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Oxidation of Titanium, Tantalum, and Niobium Films by Oxygen and Nitrous Oxide

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The oxidation, by O_2 and N_2O, of evaporated metal films of Nb, Ta, and Ti has been studied in the temperature range 195–473 K. Fast dissociative adsorption of N_2O, which was accompanied by N_2 evolution, occurred on all the three metals at 195 K. At the latter temperature, some incorporation also occurred on Ti film, but the amount adsorbed on Nb was below that required to saturate the film surface with oxygen atoms. Oxygen adsorption on all three metals also took place rapidly at 195 K and the metals showed in general more tendency for oxygen adsorption through O_2 than N_2O. At temperatures ≥303 K, the oxidation reaction took place by either O_2 or N_2O with each film at a rate which depended both on the pressure of the reacting gas and the temperature of the metal film. The Ti film was the most, and Nb the least, active of the three metals for O_2 or N_2O oxidation. Both the activation energy (E) and the preexponential factor (A) increased as the extent of oxidation (X or Y) of each film increased so that the experimental rate remained almost constant, suggesting the operation of a compensation effect in the oxidation of the three films. The effect was likely to arise from a relationship between the heat and the entropy of adsorption, leading to a compensation between activation energy and entropy of activation (and hence the preexponential factor). Values of A and E were lower for O_2 adsorption on each film than for N_2O and this was ascribed to the higher heat of oxygen adsorption as compared with that of N_2O. On the other hand, values of A and E for the Ti film were in general smaller than the corresponding values for Ta and Nb films, such data are in parallel with the greater ease with which the oxidation of the Ti film occurred in comparison with the other two films.

Introduction

There have been quite a number of investigations on the interaction of N_2O with bulk metals, reduced powders, and metal filaments but mainly under high N_2O pressures or at elevated temperatures.[1-4] With evaporated metal films, only a limited number of studies have so far been reported using N_2O gas. Isa and Saleh[5-7] have studied the interaction of N_2O with films of Fe, Ni, W, Pd, and Pb over the temperature range 195–523 K. Adsorption of N_2O on these metals at 195 K occurred dissociatively with N_2 evolution. On Fe and Ni films, extensive oxidation took place at temperatures ≥303 K; a marked compensation existed between the activation energy and the preexponential factor of the oxidation process.

Metals Ti, Ta, and Nb of periodic groups IVa and Va are known to have strong tendencies for oxygen adsorption and the initial heats of oxygen adsorption on these metals were shown to be considerably higher than those on other transition metals.[8-10] There is a need for a more fundamental investigation of oxygen adsorption to clean surfaces of such metals under controlled conditions of temperature and pressure. Nothing is known concerning the kinetics of the oxidation of the above-mentioned three metals at low pressures and in the temperature range 195–473 K; such data may be of considerable value in accounting for the behavior of the metals in oxidation reactions. It was also attempted to discern the different tendencies of the same three metals toward O_2 and N_2O and this was estimated on the basis of the kinetic data for the oxidation of the metals by either of the two gases.

Experimental Section

The apparatus, materials, and experimental techniques have been described.[11,12] Metal films of Ti, Ta, and Nb were prepared from 0.1-mm wire which was obtained from Johnson Matthey Chemicals Ltd. The glass apparatus and the metal filaments were degassed until the rate of degassing with the reaction vessel at 673 K was $<10^{-2}$ N m^{-2} hr^{-1}. The evaporation currents were 0.6, 4.0, and 9.0 A for Ti, Nb, and Ta films, respectively, and the reaction vessel was kept open to the pumps throughout the degassing and the subsequent preparation and sintering of the film. Each film was sintered at 343 K for 20 min and, thereafter, its area was measured by krypton adsorption at 78 K. Nitrous oxide was prepared and purified as described before.[5] Oxygen was obtained from cylinders, but it was further purified before use. Mixtures of $N_2 + N_2O$ were analyzed by condensing the latter gas at 78 K and measuring the remaining pressure of N_2; the vapor pressure of N_2O at 78 K as measured by a McLeod gauge was $\sim10^{-2}$ N m^{-2}, uncorrected for thermomolecular flow.

Results

The extents of N_2O and O_2 adsorption on each film were expressed in terms of X and Y as follows

$$X = V_{N_2O}/V_{Kr} \tag{1}$$

and

$$Y = V_{O_2}/V_{Kr} \tag{2}$$

where V_{N_2O} and V_{O_2} were the volumes of N_2O and O_2 adsorbed, respectively, and V_{Kr} was the volume of krypton monolayer on the film at 78 K; the volumes were measured in units of microliters (STP).

