a depolarizer which removes H° from local cathodic sites on the anode surface. (Cd has a relatively high hydrogen overvoltage and hence hydrogen is not evolved.) Momentary protection of portions of the anode surface (local cathodic sites, uneven film formation, or film disruption) allows anodic dissolution to undermine and ultimately detach metal particles from the surface. These particles are noted in surface films on the anode and the phenomenon by which they are formed has been termed "anodic disintegration." This mechanism leads to a mathematical model which is consistent with the experimental results.

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REFERENCES

1. G. Bredig, *Z. Phys. Chem.*, **32**, 127 (1900).
2. E. F. Burton, *Phil. Mag.*, **11**, 425 (1906).
3. M. C. Del Boca, *Helv. Chim. Acta*, **16**, 565 (1933).
4. M. E. Straumanis and B. K. Bhatia, *This Journal*, **110**, 357 (1963).
5. R. L. Petty, A. W. Davidson, and J. Kleinberg, *J. Am. Chem. Soc.*, **76**, 363 (1954).
6. B. D. Laughlin, J. Kleinberg, and A. W. Davidson, *ibid.*, **78**, 559 (1956).
7. M. E. Straumanis and D. L. Mathis, *J. Less-Common Metals*, **4**, 213 (1962).
8. D. T. Sorensen, A. W. Davidson, and J. Kleinberg, *J. Inorg. Nucl. Chem.*, **13**, 64 (1960).
9. W. J. James and G. E. Stoner, *J. Am. Chem. Soc.*, **85**, 1354 (1963).
10. E. Raijola and A. W. Davidson, *ibid.*, **78**, 556 (1956).
11. M. E. Straumanis and K. Poush, *This Journal*, **112**, 1185 (1965).
12. M. L. Rumpel, A. W. Davidson, and J. Kleinberg, *J. Inorg. Chem.*, **3**, 935 (1964).
13. M. E. Straumanis and M. Dutta, *ibid.*, **5**, 992 (1966).
14. J. H. Greenblatt, *Corrosion*, **18**, 125t (1962).
15. G. R. Hoey and M. Cohen, *This Journal*, **105**, 245 (1958).
16. M. E. Straumanis and Y. Wang, *Corrosion*, **22**, 132 (1966).
17. Y. C. Sun, M. S. Thesis, University of Missouri at Rolla, 1964.
18. J. W. Johnson, C. K. Chi, and W. J. James, *Corrosion*, in press.
19. J. S. Sanghvi, M. S. Thesis, University of Missouri at Rolla, 1965.
20. B. W. Jong, M. S. Thesis, University of Missouri at Rolla, 1966.
21. C. I. Lu, M. S. Thesis, University of Missouri at Rolla, 1966.
22. Y. C. Sun, Ph.D. Thesis, University of Missouri at Rolla, 1966.
23. C. K. Wu, M. S. Thesis, University of Missouri at Rolla, 1967.
24. K. Huber, *This Journal*, **100**, 376 (1953).
25. J. L. Robinson and P. F. King, *ibid.*, **108**, 36 (1961).
26. P. E. Lake and E. J. Casey, *ibid.*, **105**, 52 (1958).

Rate-Controlling Processes in the High-Temperature Oxidation of Tantalum

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ABSTRACT

The oxidation of tantalum in the temperature range 500°-950°C is approximately linear. At atmospheric pressure, the rate constant increases with temperature in the temperature range 500°-650° and 800°-950°C, but decreases slightly as the temperature increases from 650° to 800°C. The reaction rate depends on the square root of the oxygen pressure at low pressures and high temperatures, but at lower temperatures the pressure dependence decreases as the pressure increases. On the basis of experimental evidence in the literature, it is concluded that in the temperature range 500°-800°C the rate-controlling process is a reaction at the interface between the atmosphere and a layer of tantalum pentoxide growing adherently on the metal surface. This interface reaction is preceded by an equilibrium adsorption of oxygen on the interface, the adsorption taking place with dissociation. In the temperature range 800°-950°C, the over-all linear rate is a consequence of the diffusion-controlled growth of adherent pentoxide to a critical thickness, at which the scale fails from the metal. The corollary to this conclusion is that the rate of the diffusion process must be strongly dependent on the oxygen pressure.

The oxidation of tantalum, and the not-dissimilar oxidation of niobium, has been studied extensively for both practical and theoretical reasons. The reaction kinetics are of considerable interest, since the dependence of the reaction rate on both temperature and oxygen pressure is unusual.

After an initial period (a few minutes at 950°C and a few hours at 500°C) the reaction rate becomes approximately constant (linear rate law). The linear rate constant increases with temperature from 500° to 650°C and from 800° to 950°C, but decreases slightly in the temperature range 650°-800°C. The rate constant increases with pressure, the effect decreasing as the pressure increases. Increasing the temperature increases the pressure at which the pressure-dependence starts to diminish.

The principal reaction product is tantalum pentoxide, Ta_2O_5. The oxide grows adhering to the metal surface and is formed under compressive growth stresses. Eventually these cause the scale to fail from the metal surface. Growth of adherent oxide recommences immediately on the freshly exposed metal surface, and repetition of this process produces a laminated detached scale. In addition to the pentoxide, platelets of a suboxide are formed penetrating into the metal from the scale/metal interface. Finally, oxygen also dissolves in the metal.

While the oxidation of niobium has a number of points of similarity to that of tantalum, notably in the temperature- and pressure-dependence of the rate

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constant, there are also a number of important differences. In addition to the pentoxide, stable lower oxides are formed. The platelets of a metastable suboxide are much less evident, particularly at higher temperatures. Finally, the pentoxide exhibits a phase change at approximately 800°C, and there is a clear change in the reaction kinetics associated with the change.

In this paper, the effect of a number of variables on the kinetics and reaction-product morphology are reviewed in an attempt to identify the rate-controlling processes in the oxidation of tantalum in the linear oxidation region for temperatures of 500°-950°C and oxygen pressures of 1-60,000 Torr.

Effect of Experimental Variables on Experimental Results

Impurities in the metal.—No systematic study has been made of the effect of impurities on the rate of oxidation of tantalum, but the rate constants reported by a number of investigators (1-5) over a period of 10 years using tantalum from a number of sources agree closely, suggesting that the effect of impurities is small.

