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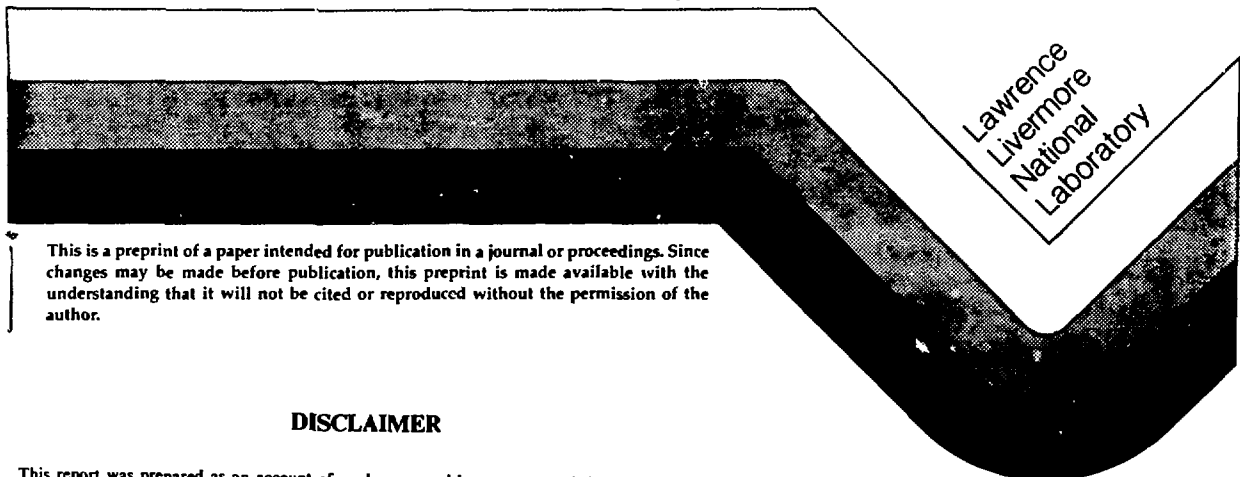
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THE REACTION OF WATER VAPOUR
WITH A CLEAN LIQUID URANIUM SURFACE

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THE REACTION OF WATER VAPOUR WITH
A CLEAN LIQUID URANIUM SURFACE

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Abstract

To study the reaction of water vapour with uranium, we have exposed clean liquid uranium surfaces to H_2O under UHV conditions. We have measured the surface concentration of oxygen as a function of exposure, and determined the maximum attainable surface oxygen concentration x_0^s as a function of temperature. We have used these measurements to estimate, close to the melting point, the solubility of oxygen ($x_0^b, < 10^{-4}$) and its surface segregation coefficient $\beta^s (> 10^3)$.

Introduction

The chemistry of and the interaction of gases with liquid metal surfaces is an important field of surface science. Metals with vapor pressures low enough to study their liquid surfaces under UHV conditions have melting point temperatures from room temperature to above $1000^\circ C$.

MASTER

Instrumentation and Techniques

High purity uranium metal (1.25 g) is melted in a small tungsten crucible under UHV conditions and the surface oxide formed by segregation of impurities to the surface is removed by filing and by polishing the surface with SiC polishing paper (1 micron) immediately before introducing the crucible into the system shown in Fig. 1. This system is held at 10^{-9} Pa by an ion pump, and kept at the desired H_2O exposure pressure by a turbomolecular pump. High purity H_2O is introduced through a leak valve from a gas inlet system evacuated by a small turbomolecular pump. The sample can be bombarded by an Argon ion gun (typically for a week to reach a surface impurity concentration of a few percent, with repeated temperature cycling between room temperature and $1200^\circ C$). Its composition is determined by a double pass Auger electron energy analyzer. Its physical appearance (i.e., uranium oxide island formation) is monitored through a microscope (10X) by a closed circuit television system, (Hitachi, charge coupled device) including a VCR. The recorded images are analyzed using a computer controlled image analyzer (Image Analyst Kevex/Kontron). The sample temperature is monitored with an optical pyrometer calibrated by using the known phase change temperatures of uranium.