Because of the very little amount of nitrogen that was retained by a film subsequent to N_2O adsorption, it was reasonable to consider the value of X as a measure of either the coverage of the surface by oxygen atoms or alternatively, when incorporation occurred, of the thickness of the oxide

layer formed. Similarly, when molecular oxygen was used, the value of Y reflected either the coverage of the film surface or of the extent of oxidation in terms of the adsorbed oxygen molecules, the same amount of oxygen uptake may be expressed by a certain value of X or by $2Y = X$ assuming dissociative adsorption of oxygen in each case.

Adsorption of N_2O. The initial adsorption of N_2O on metal films of Nb, Ta, and Ti occurred rapidly (in <1 min) at 195 K to a final pressure of 10^{-3} N m^{-2}. Further adsorption of N_2O proceeded at a rate which decreased with increasing values of X. The process of adsorption was accompanied by the evolution of gaseous N_2. The extent of N_2 desorption on Nb and Ta films was equivalent to that of N_2O adsorption; the total gas pressure always remained constant because one molecule of N_2 appeared in the gas phase for each N_2O molecule that underwent adsorption.

On the Ti film, less N_2 was desorbed than N_2O adsorbed particularly for relatively low values of X at 195 K, and this was reflected in the rapid decrease of the total gas pressure in the initial adsorption of N_2O on Ti film. This was clearly detected in the behavior of the first dose that was admitted to the clean Ti film. In the subsequent adsorption of N_2O which occurred at a measurable rate, there was a slow decrease in the total gas pressure with time as the reaction of N_2O with the film continued. Furthermore, the film of Ti was shown to be more reactive toward N_2O at 195 K than the other two metals, and this is seen in the final values of X (X_{max}) on the three films at this temperature as given in Table I. At such values of X (X_{max}), the rate N_2O uptake becomes $<10^{-4}$ µl. sec^{-1} cm^{-2} under a gas pressure of 6 N m^{-2} at 195 K.

Some N_2O desorption was observed when a Ti film which had adsorbed N_2O at 195 K to the extent $X_{max} = 4.9$ was warmed to 273 K; the amount desorbed represented only about 10% of the total gas adsorption at 195 K. Thereafter, adsorption of N_2O continued at 273 K at a rate which increased on heating the film to higher temperatures. Dissociative adsorption of N_2O, with complete desorption of N_2, was the main feature of the N_2O interaction with each of the three metals at temperatures ≥303 K. The reaction became faster as the film was heated and, at any temperature, the total gas pressure remained virtually constant as N_2O was consumed at the same rate by which N_2 was desorbed; a typical example for such behavior is shown in Figure 1. At any temperature below 520 K, the Ti film remained the most active among the three metals used in this investigation toward N_2O, *i.e.*, the rates of adsorption at 395 K, under the same pressure, on Nb, Ta, and Ti films were respectively 1.42×10^{11}, 1.46×10^{11}, and 4.2×10^{12} molecules sec^{-1} cm^{-2}.

Adsorption of Oxygen. There was a fast instantaneous adsorption of oxygen on metal films of Nb, Ta, and Ti at 195 K. Above $Y = 0.6$, the adsorption occurred at a rate which became slower as Y increased. When the rate of uptake became $<10^{-3}$ µl. sec^{-1} cm^{-2}, the amounts of oxygen adsorbed (Y_{max}) were as given in Table II.

Further interaction took place at and above 303 K. The rate of oxidation increased on increasing the temperature of the film. Above 523 K, some desorption began to occur at an extremely slow rate.

Kinetics of N_2O and O_2 Adsorption

Pressure Dependence. The rate of N_2O or O_2 adsorption on Nb, Ta, and Ti films at any temperature greater than 273 K depended on the pressure of the reacting gas. The rate of gas adsorption r_1 at an initial pressure P_1 was first determined, then the pressure was changed to P_2 at which the new rate r_2 was obtained. The dependence (n) of the rate on pressure was evaluated from the relation

$$(P_1/P_2)^n = r_1/r_2 \qquad (3)$$

Values of n thus obtained, for the pressure range 1–8 N m^{-2}, were close to unity using either N_2O or O_2. A check for the value of $n = 1$ was to plot log P_{gas} as a function of time for different films at several temperatures, typical plots of which are indicated in Figure 2.

Effect of Temperature. From the rate of N_2O (or O_2) adsorption at two different temperatures but virtually the same value of X (or Y), the activation energy of adsorption (E) was determined. Values of E for N_2O or O_2 adsorption on each metal film increased as X or Y increased as shown in Figure 3.

