

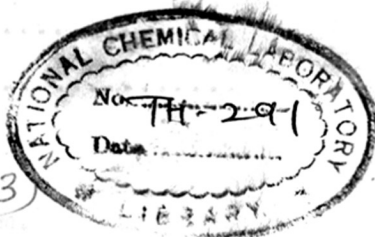
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The Oxidation and Tarnishing of Uranium, Tin,
and Zirconium Surfaces.

By

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General Introduction.

If, when a metal surface takes part in a chemical reaction, the reaction product forms a film on the surface, the initial very thin film may determine the subsequent course of the reaction. It appears that the chemical nature of the film; whether it is amorphous or crystalline; and, in the latter case, the orientation, if any, of the crystals of the film with respect to that of the crystals of the parent metal, and the texture of the original surface, may all be of importance. These factors are most easily determined by electron diffraction.

The surface films formed on a range of metals have been investigated, and in recent years much time has been devoted to the theory of how metals form such films.

The present work constitutes an experimental study by means of electron diffraction techniques of the type of films formed spontaneously or otherwise on the metallic surface and of the growth of such films, both at the solid/gas and solid/liquid interface, on the metals uranium, tin and zirconium.

PART 1.

The Oxidation and Tarnishing of Uranium
by Air, Water, Acids, Alkalis and Halides.

INTRODUCTION.

It has been known for many years that uranium forms a large number of oxides, Biltz and Muller (Z.anorg.Chem., 1927, 163, 257) and the majority of these oxides have been studied by X-ray diffraction, and their structures are reported in Metallurgical Project Report CC-1980 (Nov. 1944) of the Manhattan Project.

The results of electron diffraction studies carried out in this laboratory now show that the oxide layers on uranium form crystalline films, which have a rapid rate of growth. The oxide films can be broadly classified into two classes:

- (a) Films with a face-centred cubic structure corresponding to that of UO_2 .
- (b) Films which yield a pattern corresponding more or less to the hexagonal structure (pseudo) or orthorhombic structure of U_3O_8 or UO_3 .

The affinity of uranium for oxygen is so great that it is extremely difficult to obtain a polished surface on uranium metal free from oxide. The experimental work presented in this report deals mainly with the type of oxide film formed on polished surfaces of uranium exposed to air, and the further crystalline growth of these films.

Oxide films formed by the anodic oxidation of the polished surfaces of uranium in both acid and alkaline baths have also been investigated. Many workers have studied the structures of anodically formed films, e.g. Wood (1931) by X-ray diffraction, and Thomson (1931), Cochrane (1936) and Finch and his collaborators (1936, 1937, 1947 and 1950) by electron diffraction, but to date no work has been published about anodic films on uranium.

The formation of thin oxide films on polished uranium surfaces by the action of water and solutions containing fluoride and chloride ions will also be discussed.

The following results have been published on the structure of uranium oxides. W.F.Zachariassen has investigated the higher oxides of uranium and also the hydrated oxides. These will presumably be reported on by him. Rundle, Baenziger Wilson and MacDonald (J.Amer.Chem.Soc., 1948, 70, 99) have reported the structure of U_2O_5 as orthorhombic, $a - 8.27 \pm 0.02$ A $b - 31.8 \pm 1.1$ A, $c - 6.72 \pm 0.02$ A with 16 U_2O_5 per unit cell. They have characterised U_2O_5 as the reaction product of equimolar quantities of UO_2 and U_3O_8 .

K.B. Alberman and J.S. Anderson (J.Chem.Soc., 1949) have investigated the phase equilibria in the uranium-oxygen system between the composition limits UO_2 and $UO_{2.3}$.

The electron diffraction camera used in the following experiments was the standard Finch type. The principle and applications of electron diffraction have been discussed by Finch and Wilman (1937) so they will not be included.

EXPERIMENTAL.Mechanical Polishing of Uranium Surfaces.

The uranium samples used for mechanical polishing were both polycrystalline and macro-crystalline. The macro-crystalline specimen was prepared at Harwell from an uranium test-bar by the stress-anneal method. It was hoped to obtain a single crystal of uranium by this method, but unfortunately, the crystals so produced were not large enough to give a single-crystal electron-diffraction pattern.

The polycrystalline specimens used were cast uranium discs 2 cms. in diameter and 0.4 cm. thick.

Firstly the specimens were abraded with various grades of emery paper beginning with 1 and progressing successively to 0, 00, 000 and 0000, the lubricant in each case being benzene so as to produce a suitable face for the final polishing. Two grades of diamond dust (0/2 and 0/1) were used for the final polishing. A small quantity of diamond dust was scattered over the top of the polishing cloth, which was fixed to a mechanical polisher, and then rubbed in gently with a finger. Each sample was polished for a short time with each grade of dust, benzene being used as the lubricant and the speed of the polishing wheel being approximately 200 revolutions per minute.

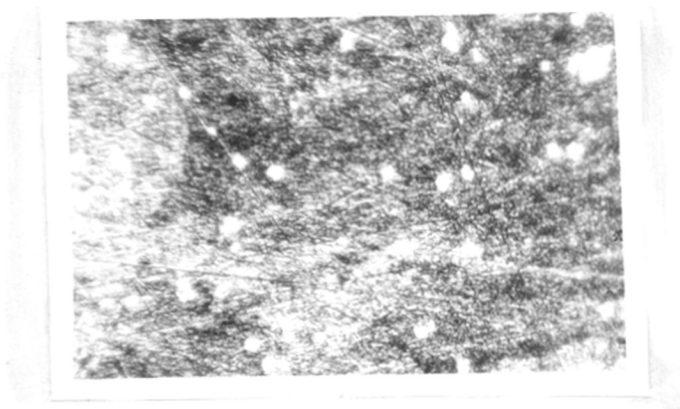


Fig. 1. x450.

The uranium surfaces so polished were silvery in appearance and almost free from scratches but having a slight waviness as shown by Fig.1. The minute cubes dotted over the surface are face-centred cubic crystals of uranium dioxide UO_2 .

Electrolytic Polishing of Uranium Surfaces.

1. Apparatus.

The apparatus used (Fig.2) for the electro-polishing of the uranium samples was similar to that used by Mott and Haines (A.F.R.F.). It consisted of a 4" diameter crystallisation dish containing the electrolyte in which was immersed a glass cooling coil, consisting of five coils of 1/4" diameter glass tubing. The solution during the polishing was kept at 15°C. by a continuous flow of tap water through these coils. The cathode consisted of a sheet of uranium 4 cms. by 6 cms. and was placed vertically in the "bath" about 4 cms. from the uranium specimen (anode) connected to the circuit by means of a stainless steel wire.

The current was drawn from the D.C. mains through a variable resistance and ammeter, with a voltmeter across the bath electrodes.

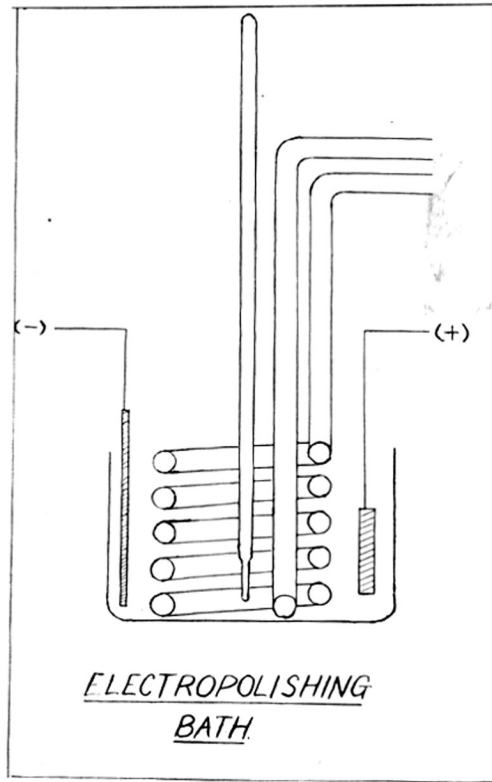


Fig. 2.

Electropolishing Bath.

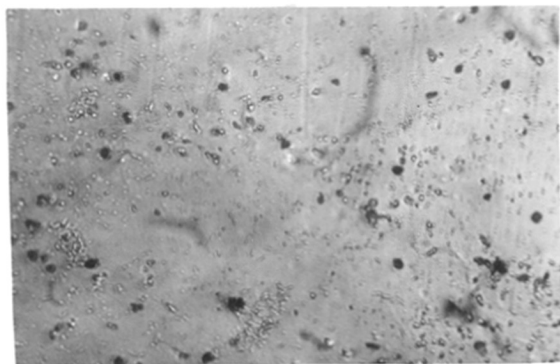


Fig. 3. x450

2. Phosphoric Acid Solution.

Several specimens were electropolished, after a rough mechanical polish to 000 emery, in a phosphoric acid solution, its composition being as follows:

Orthophosphoric Acid	50 Mls.
Conc. Sulphuric Acid	100 Mls.
Distilled water	100 Mls.

The optimum current density for polishing was found to be 0.6 to 0.65 A/cm² and the time for polishing varied from half a minute to two minutes depending on the state of the original surface.

There is a tendency for staining of the surface to occur during the electropolishing process, due to a rather viscous layer formed near the surface of the anode, (Mott and Haines, Metallurgia, 1951). This staining can be prevented by continuously brushing the surface of the specimen with a soft camel hair brush, thus disrupting the layer.

The surface obtained by this procedure is completely free of scratches and is quite flat, but there is a tendency to form pits as is shown by Fig.3. However this pitting was not sufficient to interfere with the electron diffraction patterns obtained by the reflection of a electron beam from the surface.

3. Perchloric Acid Solution.

The perchloric acid solution used was slightly stronger than that used by Jacquet (Comptes Rendus, 228, 1224, 1949) and was composed of the following:

Perchloric Acid (60% Soln.)	50 Mls.
Glacial Acetic Acid	200 Mls.

The current density used was fairly high, and of the order of 0.9 A/cm^2 . The time required to polish the samples, after a rough mechanical polish to 000 emery was approximately one minute. A smooth surface was obtained free from scratches but there was a greater tendency for the surface to become pitted, also a slight etching effect was noted.

In both cases the specimens were removed from the polishing bath, washed with distilled water, then absolute alcohol, before being transferred to the diffraction camera.

THE OXIDATION OF POLISHED URANIUM SURFACES AT ROOM TEMPERATURES BY AIR.

The uranium specimens were polished mechanically and electrolytically, as has previously been described, and then exposed to dry laboratory air for periods of time varying from 1 - 24 hours. After each period of exposure, the surface was gently rubbed with cotton wool soaked with petroleum ether, to ensure that the surface was free from grease and then transferred to the diffraction camera.

THE OXIDATION OF POLISHED URANIUM SURFACES AT ELEVATED
TEMPERATURES BY AIR.

Each of the polished uranium specimens was oxidised for a period of five minutes at temperatures of 100, 200, 280 and 300°C., in an electrically heated air oven. After each period the specimen was immediately transferred to the electron diffraction camera, where it cooled to room temperature while the camera was being evacuated.

ANODIC OXIDATION IN A SULPHURIC ACID BATH.

Before samples of polycrystalline uranium were anodised they were mechanically polished and electropolished as described previously and placed in the camera to determine the nature of the surface.

The anodising bath consisted of a 0.1 molar sulphuric acid solution; its pH, determined on a direct reading Cambridge pH meter, was 0.8.

The apparatus used for anodising was identical to the electropolishing apparatus except for a stainless steel cathode substituted for the uranium cathode, the anodising current being 0.25 A/cm².

Samples were anodised for periods of 10, 20, 30, 60, and 120 seconds, then were washed with distilled water and finally with alcohol before being transferred to the diffraction camera.

ANODIC OXIDATION IN AN ALKALINE BATH.

The repolished uranium samples were oxidised for periods of 10, 20 and 30 seconds with a current density of 0.02 A/cm^2 , and also for periods of 10, 20 and 30 seconds with a current density of 0.25 A/cm^2 .

A 0.1 M. sodium hydroxide solution was used for the anodising bath, the pH of this solution being determined on a direct reading Cambridge pH meter, was 10.7.

Immediately after the current was switched off each specimen was thoroughly washed in distilled water, so as to remove any adhering alkali and then with absolute alcohol before being transferred to the diffraction camera.

OTHER OXIDATION PROCESSES.

The resurfaced uranium samples were immersed in distilled water, 0.1 molar sodium fluoride solution and 0.1 molar potassium chloride solution, for periods ranging from 10 minutes to 24 hours. After each immersion the samples were washed in distilled water and then alcohol before being transferred to the diffraction camera.

