

II. PHYSICAL ELECTRONICS AND SURFACE PHYSICS

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A. MEASUREMENTS OF ADSORPTION OF OXYGEN ON TUNGSTEN AT LOW PRESSURE AND HIGH TEMPERATURE

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1. Introduction

The interaction of oxygen with tungsten has been studied by many investigators¹ using a variety of techniques. It is encountered in numerous technological devices, for example, incandescent and arc lamps, ionization gauges, electron tubes, thermionic energy converters, ion propulsion engines, and high-temperature vacuum furnaces, and it is considered as a classical example of high-temperature oxidation. The chemical reaction of oxygen with tungsten at high temperatures and low O₂ pressures results in the formation of volatile tungsten oxides (such as WO, WO₂, WO₃, W₂O₆) in addition to O and O₂. This reaction, which was studied previously in our laboratory, is described reasonably well by the quasi-equilibrium analysis proposed by Batty and Stickney,^{2, 3} but that analysis relies upon a semiquantitative estimate of the equilibration probability, ζ_{O_2} , defined as the probability that an impinging O₂ molecule will adsorb and be equilibrated at the tungsten surface rather than being scattered without equilibration. Batty and Stickney suggest that ζ_{O_2} depends primarily on the fraction of the tungsten surface that is not covered by oxygen, but existing experimental data are not sufficient to verify this suggestion. Although the results of flash desorption studies^{4, 5} provide valuable information on the coverage (i. e., number of oxygen atoms adsorbed per unit surface area) of oxygen on tungsten as a function of temperature, the pressure range is not sufficient to enable us to determine the dependence of coverage on pressure.

In an attempt to obtain a more complete understanding of the dependence of ζ_{O_2} on coverage, we have used Auger electron spectroscopy (AES) to perform approximate measurements of the coverage of oxygen on a polycrystalline tungsten sample as a function of sample temperature (1200-2500°K) and O₂ pressure (5×10^{-9} to 5×10^{-6} Torr).

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We believe that this is the first demonstration that chemical analysis of solid surfaces by AES is possible even at temperatures as high as 2500°K.

2. Experimental Apparatus and Procedures

The apparatus is a conventional ultrahigh vacuum system equipped with an Auger electron spectrometer (Physical Electronics Industries, Inc. cylindrical analyzer, Model 10-243). In the present study, an electron beam current of 400 μ A at 3000 eV is supplied to the sample from a gun mounted for grazing incidence. The electronic circuitry (30-kHz analyzer frequency) is essentially identical to that described by Palmberg et al.⁶

The tungsten sample is a U-shaped polycrystalline ribbon mounted on a manipulator in such a manner that only the midpoint of the U is at the focal point of the AES unit. The sample is heated resistively by direct current, and the temperature at the midpoint is measured with an optical pyrometer. The sample surface is cleaned by a combination of heating in O₂ and flashing to 2500°K; this procedure successfully reduces the concentrations of surface impurities (predominantly carbon) to a level that is below the limit of detection of AES.

Both a nude ionization gauge and a partial pressure analyzer are used to measure the O₂ pressure in an attempt to minimize the various possible errors associated with O₂ pressure measurement.⁷ The desired steady-state O₂ pressure, p_{O_2} , is attained by adjusting both the inlet valve that controls the flow of research grade O₂ into the chamber and the exhaust valve that controls the effective speed of the ion pump.

There are 7 steps in the experimental procedure: (i) Clean the surface as described above; (ii) Set p_{O_2} at the desired value; (iii) Flash the sample to 2500°K; (iv) Reduce the sample temperature, T, to the desired value, and record the Auger spectrum after steady-state conditions are attained (for temperatures above 1200°K, oxygen coverage attained a steady-state value in less than 4 min; at lower temperatures, however, the O₂-W reaction rate is so slow that we did not attempt to obtain completely steady-state conditions); (v) Reduce (or increase) T to another value and again record the Auger spectrum after attaining steady-state conditions; (vi) Repeat the fifth step for various temperatures; (vii) Repeat the entire procedure for various values of p_{O_2} in the range 5×10^{-9} - 5×10^{-6} Torr.