From the rate (r) of gas adsorption at a given temperature T, coverage X (or Y), and appropriate value of E, the value of the preexponential factor A in the Arrhenius type rate equation

$$(r)_{X (\text{or } Y), T} = A \exp(-E/RT) \qquad (4)$$

was obtained. From the values of A at various temperatures and values of X (or Y), the corresponding values of the entropy of activation (ΔS^*) were determined assuming a pressure dependence of $n = 1$. Table III shows that for approximately the same gas pressure (4–7 N m^{-2}) the values of A and ΔS^* increased as X (or Y) and E increased on each film so that the experimental rate remained almost constant. Figure 4 shows the relationship

TABLE I: Maximum Values of X (X_{max}) on Nb, Ta, and Ti films at 195 K

Film	X_{max}
Nb	0.82
Ta	1.80
Ti	4.90

TABLE II: Total Amounts of Oxygen Adsorption on Nb, Ta, and Ti films at 195 K

Film	X_{max}
Nb	1.14
Ta	2.00
Ti	2.61

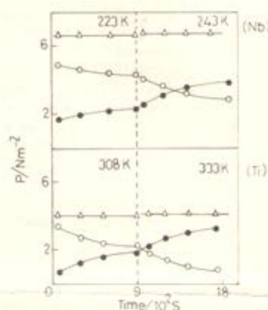

Figure 1. Interaction of N_2O with metal films of Nb and Ti at different temperatures: Δ, total pressure; O, N_2O pressure; ●, N_2 pressure.

TABLE III: Experimental Values of Activation Energy (E), Frequency (A), and Entropy of Activation (ΔS^*) at Various Values of X or Y on a Ti Film

X	Temp, K	Rate, molecules sec^{-1} cm^{-2}	E, J mol^{-1}	A, molecules sec^{-1} cm^{-2}	ΔS^*, J mol^{-1}
4.90	273	3.8×10^{12}	18.30	1.1×10^{16}	177.67
7.85	303	1.8×10^{12}	46.65	4.4×10^{19}	246.21
9.41	328	3.4×10^{12}	69.53	5.7×10^{22}	300.88
13.68	393	3.9×10^{12}	106.64	5.33×10^{25}	354.78
Y					
5.08	273	1.53×10^{12}	20.87	4.26×10^{15}	170.17
8.14	308	1.40×10^{12}	30.00	7.89×10^{16}	192.50
9.04	393	1.65×10^{12}	45.07	7.71×10^{18}	233.50
14.79	393	1.28×10^{12}	90.84	1.30×10^{24}	331.67

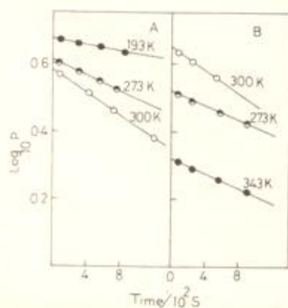

Figure 2. First-order plots for the uptake of N_2O (A) and O_2 (B) on Nb (●), Ta (○), and Ti (◓) films at various temperatures.

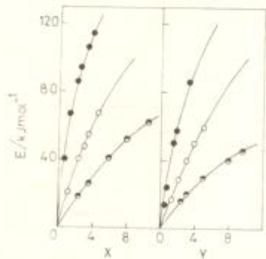

Figure 3. Activation energy (E) plotted against the extent of oxidation X and Y on films of Nb, Ta, and Ti. Symbols are as in Figure 2.

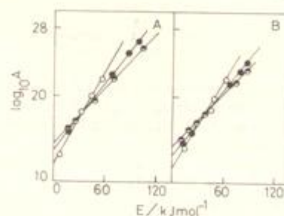

Figure 4. Compensation effect in oxidation of Nb, Ta, and Ti films by N_2O (A) and O_2 (B) gases. Symbols are as in Figure 2.

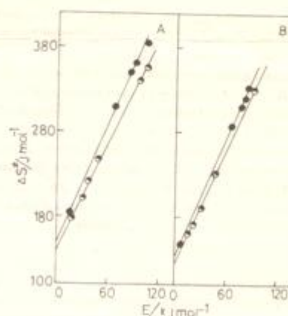

Figure 5. Variation of ΔS^* with E for N_2O (A) and O_2 (B) gases interactions with Nb and Ti films.

between log A and E and the variation of ΔS^* values with E is indicated in Figure 5. Values of A, E, and ΔS^* were obtained for each film at a given value of X (or Y) and the results were plotted in Figure 6.

Discussion

Adsorption at 195 K. Dissociative adsorption of N_2O occurred on Nb, Ta, and Ti films even at 195 K as almost all the N_2 of the adsorbed N_2O was desorbed at the same temperature. From the values of X_{max} in Table I one can conclude that surface saturation by oxygen atoms, resulting from the dissociative adsorption of N_2O, was not achieved on Nb film; the value of $X_{max} = 0.82$ suggests that the adsorbed oxygen atoms of N_2O was only sufficient to cover less than the half of the available surface sites assuming each krypton atom to occupy an area twice as large as the oxygen atom. On the other hand, the value of $Y_{max} = 1.14$ on Nb at the same temperature (Table II) indicates a complete surface saturation by oxygen. The difference in behavior may arise from the higher heat of oxygen adsorption on Nb than of N_2O.

