Fig. 1(c). A film was heated for a prolonged period below 700 °C. to try and obtain the largest possible crystals; as follows:

16 hr. at 550 °C.  
plus 15 hr. at 620 °C.  
plus 16 hr. at 660 °C.

Examination in the electron microscope showed that the film was amorphous until it had been heated finally for 16 hr. at 660 °C., when small areas were found to be crystalline. Fig. 2 is a photomicrograph of a region showing both amorphous and crystalline areas. Parts of the crystalline area gave a diffraction pattern, Fig. 3, consisting of short arcs, corresponding to the (001) plane of the reciprocal lattice of a hexagonal (or very nearly hexagonal) lattice. Diffractions of the type *hkl* and *hk2* are also visible, indicating that the crystal is flexed slightly about an axis approximately in the film. From diffractions of the type *hk0*, *a* for the hexagonal cell was found to be 6.17 Å and a mean value of *c/a* of 1.90 was calculated from the relative radii of the 220, 221, 222 and 300, 301, 302 and 303 diffractions.

The diffraction pattern obtained in the Finch camera from a film heated 30 hr. at 700 °C. is shown in Fig. 4, and is similar to Fig. 1(c) from a film heated for a shorter time at a slightly higher temperature. In the electron microscope some small areas of the film gave

patterns, Figs. 5(a) and 6(a), of a single-crystal type. Fig. 6(a) is virtually symmetrical in the intensity distribution of the spots and at first sight could correspond to a hexagonal or pseudo-hexagonal crystal with a very short reciprocal axial length, oriented with its  $c$  axis parallel to the beam. Fig. 5(a) appears to be similar in nature to Fig. 6(a), except that the distribution of the spots is markedly unsymmetrical with relation to the undeflected beam. In this case, however, the pattern would still be expected to show, at least partially, all three rows of closely spaced spots at  $60^\circ$  to each other. Since only two sets are to be seen it seems that Fig. 5(a) must be due to two crystals (one predominating) each giving a spot pattern similar to that shown diagrammatically in Fig. 5(b). Fig. 6(a) would then be interpreted as a pattern due to three single crystals, each giving a pattern similar to Fig. 5(b) but displaced in orientation to each other by  $60^\circ$  rotation round an axis parallel to the electron beam. The pattern which would result from this arrangement is shown diagrammatically in Fig. 6(b) which agrees fairly well with the experimental pattern Fig. 6(a). One of the groups of spots is shown enlarged, for example, in Fig. 6(c). Rectangular axes may be chosen (see Fig. 5(b)) to account for the pattern, and measurement gave  $a=6.20 \text{ \AA}$  and  $b=69.6 \text{ \AA}$ . The periodic intensification along the rows of spots in Fig. 5(a) occurs close to the points at which diffractions would occur from a hexagonal cell of the dimensions mentioned previously ( $a=6.17 \text{ \AA}$ ,  $c/a=1.90$ ) and it was therefore concluded that the lattice of the new structure was a superlattice of this hexagonal cell.

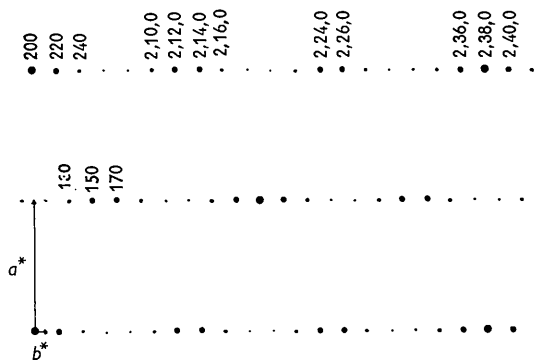


Fig. 5(b). Suggested reciprocal lattice point arrangement corresponding to spots in Fig. 5(a).