It is assumed here that N, the coverage of oxygen on the tungsten surface, is directly proportional to S_O, the peak-to-peak amplitude of the first derivative of the 509-eV oxygen Auger peak. This assumption has proved accurate for a variety of systems,⁸ and we expect that it is a valid approximation for the O-W system if the coverage is sufficiently low (e. g., less than a monolayer) and if the adsorbed O atoms do not penetrate into the lattice as a result of surface reconstruction (oxidation). The

experimental results of Musket and Ferrante⁹ show that the shape and the width of the oxygen Auger peak at 509 eV do not vary significantly with coverage on the (110) face of tungsten.

3. Experimental Results

Figure II-1 shows the first-derivative Auger spectra that we obtained for 4 values of the sample temperature, T , at one level of O_2 pressure, $p_{O_2} = 1 \times 10^{-6}$ Torr. The spectra have been displaced by an arbitrary amount in the vertical direction to prevent the curves from overlapping. A most interesting feature of these results is that the

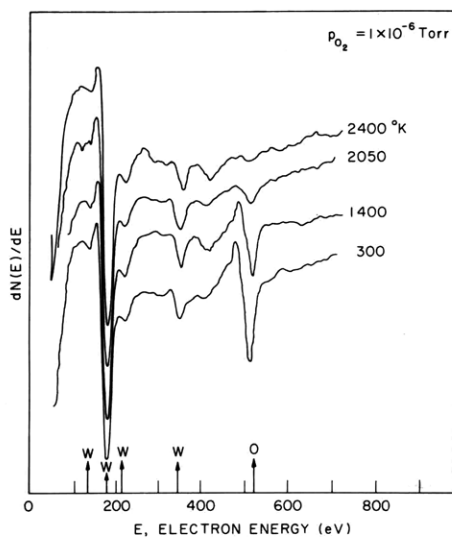


Fig. II-1.

Examples of Auger spectra recorded at various temperatures of the tungsten sample and at a constant O_2 pressure, $p_{O_2} = 1 \times 10^{-6}$ Torr.

Electron beam: 400 μ A and 3000 eV. Modulation: 30 kHz and 15 V peak-to-peak. For clarity, the curves have been displaced vertically to prevent overlapping. Arrows indicate the expected positions of tungsten and oxygen peaks based on Chang's tabulations.¹⁰

signal-to-noise ratio does not appear to be degraded when the sample is heated to high temperature. Notice that the peak-to-peak amplitude of the oxygen peak follows the expected trend of decreasing with increasing T .

From Auger spectra recorded for various choices of T and p_{O_2} , we evaluated the relative change of S_O , the peak-to-peak amplitude of the 509-eV oxygen peak. The results presented in Fig. II-2 are restricted to the range $T \geq 1200^\circ\text{K}$ because it was difficult to obtain reproducible data at lower temperatures where a surface oxide layer forms at a very slow rate.^{4, 5} The data obtained at $T \geq 1200^\circ\text{K}$ were quite reproducible and, in the few checks that we performed, did not exhibit hysteresis (i. e., the value of S_O measured for a particular choice of T and p_{O_2} was essentially the same, regardless of whether the preceding values of T and p_{O_2} were above or below the chosen values). In some cases we flashed the sample to 2500°K between each measurement at different T and p_{O_2} , but the resulting values of S_O were essentially identical to those obtained

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when the sample was not flashed between measurements.