On the Ta film, the value of X_{max} was 1.8 and this value reflects the amount of adsorbed oxygen atoms that are almost sufficient for complete coverage of the film surface. On the same assumption, one would expect $Y_{max} = 2.0$ on Ta to involve lattice penetration by oxygen in addition to surface saturation. The difference in the heat of adsorption may also account for the different behaviors of the two gases on the same metal.

On the Ti film, the adsorption and incorporation occurred almost to the same extent using either N_2O or O_2 despite the fact that the value of $X_{max} = 4.9$ corresponded to slightly less oxygen uptake than that expressed by Y_{max}

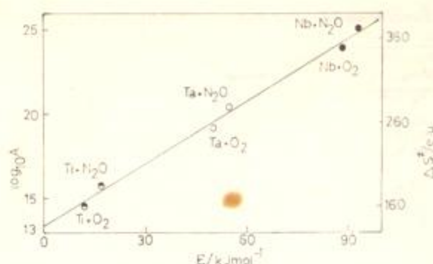

Figure 6. Compensation effect in the oxidation of Nb, Ta, and Ti films by N_2O (at $X = 2.3$) and O_2 (at $Y = 2.3$).

$= 2.6$. The small difference of about $2Y_{max} - X_{max} = 0.3$ may account for some nitrogen uptake[8] in the initial adsorption of N_2O on the Ti film at 195 K in addition to the adsorbed oxygen atoms.

The reactivity of the three metals at 195 K toward the oxygen of the adsorbed N_2O or O_2 occurred in the sequence Ti > Ta > Nb. It has been shown[9] that the initial heats of oxygen adsorption on metals of periodic group IV (as for Ti metal) are higher than on metals of other groups (*i.e.*, Nb and Ta of group V). If the oxidation process involves migration and subsequent outward diffusion of the metal ions to contact the reacting gas, then such factors as the melting point and the ionic radius may be considered to be important in deciding the ease of oxidation; the Ti metal has the lowest melting point and the smallest ionic radius[13,14] among the three metals used in this investigation. The Ti metal is known to crystallyze with a different structure (cph) than that of Ta and Nb (bcc). These and other properties of Ti probably make this metal more favorable for oxidation by either N_2O or O_2 than the other two metals.

Uptake at ≥303 K. The results of Figure 4, relating log *A* to *E*, suggest the operation of a compensation effect[15,16] which may be represented by the relation

$$\log A = UE + W \qquad (5)$$

where *U* and *W* are constants. The compensation may arise[17] from a relationship between the heat and the entropy of adsorption, and this leads to a compensation between the activation energy and the entropy of activation (and hence the preexponential factor).

The results in Figure 6 indicate a more general picture for the operation of the compensation effect in the oxidation of Nb, Ta, and Ti films by N_2O and O_2 gases. The points representing the oxidation of each metal by O_2 corresponded to lower values of log *A* and *E*, and hence to lower values of the entropy of activation, than the points representing the oxidation of the same metal by N_2O. Oxygen adsorption on each metal is likely to take place with a much higher heat of adsorption than that of N_2O. Entropy contributions arising from vibration or rotation of the adsorbed molecule are likely to be more restricted the greater the strength of adsorption; a proportionality between heat and entropy of adsorption is therefore expected. On the other hand, the activation energy of oxygen adsorption is expected to be less than that for N_2O adsorption. The relationship depicted in Figure 5 may suggest that the activated complex for N_2O or O_2 reaction with each metal becomes less restricted as the extent of oxidation increases.

The points representing the oxidation of Ti film by either N_2O or O_2 lie in general (Figure 6) lower than the corresponding points for the other two films. This may be accounted for on the basis of the heat of adsorption and certain other characteristic properties of Ti metal which have been referred to earlier in this work. Moreover, on comparison of the present results with those published previously,[5] it was found that Ti was, under similar experimental condition, as reactive toward N_2O as Fe and Ni films; the same value of *E* on Ti, Fe, and Ni metals corresponded to almost the same value of log *A*. The main difference confined in the fact that a given value of *E* for Ti film corresponded to a comparatively higher value of *X* than on Fe and Ni films. This probably assigns a higher reactivity to Ti metal than Fe and Ni. It has been found[10] that the heat of dissociative chemisorption of oxygen increased as one moved from Ni toward Ti due to the some increasing trend in the covalent contribution to metal–oxygen bond formation.

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