Insufficient observations of the other features such as scale structure and morphology were reported in most of the earlier investigations to permit evaluation of the effect of impurities on these.

Grain size.—Only one systematic study of grain-size effects has been made and that was relatively limited in scope (6). No effect of grain size on reaction rate was observed. There do appear to be differences in the scale morphology and in the suboxide platelet distribution as a function of grain size. In coarse-grained samples, long, straight suboxide plates are formed, and these produce pores in the outer detached pentoxide (7). In fine-grained samples, in contrast, the size of the platelets is limited by the grain size, and thus the voids in the pentoxide are difficult to discern. While the grosser features of the scale on coupon specimens are not obviously affected by the tantalum grain size, it has been demonstrated that, over convex surfaces, the pore lines can act as paths for tensile fractures in the detached scale (6, 7). Therefore, it is possible that the scale morphology over convex surfaces may show a grain-size dependence.

Cold work.—Cold work apparently has no effect on the linear oxidation rate in this temperature range (6). The suboxide plates appear curved in cold-worked specimens, but apart from this there is no apparent effect on oxide morphology.

Surface preparation.—Since the linear oxidation is a thick-film, steady-state process, no effect of initial surface preparation would be expected, and, in fact, none is observed (6).

Specimen shape.—It has been demonstrated that, at 820° and 925°C, ¼-in. diameter spheres oxidize more rapidly than ½-in.-diameter spheres which in turn oxidize more rapidly than coupon specimens (6). This is consistent with the tendency of coupon specimens to oxidize more rapidly at the edges and corners than at the centers of the flat faces. The scale formed over convex surfaces contains fissures normal to the metal surface penetrating inward from the outside, and it appears that these fissures are produced by tensile stresses in the outer layers of the oxide, generated by the pressure of the newly forming oxide layers beneath. There is no obvious difference at steady state in the structure of the oxide plates as a function of specimen shape.

Specimen texture.—There is a clear orientation dependence of the oxidation rate at the higher temperatures. At 925° and 820°C {110} faces oxidize more rapidly than any others; {100} faces oxidize more slowly (8). At 600° and 500°C there is no obvious effect of orientation. As a consequence, one might expect the oxidation rate to be a function of texture at high temperatures. No study of this has been made yet.

The oxide structure is clearly a function of orientation. Under steady-state reaction conditions, the suboxide platelets are always formed parallel to $\{100\}_{\mathrm{Ta}}$ throughout this temperature range. At higher temperatures the lines of pores above the platelets act as crack paths, and, if the plates lie at 45° to the surface, scale fracture under the compressive growth stresses is facilitated. As a result, the laminations in the detached scale are much thinner above {110} faces than above {100} faces (8).

Gaseous impurities.—Small amounts of gaseous impurities in the oxidizing atmosphere have not been studied in any detail, but they appear to have a negligible effect on the oxidation rate and the scale structure.

Temperature and Pressure Dependence of the Oxidation Rate

The first experiments on the pressure dependence of the oxidation rate were performed by Peterson *et al.* (1), who described their results by the empirical equation

$$\text{rate} = K_1 \frac{K_2 P_{O_2}}{1 + K_2 P_{O_2}} \qquad [1]$$

Later, Cowgill and Stringer (9) pointed out that at low pressures this reduces to

$$\text{rate} \propto K_1 K_2 P_{O_2} \qquad [2]$$

whereas experiment showed that

$$\text{rate} \propto k\, P_{O_2}{}^{1/2} \qquad [3]$$

Accordingly, these investigators (9, 3) suggested replacing Eq. [1] by

$$\text{rate} = K_1 \frac{K_2 P_{O_2}{}^{1/2}}{1 + K_2 P_{O_2}{}^{1/2}} \qquad [4]$$

This point was confirmed by Kofstad (4), who suggested a modified form of Eq. [4].

On a direct plot of rate *vs.* pressure, there is not a great deal of difference between the fit obtainable with Eq. [1] and [4]; but a plot of log rate *vs.* log pressure, by expanding the low pressure region, emphasizes the difference between the two forms.

Figure 1 shows a set of results for the oxidation of a tantalum coupon at 600°C. The full line is the best fit using Eq. [4]; with the rate in g/cm²/sec and the pressure in Torr, $K_1 = 6.53 \times 10^{-6}$, and $K_2 = 0.031$. In Fig. 2 the same equation is plotted over five orders of pressure and compared with constant pressure data from the literature. Plainly, the agreement between the various investigators is excellent: it is not possible to fit these data using Eq. [1].

The empirical Eq. [1] and [4] can be interpreted in terms of a reaction mechanism in which the rate-controlling process is linearly dependent on the ad-

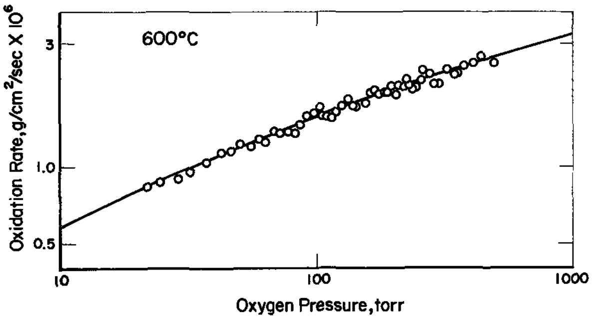

Fig. 1. Pressure dependence of the oxidation of tantalum at 600°C; data from a varying pressure experiment.

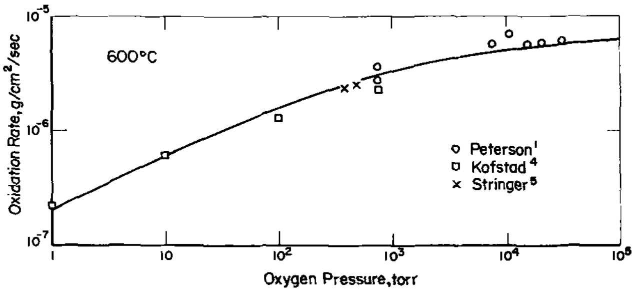

Fig. 2. Pressure dependence of the oxidation of tantalum at 600°C; constant pressure data from the literature. The curve is the same as for Fig. 1.

sorbed oxygen concentration at some interface. In the case of Eq. [1] the oxygen is adsorbed as molecules; in the case of Eq. [4] the adsorption takes place with dissociation, and the oxygen is adsorbed as atoms.