Experimental Results and Discussion

a) Surface Composition as a Function of H_2O Exposure

Fig. 2 shows the increase in oxygen surface concentration and the oxide surface coverage as a function of exposure to H_2O at three temperatures. The surface oxygen concentration is measured by Auger spectroscopy and calculated using the peak heights of the uranium peak at

186 eV and the oxygen peak at 532 eV corrected with sensitivity factors.¹
 The experiments at 1150°C and 1175°C shown here were performed at a pressure of 2.66×10^{-5} Pa, the experiment at 1200°C at 6.65×10^{-5} Pa. The slope of the oxygen surface concentration is, within experimental error, the same at all temperatures, and is

$$S = \Delta(x_{\text{oxygen}}^S / x_{\text{uranium}}^S) / \Delta \text{ (Langmuir)}$$

$$= 1.6 \times 10^{-4} \text{ (1/Langmuir)}$$

where x_i^S is the concentration of substance i at the surface.

The surface oxygen concentration is at equilibrium with the bulk oxygen concentration during the exposure: The concentration stays constant if the H₂O pressure is suddenly removed, and within the range of pressures explored the slope is not dependent on the H₂O pressure at which the experiment is performed. It was not possible to decrease the surface concentration of oxygen to zero before the start of each experiment.

Surface Segregation

The surface enrichment factor β^S is defined in the monolayer model as

$$\beta^S = (x_O^S / x_U^S) / (x_O^b / x_U^b)$$

where x_i^b is the concentration of substance i in the bulk.

$$\ln \beta^S = -E/RT$$

where E is the free energy of segregation.

M. P. Seah² gives,

$$\ln \beta^S = \{24 (T_B^m - T_A^m) + 1.86 \Omega + M 4.64 \cdot 10^7 a_B (a_A - a_B)^2\} / RT + 1.29$$

$$\text{with } \Omega = H^m / Z X_A^b X_B^b$$

where H^m is the enthalpy of mixing, Z is the coordination number, T^m is the melting point in K, a_A is the atomic radius in nanometer of substance A and M is 1 if 1 of a_A is larger than a_B and zero otherwise. Taking the ionic radii for U (.1 nm) and O (.14 nm) as given by H. Blank³ and ignoring the enthalpy of mixing, which probably would be negative and hence decreasing the surface segregation, one finds a predicted surface enrichment coefficient for oxygen in liquid uranium at 1200°C of

$$\beta^S = 8 - 106$$

The surface concentration of oxygen should increase with exposure according to the relationship

$$d/dL (X_O^S / X_U^S) = \beta^S n_L A_O / N_U$$

with

- η_{ℓ} = sticking and oxygen incorporation coefficient of H_2O on liquid uranium
 A_0 = surface area, $.52 \text{ cm}^2$
 N_U = total number of uranium atoms in the crucible, $3.163 \cdot 10^{21}$
 L = Langmuir H_{2O} , $4.8 \cdot 10^{14} \text{ H}_2\text{O}/\text{cm}^2\text{sec}$

Therefore

$$\eta_{\ell} * \beta^S = 2.028 \cdot 10^3 \text{ using the slope } S, \text{ shown above to be } 1.6^{-4}/L \text{ at } 1200^{\circ}\text{C}.$$

Since the sticking coefficient η_{ℓ} is less than 1 (to my knowledge, it has not been measured), the surface segregation coefficient is larger than 10^3 , substantially larger than the calculated value.

Solubility of Oxygen

The surface concentration of oxygen as measured by Auger analysis does not increase linearly with exposure indefinitely, but reaches a maximum value which is dependent on temperature, see Table 1. Further exposure leads to the formation of oxide islands. The oxygen concentration in the liquid metal surface does not increase. See Fig 2.

