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ORIENTED DIOXIDE FILMS ON URANIUM

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This phenomenological report deals with the formation of oriented layers of an oxide which form during oxidation without any evident relationship to the parent and underlying metal. It is offered without explanation or proposed mechanism.

In general, orientation of deposited films occurs when the supersaturation, i.e., the driving force, is too small to permit easy and frequent homogeneous nucleation. Then the films take on a growth habit characteristic either of the substrate or of their own dislocations. If the supersaturation in the vicinity of the interface is high enough, homogeneous or self-nucleation occurs and randomly oriented films occur. A common technique for obtaining oriented metal films by vapor deposition is to add an inert gas to the vapor and thus effectively lower the supersaturation at the interface by reducing the rate of arrival of vapor. Similarly, the technique for discouraging dendritic (oriented) growth during electrodeposition of a metal is to establish a large reservoir of the cation in the vicinity of the interface as a complex ion and by using high current densities; that is, by increasing the local supersaturation, to stimulate nucleation.

It is, therefore, somewhat surprising that the present phenomenon occurs at high gas pressures and less effectively at low.

Specifically, the reaction studied is the formation of uranium dioxide at several hundred degrees centigrade by relatively low pressures of water vapor. Conventional X-ray techniques were used principally for studying this reaction and examination was done at room temperatures. Stereographic projections

establish that the texture of the oriented oxide is almost exclusively the following: The (110) planes of the fluorite lattice of UO_2 are parallel to the metal surface. As background, it should be emphasized that an oriented oxide has not been seen on even single crystals of uranium except under the experimental conditions to be described below.

It was possible to form a different orientation of the UO_2 film in vacuum. Three different crystal structures of the metal could be obtained by changing the temperature but these apparently different substrates did not affect the resulting (100) fiber-like texture of the oxide. Starting with this (100) texture, the specimens formed the (110) texture when oxidized in water vapor. Therefore, the latter texture which we are reporting, does not grow in epitaxial relation to the dioxide already present.

Mehl and McCandless¹ have described the conditions under which oriented FeO films form on ferrite crystals and have indicated that the addition of hydrogen to the water vapor is necessary. Gulbransen² has confirmed this observation. This experience is reminiscent of the addition of argon or air during vapor deposition. Mehl and Lustman³ have observed that Cu_2O is oriented when formed on single crystal of copper.

One cannot establish that a stagnant layer of hydrogen formed by reaction of the water does not insulate the uranium-oxide surface from further rapid attack. In the few experiments where hydrogen was added to the water vapor, a significant effect on orientation was not noted. Further, the degree of orientation increases as the pressure of water vapor increases. Thus in these several features the phenomenon appears to be unlike the formation of oriented films previously reported.

Pertinent Crystal Structures

At 668°C with increasing temperature, the orthorhombic alpha phase⁴ changes to a complex tetragonal phase⁵. At 774°C, the latter changes to the body-centered cubic phase⁴ which is then stable up to the melting point⁶ at 1125°C. An excellent summary of the physical and chemical properties of uranium metal has been published recently⁶.

Uranium monoxide has the NaCl structure with $a_0 = 4.93 \text{ \AA}$ and the dioxide has the CaF_2 structure with $a_0 = 5.4581 \text{ \AA}$. Variation of these lattice parameters with composition has been summarized by Katz and Rabinowitch⁷.

Experimental Conditions

Both mechanically polished and electropolished as-rolled metal specimens were used. The specimens were outgassed at room temperature in the equipment for several hours in a 10^{-5} mm Hg or better vacuum. Then the silica furnace tube containing the specimen was heated to the test temperature which lay in the range of 300 to 1000°C. Droplets of water were introduced into the evacuated system through a Hg covered fine-pore sintered glass frit. The vapor pressure did not exceed the condensation pressure of water on the parts of the system which were at room temperature and thus we were limited to water pressures below about 25 mm Hg. The test pressure was determined after the water vapor had been expanded from the measuring part of the system into the hot furnace tube.

The texture of the cold-rolled metal was determined on a number of specimens prior to test. Since the several textures observed do not appear to influence the texture of the oxide, the detailed metal orientation will not be discussed here. The textures of the metal and of the oxide film were determined with the aid of a Schultz orientation goniometer⁸ adapted for use on a Norelco Type 7 (?) X-ray diffraction unit.

As a preliminary indication of the degree of orientation in the oxide the intensity of the (111), (200) and (220) lines of the oxide film were determined with a General Electric XRD-5 X-ray diffraction unit.