If this is the situation, one may expect that the temperature dependence of K_1, which is related to the rate of the rate-controlling process, will be given by a conventional Arrhenius equation

$$K_1 = K^{\circ}_1 \exp\left(\frac{-Q_1}{RT}\right) \qquad [5]$$

and the temperature dependence of K_2, which is related to the adsorption process, will be given by a Langmuir expression

$$K_2P_{O_2}{}^{1/2} = K^{\circ}_2T^{-5/2} \exp\left(\frac{Q_2}{RT}\right) \qquad [6]$$

In this expression, the $T^{-5/2}$ term arises from the temperature dependence of the concentration of the gas phase at constant pressure T^{-1} and the temperature dependence of the reciprocal of the partition function of the gas for unit volume, $T^{-3/2}$. In these expressions R is the gas constant, T is the absolute temperature, and Q_1 and Q_2 are positive energies. Conventionally, K°_2 is regarded as being independent of temperature, but the temperature dependence of K°_1 is more uncertain: it is assumed to be small in comparison with that of the exponential term. Substituting [5] and [6] into [4]

$$\text{rate} = \frac{K^{\circ}_1K^{\circ}_2T^{-5/2} \exp\left(\dfrac{Q_2 - Q_1}{RT}\right)}{1 + K^{\circ}_2T^{-5/2} \exp\left(\dfrac{Q_2}{RT}\right)} \qquad [7]$$

In this work, both K°_1 and K°_2 are regarded as being independent of temperature.

Figure 3 shows the rate constants reported in the literature by a number of investigators, corrected to a pressure of 760 Torr where necessary using the experimentally determined pressure dependence. The full line is drawn according to Eq. [7] with Q_1 = 67,700 cal/mole and Q_2 = 70,000 cal/mole. The fit is quite good over the range 500°-820°C. The $T^{-5/2}$ terms cannot be neglected, since the variation of the exponential terms is small at elevated temperatures, but the shape of the curve does not depend significantly on their inclusion: the value of Q_2 is merely altered slightly.

One would expect this mechanism to cease to operate at high temperatures and low pressures because the adsorbed surface concentration would fall so low that the adsorption step would become the rate-determining process. At 760 Torr and 800°C the volume per molecule in the gas phase is approximately 10^{-19} cm³. Assuming the sites on the adsorption interface are roughly 4 x 10^{-8} cm apart, the surface concentration will equal the mean concentration in the atmosphere adjacent to the surface when the fractional surface coverage θ falls to approximately 10^{-2}. One would not expect therefore that the mechanism would continue to describe the reaction when θ is appreciably less than this.

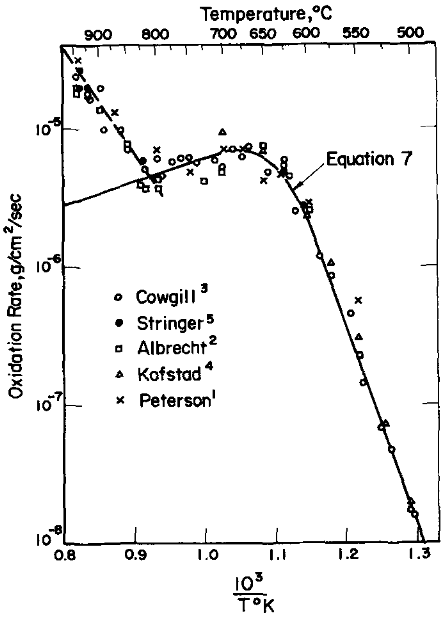

Fig. 3. Oxidation rate of tantalum as a function of temperature at an oxygen pressure of 760 Torr showing the fit of the adsorption model.

The fractional coverage of the adsorption interface θ is given by

$$\theta = \frac{K_2P_{O_2}{}^{1/2}}{1 + K_2P_{O_2}{}^{1/2}} \qquad [8]$$

and Fig. 4 shows θ calculated for the curve shown in Fig. 3. At the temperature at which Eq. [7] ceases to describe the experimental results, θ is approximately 10^{-3}, close to the estimate above. However, it must be stressed that this merely indicates that the mechanism does not continue to give a fit to the data in regions where this is physically unlikely: it does not predict or help in understanding the high-temperature process.

For the empirical fit of the data shown in Fig. 2 one calculates θ_{760} = 0.46, which is the value at 628°C according to Fig. 4. The experimental data at 650°C are shown in Fig. 5, and good fit is obtained with K_1 = 8.0 x 10^{-5} and K_2 = 0.004. These two values correspond to θ_{760} = 0.099, equivalent to a temperature of 679°C according to Fig. 4. While these agreements

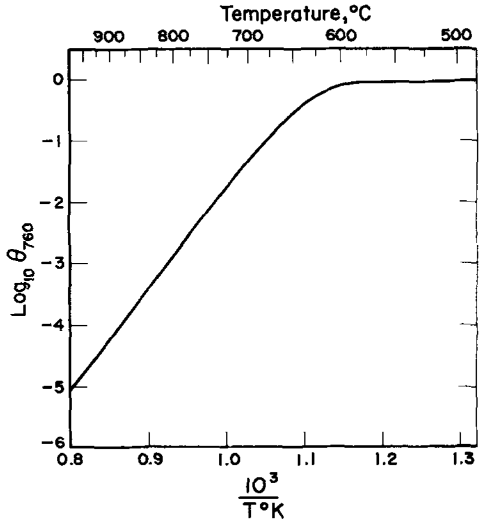

Fig. 4. Fractional surface coverage at an oxygen pressure of 760 Torr, θ_{760}, as a function of temperature.