Table 1

Run	T C	$\left(\frac{x_0^S}{x_U^S}\right) \text{ Max.}$ %	Max. Exposure L_{max}	Oxide Growth Rate %/L $1/2$	$\left(\frac{x_0^b}{x_U^S}\right) \text{ Max.}$
425	1200	13.5	844	1.7625	$6.9 \cdot 10^{-5}$
78	1175	8.0	500	1.11	$4.2 \cdot 10^{-5}$
712	1150	7.0	438	.525	$3.6 \cdot 10^{-5}$

The concentration of oxygen in the bulk is given by

$$(x_O^b/x_U^b) = \eta_L L A / N_U$$

The maximum bulk oxygen concentrations above which an oxide island appears on the surface can, therefore, be calculated by setting the sticking coefficient equal to one. They are shown in table I, and are approximately one order of magnitude lower than the solubilities reported in the literature.^[5] A more realistic sticking coefficient (.06)^[6] would lead to maximum bulk concentrations more than two orders of magnitude lower than the reported literature values.

Oxide Island Growth Kinetics

We monitor and record the surface (and the time since the beginning of the experiment) with the closed circuit television system during the exposure to water vapor. The first appearance of an oxide island (always at the liquid's highest point) is unmistakable because of the oxide's higher emissivity (see below). The Kevex/Kontron system makes a digital analysis of the brightness of the recorded images into 255 grey levels and determines the ratio between the oxide island area A (all pixels above a set grey level) and the crucible's surface area A_0 (all pixels above a set grey level). Fig. 4. shows an image of the crucible surface with a sizable oxide island, here, as is typical, settled on the rim of the crucible. A grey level analysis performed along the line in Fig 4 is shown in Fig 5. The grey levels of the oxide island can clearly be differentiated from the grey levels of the liquid uranium and the

tungsten crucible's rim. Preliminary Auger analysis data suggest that the oxide is, at least at the surface, UO , rather than UO_2 . ESCA analysis will resolve the present ambiguity. Fig 3 shows $(1 - A/A_0)$ as a function of $(\text{exposure})^{1/2}$ at two temperatures. We display the results for the run above 1200°C (the temperature is uncertain because of a failing thermocouple used in this early run) because it displays the functional dependence on H_2O exposure for oxide coverage of up to 60% of A_0 . This functional dependence is the same at the exposures shown in Fig. 2.

The volume growth of the oxide island of thickness h and area A

$$dV/dt = d(A h)/dt = A dh/dt + h dA/dt$$

cannot be observed by our techniques. One can, however, make some observations about the shape of the oxide islands: Are they spherical or are they flat? At an exposure of about 1000 Langmuir ($2.4 \cdot 10^{18}$ atoms $O/0.52 \text{ cm}^2$ if η_u is one, corresponding to $4.9 \cdot 10^{-5} \text{ cm}^3 UO_2$) after the start of oxide growth we find a coverage of about .5, i.e., $.25 \text{ cm}^2$. Hence the oxide's maximum thickness is 2 micrometer. The islands are, therefore, flat which implies that dh/dt is independent of dA/dt . Since the surface segregation coefficient of oxygen is very high, the supply of oxygen at the underside of the island may be much lower than at the edge, indeed may be insufficient to support any growth. The supply of oxygen to the oxide/liquid interface may come exclusively through the oxide from the oxide/gas interface. There are, under that assumption, two growth regimes of the thickness $h(t)$:

1) The oxygen supply to the oxide/liquid interface is limited by the supply from the gas phase:

$$dh/dt = I_{H_2O} \eta_{oxide} v_{oxide}$$

$$h = c_2 t$$

where I is the flux of gas to the oxide's top surface, η_{oxide} is the sticking and reacting coefficient of gas to oxide and v_{oxide} is the volume of oxide per oxygen atom.

2) the oxygen supply to the oxide/liquid interface is limited by the rate of diffusion through the oxide layer.

$$h = c_3 t^{1/2}$$

where c_3 is proportional to the square root of the diffusion coefficient of the reactant through the oxide. [7]