A precision and fineness of temperature control in the furnace was tolerated which was poorer than would be acceptable in a kinetic study. Inasmuch as the oxide shows the same orientation behavior at 300°C as it does at 600°C, the observed temperature variations of $\pm 10^\circ\text{C}$ probably do not have significant effect on the mechanism.

Experimental Results

The principal features of the results obtained to date are; (1) the effect of temperature and pressure, (2) effect of preformed monoxide and dioxide films and (3) a preliminary investigation of the rate law.

Most of the orientation will be indicated below in terms of the ratio of intensity of the (220) reflections of UO_2 to the intensity of the (111) reflections. A recent Bureau of Standards publication⁹ reports this ratio to be 0.49 for a random powder sample. When the (110) planes are perpendicular or parallel to the specimen surface, this ratio will be greater than 0.49. Values as high as 35 have been observed.

In order to establish what orientation was present and responsible for the high ratio, standard stereographic projections and pole figures were constructed and the identification of the texture was made from these using Wulff nets. The reader is referred to a standard text¹⁰ for details on understanding, constructing and interpreting pole figures.

Effect of Water Pressure and Temperature

There is apparently a minimum pressure of water vapor below which the

degree of orientation is small and above which the orientation is strongly developed. This critical pressure is poorly defined by our preliminary experiments. The results, which pertain to the formation of oxide in the alpha range of stability, are presented in Table I.

TABLE I

Orientation Ratio $I(220)/I(110)$ for Alpha Uranium

Temperature ($^{\circ}\text{C}$)	Pressure (mm)	Ratio
200	0.2	0.48
300	1.3	5.6
	4.2	4.7
	11.6	4.3, 5.1
400	vacuum	0.33
	0.8	5.6
	3.0	5.4
	17.0*	18.2, 35.0
	22.1*	2.4, 6.4
500	vacuum	0.31
	0.8	1.0
	5.0	12.2
	12.2	11.4
600	vacuum	0.5
	0.3	4.0
	6.2	5.2
	16.2	6.2

*Conducted with reoriented sections of rolled metal.

Whether the critical limit of water is affected by temperature cannot be established with these limited data. However, it is clear that high degrees of orientation are formed, as evidenced by this ratio of intensities, when the water pressure exceeds about 0.8 mm of mercury. Above this "critical pressure" the pressure dependence of orientation is very small.

Orientation of Dioxide Films Formed in Vacuo

One must digress from the main line of discussion to present some data which show that a (100) texture of the dioxide forms in good vacua. This behavior of uranium is important since films containing a different orientation can subsequently be oxidized in water vapor.

Experiments were carried out in vacua of 10^{-5} mm or better and at 400, 600 and 1000°C. In each of these cases, the principal orientation of the dioxide is with the (100) planes parallel to the specimen surface. However, uranium monoxide is also present in all such films formed in vacuum and what restraint it imposes on the texture of the dioxide is not known. The test data are summarized in Table II-A.

TABLE II-A

Relative Intensity of Oxide X-ray Reflection

Specimen Number	Temp. (°C)	Duration (hrs.)	Relative Intensity				Film Texture
			UO(111)	UO ₂ (111)	UO ₂ (200)	UO ₂ (220)	
2130	400	1-1/2 at 10^{-5}	20	25	160	25	(100) UO ₂
1952	600	1/2 at 10^{-6}	170	50	150	19	(100) UO ₂
1954	600	1/4 at 10^{-6}	70	20	75	7	(100) UO ₂
1802	1000	19 at 10^{-5}	210	32	50	19	(100) UO ₂

The amounts of monoxide in the films are indicated by the relative intensities of the (111) lines of the UO and UO₂, since the scattering factor for this plane of the monoxide is 91 per cent of that for the dioxide.

The observation that the (100) dioxide texture is formed in vacuo is better demonstrated by comparing the two orientation ratios computed from Table II-A. These ratios are given in Table II-B.

TABLE II-B
Comparative Orientation Ratios for Dioxide Films
Formed in Vacuum

Specimen Number	Ratio I(200)/I(111)	Ratio I(220)/I(111)
2130	6.4	1.0
1952	3.0	0.4
1954	3.75	0.3
1802	1.56	0.6

The relative ratio for intensities I(200) and I(111) in random powder samples of UO_2 is 0.48 as reported by the Bureau of Standards⁹. Although these orientation ratios by themselves do not demonstrate that the (100) texture is present and only that the films are oriented, subsequent work using stereographic projection have demonstrated that (100) texture is the correct orientation. This work will be discussed later.