In Fig. II-2, at 1200°K there is an anomalously large gap between the data for 1×10^{-8} Torr and 1×10^{-7} Torr. Although we do not have a definite explanation for this gap, we can suggest several possibilities. At the lowest pressures, the rate at which O_2 molecules impinge upon the surface may be so low that (a) the steady-state coverage

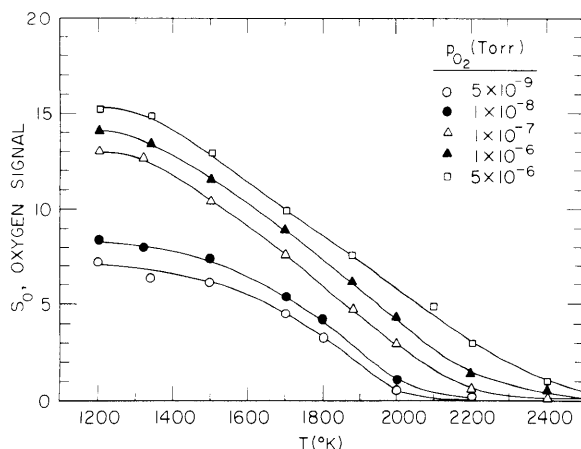


Fig. II-2.

Dependence of S_O , the peak-to-peak amplitude of the 509-eV oxygen Auger peak, on temperature of the tungsten sample and on O_2 pressure. Electron beam and modulation conditions as in Fig. II-1.

may be lowered significantly because the electron beam used for Auger spectroscopy produces electron-stimulated desorption (ESD) of oxygen from tungsten;¹¹ and/or (b) the allowed "equilibration period" (~ 5 min) may not be sufficient to ensure that steady-state conditions are fully attained. Existing data show that the ESD rate increases markedly with increasing coverage,¹¹ thereby providing a possible explanation of the observation (see Fig. II-2) that the gap between the data for 1×10^{-8} Torr and 1×10^{-7} Torr increases with increasing coverage. Since ESD data are not available for the high electron energies and high temperatures employed in this study, we can do no more than provide a rough estimate of the magnitude of the ESD rate R_e relative to the oxygen impingement rate Z expressed in terms of O atoms rather than O_2 molecules. Assuming an electron beam current of $I \approx 400 \mu A$, a beam cross-sectional area of $A \approx 1 \times 10^{-2} \text{ cm}^2$, a coverage of $N \approx 1 \times 10^{15} \text{ atoms/cm}^2$, and an ESD cross section of $Q \approx 1.5 \times 10^{-20} \text{ cm}^2$ (see Musket¹²), we obtain

$$R_e/Z \approx 6 \times 10^{-9}/p_{O_2}, \quad (1)$$

where p_{O_2} is the O_2 pressure in Torr. As shown by Madey and Yates,¹¹ $R_e = QNI/\epsilon A$, where ϵ is the electronic charge. The very approximate relation (1) predicts that $R_e/Z \approx 0.6$ at $p_{O_2} = 1 \times 10^{-8}$ Torr, and we would therefore expect that ESD would produce a significant reduction in the coverage (especially because the sticking probability

is significantly less than unity at high coverages, and hence the adsorption rate is considerably smaller than the impingement rate Z). Because of these uncertainties in the data obtained at the lowest pressures and temperatures, our discussion favors the data for higher pressures and temperatures.

To obtain a rough evaluation of the constant of proportionality between S_O and N , we shall use the results of Ptushinskii and Chuikov⁴ to estimate the coverage at one particular choice of T and p_{O_2} . At 1600°K and 1×10^{-7} Torr their data¹³ indicate that $N \approx 1.1 \times 10^{15}$ oxygen atoms/cm² (with all O atoms on the surface counted, regardless of their molecular state of adsorption). Since $S_O \approx 9$ for the same state in Fig. II-2, the resulting estimated relation is

$$N \approx 1.2 \times 10^{14} S_O. \quad (2)$$

We emphasize that this relation is very approximate because of various uncertainties; furthermore, a slightly different proportionality constant is obtained if we select a different temperature for fitting our data to those of Ptushinskii and Chuikov.