The degree to which the polished surfaces of each specimen had tarnished after the various periods of immersion in the above solutions was noted, so that the relative rate of film growth could be roughly estimated.

The pH of the above solutions was determined as previously described, before the specimens were immersed.

THE OXIDATION OF URANIUM IN AN ELECTRIC ARC.

A direct current electric arc was struck between two freshly cleaned uranium electrodes, both being 0.4 cm. in diameter. The uranium oxide smoke so produced was collected on a collodion film, supported on a nickel gauze, held 14 ins. vertically above the arc.

When sufficient oxide had been deposited, the specimen was transferred to the diffraction camera.

Several specimens were prepared with different times of deposition and arc currents.

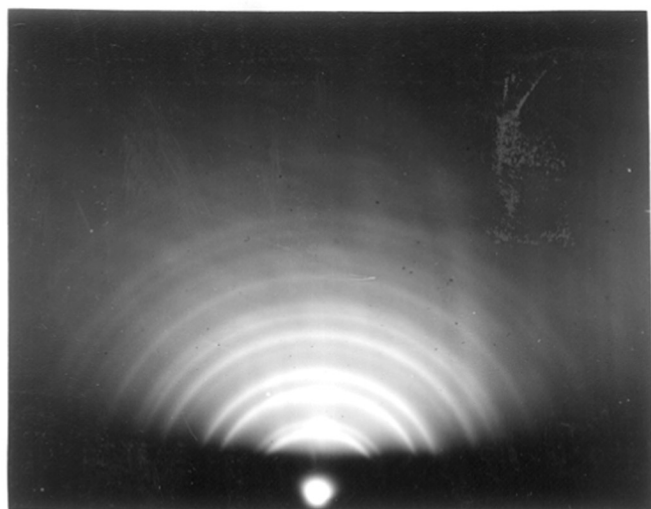


Fig. 4.

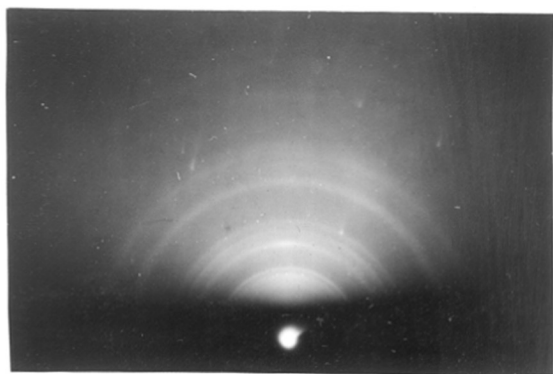


Fig. 5.

RESULTS.The Structure of Mechanically Polished Uranium Surfaces.

When polycrystalline uranium was mechanically polished with emery and diamond dust, the nature of the surface layer varied considerably with the conditions of polish.

It was found from the interpretation of electron diffraction ring patterns that if the surface was polished for short periods of about a minute with fine diamond dust, and the specimen immersed in benzene, the polished surface layer was found to consist of a polycrystalline film. The net plane spacings, calculated from the ring radii in Fig.4 were compared with the available X-ray data, and were found to correspond closely to the net plane spacings of UO_2 determined by X-rays at I.C.I., Winnington. The net plane spacings for Fig.4 are shown in Table 1.

If the specimen became warm due to insufficient lubrication or was polished for periods of five minutes or longer, the surface layer remained crystalline, but diffraction patterns (Fig.5 and Fig.9h) showed that the structure of the surface film was similar to the structure of the film obtained by electropolishing uranium.

Diffraction patterns obtained from the surface of uranium after it had been polished for eight minutes with 0/1 grade diamond dust showed strong orientation as is shown

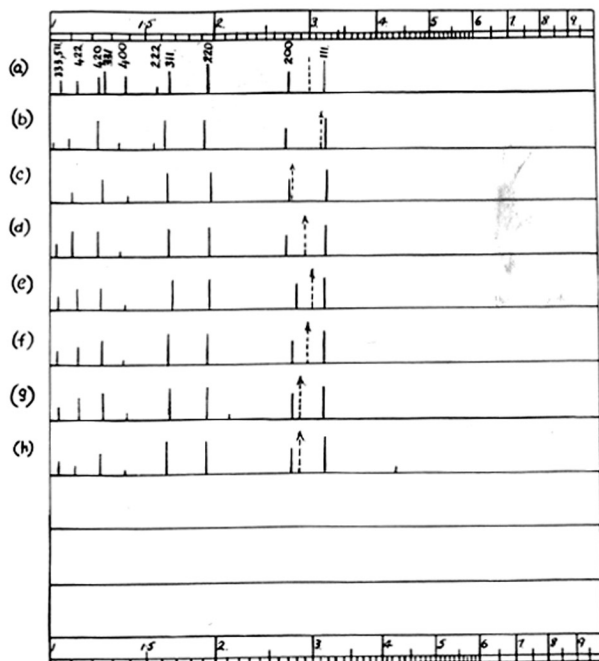


Fig. 6.

A comparison table showing the relative intensities of rings and the net plane spacings of UO_2 type ring patterns.

- (a). Calculated lattice spacings and indices of UO_2 from X-ray data.
- (b).- (h). Lattice spacings and ring intensities of UO_2 type ring patterns from oxidised uranium surfaces, the arrow indicating the degree to which each graph had to be displaced from the 3.0 position in order to correspond to pattern (a). This displacement lies within the limits of variation due to inaccuracy of high tension voltage and camera length measurements.

Table 1.

Intensity	Plane spacing d. in A.	hkl plane.	X-Ray spacings d. in A.
V.S.	3.040	111	3.164
S.	2.595	200	2.737
V.S.	1.830	220	1.932
V.S.	1.557	311	1.646
W.	1.478	222	1.573
W.	1.270	400	1.364
V.S.	1.175	331	1.250
M.	1.043	422	1.112
M.	0.976	333,511	1.049
M.	0.853	400	0.964
W.	0.766	531	0.922

V.S.-very strong. S.-Strong. M.-Medium. W.-Weak.

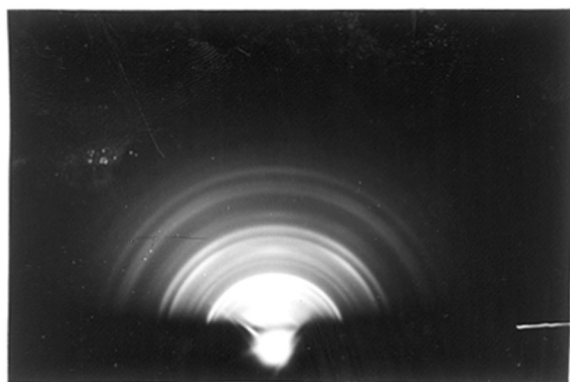


Fig. 7.

in Fig.7 and Fig.9(g).

The pattern shown in Fig.7 could not be fully indexed, due to the unavailability of X-ray intensity data. The arcing of some of the diffraction rings suggests that the surface film was composed of more than one oxide, the lower order oxide tending to become orientated.

The Oxidation of Mechanically Polished Surfaces of Uranium
at Room Temperature by Air.

Diffraction patterns of the surface layer revealed that its composition remained the same as the initial film for periods of exposure up to 24 hours. Film growth was considerable during this exposure period, as was indicated by the progressively less clear shadow edge on the different patterns and the colour of the tarnished surface. After twenty-four hours exposure to the atmosphere the polished surface tarnished to a dark brown appearance.

THE Oxidation of Mechanically Polished Uranium Surfaces
at Elevated Temperatures by Air.

When the film was mechanically polished uranium is composed of polycrystalline uranium UO_2 , its structure and composition remain unchanged on being heated to different temperatures up to $300^\circ C$. The net plane spacings of

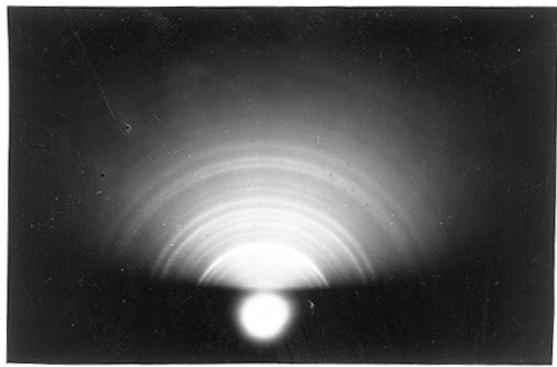


Fig. 8.

Table 2.

Intensity	Plane spacings d. in Å.	hkl plane.	X-ray spacings d. in Å.
V.S.	3.48	111	3.164
S.	2.99	200	2.737
V.S.(diff)	2.15	220	1.932
V.S.	1.79	311	1.646
V.W.	1.505	400	1.364
S.(diff)	1.35	331	1.250
M.	1.19	422	1.112
W.(diff)	0.99	531	0.923

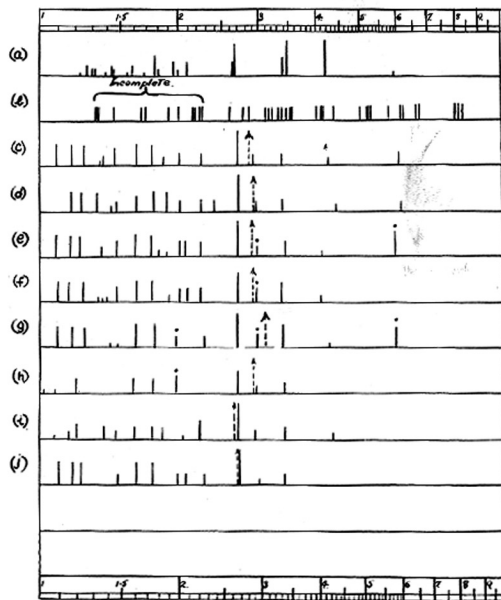


Fig. 9.

- (a) Calculated lattice spacings of $U_3 O_8$ from X-ray data.
- (b) Calculated lattice spacings of $U_2 O_5$, incomplete below 2.5 A.
- (c)-(j) Lattice spacings of ring patterns obtained from the higher oxides of uranium, the arrow indicating the degree to which each graph had to be displaced from the 3.0 position in order to correspond to patterns (a) and (b).

Spots above lines indicate that the diffraction rings are arced.

diffraction patterns obtained are illustrated by Fig.6(c) and are tabulated in Table 2.

If the polishing conditions are such as to form a surface layer having a structure similar to the structure of the film obtained by electropolishing uranium then the film behaves in a manner similar to that described later in these results.

The Structure of Electropolished Uranium Surfaces.

In all cases, when polycrystalline uranium was electropolished in either phosphoric-sulphuric acid or perchloric-acetic acid polishing baths, electron diffractions obtained from the resulting surface film showed it to be polycrystalline.

Electron diffraction patterns obtained from electropolished uranium surfaces were similar to Fig.8. The surfaces of these specimens was silvery in appearance, and it remained bright for a considerable time during further exposure to air at room temperature.

From the measurement of diffraction ring radii, the net plane spacings were calculated and were compared with the X-ray powder data obtained by I.C.I., Winington from U_3O_8 and the data for U_3O_8 listed in the A.S.T.M. X-ray diffraction index. These results are tabulated in Table 3.

Table 3.

Radii (cms)	Density	Spacings d. in Å	Diffraction indices hkl.	Calculated spacing d. in Å.	X-ray Intensity U ₃ O ₈ .
0.472	W.	5.960	031 U ₂ O ₅	5.68	-
0.652	W.	4.320	012 U ₂ O ₅	4.35	-
0.842	M.	3.34	200 U ₃ O ₈	3.35	50
0.963	S.	2.92	062 U ₂ O ₅	2.84	-
1.060	VVS.	2.65	300,201 U ₃ O ₈	2.64	90
1.284	M.	2.19	093 U ₂ O ₅	1.89	-
1.415	M.	1.98	-	-	-
1.616	VS.	1.74	331,132 U ₃ O ₈	1.78	60
1.762	VS.	1.59	261 U ₃ O ₈	1.58	30
1.950	MW.	1.44	0124 U ₂ O ₅	1.42	-
2.325	S.	1.21	-	-	-
2.437	S.	1.15	-	-	-
2.611	S.	1.076	-	-	-

VVS.-very very strong. VS.-very strong. S.-strong.

M.-medium. W.-weak.