The area growth of the oxide island may be controlled by the rate of the oxide formation reaction at the perimeter, by diffusion of oxygen to the perimeter or by the supply of oxygen from the gas to the liquid surface. If we make the latter hypothesis, then

$$h \, dA/dt = I_{H_2O} \eta_{oxide} v_{oxide} (A_0 - A) = c_1 (A_0 - A)$$

To describe the very early growth of the oxide island we neglect A in comparison to A_0 , and use the relationship from 1) above and get

$$dA/dt = A_0 c_1/c_2 t$$

$$A(t) = A(t_0) A_0 c_1 c_2^{-1} \ln(t/t_0)$$

i.e., A(t) increases linearly with time when (t/t_0) is close to one. If A cannot be neglected in comparison to A_0 , the solution is

$$A(t) = A_0 c_1/(1-c_2) + [A(t_0) - c_1$$

$$A_0/(1-c_2)A_0][t/t_0]^{1/c_2}$$

Data for oxide growth with (A/A_0) less than .01 show that A grows linearly with time; they are not precise enough to be conclusive, however.

To describe the growth of the island under conditions where the growth of h is diffusion controlled, we use relationship for $h = c_3 t^{1/2}$ from above and get

$$c_3 t^{1/2} dA/dt + c_1 A = c_1 A_0$$

$$1 - A/A_0 = \exp - 2 c_1 t^{1/2}/c_3$$

This functional form is represented by the straight lines in Fig. 3, and clearly fits the data very well. It is a form typical for phase transformations in metals (Avrami's law)^[8]. The good fit implies that the growth of $h(t)$ is diffusion controlled whereas in the pressure range explored here the lateral growth is limited solely by the arrival rate of reactant to the remaining liquid surface. For small values of the exponent the slope of A/A_0 vs. $t^{1/2}$ is $2 c_1/c_3$. That slope and the slope of the lines in Fig. 2 should change with the square root of the exposure pressure.

Emissivity Estimates of Liquid Uranium and Uranium Oxide

The light intensity emitted from objects held at the same temperature is proportional to the emissivity. If we assume that the temperature is constant and that the response of the camera to light intensity is linear, then the grey levels shown in Fig. 5 are directly proportional to the emissivity. With these assumptions we find that the emissivity of liquid uranium is .91 of the emissivity of the tungsten rim, and the oxide formed has 1.3 times the emissivity of the tungsten rim. (We do not know whether the surface of the crucible's rim is pure tungsten or some W-U reaction product.) This is a low estimate for the emissivity of the uranium oxide formed, since uranium oxide is a good insulator and the heat flow from the oxide surface is higher, and hence the temperature on the surface of the oxide island is lower than the temperature of the liquid uranium. Since the intensity is proportional to the fourth power of the temperature, a small temperature drop across the thickness of the oxide may lead to a substantial under-estimation of the emissivity. There is visible evidence of the increased heat flow from the oxide surface; the temperature of the liquid uranium along the oxide rim is lowered.

It is obvious that the television camera is a very crude pyrometer, albeit with high spatial resolution.

Conclusion

This is the first set of measurements describing the reaction of water vapor with liquid uranium. It is apparent that the tools and techniques used can supply information of scientific and practical interest. To make full use of the data on solubility and surface segregation, independent measurements of the sticking coefficient of H_2O on the liquid metal and the oxide surface must be made.

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Acknowledgment

Ed Schmitt prepared the uranium samples, built and maintained the vacuum system, and took data. We acknowledge his contribution to his work. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