Oxidation of Preformed Films

Starting with a film with the (100) texture, it was possible to oxidize the metal further in water vapor and develop the (110) orientation. Admittedly the texture was more incompletely formed when preformed layers were present.

As a basis for comparison, a metal coupon was oxidized in vacuum at 600°C and examined by X-ray diffraction to establish the nature of the film. A mechanically polished coupon of the same rolled metal stock was placed with the vacuum-treated specimen in the furnace at 600°C and oxidized for one hour at a water pressure of 0.3 mm. After X-ray examination, the two coupons were replaced in the furnace and oxidized at 600°C for one hour at a pressure of 6.2 mm. The data in Table III illustrate the observation that the (110) texture, characteristic of water vapor, will develop if sufficient water is present.

A similar experiment was conducted at 400°C and the pertinent data are recorded in Table IV.

TABLE III

Comparison of the Degree of Orientation Formed on Oxidation
of Preformed Film at 600°C

Specimen Number	Treatment Given	Orientation Ratio*	
		I(220)/I(200)**	I(220)/I(111)
1952	Vacuum, 1/2 hr	0.25, 0.09	1.6, 3.8
1952	Vacuum, 1 hr	0.25, 0.20	1.7, 3.3
1952a	Vacuum + 0.3 mm	0.23, 0.30	2.0, 1.5
1952b	Vacuum + 0.3 mm + 6.2 mm	0.45, 0.48	0.79, 0.83
1966	0.3 mm	0.74, 0.89	5.4, 4.0
1966a	0.3 mm + 6.2 mm	1.29, 1.86	4.0, 4.0

*Values obtained parallel to the rolling direction given first.

**Random orientation would give 1.02.

TABLE IV

Oxidation of Preformed Film
at 400°C

Specimen Number	Preliminary Treatment	Water Pressure (mm)	Orientation Ratios	
			I(200)/I(111)	I(220)/I(111)
2130	Electropolished	vacuum	6.4	1.0
2131	Vac. Annealed	28.4	0.3	1.0
2132	Electropolished	28.4	0.6	1.8

Tables III and IV indicate that the (110) texture is being produced at the expense of the (100) texture initially present.

The significance of these data is that they demonstrate that the development of the (110) texture is not dependent upon the randomness or the previous orientation of any film present. A logical explanation is that the

characteristic water texture is the result of competing growth rates.

The data do not need to be discussed here but there is evidence which suggests that oxidation occurs slower on the filmed specimens. This may be due to the presence of monoxide in the films formed in vacuum.

Orientation of the Underlying Metal

Even with a cubic metal three mutually perpendicular planes do not belong to the same crystallographic family, in general. The planes (100), (010) and (001) are perpendicular but in a more general case planes such as (211), (121) and (112) are not orthogonal to each other but do have common dihedral angles. In the case of an orthorhombic metal, such as uranium, a group of planes related by the permutation of their Miller indices, such as the (211) group just mentioned, the planes do not have common dihedral angles. In addition, two mutually perpendicular planes, if perpendicular to a third, such as say (101), will bear little relation to each other in terms of their Miller indices. Therefore, the significance of the experiments to be described below is that the (110) dioxide texture was formed on three mutually perpendicular surfaces of uranium, and that these surfaces did not have a common orientation which resulted from rolling the metal. Complex rolling textures are formed.

Study has established that the oriented oxide is formed with essentially no relation to the underlying metal. Transverse and longitudinal sections have been made of some previously studied metal specimens. These were bolted together to present different specimen surfaces and the oxide layers removed. When oxidized as before, highly oriented dioxide films are formed with the (110) plane of the oxide parallel to the specimen surface but without directionality

in that plane. The pertinent test data are presented in Table V.

TABLE V

Orientation Ratios and Test Conditions

Specimen Number	Preliminary Treatment	Water Pressure	Ratio of Intensities*	
			220/111	200/111
2130 (W-6-E)	Electropolished	vacuum	1.0	6.4
2131 (W-6-E)	Vac. anneal	28.4 mm	1.0	0.30
2132 (W-5-E)	Electropolish	28.4	1.80	0.59
2133 (W-4-I)	Electropolish	17.0	18.2	1.47
2134 (W-7-I)	Electropolish	17.0	35.0	2.70
2135 (W-4-E)	Front, electropolish	22.1	2.4	0.26
2135 (W-7-E)	Back, after mech. polish	22.1	2.7	0.27
2136 (W-7-E)	Electropolish	22.1	6.4	0.5

*For random samples 220/111 is 0.49 and 200/111 is 0.48.