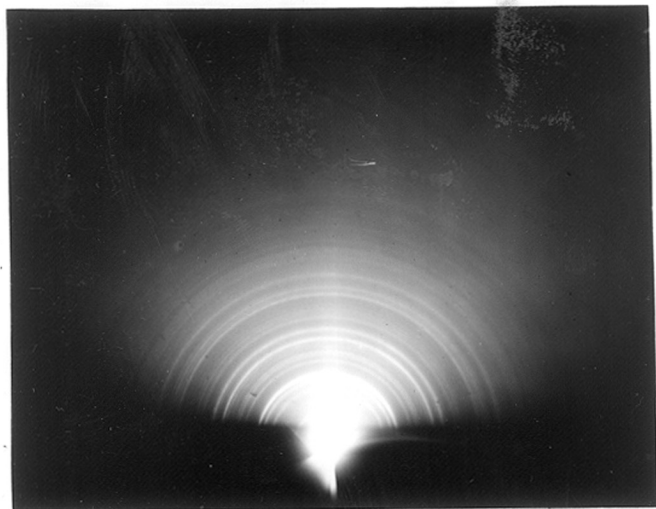


Fig. 10.

The structure of U_3O_8 according to available data (private communication from A.E.R.F.) is orthorhombic with the following parameters:

a - 6.70 A.

b - 11.94 A.

c - 4.14 A.

There are two molecules per unit cell, with uranium atoms at 000 , $1/2 \ 1/2 \ 0$, $0 \ 1/3 \ 0$, $1/2 \ 1/6 \ 0$, $0 \ 2/3 \ 0$, $1/2 \ 5/6 \ 0$. As the scattering power of oxygen is small in comparison to that of uranium, the positions of the oxygen atoms have apparently not been calculated. However some weak diffractions in both X-ray and electron diffraction patterns appear to be attributable to the scattering of the oxygen atoms

It can be mentioned here that orthorhombic U_3O_8 has a pseudo hexagonal structure similar to that of the hexagonal UO_3 , for which $a = 3.96$ A., $c = 4.160$ A., (private communication from A.E.R.F.).

From the above information, the general expression for the structure factor and the net plane spacings of U_3O_8 were determined as follows:

According to the positions of the uranium atoms in the lattice, it appears that if the oxygen atoms are neglected, the structure of U_3O_8 can be represented as having a pseudo ortho-hexagonal lattice (lattice points at 000 and $\frac{1}{2}\frac{1}{2}0$), three such atomic (uranium) lattices interpenetrating and starting

from these points, with uranium atoms in the following positions:

$$000, 0 \frac{1}{3} 0, 0 \frac{1}{3} 0.$$

The structure factor S^2 is thus:

$$S^2 = G_1^2 \cdot G_2^2 \cdot U^2$$

where

$$G_1^2 = \left[1 + \cos 2\pi \left(\frac{h+k}{2} \right) \right]^2$$

and

$$G_2^2 = \left[1 + 2 \cos 2\pi \left(\frac{k}{3} \right) \right]^2$$

on substituting

$$G_1^2 = 4 \text{ if } h+k = 2n \quad \text{if } k = 0 \quad 3n \quad G_2^2 = 3^2 = 9$$

$$G_1^2 = 0 \text{ if } h+k \neq 2n \quad k = 3n \pm 1 \quad G_2^2 = 0$$

From the above it follows that diffractions occur if $(h+k)$ is even, and simultaneously if k is a multiple of 3.

The net plane spacings 'd' for U_3O_8 were calculated from the above orthorhombic axes and from the equation:

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

Where 'd' is the net plane spacing. These spacings are shown in Table 4. The spacings for 'd' given in the A.S.T.M. X-ray data agree with most of these spacings, but there are small variations occurring in the data supplied by I.C.I., Winnington, shown in Table 4.

As there is some doubt whether the faint diffractions in the X-ray powder patterns are caused by the oxygen atoms in

Table 4.

X-Ray Powder Pattern Data and Calculated Spacings
for U₃O₈

Intensity I.C.I.	d. in Å. I.C.I.	d. in Å. A.S.T.M.	Intensity A.S.T.M.	Calculated d in Å	hkl
W.	8.65				
W.	6.92				
V.W.	5.86	5.87	10		
V.St.	4.12	4.15	100	4.14	001
V.W.	3.68				
V.St.	3.38	3.43	100	3.45	130
	3.36	3.36	50	3.35	200
V.St.	2.61	2.64	90	2.64	131
		2.61	40	2.61	201
V.W.	2.19				
M.	2.05	2.07	40	2.07	002
W-M.	1.97	1.99	20		
M.	1.93	1.95	40	1.95	330
				1.79	202
				1.78	331
St.	1.76	1.77	60	1.77	132
W.	1.70	1.71	20	1.71	260
V.W.	1.67	1.68	10	1.67	400
W.	1.57	1.58	30	1.58	261
V.W.	1.54	1.55	10	1.55	401
V.W.	1.50				
		1.44	20		
M. (broad)	1.41	1.42	30		
W.	1.37	1.38	10	1.38	003
				1.36	190
W.	1.31	1.32	20		
V.W.	1.30	1.30	20		
M.	1.27	1.28	30	1.28	460
				1.27	530
				1.21	531
				1.15	062
				1.12	333
				1.11	600
				1.08	532
				1.06	403
				1.04	461
				1.03	004
				1.01	134
				0.98	204

Table 5.

Calculated Lattice Spacings for U₂O₅.

Calculated d. in Å.	hkl	Calculated d. in Å.	hkl
10.60	030	3.36	002
8.27	100	3.30	022
8.02	110	3.20	032
7.95	040	3.12	120, 112
6.72	001	3.06	122
6.59	011	2.83	062
6.37	050	2.76	300
6.19	021	2.59	222
5.68	031	2.26	003
5.22	101	2.24	013
5.16	111	2.16	113, 103
5.14	040	2.14	123
4.96	121	2.00	440
4.35	012	1.90	093
4.13	200	1.68	004, 014
4.11	210	1.64	114, 124
4.00	220	1.43	0,12,4
3.53	201	1.34	005, 015
3.51	211	1.33	115
3.44	221	1.32	125

the cell, or show the presence of another phase, the net plane spacings of U_2O_5 were calculated from the axial dimensions recorded by R.F.Rundle and co-workers (U.S.A.E.C. M.D.D.C. 1608) and compared with U_3O_8 data.

The unit cell is reported as orthorhombic,

$$a = 8.27 \pm 0.2 \text{ \AA.}$$

$$b = 31.8 \pm 0.1 \text{ \AA.}$$

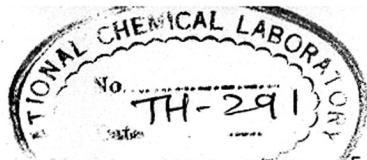
$$c = 6.72 \pm 0.02 \text{ \AA.}$$

with 16 U_2O_5 per unit cell.

The values for the net plane spacings of U_2O_5 , calculated from the above data are shown in Table 5, and are plotted on a logarithmic scale in Fig.9(b). This table is incomplete below 2.5 \AA. , and as the positions of the uranium atoms are lacking, it is not clear what are the relative intensities of the diffractions. Owing to the close relationship of the axial dimensions of U_2O_5 and U_3O_8 the difference of intensities between some of the electron diffraction rings and X-ray intensities is apparently due to U_3O_8 diffractions superimposed on U_2O_5 diffractions.

The Oxidation of Electropolished Uranium Surfaces
at Room Temperatures by Air.

The electropolished surface of the uranium specimen was exposed to the atmosphere for periods from five minutes to twenty-four hours. Diffractions showed that there was



no change in the composition of the surface film [Fig.9(d) compared with Fig.9(c)]. However, the growth of the film is quite noticeable from the tarnished appearance of the surface. After twenty-four hours, the polished surface had tarnished from a silvery appearance to a dark blue colour. The shadow edge in the electron diffraction pattern had also lost its sharpness, indicating that the surface film had grown uneven.

Oxidation of Electropolished Uranium Surfaces at
Elevated Temperatures by Air.

From the diffraction patterns obtained, it appears that heating tends to cause growth of an orientated surface film. When polished uranium surfaces were heated to temperatures of the order of 200°C . for 5 minutes, the diffractions were similar to Fig.9(c) and (d). On heating above 200°C . and below 280°C . the surface of the film tended to consist of preferentially orientated crystals, giving first and second order arcs in the line of incidence, as is shown by Fig.10 and Fig.9(e). In Fig.10 the arcs in the plane of incidence correspond to the first and second order Bragg reflections from a net plane spacing of 6.15 A., and parallel to the surface. These arcs correspond in position to 031 and 062 diffractions of U_2O_5 , and are not accounted for by any U_3O_8 diffractions.

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This fact appears to indicate that the surface layer was composed of a mixture of U_2O_5 and U_3O_8 , the U_2O_5 having a lower oxygen content will tend to orientate itself in preference to the higher oxide.

The Anodic Oxidation of Polished Polycrystalline Uranium in Sulphuric Acid at Room Temperatures.

When polished polycrystalline uranium is oxidised anodically in a sulphuric acid solution, the film formed on the polished surface varied in colour from a brownish tinge to a light brown colour, the depth of colouring depended upon the time of anodising. During the anodising, evolution of oxygen took place at the anode.

Electron diffraction patterns obtained by anodising the polished surface of uranium in 0.1 M sulphuric acid (pH 0.9) with a current density of 0.25 A/cm^2 for 10 seconds, were similar to Fig.4. For longer periods of anodising the surface film yielded electron diffraction patterns similar to Fig.8.

The results obtained from anodising in a sulphuric acid solution at the same current density for different periods of time are shown in Table 6.

It is evident from Table 6 that whatever the state of the surface of the uranium substrate, after a short period of anodising in acid solution, a film of randomly distributed UO_2 is formed initially, which on more prolonged anodising changes to the higher oxides of uranium.

Table 6.

Substrate	Temp. °C.	c.d.in amp./ sq.cm. ²	Time secs.	Composition	Orient- ation.	Appear- ance.
Electropolished Uranium.	15	0.25	10	UO ₂	Random	Faint brown tinge.
"	15	0.25	60	U ₂ O ₅ + U ₃ O ₈	Random	light brown
"	15	0.25	120	U ₂ O ₅ + U ₃ O ₈	Random	brown
Mechanically polished Uranium.	15	0.25	10	UO ₂	Random	Faint brown tinge.
"	15	0.25	20	U ₂ O ₅ + U ₃ O ₈	Random	light brown
"	15	0.25	30	U ₂ O ₅ + U ₃ O ₈	Random	light brown

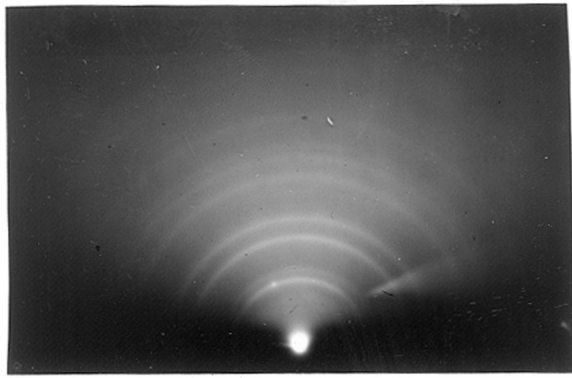


Fig. 11.

The Anodic Oxidation of Polycrystalline Uranium
in Sodium Hydroxide Solution at Room Temperatures.

Polished surfaces of polycrystalline uranium were oxidised anodically in 10 per cent sodium hydroxide solution (pH 10.7) at room temperatures, the current density being varied from 0.08 to 0.25 A/cm².

Electron diffraction patterns similar to Fig.11 showed that films of randomly distributed UO₂, F.C.C., $a = 5.45 \text{ \AA}$., were formed at the lower current density, and on anodising at the higher current density, patterns similar to Fig.8 showed that the surface films formed consisted of the higher oxides of uranium.

The effects of varying the current density and time of specimen in the anodising bath on the surface films formed on polycrystalline uranium are shown in Table 7. These results show that the nature of the surface film formed by anodising uranium in an alkaline solution is independent of the condition of the mode of polishing of the uranium surface.

The Oxidation of Polished Surfaces of Uranium in
Distilled Water at Room Temperatures.

Polished specimens of polycrystalline uranium were immersed in boiled-out distilled water at room temperatures

Table 7.