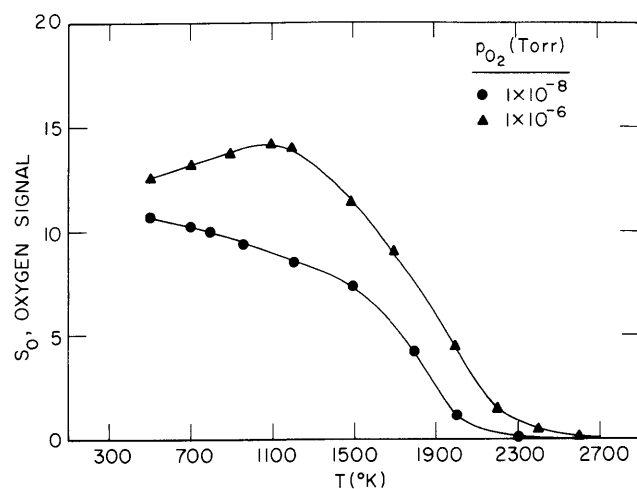


Fig. II-3.

Extension of Fig. II-2 to lower temperatures. Data below 1200°K do not correspond to steady-state conditions and may be influenced by electron-stimulated desorption.

Although the data taken below 1200°K are inaccurate because steady-state conditions were not fully obtained, Fig. II-3 is included, since the results for $p_{O_2} = 1 \times 10^{-6}$ Torr exhibit an interesting maximum at $\sim 1100^\circ\text{K}$. This maximum is consistent with results based on flash desorption measurements,^{4, 5} and it is suspected to be a consequence of the fact that the surface oxidation rate is highest in the vicinity of 1100°K . The absence of a maximum in the curve for $p_{O_2} = 1 \times 10^{-8}$ Torr is most likely to be associated with the problems just discussed.

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4. Discussion

A principal objective of the present study was to determine whether ζ_{O_2} , the equilibration probability defined by Batty and Stickney,³ depends primarily on coverage N , as was previously suggested. Since they did not have data on N , they adopted an expression given in terms of T ($^{\circ}K$) and p_{O_2} (Torr):¹⁴

$$\zeta_{O_2} = 80(p_{O_2})^{-0.3} \exp(-18400/T). \quad (3)$$

(Note: Since values of ζ_{O_2} greater than unity are absurd, we shall assume $\zeta_{O_2} = 1$ when Eq. 3 yields $\zeta_{O_2} > 1$.) We have used this equation to construct Fig. II-4 in the following manner. Each data point in Fig. II-2 represents the value of S_O corresponding to particular choices of T and p_{O_2} . By using Eq. 3 to calculate ζ_{O_2} for the same T and p_{O_2} , we obtain the values of ζ_{O_2} corresponding to various values of S_O . The results are shown in Fig. II-4. If ζ_{O_2} depends primarily on the coverage N and N is directly proportional to S_O , then the points plotted in Fig. II-4 should form a single curve corresponding to the functional relationship $\zeta_{O_2}(N)$. Therefore we have attempted to draw a smooth curve through the points, but ignored the unreliable points for 5×10^{-9} and 1×10^{-8} Torr in the range $S_O \gtrsim 5$. The scatter is sufficiently large that these results provide only marginal support of the suggestion that ζ_{O_2} depends primarily on coverage.

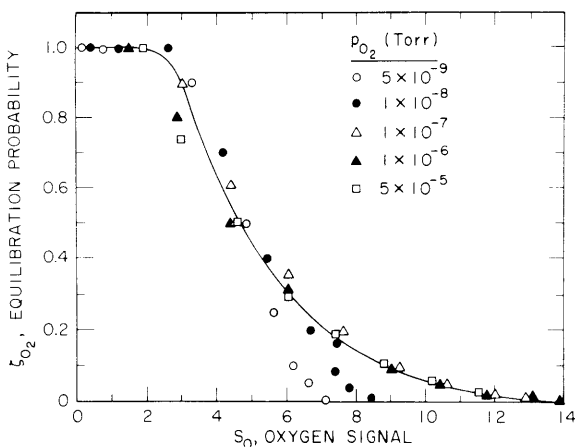


Fig. II-4.

Relationship between the equilibration probability ζ_{O_2} and the oxygen coverage (assumed to be directly proportional to S_O).

Since the results are not conclusive, we shall not include a detailed description of our attempts to find a model that would yield a ζ_{O_2} - N relationship in agreement with the

results shown in Fig. II-4. The simplest forms of the popular models suggested by Roberts¹⁵ and by Kisliuk¹⁶ do not agree closely over the entire range with the present results.