It is not possible to obtain any useful data concerning the  $c$  axis from Figs. 5(a) and 6(a), but it seems reasonable to assume that  $c$ , like  $b$ , is approximately simply related to the  $c$  axis ( $11.7 \text{ \AA}$ ) of the hexagonal cell. However, when net-plane spacings were calculated for an orthorhombic cell with

$$a=6.20, b=69.6, c=11.7 \text{ \AA}$$

and compared with the experimental ring pattern,

it was found that only  $hkl$  diffractions with  $l=3n$  were present. Since we have no evidence concerning the presence or absence of screw-axes a value for  $c=11.7/3=3.90 \text{ \AA}$  was used in the calculated net-plane spacings shown in Table 1. The agreement between observed and calculated spacings is satisfactory.

#### 4. Summary and discussion

These experiments show that appreciable mobility of tantalum oxide molecules does not occur below about  $700^\circ\text{C}$ . in an amorphous film free from the metal surface. After heating the film for about  $\frac{1}{2}$  hr. at  $710^\circ\text{C}$ . it is converted almost entirely to crystalline oxide, whereas after 16 hr. at  $660^\circ\text{C}$ . only small areas of the film became crystalline. It is evident from the diffraction patterns obtained that once crystallization commences the growth of the crystals is very rapid, since no intermediate stage showing a gradual sharpening of the haloes was observed. This is also indicated in the photomicrograph Fig. 2, showing an amorphous area of the film adjacent to an area showing fairly large ( $\sim 0.1 \mu$ ) crystals. This is in contrast to some other amorphous oxides where a gradual increase in crystal size occurs throughout the film during heat treatment at about the crystallizing temperature (e.g.  $\text{BeO}$  and  $\text{Al}_2\text{O}_3$ , Kerr, 1956).

The weaker rings in the electron-diffraction pattern from the crystallized film did not correspond well with previous X-ray data for  $\text{Ta}_2\text{O}_5$ . Experiments indicated, however, that few if any impurities were introduced during the treatment of the film and specimens were therefore examined in the electron microscope to attempt to obtain diffraction patterns from small monocrystalline areas. It was found that when initially crystallized, the oxide had a hexagonal (or pseudo-hexagonal) structure with  $a=6.17 \text{ \AA}$  and  $c/a=1.90$ . When a film was heated for a longer period at a higher temperature, however, the structure became more complicated and was found to correspond to an orthorhombic (or pseudo-orthorhombic) cell with

$$a=6.20, b=69.6, c=3.90 \text{ \AA}.$$

It seems likely that one or both of these structures, and probably previous X-ray patterns, correspond to a non-stoichiometric composition near  $\text{Ta}_2\text{O}_5$  with a slight excess or deficiency of oxygen.

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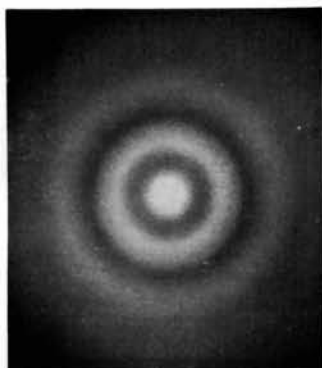


Fig. 1(a).



Fig. 1(b).

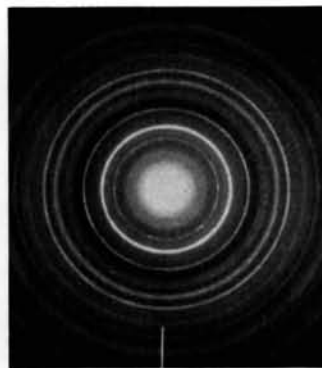


Fig. 1(c).



Fig. 2.

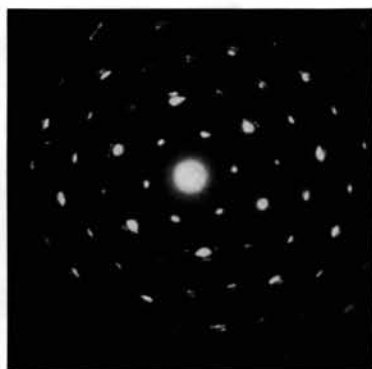


Fig. 3.