Substrate	Temp. °C.	c.d. Amp/ sq. cm.	Time secs	Composition	Orient- ation.	Appearance
Electro- polished Uranium.	15	0.08	10	UO ₂	Random	silvery
	15	0.08	20	UO ₂	"	silvery
	15	0.08	30	UO ₂	"	slight brown tinge
	15	0.08	60	UO ₂	"	light brown
	15	0.25	10	U ₂ O ₅ + U ₃ O ₈	"	light brown
	15	0.25	20	U ₂ O ₅ + U ₃ O ₈	"	light brown
Mechanically polished Uranium.	15	0.08	10	UO ₂	"	slight brown tinge
	15	0.08	20	UO ₂	"	slight brown tinge
	15	0.25	10	U ₂ O ₅ + U ₃ O ₈	"	light brown
	15	0.25	20	U ₂ O ₅ + U ₃ O ₈	"	light brown

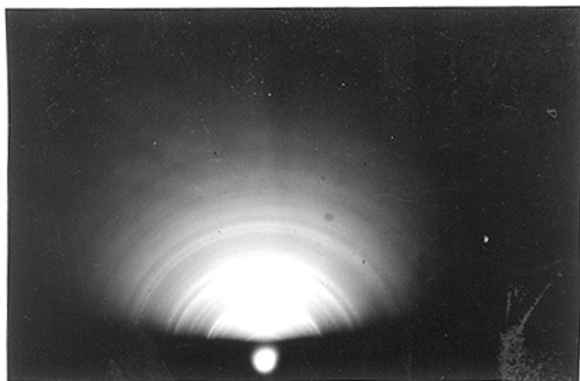


Fig. 12.

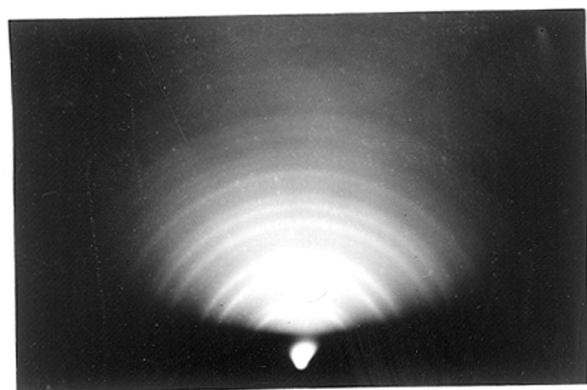


Fig. 13.

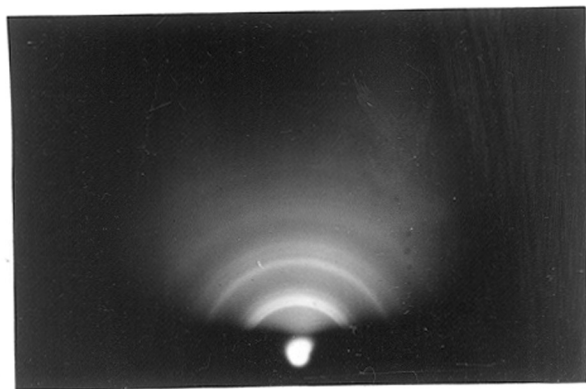


Fig. 14.

for periods from one hour to twenty four hours. The results are shown in Table 8.

Both mechanically and electrolytically polished surfaces of the uranium, after short immersion in distilled water, yielded electron diffraction patterns similar to Fig.12, thus showing that a film of UO_2 had grown. The pattern Fig.13 due to UO_2 is quite sharp, showing that the randomly distributed crystals were several hundred angstroms in diameter. The UO_2 film continued to grow on longer periods of immersion until after 24 hours immersion diffraction patterns (Fig.14) consisting of UO_2 rings together with additional rings were obtained. The values of the net plane spacings are given in Table 9.

It is apparent from the diffuseness of the outer diffraction rings that the film growth had been considerable and that the surface of the film had grown uneven. As there are insufficient X-ray data available, it has not been possible to index the additional rings occurring in Fig.14.

The Oxidation of Polycrystalline Uranium in Aqueous Fluoride Solutions at Room Temperature.

Both mechanically polished and electropolished specimens of uranium were immersed in 0.1 M sodium fluoride solution at $15^\circ C$. for periods between 10 minutes and 2 hours.

Table 8.

Substrate both Mechanically and Electrolytically
polished Uranium.

pH of water	Time in hours.	Appearance of film	Figure
6.1	1	slight brown tinge.	13
6.1	2	slight brown tinge.	13
6.1	3	light brown.	13
6.1	6	light brown.	13
6.1	24	brown.	14

Table 9.

Intensity	Plane Spacings d. in Å.	hkl	X-ray Spacings of UO ₂ . d. in Å.
VS. (add.ring)	3.58	-	-
VS.	3.24	111	3.164
M+	2.85	200	2.737
VS	1.98	220	1.932
M. (add.ring)	1.81	-	-
M-	1.67	311	1.646

It was apparent that the fluoride solution had far more action on the polished uranium surface than had exposure to air, as was shown by the increased rate of tarnishing, as shown in Table 10.

The net plane spacings of the compound formed were calculated from the diffraction ring radii, and are shown in Table 11. The diffraction patterns were thus due to randomly disposed UO_2 , F.C.C., $a = 5.45$ A. Fig.6(c) shows the relative intensities and the face-centred cubic arrangement corresponding to these ring patterns such as Fig.7.

Electron diffraction patterns revealed that after a short immersion in a fluoride solution at room temperature a film of randomly disposed UO_2 crystals was formed on the polished uranium surface, and this film continued to grow as such on longer periods of immersion.

The Oxidation of Polycrystalline Uranium in Aqueous Chloride Solutions at Room Temperatures.

The interpretation of the electron diffraction patterns obtained from the films formed on the polished polycrystalline uranium surfaces by the action of aqueous potassium chloride solutions at room temperatures showed that these films were identical to the films formed on polished

Table 10.

Substrate	Conc. of NaF	Time of Immersion.	Appearance
Mechanically Polished Uranium.	0.1 M	10 mins.	greenish tinge.
	0.1 M	2 hrs.	greenish-brown.
Electropolished Uranium.	0.1 M	10 mins.	greenish tinge.
	0.1 M	2 hrs.	greenish-brown.

Table 11.

Intensity	Plane Spacings d in Å.	hkl	X-ray Spacings d in Å.
VS	3.22	111	3.164
S +	2.80	200	2.737
VS	1.96	220	1.932
VS	1.67	311	1.646
VW	1.38	400	1.364
S(diff)	1.26	331	1.250
S -	1.14	422	1.112
M	1.05	333 511	1.049

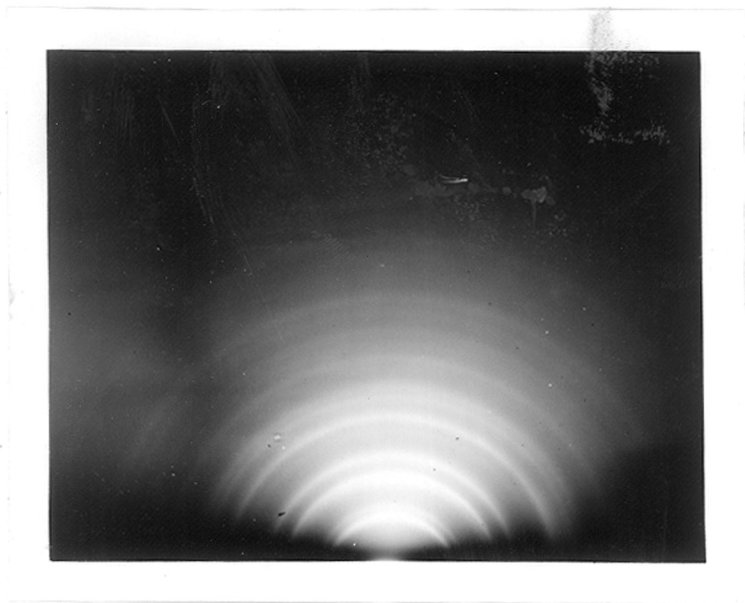


Fig. 15.

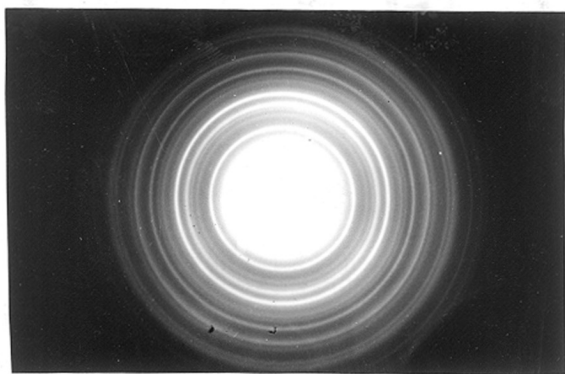


Fig. 15a.

uranium surfaces by the action of aqueous fluoride solutions. The net-plane spacings of the electron diffraction ring patterns obtained (Fig.15) are shown in Table 12.

From the experimental results shown in Table 12 it can be concluded that the electron diffraction ring patterns obtained from the surface films formed on polished uranium surfaces in aqueous chloride solutions at room temperatures was due to randomly disposed UO_2 (F.C.C., $a = 5.45 \text{ \AA}$) crystals.

The degree to which the polished polycrystalline surface of uranium was tarnished by aqueous chloride solution over a period of two hours is shown in Table 13.

The Oxidation of Uranium in an Electric Arc.

The transmission electron diffraction patterns obtained from all the specimens prepared by this method were similar to Fig.15a. The net plane spacings of these electron diffraction ring patterns (Table 14) when compared with existing X-ray data show that the electron diffraction ring patterns obtained were due to randomly disposed U_3O_8 .

These patterns have three extra rings which cannot be indexed as U_3O_8 diffractions, and thus are probably due to a small percentage of some other phase being present.

Table 12.

Intensity	Plane Spacings d in Å.	hkl	X-Ray Spacings d in Å.
VS	3.27	111	3.164
S+	2.82	200	2.737
M	2.37	-	-
VS	1.98	220	1.932
VS	1.69	311	1.646
FW	1.52	-	-
FW	1.39	400	1.364
S	1.27	331	1.250
S-	1.13	422	1.112
M	1.07	333	1.049
		511	

Table 13.

Concentration of KCl - 0.1 M. pH of Solution - 9.0

Substrate	Time of Immersion.	Orientation	Appearance
Mechanically Polished Uranium.	10 mins.	Random	Silvery with very slight brown tinge.
	2 hours	Random	Light brown.
Electropolished Uranium.	10 mins.	Random	Silvery surface.
	20 mins.	Random	Slight brown tinge.
	2 hours.	Random	Light brown colouration.

Table 14.

Intensity	Plane Spacings d in Å.	hkl	Calculated Spacings of U ₃ O ₈ d in Å.
M	4.62	-	-
S	3.99	001	4.14
VS	3.28	200	3.35
VS	2.54	201	2.61
MW	2.15	-	-
W+	2.01	002	2.07
VS	1.90	330	1.95
VS	1.72	202,331,132	1.79,1.78,1.77
W	1.64	260	1.71
W	1.53	261	1.58
W	1.47	401	1.55
S	1.38	-	-
S(diff)	1.24	460	1.28
M	1.19	531	1.21
W-	1.14	062	1.15
S	1.10	600,532	1.11
S	1.05	403	1.06
M+	0.95	602	0.96
M	0.91	334	0.91
M	0.89	264	0.88

Discussion.

The present experiments provide information concerning the growth and nature of thin oxide films on polished uranium surfaces. The electron diffraction patterns reveal that the surface oxide films on uranium are polycrystalline and have a rapid rate of growth, so that mechanically or electrolytically brightly polished surfaces of uranium tarnish rapidly.

The composition of the surface film produced on polished uranium depends primarily on the duration and vigour of polishing rather than on whether the polishing was carried out mechanically or electrolytically. Further, in the case of mechanical polishing the use of an oxygen excluding lubricant, such as benzene, favoured the formation of UO_2 rather than that of a higher oxide.

When a thin film of UO_2 is formed, further oxidation by air at room temperature or temperatures up to $300^\circ C$. only affects the rate of growth of the film without changing its composition.

In all other cases when uranium was polished either mechanically or electrolytically, surface films of the higher order oxides of uranium were formed. The electron diffraction patterns obtained from these surface films were difficult to index, due to the lack of data available about the higher

oxides of uranium.

Relative to the X-ray diffraction data given (A.E.R.E.) of the surface layer, the strong rings of the electron diffraction patterns correspond to the calculated uranium atom positions in the U_3O_8 cell, with the exception of the three inner rings. Of these three, the 5.80 Å. diffraction ring can be indexed as (110) U_3O_8 , the other two cannot be diffractions of the U_3O_8 structure, but correspond reasonably well to calculated U_2O_5 spacings. Taking into account the weakly scattering oxygen atoms, it would be possible to detect faint rings in the positions defined by the U_3O_8 unit cell in addition to those which correspond to scattering by the uranium atoms only.