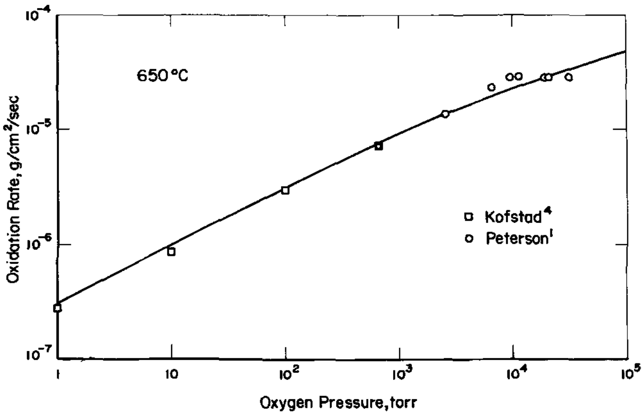

Fig. 5. Pressure dependence of the oxidation of tantalum at 650°C.

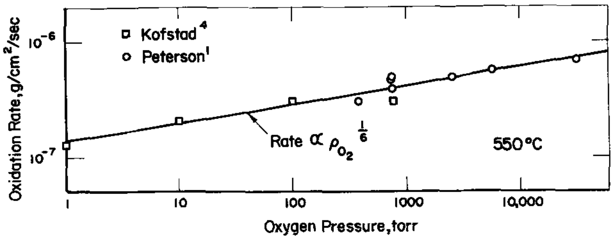

Fig. 6. Pressure dependence of the oxidation of tantalum at 550°C.

are not exact, they are sufficiently close to be satisfactory.

There are some important defects in the theory, however. Equations [4] and [7] imply that, as the pressure changes, the general form of the temperature dependence remains the same, and, in particular, that the negative slope of the higher temperature range remains the same. Kofstad's data (10) suggest that this is not so; at 10 Torr and below the rate increases slightly with temperature in the range 650°-800°C. No other investigation in this temperature and pressure range has been reported.

At 550°C one would expect θ_{760} to be in the range 0.92-0.98, but the published data of Kofstad (4) and Peterson (1) shown in Fig. 6 are better fitted by an equation of the form

$$\text{rate} \propto P_{O_2}^{1/6} \qquad [9]$$

However, this may be fortuitous. Kofstad's data alone are not inconsistent with Eq. [4] and correspond to a high value of θ.

Scale Morphology

It is clear that the properties of the tantalum pentoxide scale vary as a function of temperature. At the low temperatures the scale is soft and weak, and the layers in the laminar detached scale are thin. At high temperatures the scale is hard and strong, and the layers are much thicker. Actually, the scale is most fragmentary at about 600°C; the scale formed at 500°C appears to be far more coherent with a greater layer thickness, and the scale at 820°C is clearly much more continuous. Typical scales are shown in Fig. 7. Because of this, it is tempting to suggest that the origin of the maximum in the rate of 650°C and the anomalous temperature dependence between 650° and 800°C is related to the changing properties of the scale. In fact, this suggestion has been made by Aylmore, Gregg, and Jepson (11) in the case of niobium.

If the oxidation is assumed to take place by the repeated (parabolic) diffusion-controlled growth of adherent scale layers to a critical thickness at which they fail, an average linear rate constant K_l will result

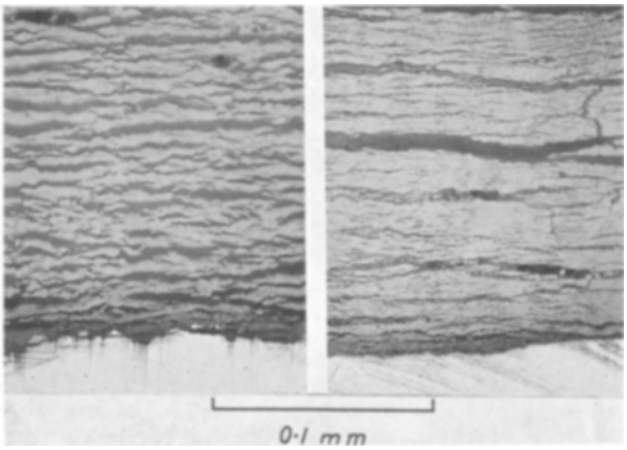

Fig. 7a. Cross sections of oxidized samples showing the lamina thickness in the detached pentoxide. Sample oxidized at 500°C, 450 Torr.

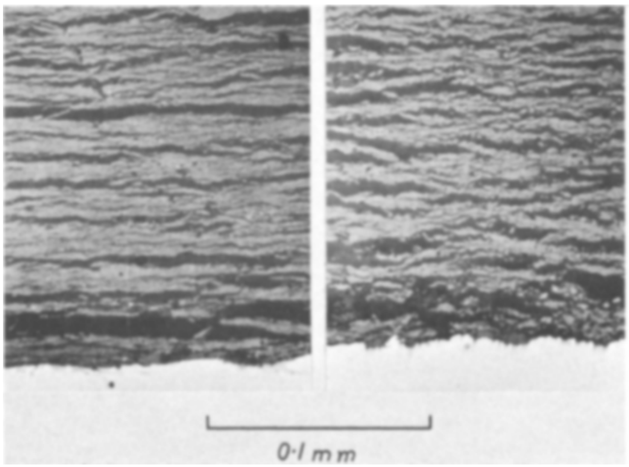

Fig. 7b. Oxidized at 600°C, 450 Torr

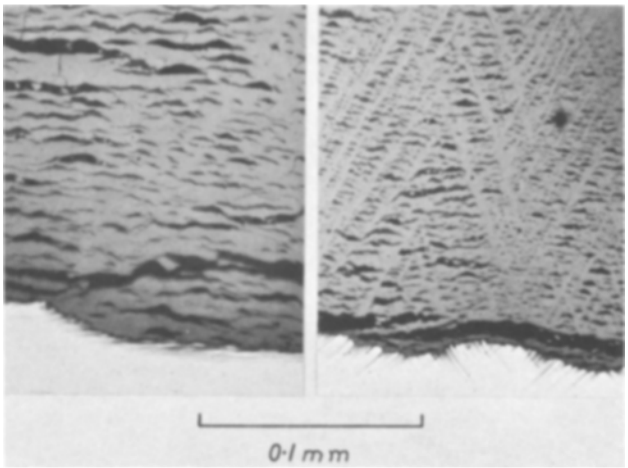

Fig. 7c. Oxidized at 820°C, 450 Torr

which is related to the parabolic rate constant K_p and the critical scale thickness w_c

$$K_l = \frac{K_p}{w_c} \qquad [10]$$

If the anomalous temperature dependence is solely a result of the change in the scale properties, one can easily calculate, using Eq. [9] and Fig. 3, the sort of change one would need to see in the critical scale thickness. Between 600° and 800°C the scale should increase in thickness by approximately 100 times. It is extremely difficult to obtain a quantitative measure of the layer thickness because of the wide variation from point to point, the loss of resolution due to multiple reflection in the oxide, and the indeterminate effects of cooling; but it is difficult to obtain a value of greater than 10 times for the change in the layer thickness in this temperature range.

