JOURNAL OF MATERIALS SCIENCE 9 (1974) 985–988

Relationship between activation energies for the thermal oxidation of metals and the semiconductivity of the oxides

ASHOK K. VIJH
Hydro-Quebec Institute of Research, Varennes, P.Q., Canada

The activation energies for the thermal oxidation of metals appear to be inversely related to the band gaps, heats of formation per equivalent and the electronic conductivity of the oxides formed. An attempt is made to develop the theoretical significance of these correlations in the context of a general discussion of some fundamental aspects of the thermal and the anodic oxidation of metals.

1. Introduction

An interesting problem in the thermal oxidation of metals to yield oxides is the delineation of the factors that appear to be correlated to the magnitudes of the activation energies for the oxidation process. On the basis of an earlier suggestion of Rideal and Wansbrough-Jones [1], Ward and Bharucha [2] have shown that the activation energies for the oxidation of several metals appear to be related to their work functions. The growth of oxide during the high temperature oxidation proceeds through the ionic conduction so that factors bearing on this ionic conduction should be related to the activation energies for the oxidation.

2. Statement of the argument

The electronic conduction in semiconductors is given by the equation [3]:

$$\sigma = \sigma_0 \exp(-E_g/2kT) \qquad (1)$$

where σ is the electronic conductivity at the absolute temperature, T; E_g is the activation energy for the electronic conduction and is thus the "thermal" band gap; σ_0 is the limiting electronic conductivity for the material when $T \rightarrow \infty$; k is the Boltzmann constant. High values of E_g, as, for example, in the oxides of Al, Ta, Nb, Zr etc, signify that very high temperature-gradients (or fields) can be built across these oxides before an appreciable electronic conduction can result. Since for these high band gap materials, the electronic conduction is rather slight, the application of high temperature (or the field) results in the movement of ions in the oxide. The ionic current associated with this thermally- or field-assisted ionic conduction is represented, in its empirical form, by the equation [3].

$$i = A \exp B(V/D) \qquad (2)$$

where i is the ionic current (i.e. ionic conduction); (V/D) is the average value of the applied field operating across the oxide since V is the voltage drop across the oxide and D is its thickness; A and B are constants containing appropriate functions of temperature.

The above empirical equation can also be derived in a form, as reviewed previously [3], based on mechanistic considerations regarding the field- and thermally-assisted motion of ions over the appropriate activation energy barriers. This equation may be written, in its most simplified form, as [3]:

$$i = n\nu Z \exp - \left(\frac{E - Za(V/D)}{kT}\right) \qquad (3)$$

where n is the density of the mobile ions within the oxide; ν is a frequency factor and denotes the number of times the ion may jump the appropriate activation energy barrier, provided that it is sufficiently activated either by temperature or by field or by photo-stimulation; Z is the effective charge on the mobile ion; E is the height of the activation energy barrier; a is the distance between the position of minimum energy (initial state) and the maximum energy (activated state) of the mobile ion.

In Equation 3, when n, ν, Z, E, a and k are constants, the ionic current i depends on (V/D) and T. At constant temperature, a higher value of the applied field (V/D) makes the activation energy E much lower, thus increasing the ionic conduction current i. For oxides of low electronic conductivity, it is clear that very high fields, (V/D), can be built across them (before noticeable electronic currents commence to flow) with the consequent increase in the ionic current, i. Similarly, for constant (V/D) (as, for example, in the thermal oxidation of metals), a higher value of temperature, T, would tend to produce insignificant electronic currents up to rather high temperatures, whereas substantial ionic currents would flow before even negligible electronic conductions occurs.

In conclusion, then, high band gap materials show low electronic conduction and, under conditions of significant applied temperature or field, can sustain appreciable ionic conduction [3-8]; the latter would signify a low activation energy for the oxidation process, assuming that the oxide growth is controlled by the field- or thermally-assisted diffusion of ions within the growing oxide. From the foregoing arguments and assumptions, a situation emerges in which low electronic conduction (i.e. high E_g values) herald higher ionic conduction and thence a lower activation energy for the process of the oxidation of metals. The following sections show that this line of reasoning is roughly sustained by the available experimental data.