Another possibility not to be overlooked is that superlattices may be formed of composition intermediate between these oxides, as suggested by the close relationship between the U_3O_8 lattice dimensions and the U_2O_5 lattice dimensions reported by Rundle and co-workers (United States Atomic Energy Commission MDDC-1608), the U_2O_5 having a pseudo unit cell $a = 4.14$ Å., $b = 3.96$ Å., $c = 6.72$ Å.

There is a slight discrepancy in the intensity of U_3O_8 diffraction rings relative to the X-ray powder pattern data given, but the plane spacings agreed well. The intensity variation was probably due to some U_2O_5 diffractions being superimposed on U_3O_8 diffractions. The average composition

of the surface layer was thus possibly intermediate between U_2O_5 and U_3O_8 .

The surface layers on polycrystalline uranium remain unchanged when the layer becomes thicker by oxidation by exposure to air at room temperatures, but growth of U_2O_5 crystals in preferential orientation with the (031) planes of U_2O_5 parallel to the surface occurred after oxidising at $280^\circ C$. for 5 minutes, while at higher temperatures only random surface films are formed. The preferential orientation of U_2O_5 is presumably accounted for by the fact that U_2O_5 having the lower oxygen content of the higher oxides will tend to orientate when favourable conditions are obtained. Another possible explanation of the orientation of U_2O_5 is that a layer of U_2O_5 is formed on the uranium surface and further oxidation produces a randomly disposed crystalline film consisting of U_2O_5 and U_3O_8 .

Distilled water solutions of fluorides and chlorides produced films of UO_2 which remain unchanged after further film growth in such solutions. Uranium surface films obtained after 24 hours immersion in distilled water gave diffraction patterns with additional rings, but these rings could not be correlated with any of the available data. It is possible that these rings were due to hydrated oxides of uranium such as $UO_2(OH)_2$ or $UO_4 \cdot 2H_2O$, being formed by the

reaction of UO_2 with water. These additional rings only appeared when thick films of UO_2 had been formed so it is not likely that the uranium substrate had any influence on their formation.

Surface films of UO_2 formed by immersion of uranium in fluoride and chloride solutions can be attributable to the formation of an oxyfluoride or oxychloride which immediately decomposes on formation into UO_2 .

The films formed anodically at moderately high current densities on polished uranium surfaces were identical in composition to the surface layer produced when uranium is electropolished. A surface layer of randomly disposed oxides of uranium produced when polycrystalline uranium is electropolished is probably due to the uranium surface being anodised simultaneously with the polishing operation.

Low current densities effect the formation of randomly disposed crystals of UO_2 . Apparently anodising under these conditions has a similar effect to distilled water, fluoride and chloride solutions on the polished uranium surfaces.

Smoke patterns obtained by heating uranium to very high temperatures (electric arc) reveal that the highest oxide of uranium (U_3O_8) is the only oxide formed, which suggests that this oxide is the most stable of the uranium oxides, and which when once formed at a high temperature does not change its composition on cooling.

PART II.

181 The Surface Oxidation and Tarnishing of Tin.

Introduction.

If the surface of tin is exposed to air, a compact oxide film is formed. With the aid of electron diffraction, investigations have been made as to what effect 0.2% of indium has on the oxide layers formed on tin surfaces.

Results obtained by L. Kenworthy (Trans. Faraday Soc., 31, 1334, 1935) on the effect of impurities on the corrosion of tin indicate that the purer the tin the greater is its corrosion resistance.

Previous workers have shown by electron diffraction, e.g. H.K. Acharya (Ph.D. Thesis, 1948) that the oxide layer formed on tin surfaces at room temperature is amorphous, but on heating to temperatures above 100°C., this amorphous layer will be transformed into the monoxide, and at higher temperatures still it will finally convert into the dioxide.

The results of the present experiments show that the oxide layers formed by exposure to air at room temperature or by anodising on both pure tin and tin containing a small percentage of indium as an impurity were amorphous, and were formed immediately the metal surface comes in contact with the air. When first formed this film is extremely thin, but on prolonged exposure to air, electron diffraction patterns reveal that the film grows to the order of 2,000 Å. in thickness.

The growth of these amorphous films can be greatly accelerated by anodising the surface, but films produced in this way grow unevenly and are slightly porous.

A considerable amount of work has been done on the effect of heating thin oxide films of tin. In 1932, Bragg and Darbyshire found that tin foil heated in a gas flame yielded electron diffraction patterns characteristic of tetragonal stannic oxide. It was noted by Steinheil in 1934 that heated tin foil generally yielded electron diffraction patterns of stannic oxide, but in some cases diffraction patterns of stannous oxide were obtained. Jenkins (1935) prepared films of tin oxides and found that films formed just above the melting point of tin consisted almost entirely of stannous oxide, the crystals being partially oriented with their [001] faces in the plane of the film. He also found that if these films were formed at a higher temperature, they were composed of the dioxide (SnO_2).

Results given below reveal that the thin films formed by heating tin foil can be either amorphous or crystalline, and stannous or stannic oxide, depending on the temperature to which the tin foil is heated.

The whole assembly heated by a temperature of 350°C .

While the heating of the block was in progress, the

Experimental.

Preparation of Single Crystal Specimens of Tin and Tin-Indium Alloy.

The specimens of pure tin and 0.2% tin-indium alloy used in these experiments were supplied by the Tin Research Institute. Two methods were used for growing single crystals from these specimens, both methods being modifications of the method used in this laboratory for growing single crystals of light metals.

Method A.

Consisted of casting the specimens from a melt onto a clean glass slide, held at a temperature about 10° higher than the melting point of tin in an insulated brass casting block.

The glass slide was thoroughly cleaned first with benzene to remove any grease and then with sulphuric-chromic acid cleaning solution and finally washed with distilled water. The glass was then dried with a filter paper and placed on an insulated brass block. Another insulated brass block containing a cavity was then placed over the glass slide, and the whole assembly heated to a temperature of 250°C.

While the heating of the block was in progress, the specimens of tin and tin-indium were melted in cleaned

porcelain crucibles to 250°C. When both were in equilibrium at this temperature, the upper brass block was quickly removed and the specimens were poured onto the glass slab, making sure that the oxide scum on top of the metal in the crucibles was retained therein. The upper brass block was then replaced and the whole assembly allowed to cool at a rate of about one degree per minute.

After cooling the metal surfaces, in contact with the glass, had a very smooth and mirror-like appearance, while the sections of the specimens exposed to the atmosphere had tarnished considerably, and gave rise to red, green, and blue interference colours.

Method B.

This method is similar to method A except the process was carried out in an atmosphere of hydrogen, and the specimens were cast in glass moulds.

Two glass rings were cut and ground $3/8$ " dia. and $1/2$ " high and together with the glass slab were cleaned as described above. This assembly was placed in a sealed electrically heated furnace, containing an inlet and an outlet tube and also a thermocouple.

The furnace was heated to a temperature of 250°C. and the molten specimens cast into the glass moulds. The furnace

was then sealed and hydrogen passed through and burnt at the outlet, so as to ensure that air was excluded during cooling. Cooling was timed so that the furnace would take approximately 24 hours to cool down to room temperature.

Specimens obtained by this second method had a very bright appearance and the surfaces were free from interference colours. However, electron diffraction patterns revealed that the specimens were not wholly single crystals but that there was a small percentage of polycrystalline tin present as well.

Atmospheric Oxidation of Single Crystals of Tin and Tin-Indium Alloy.

After the initial electron diffraction patterns were obtained from the cleaned surfaces of the cast specimens, the specimens were exposed to dry air for similar periods of time varying from one hour to 24 hours. At the different time intervals the specimens were transferred to the diffraction camera and their electron diffraction patterns recorded. In this way a comparison of the rates of corrosion between pure tin and tin-indium was obtained.

The above experiments were repeated on the electropolished surfaces of the specimens so that a similar comparison could be obtained.

Surface Preparation of the Single Crystals by
Electropolishing.

The flat surfaces obtained by casting the specimens on a glass slab were electropolished in a perchloric acid-acetic acid solution of the following composition:

Perchloric Acid	100 Mls.
Acetic Acid	350 Mls.

The apparatus used for electropolishing is shown in Fig.2, a sheet of pure tin being used as the cathode. During the polishing it was found advisable to brush the surface being polished with a camel hair brush, otherwise parts of the surface tend to tarnish to a dark brown colour. The conditions for polishing were 0.10 A/cm^2 for 5 minutes, the temperature of the bath being kept constant at 15°C . by means of the glass cooling coil. If the temperature of the bath is allowed to rise above 20°C . there is an increased tendency for the surface to tarnish, and even with constant brushing it is difficult to keep the surface clean.

After polishing the specimens were thoroughly washed in absolute alcohol, then given a quick etch in 5% hydrochloric acid solution, washed again in absolute alcohol, and finally transferred to the diffraction camera while still wet with alcohol.

The Anodic Oxidation of Smooth Surfaces of Tin
and Tin-Indium Alloy.

Clean surfaces were obtained on the tin and tin-indium specimens by again electropolishing them so as to remove any corrosion products present, and then diffraction patterns were taken so that the state of the surface could be determined before anodising.

The anodising of these surfaces was effected in a 10% sulphuric acid bath at a potential which was varied from one to five volts. The time of anodising was also varied from five seconds to one minute, after which the specimens were washed with boiled distilled water and then with absolute alcohol before being placed in the diffraction camera.

Heating of Tin foil in Air at Different Temperatures.

Specimens of pure tin foil were supported on clean nickel gauze grids and heated at different temperatures by means of a bunsen flame. No accurate determination of the temperature to which the specimens were heated could be made by this method, but approximate values could be obtained by noting the appearance of the film as it formed.

The specimens were then transferred to the electron diffraction camera and transmission diffractions were recorded.

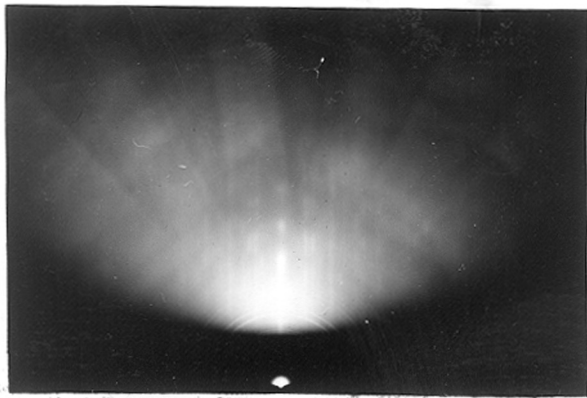


Fig. 16.

Results.Surface Structure of Cast Tin and Tin-Indium Single Crystals.

With both the cast single crystal specimens of tin and tin-indium the surface in contact with the glass during preparation was very smooth and mirror-like in appearance. Electron diffraction patterns obtained from these cast surfaces showed well defined Kikuchi lines, indicating that the single crystals had a high degree of perfection.

From analysis of these Kikuchi line patterns, similar to Fig.16, it was revealed that there was no specific orientation of the tin crystal faces in relation to the glass surface on which they were cast. Acharya (1948) in this laboratory observed that on crystallising tin from a melt the (100) face of the crystal was approximately parallel to the glass surface on which it was cast. This may be due to different cooling conditions of the furnace, bringing about in the former case solidification at the more rapidly cooled upper section of the melt, than at the glass-tin interface.

There was no indication from the patterns obtained that the 0.2% indium impurity had any effect on the crystallising habit of the tin.

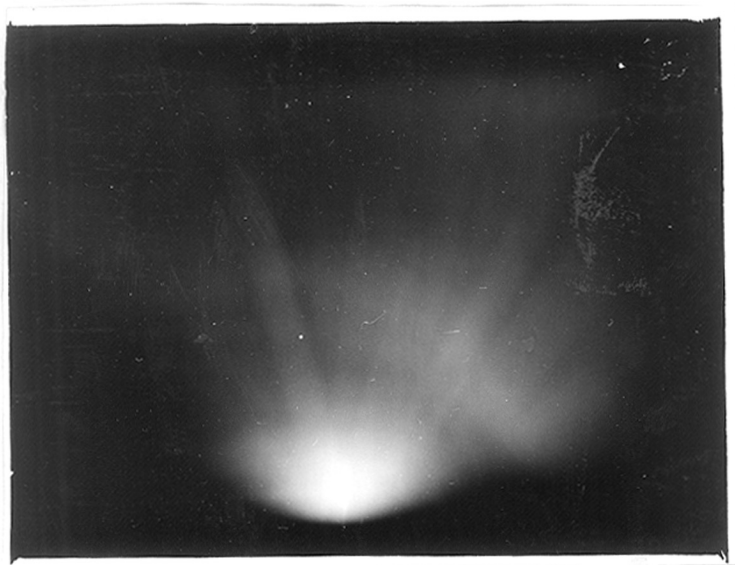


Fig. 17.