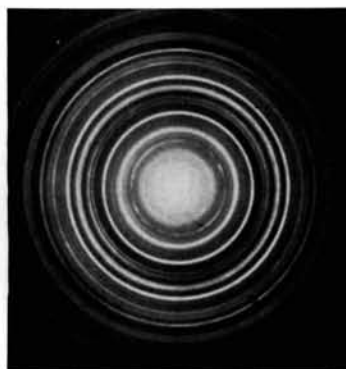


Fig. 4.

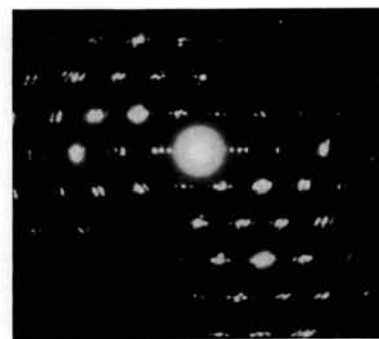


Fig. 5(a).

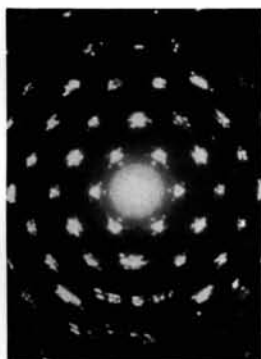


Fig. 6(a).

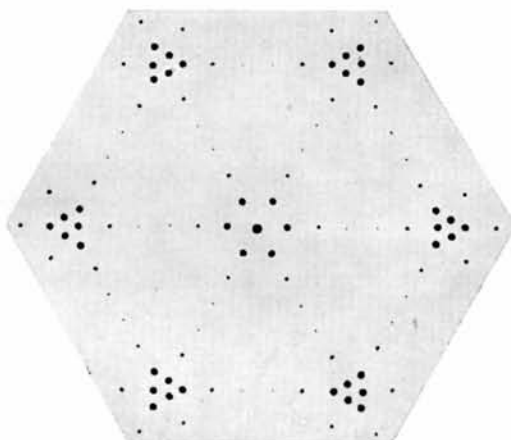


Fig. 6(b).

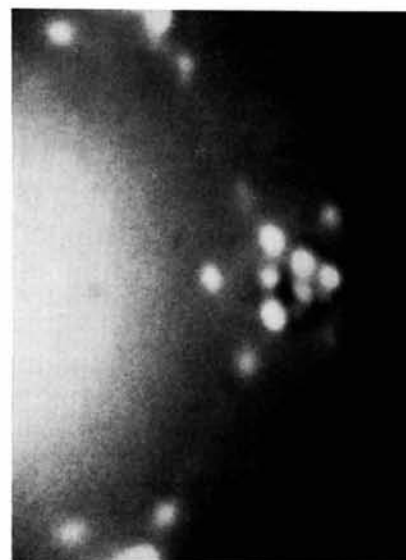


Fig. 6(c).

Fig. 1. Electron diffraction patterns from stripped anodic tantalum oxide film; (a) as prepared, (b) and (c) after heating in air for  $\frac{1}{2}$  hr. at 650 °C., and for a further  $\frac{1}{2}$  hr. at 715 °C., respectively.

Fig. 2. Ta oxide film heated in air 16 hr. at 660 °C.; partly crystallized; electron micrograph, 40,000 $\times$ .

Fig. 3. As Fig. 2 but electron diffraction in el. microscope, from a small crystalline area.

Fig. 4. Electron diffraction pattern (in Finch camera) from a Ta oxide film heated in air 30 hr. at 700 °C.

Fig. 5(a). Pattern (in el. microscope) from small area of spec. of Fig. 4.