In view of experimental results obtained previously in our laboratory,^{17, 18} we would expect that the present data (Fig. II-2) could be correlated in terms of the parameter T/T_R^* , where T is the sample temperature and T_R^* is the saturation temperature corresponding to the oxygen pressure p_{O_2} in our experiments (that is, T_R^* is the temperature at which the equilibrium vapor pressure of liquid oxygen is equal to p_{O_2}). Engelmaier and Stickney¹⁷ adopted the following relationship between T_R^* and p_{O_2} based on available vapor-pressure data for O_2 :

$$\log_{10} p_{O_2} = 9.25 - \frac{486.45}{T_R^*}. \quad (4)$$

Using this equation, we have transformed the data in Fig. II-2 to obtain Fig. II-5. Notice that T/T_R^* can be used very successfully to correlate the data if we ignore the unreliable points for 5×10^{-9} and 1×10^{-8} Torr in the range $S_O \gtrsim 5$.

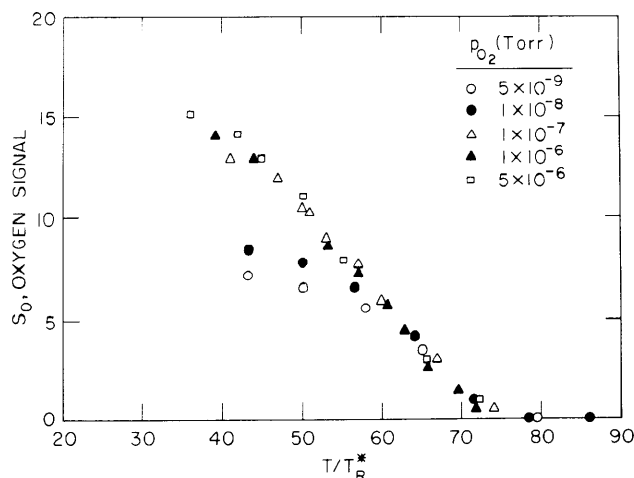


Fig. II-5. Correlation of the oxygen coverage data by means of the parameter T/T_R^* .

We have also attempted to describe the data in Fig. II-2 by means of kinetic models. Since the kinetics of the O-W interaction appear to be extremely complex, we consider only the low-coverage region where the predominant desorption product is atomic oxygen.¹⁻⁵ Under steady-state conditions, the rates of adsorption and desorption may be

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equated to give

$$2\xi_{O_2} p_{O_2} (2\pi m_{O_2} kT')^{-1/2} = \nu N \exp(-E/RT), \quad (5)$$

where m_{O_2} is the molecular mass of O_2 , k is Boltzmann's constant, T' is the temperature of the O_2 gas ($\sim 300^\circ K$), ν is the frequency factor in the assumed first-order form of the desorption rate, E is the desorption energy for O on W, and T is the temperature of the tungsten sample. Under the assumption that ν is a constant and ξ_{O_2} is a function of coverage alone, partial differentiation of the logarithm of Eq. 5 leads to

$$[\partial(\ln p_{O_2})/\partial(1/T)]_N = -E/k. \quad (6)$$

Therefore, by replotting the data in Fig. II-2 in the form $\ln p_{O_2}$ vs $1/T$ for various choices of N (choices of S_O), we may evaluate $E(N)$ from the slopes of the lines of constant coverage. This has been done in Fig. II-6, where for convenience we have expressed the coverage in terms of θ , the fractional coverage, defined by utilizing Eq. 2 together with the assumption that a monolayer contains 1.2×10^{15} atoms/cm⁻² (as suggested by King et al.⁵). That is,