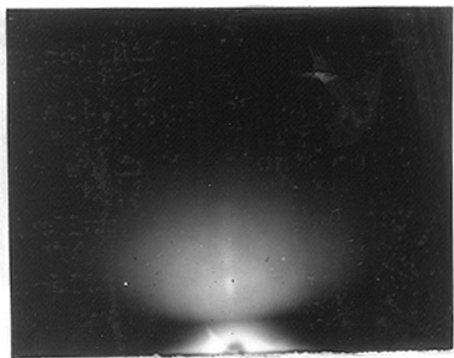


Fig. 18.

Atmospheric Oxidation of Tin and Tin-Indium Single Crystals
at Room Temperatures.

The specimens of both pure tin and tin + 0.2% indium were allowed to stand in laboratory air for periods of time from 10 minutes to 24 hours.

Electron diffraction patterns similar to Fig.17 reveal that after a short exposure to the atmosphere of approximately 10 minutes a diffuse halo appears round the central part of the patterns, partly obliterating the Kikuchi line patterns, and revealing that a very thin amorphous layer is formed on the surface of both the tin and tin-indium specimens.

After 24 hours exposure to the atmosphere, electron diffraction patterns obtained from the oxidised surfaces revealed that the initial amorphous layer had increased considerably in thickness, as is shown in Fig.18. Fig.18 shows several Laue zone spots in the plane of incidence of the electron beam, indicating that the amorphous layer formed after 24 hours exposure to air at room temperatures is still thin enough to allow an electron beam to pass through and give diffractions from the underlying metal.

This amorphous layer is thus apparently of the order of 50 A. thickness and displays first order interference colours.

From the patterns obtained, there was no evidence that the incorporating of 0.2% indium with tin has any effect on the rate with which tin surfaces will oxidise.



Fig. 19.

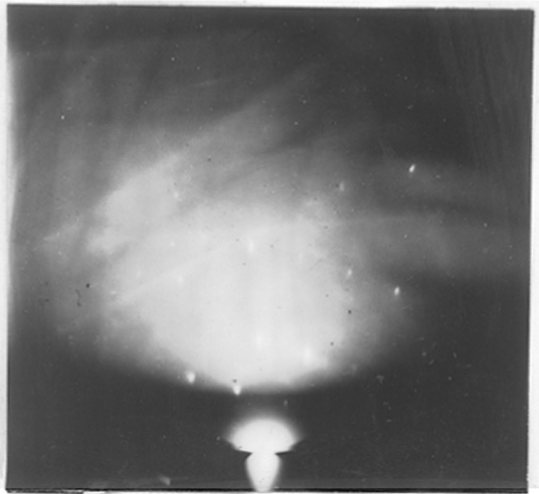


Fig. 20.

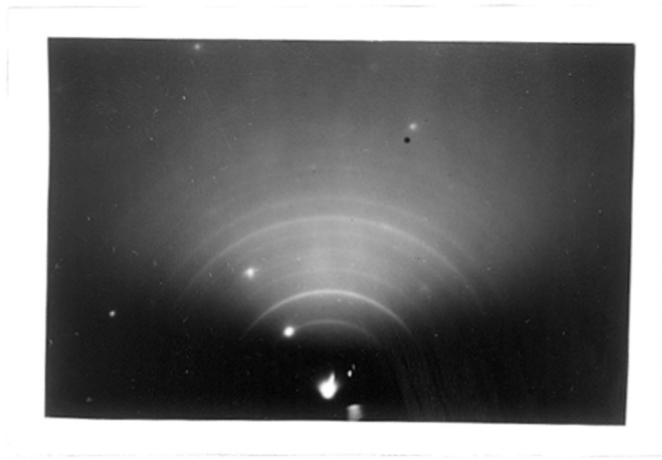


Fig. 21.

Table 15.

Intensity	Plane Spacings d in Å.	hkl	X-ray data for Sn c/a = 0.546	
			d in Å.	I/I ₀
VS	2.88	300	2.95	100
		310	2.81	80
		330	2.08	60
S	2.03	401	2.02	70
		420	1.98	40
M	1.65	003,412	1.60	20
M	1.49	441,213	1.49	60
M-	1.43	502,432	1.44	60
		541	1.34	20
M-	1.29	403	1.31	40
		532	1.29	20
S	1.16	004	1.21	60
M	1.05	314	1.10	40
		334	1.04	40
		424	1.03	20

The Structure of Electropolished Tin and Tin-Indium
Surfaces.

The electropolishing technique previously described using a perchloric acid-acetic acid electrolyte, produced extremely bright, smooth surfaces on both the tin and tin-indium specimens and good Kikuchi line patterns were obtained by electron diffraction.

Analysis of these patterns, similar to Figs.19 and 20, showed that the surfaces were free of oxide and that there was no specific orientation of the tin crystals in the specimens.

Diffraction patterns revealed that there was very little difference in the nature of surfaces prepared either by direct casting on smooth glass or by electropolishing mechanically prepared smooth surfaces.

An electron diffraction pattern, as shown by Fig.21, obtained by the diffraction of electrons from an electropolished surface of one of the tin specimens, revealed a ring pattern superimposed on a Laue spot pattern. Analysis of the ring pattern and comparison with A.S.T.]M. X-ray data is shown in Table 15.

The ring pattern corresponds to that of polycrystalline tin (tetragonal, $a = 5.819 \text{ \AA}$, $c = 3.175 \text{ \AA}$, $c/a = 0.546$), thus the surface was not a single crystal, but contained polycrystalline tin, the beam penetrating small peaks of

polycrystalline tin on the surface and also being diffracted from the single crystal.

Oxidation by Air of Electropolished Surfaces of Tin and Tin-Indium at Room Temperatures.

Electron diffraction patterns obtained from oxidised electropolished surfaces of both pure tin and tin containing 0.2% indium by air at room temperatures were similar to Figs. 17 and 18. Thus it was apparent that the oxidation process of electropolished surfaces was similar to that of cast surfaces.

The Anodic Oxidation of Single Crystal Surfaces of Tin and Tin-Indium.

On anodising the specimens of tin and tin-indium in a dilute sulphuric acid electrolyte the shiny surfaces lost their brilliance and showed second order red, blue and brown interference colours. Electron diffraction patterns similar to Figs. 17 and 18 shows these films produced by anodising to be amorphous.

The growth of these films on both the tin and tin-indium samples was extremely rapid, anodising for a period of about thirty seconds produced films sufficiently thick to prevent an electron beam from passing through and giving a

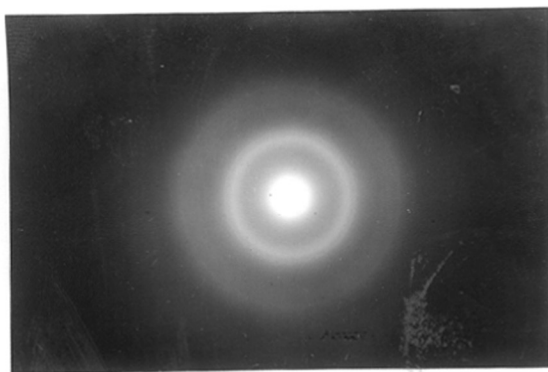
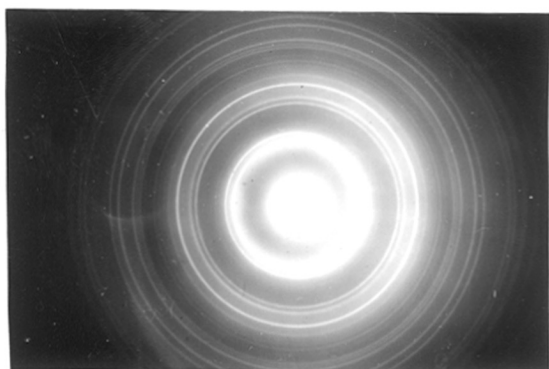
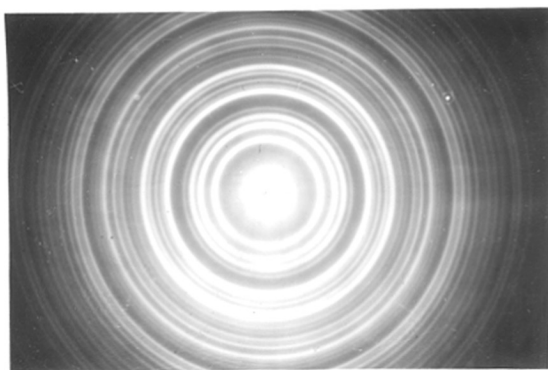


Fig. 22.



SnO

Fig. 23.



SnO₂

Fig. 24.

pattern of the underlying metal structure.

A slight waviness in the shadow edge of diffraction patterns obtained from thick surface films indicated that the surface layer had grown unevenly.

Effect of heating Tin foil in Air at Different Temperatures

Electron diffraction patterns obtained from tin foil which had been very gently heated to a temperature below about 130°C. revealed that an amorphous layer was obtained, which yielded a pattern consisting of diffused haloes as is shown in Fig.22. Several rings however are visible in the haloes, indicating that some crystallisation had taken place.

When tin foil was heated at a slightly higher temperature than that required to form an amorphous layer, sharp ring patterns similar to Fig.23 were obtained by electron diffraction. The net plane spacings of these rings were calculated, and on comparison with X-ray data, were found to agree with the net plane spacings of α . stannous oxide (tetragonal, $a = 3.209$, $c = 5.314$, $c/a = 1.65$), as is shown in Table 16. Table 16 shows that the values obtained correspond closely to those of α . SnO. There are several weak diffractions which cannot be indexed as SnO diffractions.

On strong heating of tin foil a tarnished film was

Table 16.

Intensity	Plane Spacings d in Å.	hkl	X-ray Data for SnO	
			d in Å.	I/I ₀
VS	2.88 ✓	101	2.97	100
VS	2.58 ✓	110	2.66	25
W	2.24 ✓	002	2.39	5
W-	1.94 ✓	-	-	-
VS	1.82 ✓	200	1.89	15
S	1.72 ✓	112	1.79	30
VVS	1.54 ✓	003,211	1.59	40
M-	1.43 ✓	103,202	1.48	15
W-	1.36 ✓	-	-	-
W-	1.33 ✓	-	-	-
M	1.28 ✓	220	1.33	5
W	1.23 ✓	-	-	-
M	1.17 ✓	321	1.22	5
M	1.15 ✓	400	1.19	5
M-	1.12 ✓	222	1.17	10
M-	1.03 ✓	411	1.07	5
S-	0.98 ✓	-	-	-
W	0.95 ✓	-	-	-

Table 17.

Intensity	Plane Spacings d in Å.	hkl	X-ray Data for SnO ₂ Tetragonal c/a = 0.6727	
			d in Å.	I/I ₀
VVS	3.32	110	3.35	80
VVS	2.59	101	2.64	80
VS(diff)	2.28	200	2.37	50
		111	2.31	20
S	2.08	-	-	-
VVS	1.73	211	1.76	100
M	1.65	220	1.67	60
S-	1.56	002	1.59	50
S-	1.47	310	1.50	60
-	-	112	1.44	60
S	1.39	301	1.41	60
M	1.29	202	1.32	50
W+	1.24	-	-	-
S-	1.19	321	1.21	60
-	-	400	1.18	40
S-	1.13	222	1.15	60
-	-	330	1.12	50
S	1.06	312	1.09	60
		411	1.08	60
M	1.04	420	1.06	50
M	1.01	103	1.04	50
W	0.99	-	-	-

obtained, which yielded diffraction patterns similar to that shown in Fig. 24. The ring radii of these patterns were measured and the net-plane spacings calculated, and were found to agree with the X-ray data for SnO_2 (tetragonal, $a = 4.735$, $c = 3.185$, $c/a = 0.673$), with several additional rings which can be indexed as SnO diffractions.

The values of the net plane spacings are given in Table 17.

Figs. 22, 23 and 24 reveal that the oxide layer formed by tin is dependent on the temperature at which it is formed, firstly producing an amorphous layer at temperatures below about 130°C ., which changes to alpha stannous oxide at slightly higher temperatures and finally yielding stannic oxide at high temperatures.

Discussion.

The two methods employed for growing single crystals of tin (pure and impure) produced specimens which yielded Kikuchi line patterns which showed that the crystals so produced had a high degree of perfection. The cast surfaces of these specimens were extremely bright and smooth, and results showed that these surfaces were equally suitable for electron diffraction studies as were surfaces prepared by electro-polishing mechanically smoothed surfaces.