However, the qualitative parallel between the temperature dependence of the rate and that of the scale layer thickness is interesting and may well be significant.

Suboxide Structure and Morphology

Since the suboxide or suboxides are metastable at all temperatures, one cannot prepare them in bulk to examine their properties. The metal + suboxide/pentoxide interface is irregular, and one must polish some way back from the interface to obtain good x-ray results, but the volume fraction of the suboxide is too small even at very short distances from the interface and the structures appear to be too close to that of tantalum itself to obtain reasonable results. Further, all one's observations of necessity must be made on specimens cooled from reaction temperature. Studies have been made on the structure of the suboxides formed in the very early stages of the oxidation, prior to the complete coverage of the surface by the pentoxide, using high-temperature x-ray diffraction and hot-stage metallography (12). It is dangerous to assume, however, that these suboxides are the same as those present in the steady-stage process (8) since, for example, the growth stresses associated with the adherent Ta_2O_5 are absent.

Recently, Stringer (7) pointed out that, above suboxide platelets lying more or less normal to the metal/oxide interface, lines of pores are formed in the pentoxide and argued that the existence of these pore lines in the scale is evidence for the presence of the platelets at reaction temperature. Using this as an indication, it appears very likely that all the platelets observed in cross sections of specimens cooled from steady-state reaction in this temperature range were present at temperature and have not precipitated on cooling. Pore lines are evident in scales formed at 600°-950°C, although as the temperature decreases they become more difficult to see.

All the platelets formed during the steady-state (linear) reaction in the temperature range 500°-925°C are parallel to $\{100\}_{Ta}$ (8).

Finally, Fig. 8a shows, in polarized light, a section through the broad part of a platelet in a specimen oxidized at 925°C, 450 Torr. There is evidence of an internal structure, which might suggest a transformation in the platelet on cooling. However, the same type of internal structure is observed in platelets formed throughout the whole temperature range, (Fig. 8b shows the internal structure in plates formed at 500°C) so that any transformation must take place below 500°C. It is also possible that this is a domain structure formed at temperature, but so far it has not been possible to determine this.

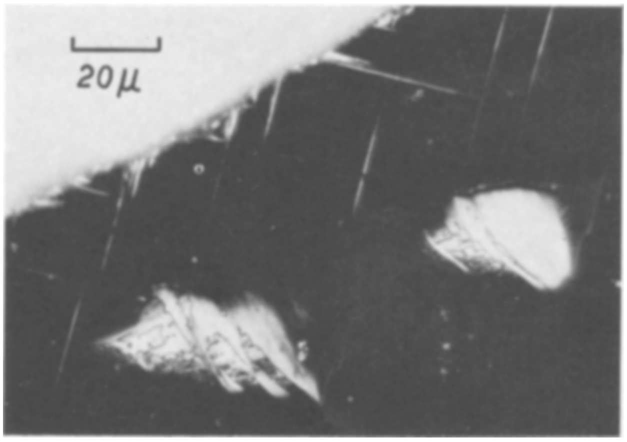

Fig. 8a. Internal structure in suboxide plates visible in polarized light; oxidized at 925°C, 450 Torr.

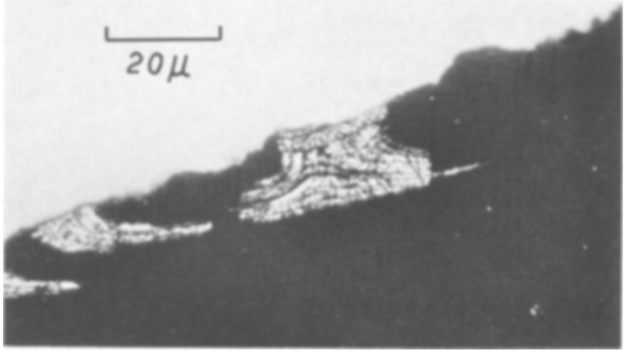

Fig. 8b. Oxidized at 500°C, 450 Torr.

It appears, therefore, that one cannot interpret the observed temperature dependence of the rate constant in terms of a change in structure or habit of the suboxide. Every indication is that they are the same throughout the whole temperature range. While the number of platelets seems a little less at 950°C than at lower temperatures, there appear to be at least as many at 800° as at 600°C, so that again one cannot explain the anomalous temperature dependence in terms of varying volume fraction of suboxide at the interface.

Scale Failure Modes

The scale grows adhering to the metal surface, and in cross section it appears that both Ta_2O_5/Ta and Ta_2O_5/suboxide interfaces may exist. However, it may be that a very thin layer of suboxide is present between the pentoxide and the metal, and in fact in polarized light a bright line is often visible between the metal and the adherent oxide, both of which appear dark. The dark coloration of the adherent pentoxide in polarized light is of interest. It also appears dark in oblique (dark-field) illumination but white in normal illumination, whereas the detached oxide appears white in all illumination. The color is darkest at the oxide/metal interface and becomes lighter away from the interface (5). The effect may be due to a stoichiometry gradient across the scale, but the striking similarity between polarized light and dark-field illumination suggests that the effect may be due to the absence of internal reflection from flaws in the oxide.

An adherent scale growing under compression on a metal surface may fail either by shear or by blistering from the metal surface. Clearly, shear is a much easier process and is probably much more common; blister-type fractures are sometimes observed, however. For tantalum oxidized at 925°C, 450 Torr, it has been observed that above $\{110\}_{Ta}$ faces the oxide lamellae are much thinner than those above the $\{100\}_{Ta}$ faces, and that this occurs because the pore lines which result from the oxidation of the suboxide plates act as crack paths (8). At 820°C this feature is still evident, but at lower temperatures there is no obvious dependence of laminar thickness on orientation. This may be because a new mode of scale failure operates at low temperatures, or may suggest that a single crack, once nucleated, propagates over a large distance. The oxidation rate is also a function of surface orientation, and in general the faces with the thinnest layer thickness oxidize most rapidly.