3. Correlation between the activation energies and semiconductivity

In Fig. 1, the activation energy, E, values for the oxidation of metals [2] have been plotted against the band gap, E_g, values [3] of the oxides of the shown metals. A high E value is generally associated with the low E_g value, although zirconium departs from the shown trend. Since band gap values are available for a limited number of oxides only, it is of interest to explore this relation further by plotting the E values against the corresponding (exothermic) heats of formation per equivalent, $-\Delta H_e$; the $-\Delta H_e$ value for a material is roughly equal to half the band gap [4]. In Fig. 2, one observes that high E values correspond to low $-\Delta H_e$ $(= \frac{1}{2} E_g)$ values.

One may correlate E values not only with the E_g values of the oxides (as in Figs. 1 and 2), but also with the direct values of high temperature electronic conductivity of the oxides (through Equation 1) for which the data are available [3] (Fig. 3). Here again, highly insulating oxides such as Al_2O_3 and TiO_2 exhibit low magnitudes

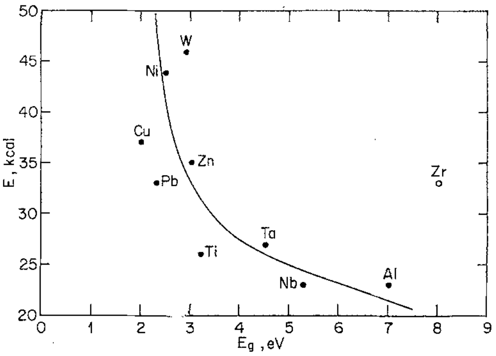

Figure 1 A plot of the activation energy for the high temperature oxidation of metal, E, versus the band gap, E_g, value of the oxide formed for the shown metals. The data are given in Table I together with the source references.

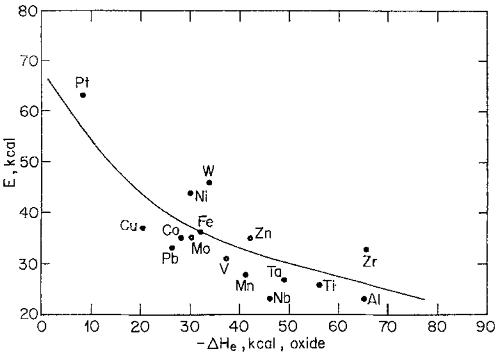

Figure 2 A plot of E versus the heats of formation per equivalent, $-\Delta H_e$, values of the oxides of the shown metals. See Table I for data and references.

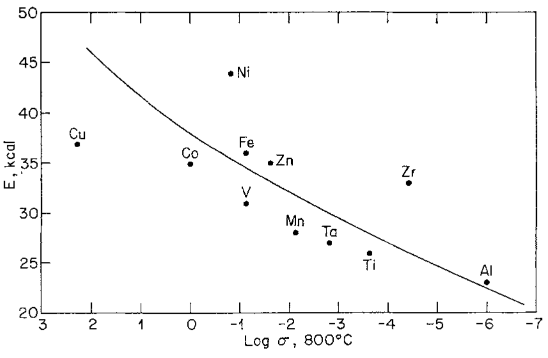

Figure 3 A plot of E versus log σ, 800°C (where σ is the electronic conductivity for the oxides of the shown metals). See Table I for data and references.

of E whereas relatively conducting oxides (e.g., of Cu, Ni and Co) show high E values, although a large scatter in this correlation permits the establishment of a rough trend only. The data, and the source references, used in the construction of Figs. 1 to 3 have been presented in Table I here.

TABLE I

Metal	E (kcal)	$-\Delta H_e$ (kcal)	E_g (eV)	Log σ (800° C)
Pt	63	$\simeq$ 8	—	—
W	46	33.5	2.9	—
Ni	44	29.2	2.5	−0.8
Cu	37	20.0	2.0	2.3
Fe	36	32.1	—	−1.1
Mo	35	30.1	—	—
Co	35	28.6	—	0
Zn	35	41.6	3.0	−1.6
Zr	33	65.4	8.0	−4.4
Pb	33	26.1	2.3	
V	31	37.3	—	−1.1
Mn	28	41.4	—	−2.1
Ta	27	48.9	4.5	−2.8
Ti	26	56.4	3.2	−3.6
Nb	23	46.5	5.3	—
Al	23	65.3	7.0	−6

Notes: 1. The E values are from Ward and Bharucha [2]; the value for Cr not used since it was concluded to be suspect in this compilation [2].
2. The E_g and $-\Delta H_e$ values are from [4] and the papers cited therein.
3. The log σ values (where σ is the electronic conductivity) are from [4] and the papers cited therein.