The atmospheric oxidation of the surfaces of single crystals of tin and tin containing 0.2% indium as an impurity at room temperatures, produced an amorphous layer in all cases which was extremely thin when first formed, and grew evenly to a thickness of several hundred angstroms after 24 hours exposure.

The rate of growth of this amorphous layer was approximately the same on pure tin as it was on tin containing 0.2% indium, so it appears that this small percentage of indium has very little, if any, effect on the surface oxidation of tin.

Results obtained by L. Kenworthy (Trans. Faraday Soc., 31, 1334, 1935) on the oxidation of pure tin and tin containing 0.2% copper or 2.2% antimony, would seem to indicate, however, that refinement of the metal increases its corrosion resistance. His results also showed that the surface of tin tarnishes at a slow but uniform rate, any film present is not of a completely protective nature.

The anodic oxidation of polished and cast surfaces of the above specimens produced surface films which were amorphous in nature. However, the rate of growth of films produced in this way was far more rapid than that of films formed by atmospheric oxidation at room temperatures. Anodising for a few seconds at low potentials produced films

of similar thickness to those produced by atmospheric oxidation in 24 hours. Also the surface of the film caused by anodising was more uneven, as was shown by the waviness of the shadow edge in diffraction patterns and the film appeared to be less cohesive than atmospherically formed films.

The type of films formed on tin at various temperatures was determined by heating very thin tin foil at different temperatures. These experiments showed that an amorphous oxide formed up to temperatures of approximately 130°C., while at higher temperatures the layer crystallised and yielded electron diffraction patterns of polycrystalline alpha stannous oxide (tetragonal, $a = 3.209$, $c = 5.314$, $c/a = 1.65$), and finally at temperatures about the melting point of tin, the dioxide (SnO_2 , tetragonal, $a = 4.735$, $c = 3.185$, $c/a = 0.673$) was formed.

PART III.

The Surface Oxidation of Zirconium.

Introduction.

Zirconium is a highly reactive metal and has a great affinity for both oxygen and nitrogen at temperatures above 400-450°C. (Miller, 1951). When heated to above 865°C. (W.G.Burgers and J.J.A.Ploos van Amstel) zirconium changes from an α -hexagonal into a β -cubic structure. This transition point is raised to as high as 1550°C. by the homogeneous absorption of up to 10 atoms percent of oxygen or nitrogen.

Because of the above facts, large single crystals of zirconium have not yet been prepared, even by the stress-anneal method and so in this present work, only the oxidation of polycrystalline zirconium surfaces could be investigated.

The oxidation products of zirconium have been studied, both as surface films on the metal and in a powder state detached from the metal.

Cohn (1935) lists the forms of pure zirconium dioxide as follows:-

Modification	Crystal System	Unit Cell.
C. Baddeleyite	Monoclinic	$a = 5.21, b = 5.26 \text{ \AA.},$ $c = 5.37 \text{ \AA.}, \quad = 80^{\circ}32'$
B.	Tetragonal	$a = 5.07 \text{ \AA.}, c = 5.16 \text{ \AA.}$
A ₂ /A ₁ glassy	Trigonal	$a = 3.60 \text{ \AA.} \quad c/a = 1.633.$

According to Cohn the monoclinic form is stable between room temperature and 100°C. and is obtained by slowly cooling pure zirconium in an oxidising atmosphere from temperatures between 600°C. and 1900°C. The tetragonal form appears at 1000°C. and is reported to be preserved at room temperatures after extremely rapid quenching. A_2 is formed by heating pure zirconia for a long time at 1900°C. or above. The transition of the monoclinic form is irreversible. A_2 changes to A_1 , another trigonal form, reversibly at 625°C.

Clark (1937) working with the oxy-salts and hydroxides of zirconium obtained X-ray diffraction patterns of zirconium dioxide after these salts had been heated to above 500°C. At this temperature the tetragonal form of ZrO_2 was formed which was converted into the monoclinic modification at about 650°C. X-ray diffraction also revealed that the zirconium dioxide had an extremely small crystal size.

Hickman (1948) reports the dioxide of zirconium as existing in at least three modifications: monoclinic, cubic, and tetragonal. The A.S.T.M. X-ray card index (1950), apparently relying on the above authors, lists zirconium dioxide in the following modifications:-

<u>Crystal System.</u>	<u>Unit Cell.</u>
Monoclinic.	$a = 5.21 \text{ \AA.}, b = 5.26 \text{ \AA.}, c = 5.375 \text{ \AA.},$ $= 99^{\circ}28'.$
Monoclinic.	$a = 5.17 \text{ \AA.}, b = 5.26 \text{ \AA.}, c = 5.30 \text{ \AA.},$ $= 80^{\circ}8'.$
Cubic.	$a = 5.103 \text{ \AA.}$
Tetragonal.	$a = 5.07 \text{ \AA.}, c = 5.16 \text{ \AA.}, c/a = 1.018.$

In this present work, investigations have been made to determine what oxide is initially formed on zirconium, and the effects of prolonged oxidation at room temperatures and temperatures to 700°C. on the surface layer.

The effect of anodising zirconium surfaces in various electrolytes has also been studied.

Experimental.

Preparation of Zirconium Surfaces.

As it was not possible to obtain single crystals of zirconium, specimens of polycrystalline zirconium were cut from a $3/8$ inch diameter zirconium rod, obtained from Munex Ltd., and analysed as chemically pure, except for some half percent of hafnium, which is always associated with zirconium. The six specimens so obtained were abraded with various grades of emery paper to develop a flat surface. In all cases, benzene was used as a lubricant. The specimens were then washed with distilled water and prepared by the following methods:-

Mechanically Polished Surfaces.

After being abraded to 000 emery the surfaces were polished with alumina powder on a polishing wheel. After polishing, the specimens were washed thoroughly with distilled water to remove any adhering alumina powder and then stored under benzene ready for use.

Various grades of diamond dust were also tried as polishing agents, but it was found by electron diffraction examination that the surfaces became impregnated with diamond dust, which could not be removed from the surface by rubbing

it with a filter paper soaked in benzene.

Electropolished Surfaces.

Various electrolytes and polishing techniques have been tried, but so far none of these have proved successful. A.E.R.E., Harwell have developed a method for electropolishing zirconium (private communication) but as yet it is not known whether this method will be suitable for preparing specimens to be used in electron diffraction experiments.

Etched Surfaces of Zirconium.

Due to the corrosion resistant properties of zirconium, the use of most of the normal etching agents was impracticable. Mechanically polished zirconium surfaces were etched in 10% hydrofluoric acid at room temperatures (time: 10 secs.). This reagent gave suitably etched surfaces for examination by electron diffraction. After etching, the specimens were rapidly washed with distilled water and transferred to the diffraction camera under benzene.

Anodic Oxidation of Zirconium.

Fresh surfaces of zirconium were prepared by mechanical polishing with alumina, and then anodised in sulphuric acid (10%), boric acid or ammonium borate electrolytes, at

potentials varying from 5 volts to 80 volts, each specimen being anodised for a period of two minutes. The anodised surfaces displayed interference colours, the colour being dependent on the anodising voltage. The electrical properties of films formed by anodising zirconium have been investigated at A.E.R.E., Harwell (private communication). Standard colour charts have been obtained from anodising at potentials from 5 volts to 200 volts at four volt intervals. These charts show that the anodised surface of zirconium changes colour from brown at 5 volts, through purple, blue, white, yellow, salmon, red, purple to blue at 80 volts. On anodising at higher voltages, these colours are repeated in roughly the same order.

The thickness of the anodised films, formed after two minutes anodising in any of the above electrolytes, at different potentials has also been measured at A.E.R.E., Harwell (private communication), by both optical and capacity measurements, and results obtained show that the film thickness increases at a rate of 20 angstroms per volt.

Dry Oxidation at Room Temperatures.

Both mechanically polished and etched surfaces of zirconium were exposed to air (silica-gel dried) for times varying from a few seconds to 24 hours. After each exposure,

the surface was washed in benzene and then placed in the diffraction camera.

Thermal Oxidation of Mechanically Polished Zirconium Surfaces.

The specimens of zirconium were polished as above and then oxidised in dry air at room temperatures for a short time so as to form an oxide layer. The specimens were then heated to temperatures of 300, 400, 500, 600, and 700°C. respectively in a vacuum of 10^{-5} mm. of mercury for 15 minutes. After heating to the desired temperature, they were cooled to room temperature while still under vacuum, and then transferred to the diffraction camera for investigation.

The Oxidation of Zirconium in an Electric Arc.

Smoke films of zirconium oxide were formed on collodion films supported on cleaned nickel gauze by collecting the "oxide smoke" from an electric arc burning between two spectroscopically pure rods of zirconium, in a similar manner to that described in Part I for uranium.

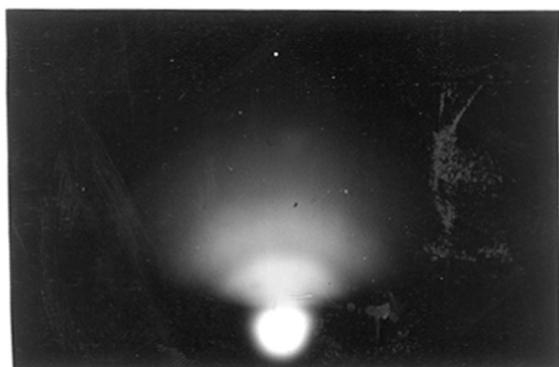


Fig. 25.

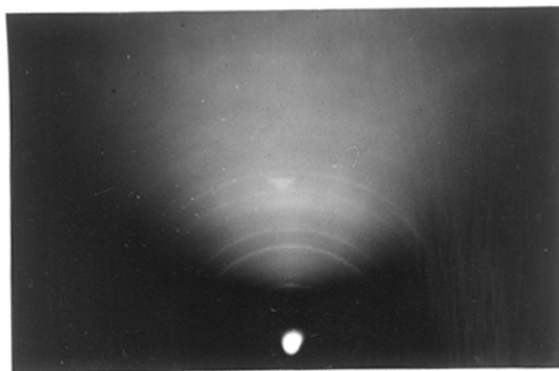


Fig. 26.

Results.

The Structure of the Initial Film formed on Mechanically Polished Zirconium Surfaces.

The surfaces of zirconium polished mechanically in the way described above, yielded the patterns shown in Figs. 25 and 26. The diffuse haloes in Fig. 25 indicate that the surface layer is amorphous. There are, however, also signs of a micro-crystalline structure being present, as several diffuse bands appear in the haloes. The net-plane spacings of these bands agree reasonably well with the net-plane spacings of the 111, 200, and 220, 311, 222 planes of a zirconium dioxide of cubic structure ($a = 5.1 \text{ \AA.}$).

On scanning the surface with the electron beam, there was a spasmodic appearance of sharp ring patterns as shown in Fig. 26. This ring pattern can be indexed as polycrystalline zirconium dioxide (cubic, $a = 5.103 \text{ \AA.}$), Table 18. Powdered graphite was blown onto the surfaces of several of these specimens so that the diffractions yielded by the graphite could be used as standard for lattice dimension comparison purposes. It was thus shown that the net-plane spacings of the zirconium dioxide lattice (assuming $a = 5.1 \text{ \AA.}$) lay within the limits of variation of λL . Thus Figs. 25 and 26 suggest that the initial surface film is

Table 18.

Intensity	Plane Spacing d in A*	hkl	X-Ray Data ZrO ₂ , Cubic, a = 5.103 A	
			d in A.	I/I ₀
S.	2.94	111	2.96	100
M.	2.55	200	2.56	24
S.	1.79	220	1.81	80
S-	1.52	311	1.54	60
W.	1.46	222	1.48	10
W.	1.23	400	1.28	12
M.	1.13	331	1.17	20
M.	1.01	422	1.04	16

* Relative d₁₁₀ of graphite taken as 1.230 A.

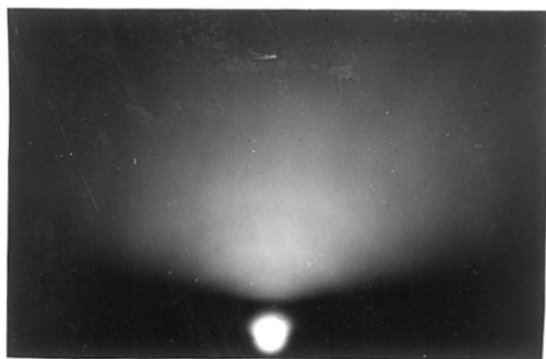


Fig. 27.

mainly amorphous but also contains crystallites of the cubic modification of ZrO_2 .

Etched Mechanically Polished Surfaces.