Fig. 6. (a) As Fig. 5(a), but another small area of specimen; (b) diagram representing diffraction spot positions in central part of Fig. 6(a); (c) enlargement of spot group to right of centre in Fig. 6(a).

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## The Crystal Structure of Sodium Pyruvate\*

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Sodium pyruvate,  $\text{CH}_3\text{COCOONa}$ , crystallized from aqueous solution, is monoclinic, space group  $P2_1/a$ , with four molecules per unit cell of dimensions

$$a = 22.25, b = 5.31, c = 3.71 \text{ \AA}; \beta = 98.2^\circ.$$

The detailed structure has been determined by two-dimensional Fourier syntheses, and refined by the method of least-squares.

The plane containing the methyl carbon, the keto group and the carbon of the carboxylic group makes an angle of  $18.1^\circ$  with the plane of the C-COO group. This suggests that there is no appreciable degree of conjugation across the central C-C bond, a fact that is confirmed by the observed central C-C bond length,  $1.579 \pm 0.045 \text{ \AA}$ , which is close to the standard single C-C bond length.

Strong Na-O bonds tie the molecules into infinite layers parallel to the (100) planes. Any one layer of molecules is linked with the neighbouring layers by strong Na-O bonds on one side and van der Waals bonds on the other.

### Introduction

The  $\alpha$ -keto acid analogs of amino acids are of considerable biochemical interest as intermediates in the biosynthesis and degradation of amino acids. They have unusual properties and are formed in the course of enzymatic oxidative deamination and transamination reactions. Although considerable work has been reported on the structure of amino acids, little attention has been given so far to the  $\alpha$ -keto analogs. With a view to providing structural information which might throw light on their chemical characteristics, we have undertaken a programme to determine the structures of some of these compounds. In what follows, we report the structure analysis of the sodium salt of the simplest keto acid, i.e. pyruvic acid.

### Experimental details

The crystals of sodium pyruvate were obtained from aqueous solution. They are monoclinic and grow as very thin plates, parallel to the (100) face. There is strong cleavage parallel to the plates. The crystal and physical data obtained are as follows:

$$a = 22.25, b = 5.31, c = 3.71 \text{ \AA}; \beta = 98.2^\circ.$$

The axial lengths were determined from the rotation

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photographs along the three axes, and the  $\beta$  angle from a Laue photograph, taken with X-rays, travelling parallel to the  $b$  axis.

The observed density at  $25^\circ\text{C}$ ., measured by the flotation method is  $1.718 \text{ g.cm.}^{-3}$ , and the calculated density for four molecules of  $\text{CH}_3\text{COCOONa}$  per unit cell is  $1.684 \text{ g.cm.}^{-3}$ .

The systematic absences are:  $0k0$  for  $k$  odd and  $h0l$  for  $h$  odd, so that the space group is uniquely determined as  $P2_1/a$ . The linear absorption coefficient  $\mu$  for Cu  $K\alpha$  radiation is  $23.7 \text{ cm.}^{-1}$ . Reflexions of the type  $hk0$ ,  $h0l$  and  $0kl$  were obtained from  $10^\circ$  or  $15^\circ$  oscillation photographs, using Cu  $K\alpha$  radiation and the multiple-film technique. Of the 153 possible reflexions in the  $hk0$  zone, 122 were observed while in the  $h0l$  and  $0kl$  zones, 93 and 19 reflexions were observed out of possible 105 and 27, respectively. The specimens used were flakes of roughly  $(0.7 \times 1.1) \text{ mm.}^2$  area. Intensities were measured visually, using intensity scales made with the same crystals. Corrections for Lorentz and polarization factors were applied and that for absorption was neglected. On account of the flakiness of the crystals, the shapes and sizes of the spots were not uniform, and this seems to be a serious source of error in the estimation of integrated intensities.

Wilson's method (1942) was used to obtain preliminary values for the scale factors and the temperature factors. These values were improved during the later