The oxidation rate is also a function of surface curvature at higher temperatures, and there is some evidence to suggest that the layer thickness also varies with surface curvature. Stringer (6) reported that at 820° and 925°C ¼-in.-diameter spheres oxidized more rapidly than ½-in.-diameter spheres which in turn

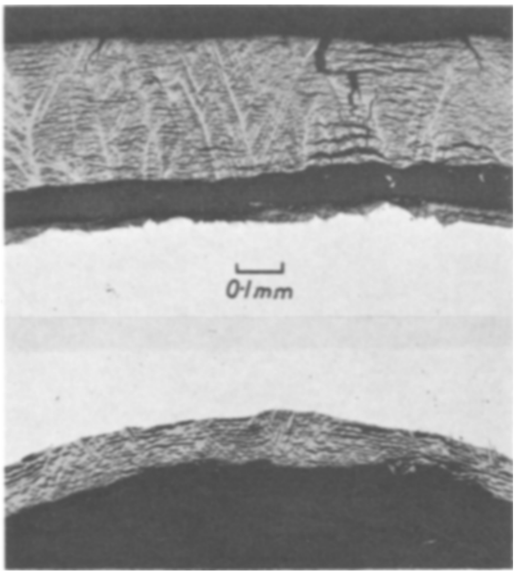

Fig. 9. Scale formed on the outer (upper photograph) and inner (lower photograph) surfaces of a tantalum tube oxidized 100 min at 820°C, 420 Torr; outer radius 6.35 mm, inner radius 1.45 mm, length 9.5 mm.

oxidized more rapidly than coupons. There was no detectable effect of surface curvature on the rate at 600°C. The scales on the spheres contained large radial fissures, apparently due to the tensile stresses produced in the outer layers of the scale by the outward pressure of the newly forming oxide.

Figure 9 shows the scale formed on the outer and inner surfaces of a cylinder oxidized at 820°C. The outer radius of the tube was 6.35 mm, the inner radius was 1.45 mm, total length was 9.5 mm. The cylinder was machined from bar stock and recrystallized, using the same preparation techniques that were used for the spheres (6) to eliminate any possibility of texture effects. The total oxide thickness was approximately three times greater on the convex outer surface than on the concave inner surface. The difference in rate diminishes as the inner radius increases; Figure 10 shows the scale formed on the outer and inner surfaces of a cylinder of internal radius 5.87 mm and external radius 6.35 mm, oxidized at 820°C. The difference in rate is negligible, although the scale formed on the outer surface contains the radial fissures and that on the inside does not. Clearly, the radial fissures do not affect the oxidation rate, and thus the difference in rate for the smaller radius must lie in the scale-fracture process at the interface. The scale layers on the concave surface are thicker in the case of the smaller diameter cylinder, but apparently not as much as three times greater. However, this cannot be determined quantitatively with any great precision. The general effect is much the same at 925°C

Although it is difficult to make categoric statements on the basis of cooled and sectioned samples, it seems likely that the interfaces present in the system are

atmosphere/Ta_2O_5
Ta_2O_5/suboxide
suboxide/Ta

and, possibly,

Ta_2O_5/Ta

One cannot dismiss the possibility of very thin layers of other suboxides, but no evidence for these has been produced. Interfaces between the atmosphere and the metal and between the atmosphere and the suboxides either do not exist or are transitory.

Rate-Controlling Processes

Plainly, the "repeated-parabolic" scaling model described before accords well with the anisotropy of

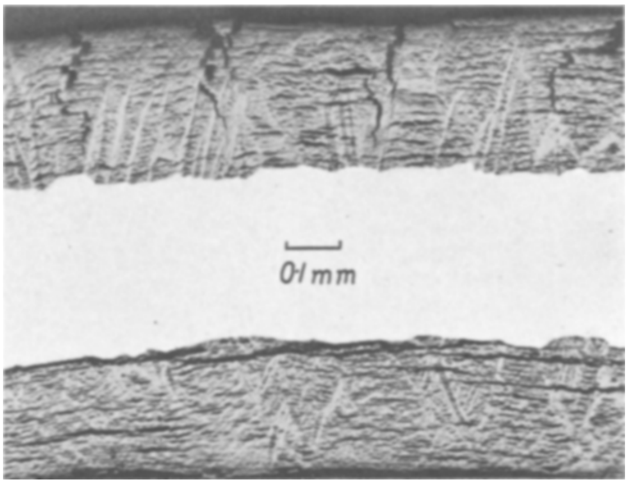

Fig. 10. Scale formed on the outer (upper part) and inner (lower part) surfaces of a tantalum tube oxidized 90 min at 820°C, 420 Torr; outer radius 6.37 mm, inner radius 5.86 mm, length 6.34 mm.

oxidation at elevated temperatures, and numerically the agreement is fair: at 925°C the {110} faces oxidize 5 to 10 times as fast as the {100} faces, and the scale laminations over the {100} faces are 5 to 10 times thicker than those over the {110} faces. If one accepts that failure of the scale is easier on a convex than on a concave surface, it also accords with the curvature-dependence of the oxidation rate at high temperatures, although here the quantitative fit is less easy to evaluate.

However, while qualitatively the variation in laminar thickness parallels the temperature dependence of the rate constant, the quantitative agreement is poor. In addition, it is difficult to reconcile the high pressure dependence of the linear rate constant with this model.

The defect structure of Ta_2O_5 is apparently complicated. Hartmann (13) reported that it was an n-type semiconductor, and, since marker experiments indicate a mobile anion, it was generally assumed that oxygen vacancies were mobile. However, Kofstad (14) has shown that the oxide is p-type at higher oxygen pressures and n-type at lower oxygen pressures, the transition pressure increasing as the temperature increases. An n-type oxide would not be expected to show a significant dependence of diffusion-controlled growth on the oxygen pressure, but a p-type scale should exhibit pressure-dependent growth. The magnitude of the pressure dependence depends on the detailed defect structure, but Kofstad (10) has shown that at pressures in the range 1-760 Torr at 900°C there is an initial parabolic growth of Ta_2O_5 for which

$$K_p \,\alpha\, P_{O_2}{}^{1/5.5} \qquad [11]$$

While the critical scale thickness would not be expected to show any direct dependence on the oxygen pressure, it might depend on the rate of the diffusion-controlled growth, thus enhancing the apparent pressure dependence of K_l. However, it would be very surprising if w_c varied as $(K_p)^{-2}$, which would be required to give the observed pressure dependence of K_l.