The zirconium specimens were etched in 10% hydrofluoric acid from 10-20 seconds to remove the distorted surface layers caused by mechanical polishing. Surfaces so treated were etched uniformly to a not too rough surface, but in places were slightly pitted.

Fig.27 shows the electron diffraction patterns obtained from these etched surfaces. These patterns contained a number of ring diffractions which on analysis were shown to be due to zirconium (hexagonal, $a = 3.23 \text{ \AA}$., $c = 5.14 \text{ \AA}$., $c/a = 1.59$). The high intensity of the general background scattering suggests that the surface was covered with a thin amorphous layer, thin enough however to allow an electron beam to pass through and give diffractions of the underlying metal.

The Anodic Oxidation of Mechanically Polished Zirconium Surfaces.

All specimens anodised for a period of two minutes displayed interference colours, which were dependent on the anodising voltage. After about half a minute the anodising

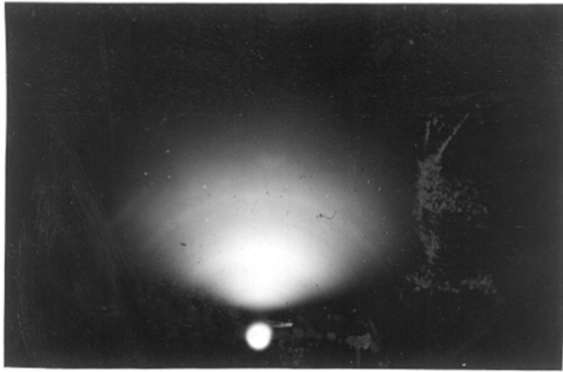


Fig. 28.

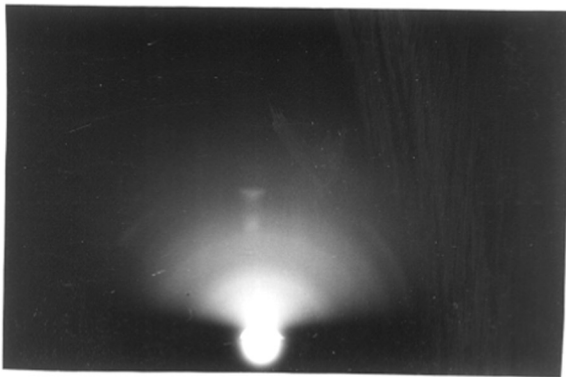


Fig. 29.

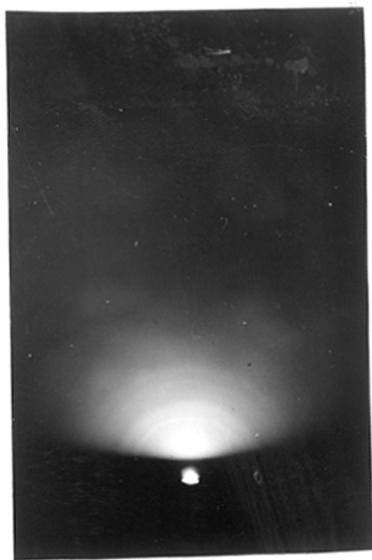


Fig. 30.

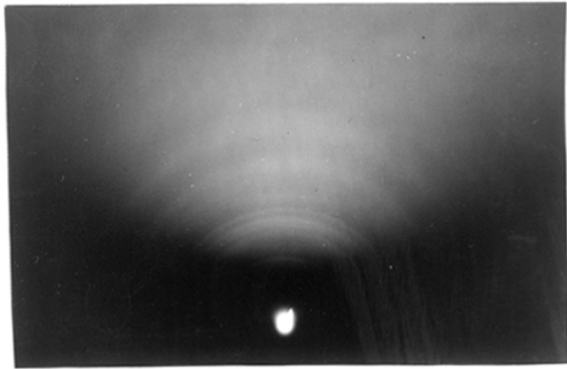


Fig. 31.

voltage dropped rapidly to almost zero, showing that the films so formed were insulating and of a definite thickness. The use of different electrolytes appeared to have no effect on the type of film formed as is shown by Figs. 28, 29, and 30.

The diffraction patterns obtained from mechanically polished zirconium anodised in ammonium borate is shown in Fig. 28, the patterns obtained from surfaces anodised in boric acid were similar to Fig. 29 and the high voltage diffractions (120 KV.) from polished zirconium surfaces anodised in 10% sulphuric acid were similar to Fig. 30. The net plane spacings of ring diffractions shown by Figs. 28-30 correspond to X-ray data for the cubic modification of ZrO_2 ($a = 5.10 \text{ \AA}$).

Analysis of these diffraction patterns revealed that the surface layer formed by anodising mechanically polished zirconium in either ammonium borate, boric acid or sulphuric acid consisted of micro-crystalline zirconium dioxide (cubic, $a = 5.103 \text{ \AA}$), apparently with some amorphous material present.

Dry Oxidation of Mechanically Polished Zirconium at Room Temperatures.

Mechanically polished zirconium surfaces were exposed to air for times varying from one minute to 24 hours. Electron diffraction patterns showed that after the initial film had formed no noticeable change took place after further

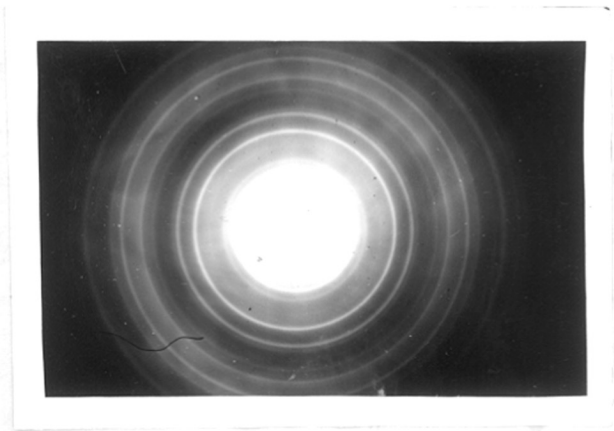


Fig. 32.

exposure to air at room temperatures.

The oxide layer on zirconium apparently forms immediately the metal is exposed to the atmosphere and grows rapidly until a highly resistant layer is formed of a specific thickness.

The Thermal Oxidation of Mechanically Polished Zirconium Surfaces.

The surface layers on zirconium after being heated to temperatures between 300°C. and 700°C. displayed interference colours, varying from a yellowish tinge to brown, which indicated that the surface layer had increased in thickness.

Electron diffraction patterns obtained from surfaces heated between 300°C. and 600°C. showed the film to be amorphous. Patterns obtained from films heated to 600°C. showed evidence of crystallisation on a micro scale. Films heated to 700°C. gave ring diffractions with much background similar to Fig.31. These patterns did not correspond to the cubic, tetragonal or monoclinic forms of ZrO_2 or mixtures of these oxides. The material has not yet been identified.

The Thermal Oxidation of Pure Zirconium in an Electric Arc.

Zirconium oxide smoke obtained by burning pure zirconium in an electric arc in air gave transmission electron diffractions as in Fig.32. Analysis of these ring patterns by comparing

the net plane spacings of rings obtained with A.S.T.M. X-ray diffraction data (Table 19) showed that the oxide formed by zirconium at high temperatures near an electric arc to be the cubic modification ($a = 5.103 \text{ \AA.}$) of zirconium dioxide.

Table 19.

Intensity	Plane Spacings	hkl	X-Ray Data ZrO ₂ , Cubic, a = 5.103 Å	
	d in Å.		d in Å.	I/I ₀
V.S.	3.08	111	2.96	100
M.	2.68	200	2.56	24
W.	2.19	-	-	-
V.S.	1.88	220	1.81	80
S.	1.60	311	1.54	60
W.	1.52	222	1.48	10
W.	1.42	-	-	-
M-	1.32	400	1.28	12
W-	1.26	-	-	-
M+	1.21	331	1.17	20
M.	1.08	422	1.04	16
M-	1.01	331, 511	0.98	14
W-	0.93	400	0.90	5
S	0.89	531		
M	0.83	442, 600		
M	0.80	620		

Discussion.

The object of the above experiments was to determine:-

- a. The structure and nature of the initial films formed in air at room temperatures;
- b. The effect of anodic oxidation processes;
- c. The effect of thermal oxidation on these films.

Electron diffraction patterns obtained from mechanically polished surfaces of zirconium reveal that the initial film formed is amorphous, but often contains crystallites of the cubic modification of zirconium dioxide. It appears that this initial film forms immediately after exposure of the cleaned zirconium surface to the atmosphere, and that it grows rapidly to a specific thickness and in so doing forms an impervious layer on the zirconium, making the latter very resistant to further oxidation or chemical attack. Thus no additional changes were noted in the growth or structure of this surface layer after 24 hours exposure to dry air at room temperatures.

Even after etching the polished zirconium surface with hydrofluoric acid, and the immediate transfer of the specimen immersed in benzene to the diffraction camera, diffraction patterns indicating the presence of an amorphous layer were obtained.

The present investigations of the surface layers formed

on polycrystalline zirconium by anodising in various electrolytes have led to the conclusion that such surface layers are crystalline zirconium dioxide present as the cubic modification though apparently still containing some amorphous oxide.

Experiments carried out at A.E.R.E., Harwell on the refractive index of the surface films on anodised zirconium suggest that the refractive index of these films is approximately the same as the refractive index of the monoclinic modification of zirconium dioxide (private communication). This discrepancy in results may be due to the fact that electron diffraction patterns reveal the nature and structure of only the surface regions to a depth of a few angstroms and do not give a general picture of the whole film. The matter is now being subjected to the test of further experiment.

Since the anodised films display interference colours, the nature of which depend only on the anodising voltage, it would appear that they grow to a voltage-limited thickness which is a function of the insulating properties of these films

An experiment carried out by impregnating the initial surface layer with diamond dust and then anodising for two minutes, revealed that the diamond dust remained on the outward surface of the film, thus showing that the film had

grown from the metal/oxide interface and not from the oxide/air interface.

The thermal oxidation of zirconium up to temperatures of approximately 600°C. resulted in the formation of a thick amorphous films, which were extremely hard and could only be removed from the metal by vigorous abrasion with emery.

The diffraction pattern from crystalline surface layers formed on zirconium heated at 700°C. did not correspond to the cubic ZrO_2 and it was not identifiable as either tetragonal or monoclinic ZrO_2 , although Clark (1937) obtained tetragonal ZrO_2 from $ZrOCl_2 \cdot H_2O$ heated at 500°C. and this converted to monoclinic ZrO_2 above 650°C.

Further work is being carried out on the thermal oxidation of zirconium surfaces to investigate whether any further changes occur on prolonged heating.

General Summary.

The oxidation of polished surfaces of uranium and certain other metals has been investigated.

The present experiments show that the surface oxide layers formed on uranium by air, distilled water, fluoride and chloride solutions to be polycrystalline, and having a rapid rate of growth. The composition of these films varied, being either the dioxide of uranium (UO_2) or a mixture of the higher oxides (U_3O_8 with possibly U_2O_5). It has been established by electron diffraction that the dioxide of uranium is formed when uranium is polished under benzene, or when oxidised by aerated water, dilute oxidising solutions or anodised at very low current densities. Surface layers composed of the higher oxides of uranium are produced when uranium is electropolished, mechanically polished in air, or when anodised at high current densities. The oxidation product resulting from burning uranium in an electric arc was found to be almost wholly U_3O_8 . The exact nature of the higher oxide films has not been determined, as the available data are inconclusive, but it is probable that their composition is somewhere between the U_2O_5 and U_3O_8 phases.

The oxide layers formed on tin single crystals by air at room temperatures were found to be amorphous, and there

was no detectable change in the rate of formation when tin was alloyed with 0.2% indium. Anodising also caused the formation of amorphous films, but these were less cohesive than atmospherically formed films. Thermal oxidation of tin foil showed that amorphous layers were stable to approximately 130°C., converting to SnO at slightly higher temperatures and finally to SnO₂ at temperatures about the melting point of tin.

Diffractions from air-oxidised zirconium surfaces showed the films to be amorphous and which grew rapidly to a specific thickness, and that these films often contained crystallites of cubic ZrO₂. These films remained amorphous after being heated to about 600°C. for 15 minutes, but crystallised when heated to higher temperatures. These crystalline films were not identifiable as either the cubic, tetragonal or monoclinic modifications of ZrO₂ as quoted in the literature. High temperature (electric arc) oxidation of zirconium resulted in the formation of cubic ZrO₂. Anodised surfaces of zirconium consisted of the cubic modification of ZrO₂, though they apparently still contained some amorphous oxide.

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