In run 2130, the electropolished specimen was heated in vacuum at 400°C for 90 minutes prior to oxidizing it in water vapor. The orientation appears to be (100) texture, namely with (100) UO_2 planes parallel to the specimen surface. This orientation has been associated above with monoxide formation. The simultaneous oxidation of specimens 2130 and W-5-E for 5 minutes (to form 2131 and 2132) shows that in spite of a previous dioxide orientation, the (110) planar dioxide orientation is formed in water vapor and apparently at the expense of the (100) orientation.

Specimens 2133 and 2134 are transverse sections of rolled metal bolted together so that the rolling direction is perpendicular to the specimen surface. Hence the (010) alpha planes were parallel to the specimen surface in contrast to the (102) alpha planes in as-rolled sheet. Table V shows that very strong dioxide orientations resulted from heating at 400°C for 40 minutes.

Data for pole figures were obtained. In both specimens, the (110) dioxide planes are parallel to the specimen surface but there is no evidence of directional orientation within this plane.

In the last group of experiments described in Table V, longitudinal sections of rolled specimens were employed. Thus the (102) alpha planes were perpendicular to the specimen surface. Except for the back of specimen 2135, the (110) dioxide plane was found to be oriented parallel to the specimen surface. The back side of electropolished specimens develops a white film which apparently is dioxide with a slight preferred orientation. After oxidation in water vapor, the (110) orientation was poorly developed on the back side, but a loose rust-colored oxide was noticeable. After polishing off this rust-colored material, the (110) orientation was observable.

Pole Figures

Several pole figures have been constructed for specimens (mechanically polished) exposed in good vacuum at 600°C. Here the metal is oxidized by the leakage gas. Both dioxide and monoxide are present in the film.

TABLE VI

Analysis of the Pole
Figures for Vacuum Treated Specimens

Specimen Number	Duration Hours	Plane Investigated	Plane Parallel	Direction in Plane	Remarks
1954	0.25	(200) UO ₂	(100)	none	
		(111) UO ₂	(100)		slight orientation
		(112) α-U	(102)	[010]	also others
1953	16	(111) UO ₂	(111)	none	
1955	168	(111) UO ₂	not (110)	none	
		(111) UO	slight	-	
		(110) UO	slight	-	

Specimen (1954) was subsequently exposed to water vapor at 600°C. Pole figures constructed using the (200) and (110) planes of UO_2 show that the (110) planes are parallel to the specimen surface. In the directions [001] and [112] within the (110) plane of UO_2 , the intensities were slightly higher but one must conclude that there is essentially no directionality within the plane.

Specimens from several runs in water vapor at 600°C were also examined and their pole figures analyzed as shown below.

TABLE VII

Pole Figure Analysis of Specimens Oxidized in Water Vapor

Specimen Number	Pressure H_2O , mm	Temp. °C	Ratio 220/111	Plane Investigated	Plane Parallel	Direction in Plane
1970	16.2	600	6.2	(110) UO_2 (111) UO_2 (100) UO_2	(110) (110) (110)	none slight [001] mod. [001]
1966	0.3	600	5.4	(110) UO_2	(110)	none
1975	1.3	300	5.6	(100) UO_2	(110)	slight [001]

The evidence, although slight, suggests the preferred direction is [001] within the (110) plane of UO_2 .

Statistical analysis of the pole figure intensities has been made on two electropolished specimens mentioned previously. The orientation "index" as recommended by Professor Brick is the standard deviation of intensities above background divided by the gross average intensity above background. This index does not clearly differentiate between simple and complex textures, however where a simple texture is present, the index is

usually higher. The pertinent data are:

<u>Specimen</u>	<u>Treatment</u>	<u>Pressure</u>	<u>Index</u>	<u>Texture</u>
W-7-1	400°C, 0.25 hr	17 mm	0.386	(110) UO ₂
W-8-1	400°C, 3 hr	6.9 mm	0.190	(110) UO ₂

These orientation "indices" are comparable to those for rolled uranium. Although some directionality was present in the oxide it was not sufficiently strong to justify assigning a definite orientation relationship between the oxide and the metal.

Rate Law

Preliminary investigation of rate law has been made. The consumption of water vapor releases hydrogen at 400°C and these low pressures and thus the reaction can be followed manometrically. After a few minutes at 400°C, the reaction virtually ceases. The available data indicate that a logarithmic law is obeyed.

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