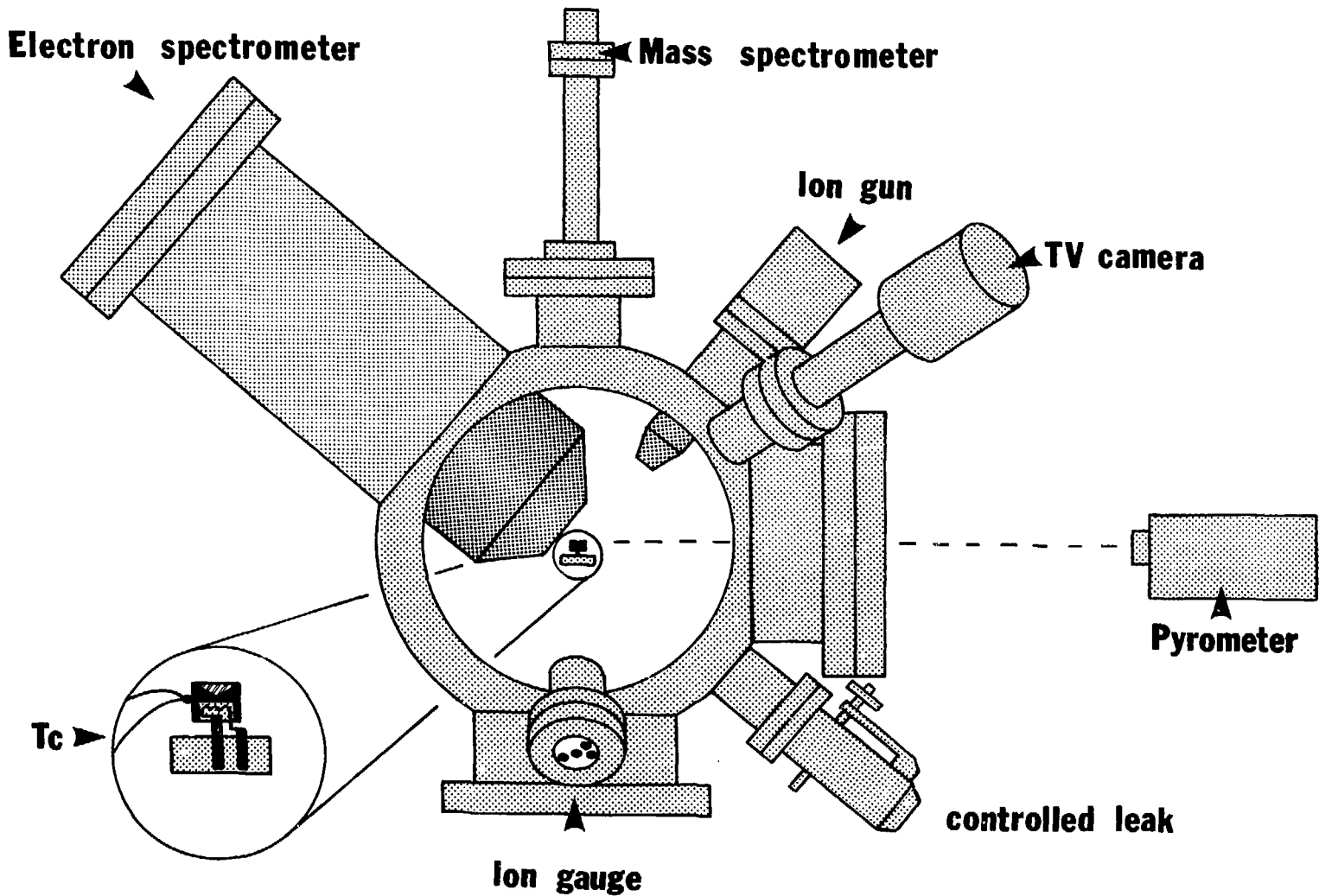


Fig. 1 The Experimental System

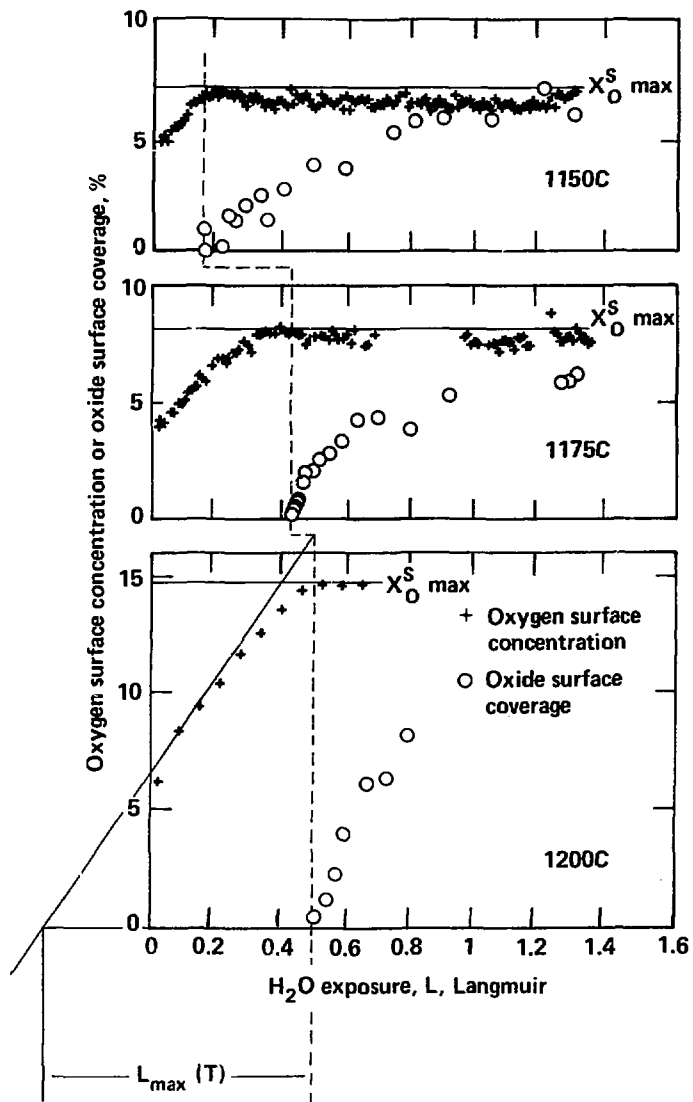


Fig. 2. Oxygen Surface Coverage and Oxide Surface Coverage as F(Exposure)