A linear reaction rate may also result from an interface controlled process. In this event, the reaction rate is linear on a microscopic scale; the adherent growth of the scale to the critical thickness is also linear. There is, of course, nothing in the scale morphology incompatible with this concept.

If the adherent Ta_2O_5 layer is very thin, so that transport through it is very rapid in comparison with the reactions at the pentoxide/metal + suboxide interface, the oxygen activity at this interface would equal that at the atmosphere/pentoxide interface, and so a rate-controlling process at the inner interface would not be incompatible with the observed pressure dependence of the reaction. However, in general, some oxygen-activity gradient must exist across the adherent layer to provide the driving force for the oxygen flux required by the reactions at the inner interface, and so one would expect the oxygen activity at the inner interface to be rather less than that at the outer scale/atmosphere interface. This would have the effect of reducing the apparent pressure dependence of the reaction.

It would appear more likely, therefore, that the rate-controlling process is a reaction at an interface in direct contact with the atmosphere, although one cannot at this stage reject the alternative possibility. The observed temperature dependence may then be explained in one of two ways:

(*A*) The reaction interface or the interface process changes abruptly at 800°C. Below this temperature, oxygen is adsorbed on an interface, dissociating as it is adsorbed. The agreements with the adsorption model in the range 500°-800°C are regarded as real; the apparent disagreements, in the low temperature-pressure dependence, for example, are due to experimental variations between the different investigators. Above 800°C the rate-controlling process is situated at a different interface, again between the atmosphere and one of the solid phases; or, alternatively, there is a change in the rate-controlling process at the original interface. There is insufficient evidence to indicate whether or not an adsorption process precedes this high-temperature reaction.

(*B*) Again there are two reaction interfaces involved, but in general both are present simultaneously. As the temperature is raised the relative area of one increases. The low-temperature temperature dependence is then typical of one of these processes, and the high-temperature temperature dependence of the other. The anomalous temperature range is where both contribute to a significant extent, and is thus a transition region. The low-temperature process is independent of the oxygen pressure, and the high-temperature process depends on the square root of the oxygen pressure. Increasing the pressure at any temperature increases the relative contribution of the low-temperature process, so the adsorption-type pressure-dependence curves again represent transition processes. All the numerical fits with the adsorption model are regarded as fortuitous. This model is much more qualitative than the first.

It is possible to combine the features of these models: one can regard the temperature dependence as being due to a gradual transition in rate-controlling mechanism, but accept that one or both of these processes involve an adsorption step.

However, as discussed earlier, there is every indication that the oxide and suboxide structure and morphology is essentially the same throughout the whole temperature range, and that, in particular, the only interface between the atmosphere and a solid phase is between the gas and the adherent pentoxide layer. For the high-temperature process, furthermore, it is extremely difficult to see how an interface process can show such a clear dependence on the surface curvature or on the scale failure process.

Conclusions

On the basis of the arguments presented above, it appears that the only tenable model for the oxidation involves two distinct processes.

In the range 500°-800°C the fit with the adsorption model seems far too good to be accidental. Not only can the temperature dependence in this range be explained, but the values of θ calculated from the temperature dependence at constant pressure agree quite well with those calculated from the pressure-dependence data at constant temperature. In addition, the process ceases to operate at about the temperature one would expect from a rough calculation.

Since the only interface with the atmosphere is at the outer surface of the adherent Ta_2O_5 layer, the adsorption must take place there. If one accepts that no internal interface process can show a linear dependence on the oxygen concentration at that interface, it follows that the rate-controlling process must also be at the Ta_2O_5/atmosphere interface. The reactions at this interface may be written

$$O_2/\text{gas} \rightarrow 2\,O_{\text{ads}} \qquad [12]$$

$$O_{\text{ads}} + O\square/\text{x} \rightarrow O/Ta_2O_5 \qquad [13]$$

or,

$$O_{\text{ads}} \rightarrow O\triangle/\text{x} \qquad [13a]$$

Here the subscript x indicates the outer surface of the adherent scale layer. The ionicity of the species has not been considered, The oxygen vacancies are produced (or oxygen interstitials are consumed) in the scale-forming process at the metal/scale interface

$$2Ta/_{\text{metal}} \rightarrow Ta_2O_5 + 5\,O\square/\text{o} \qquad [14]$$

or

$$2Ta/_{\text{metal}} + 5\,O\triangle/\text{o} \rightarrow Ta_2O_5 \qquad [14a]$$

$$O\square/\text{o} \xrightarrow{\text{diffusion}} O\square/\text{x} \qquad [15]$$

$$O\triangle/\text{x} \xleftarrow{\text{diffusion}} O\triangle/\text{o} \qquad [15a]$$

Similar equations involving possible suboxides may be written, but they do not affect the over-all mechanism. Equation [13] is regarded as the slow step in this sequence.

However, while it is less likely, the reactions at the outer interface may be rapid and the diffusion through the adherent oxide very rapid, and, provided the adherent layer is thin enough, the oxygen activity may be effectively the same at the inner interface as at the outer.

The reaction mechanism clearly alters above 800°C, and, because of the dependence of the rate on surface curvature and because of the apparent correlation between laminar thickness and the linear rate, one must conclude that above 800°C the linear rate is a result of a repeated parabolic process, with the diffusion step (Eq. [15]) being the slow process.

In fact, Kofstad (10) has shown that the initial nonlinear reaction at 900°C is parabolic and that at higher temperatures and lower pressures the rate curves do have the appearance of repeated parabolas. This is probably due to the fact that w_c increases as the temperature is increased so that the "smoothing out" of the repeated parabolae to an over-all linear rate is not possible. The activation energy of the high-temperature process contains the temperature dependence of the parabolic growth rate and the temperature dependence of the scale layer thickness. Since the latter clearly increases with temperature, the real temperature dependence of the parabolic rate constant must be greater than that of the linear rate. The activation energy for the linear rate is approximately 35,000 cal/mole, while Kofstad (10) gives an activation energy of 45,000 cal/mole for the initial parabolic rate in the range 900°-1050°C.