It may thus be concluded that a high electronic conductivity of the oxide generally leads to a low activation energy for oxidation of the corresponding metal by creating conditions favourable for a facile ionic conduction (Figs. 1 to 3).

4. Discussion

It is clear that the approximate theoretical basis of Fig. 1 arises from the discussion of Equations 1, 2 and 3, as presented above. Fig. 2 is really a restatement of Fig. 1, since $E_g = -2\Delta H_e$ as shown previously [3, 4, 9]; this figure is presented only to show the validity of the present line of argument even for those oxides for which the E_g values are not available, i.e., the correlation, $E_g - -2\Delta H_e$, permits the examination of Fig. 1 for many more metals, as in Fig. 2. And, finally, Fig. 3 confirms yet again the present viewpoint since E_g is related to log σ through the Equation 1. In summary, the correlation of the activation energy for the oxidation of metals, namely, E is demonstrated to be related to the semiconductivity of the oxides by three separate (but inter-related) indicators of semiconductivity, i.e., E_g, $-\Delta H_e$ ($= \frac{1}{2} E_g$), and the log of electronic conductivity (see Figs. 1 to 3 and Equations 1 and 2).

It should be emphasized here that the foregoing line of reasoning is quite valid for oxides such as Al, Zr, Nb, Ta, Fe, Ti, W and Zn etc., i.e., the oxides for which there is some evidence that the oxide growth proceeds by the temperature- or field-assisted migration of ions within the oxide. However, for the case of metals such as Pt, Cu and Pb, and perhaps also some other metals, the foregoing considerations are perhaps not rigorously applicable because the oxide growth on these metals probably does not occur by the diffusion of ions within the oxide. Some recent evidence [10] from the work on the anodic oxidation of metals suggests strongly, however, that even for the case of Pt, the oxide growth occurs by the same mechanism as that observed on Ta, namely, the ionic conduction brought about by the applied field operating across the oxide. In the light of this work [10], it is perhaps not inappropriate to suggest that even in the thermal oxidation of metals, oxide growth on Pt, Cu and Pb etc., by thermally-assisted ionic conduction is not impossible. This suggestion is particularly attractive in view of a recent report [11] in which it was demonstrated that the thermal and the anodic oxide growth processes on metals basically involve events which are quite comparable. However, in the absence of some further clear-cut data bearing on this point, it should be stated that the rough trends followed by metals such as Pt, Cu and Pb in Figs. 1 to 3 should perhaps be treated as fortuitous at the present time.

References

1. E. K. RIDEAL and O. H. WANSBROUGH-JONES, *Proc. Roy. Soc. (London)* **A123** (1929) 202.
2. A. F. H. WARD and N. R. BHARUCHA, *Rec. Trav. Chim. Pays-Bas* **72** (1953) 735.
3. A. K. VIJH, "Electrochemistry of Metals and Semiconductors" (Marcel Dekker, New York, 1973).
4. *Idem*, in "Oxides and Oxide Films", Vol. 2, edited by J. W. Diggle (Marcel Dekker, New York, 1973).
5. L. YOUNG, "Anodic Oxide Films" (Academic Press, New York, 1961).

6. T. P. HOAR, in "Modern Aspects of Electrochemistry", Vol. 2, edited by J. O'M. Bockris (Butterworths, London, 1959).
7. J. W. DIGGLE, T. C. DOWNIE and C. W. GOULDING, *Chem. Rev.* **69** (1969) 365.
8. F. J. BURGER and L. YOUNG, in "Progress in Dielectrics", Vol. 5 (Heywood, London, 1962).
9. A. K. VIJH, *J. Mater. Sci.* **5** (1970) 379.
10. J. L. ORD and F. C. HO, *J. Electrochem. Soc.* **118** (1971) 46.
11. A. K. VIJH, *J. Mater. Sci.* **8** (1973) 1669.

Received 26 September and accepted 31 December 1973.