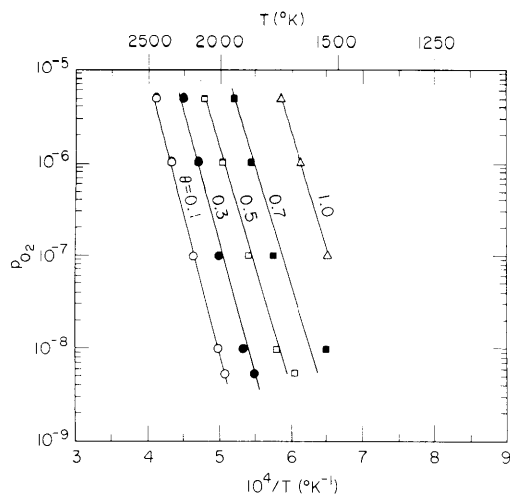


Fig. II-6.

Pressure-temperature plots of data in Fig. II-2 for various values of coverage. For convenience, the coverage is described in terms of the fractional coverage θ , based on the assumption that $\theta = 1$ corresponds to $N \approx 1.2 \times 10^{15}$ atoms/cm⁻².

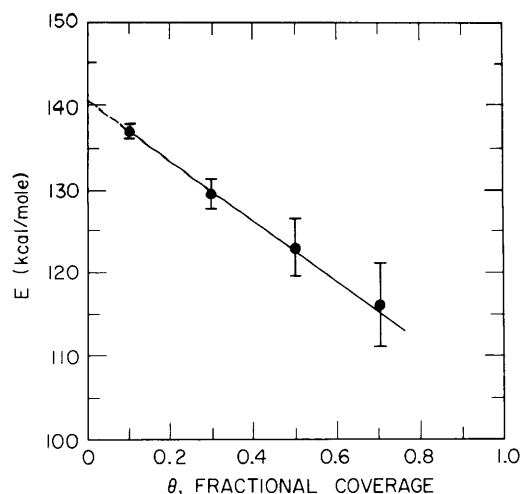


Fig. II-7.

Variation of the desorption energy with coverage, as estimated from the slopes of the constant-coverage lines in Fig. II-6. Bars indicate the estimated uncertainty in determining the slopes.

$$\theta = N/1.2 \times 10^{15} = 0.1 S_{\text{O}}. \quad (7)$$

From the slopes of the lines in Fig. II-6, we have evaluated E vs θ in Fig. II-7. Notice that extrapolation of E to the limit of zero coverage yields ~ 140 kcal/mole (~ 6.1 eV), which is consistent with the values obtained by other investigators using different techniques.^{4, 5, 17-20}

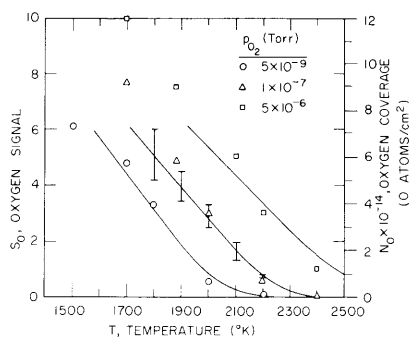


Fig. II-8.

Comparison of a simple, semiempirical model (solid curves) with experimental data from Fig. II-2 on the dependence of coverage on T and p_{O_2} . Bars on the curve for $p_{\text{O}_2} = 1 \times 10^{-7}$ Torr are included to illustrate the effects of uncertainties associated with the desorption energy (Fig. II-7).

With these data on E vs coverage and with Eq. 3 (Batty and Stickney's approximate expression for ζ_{O_2}), Eq. 5 provides a relationship between N , T , and p_{O_2} in terms of only one adjustable parameter, ν . This relationship is plotted in Fig. II-8 for $\nu = 4 \times 10^{13} \text{ s}^{-1}$, which was selected because it leads to the best overall agreement of the curves with the experimental data. The magnitude of ν appears to be reasonable for a frequency factor in a first-order desorption model. In view of the many assumptions and uncertainties associated with both the model and the experimental data, the agreement exhibited in Fig. II-8 is about as good as we could hope for. The curves have not been extended above $S_{\text{O}} \gtrsim 6$ because the model is invalid at higher coverages where the desorption rates for oxides (WO_2, WO_3) are no longer negligible.

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