However, in this range the linear rate constant depends on the square root of the oxygen pressure (approximately). According to Kofstad (10) the parabolic rate constant varies as $P_{O_2}{}^{1/5.5}$ at pressures above the n → p transition and is independent of pressure at pressures well below the transition. Therefore, for the linear rate to exhibit the observed pressure dependence, the critical scale thickness w_c (which cannot depend directly on oxygen pressure) must depend on the rate, and in fact

$$w_c \;\alpha\; (K_p)^{-2} \;\alpha\; P^{-1/3} \qquad [16]$$

It is extremely difficult to measure w_c with any accuracy, but at 1000°C Kofstad's data (10) show no obvious pressure dependence of the scale thickness at the break-away from the initial parabola. At 1200°C w_c is approximately 1.5 times as great at 1 Torr as at

10 Torr; Equation [16] gives a value of 2.15. While the data are clearly insufficient to confirm or deny the model, they are equally clearly not inconsistent with it.

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REFERENCES

1. H. C. Peterson, W. M. Fassell, and M. E. Wadsworth, *J. Metals*, **6**, 1038 (1954).
2. W. M. Albrecht, W. D. Klopp, B. G. Koehl, and R. I. Jaffee, *Trans. AIME*, **221**, 110 (1961).
3. M. G. Cowgill, Ph.D. Thesis, Liverpool, 1963.
4. Per Kofstad, *J. Inst. Metals*, **90**, 253 (1961-1962).
5. J. Stringer, *This Journal*, **112**, 1083 (1965).
6. J. Stringer, Proc. Journees Int. Sur l'Ox. des Metaux, Brussels, 1965, To be published.
7. J. Stringer, *J. Less Common Metals*, **11**, 111 (1966).
8. J. Stringer, *ibid.*, to be published.
9. M. G. Cowgill and J. Stringer, *ibid.*, **2**, 233 (1960).
10. Per Kofstad, *Tidskrift for Kjemi, Bergvesen, og Metallurgi*, **6**, 127 (1963).
11. D. W. Aylmore, S. J. Gregg, and W. B. Jepson, *This Journal*, **107**, 495 (1960).
12. Per Kofstad and O. J. Krudtaa, *J. Less Common Metals*, **5**, 477 (1963).
13. W. Hartmann, *Z. Physik*, **102**, 709 (1936).
14. Per Kofstad, *This Journal*, **109**, 776 (1962).

Carburization of Fe-Cr Alloys During Oxidation in Dry Carbon Dioxide

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ABSTRACT

Iron-chromium alloys (1-15 w/o [weight per cent] Cr) oxidized in dry carbon dioxide at 700°, 900°, and 1100°C form duplex scales which are similar in structure to those generated in H_2O-Ar atmospheres, *i.e.*, a detached but continuous outer layer of iron oxides (predominantly FeO) and a porous inner layer of FeO and Fe-Cr spinel particles. Carburization accompanies this oxidation at all temperatures, and the resulting microstructural changes, the carbides formed, the hardness increases and the carbon content of homogeneous specimens are related to the equilibria of the Fe-Cr-C system. The carburization and the continued high oxidation rates, in spite of the detached duplex structure of the scale, require that a gaseous transfer of oxygen and carbon occur within the voids separating the outer and inner oxide layers. This requirement suggests a carbon permeation of the dense outer scale and the generation of a CO_2-CO atmosphere in these voids which is carburizing as well as oxidizing to the alloy.

The high-temperature oxidation of iron-chromium alloys in carbon dioxide produces two-layered scales which are very similar in structure to those generated on these alloys in atmospheres of H_2O-Ar (1). An example of this scale structure is illustrated by the micrograph of Fig. 1. The outer layer of iron oxides is dense and crack-free while the inner layer of wustite and an Fe-Cr spinel is relatively porous. The oxidation process generates large voids between the outer and inner scale layers, but the extension of these voids does not appear to alter the high oxidation rates of these alloys. In fact, these rates are comparable to that of pure iron where the scale remains rather adherent and the diffusion of iron is unhindered by voids.

Within the proper experimental limits of time and temperature linear rates are observed for the oxidation of iron in CO_2-CO mixtures, and there is general agreement that the reaction at the gas:oxide interface is the rate determining process (2-4). Thus, the diffusion of iron through the oxide is sufficiently rapid to preclude the observation of parabolic oxidation rates. Similarly, the oxidation rates of Fe-Cr alloys indicate that an adequate flux of iron to the gas:oxide interface is maintained in spite of the extensive voids separating the outer from the inner scale layer. Although this detachment is never complete, the remaining columns of oxide connecting the two layers appear to be adequate as diffusion paths for the iron required by the oxidation reaction at the outer-oxide:gas interface. Since the integrity of the outer detached scale layer is preserved, an alternative source of iron must be provided to augment the "normal" diffusion process through the connecting oxide columns if the high oxidation rates are to be sustained.

The experimental evidence in the previous study of the oxidation of Fe-Cr alloys in water vapor indicated a substantial contribution to the iron flux in the

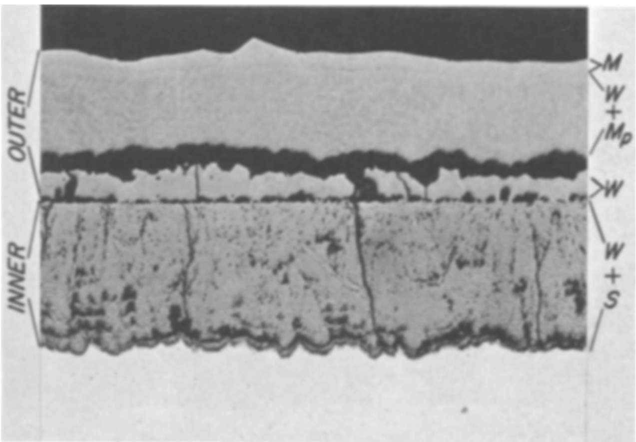

Fig. 1. Unetched microstructure of a typical two-layered scale, from Fe-15Cr alloy oxidized for 24 hr at 900°C in 1 atm of dry CO_2. Magnification approximately 60X.