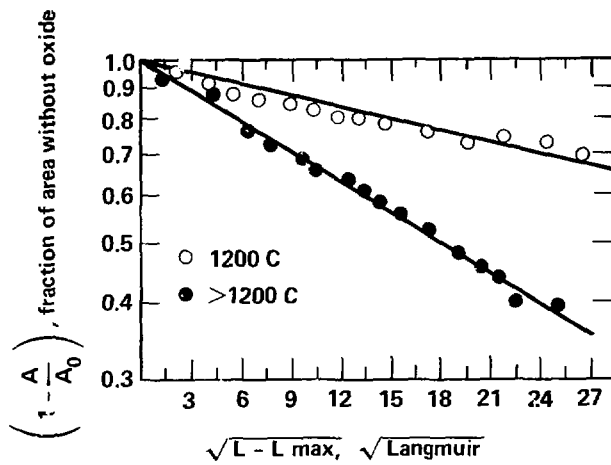


Fig. 3. Oxide Surface Coverage as a Function of Exposure^{1/2}

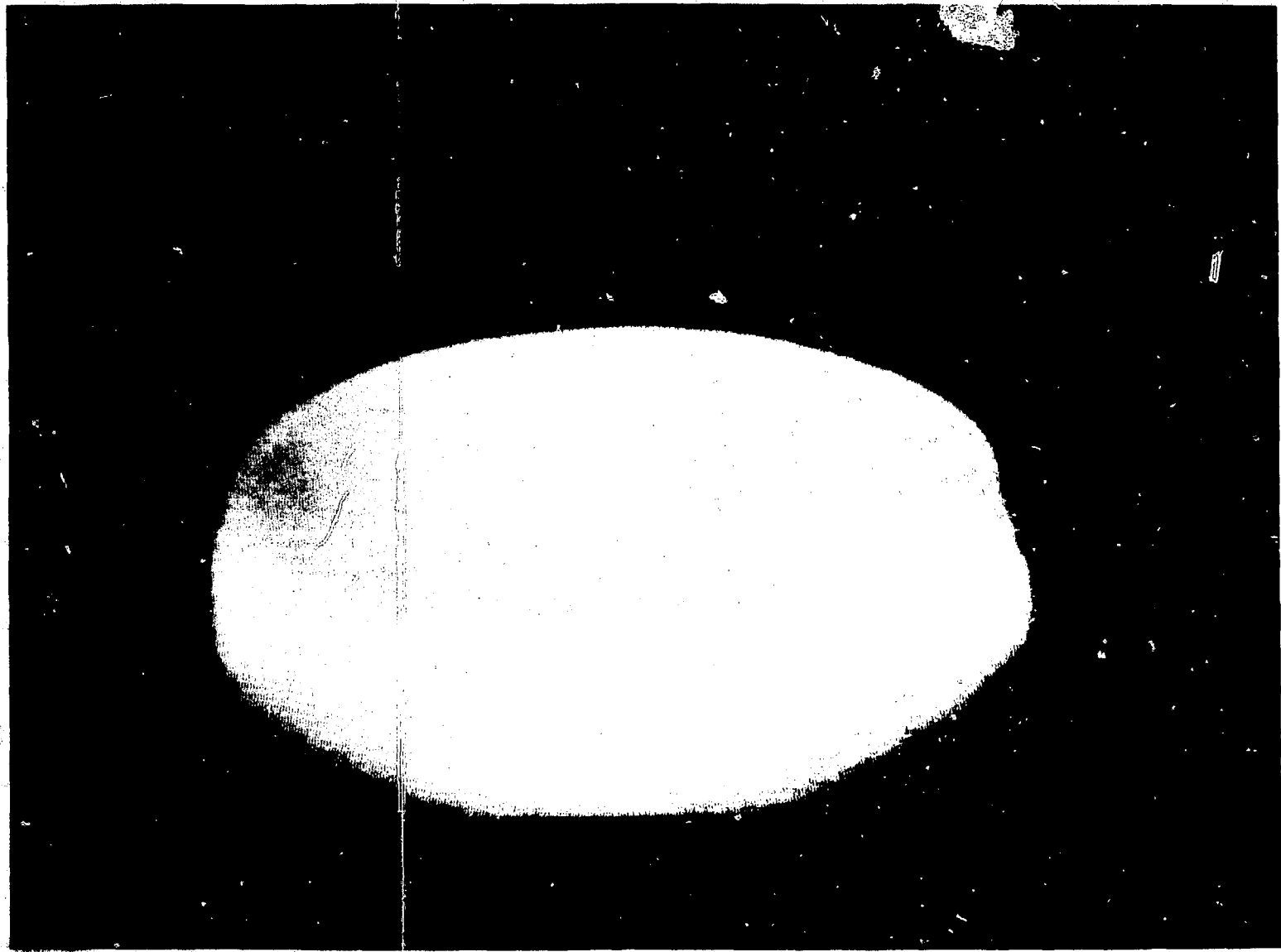


Fig. 4 Video Image of a Reacted Surface

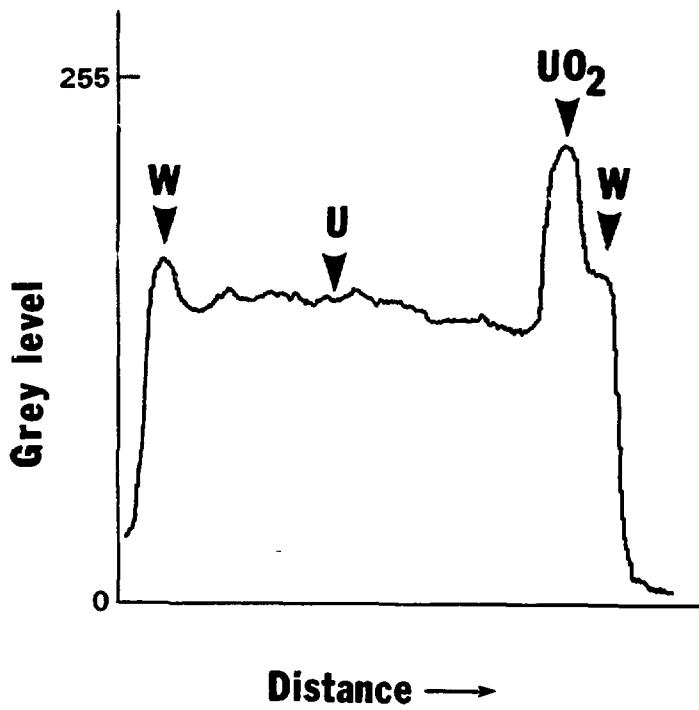


Fig. 5 Grey Level Distribution Along the Line in Fig. 4