Acknowledgements

I would like to thank R. R. Monchamp for his continued support and helpful suggestions, S. R. Bolin for technical consultation, O. J. Guentert for probe analysis of the inclusions, and A. Goguen, K. Hartnett, and L. Kalian for their assistance in growing the crystals.

References

1. E. M. LEVIN, *J. Amer. Ceram. Soc.* **50** (1967) 381.
2. L. G. VAN UITERT, R. C. LINARES, R. R. SODEN, and A. A. BALLMAN, *J. Chem. Phys.* **36** (1962) 702.
3. L. H. BRIXNER and E. ABRAMSON, *J. Electrochem. Soc.* **112** (1965) 1.
4. A. A. BALLMAN, R. C. LINARES, JUN, and L. G. VAN UITERT, US Patent 3, 152, 085 (1964).
5. W. PHILLIPS and R. J. PRESSLEY, *Amer. Ceram. Soc. Bulletin* **46** (1967) 366.
6. K. MUTO and K. AWAZU, *Japan J. Appl. Phys.* **8** (1969) 1360.
7. R. PUTTBACH, personal communication.
8. V. I. POPOV, KH. S. BAGDASAROV, I. N. BUSEVA, and M. V. MOKHOSOEV, *Sov. Phys. Cryst.* **13** (1969) 974.
9. H. M. DESS and S. R. BOLIN, *Trans. Met. Soc. AIME* **239** (1967) 359.
10. J. J. RUBIN and L. G. VAN UITERT, *J. Appl. Phys.* **37** (1966) 2920.
11. E. A. MAUNDERS and L. G. DESHAZER, *J. Opt. Soc. Amer.* **61** (1971) 684.
12. R. C. PALILLA, A. K. LEVINE, and M. RINKEVIC, *J. Electrochem. Soc.* **8** (1965) 776.
13. J. R. O'CONNOR, *Appl. Phys. Letters* **9** (1966) 407.
14. C. D. BRANDLE, D. C. MILLER, and J. W. NIELSEN, *J. Crystal Growth* **12** (1972) 195.

Received 9 March
and accepted 22 March 1973

A. D. MORRISON*
Raytheon Co.,
Special Microwave
Devices Operation,
Waltham, Mass., USA

---

*Present address: Tyco Laboratories Inc, Waltham, Mass, USA.

A correlation between thermal and anodic oxide growth behaviour on some metals

A systematic and comprehensive investigation of the comparative thermal oxidation behaviour of the elements of the periodic table has been recently reported by Stone [1]. A parameter, T_p, was chosen as the measure of the comparative ease of oxidation; this T_p is the temperature for every element, in °C, at which a weight change of 1 mg cm^{-2} 4h^{-1} was achieved. The parameter T_p is thus only a *rough* index of the relative oxidation rates of metals because it fails to take into account the differences in the densities of oxides; thus the same rate of weight gain may not correspond to the same *amount* (e.g., in milliequivalent or millimoles) of oxide formed under the same conditions. However, for the purposes of comparison of relative trends of various metals for the thermal oxide growth process, T_p is indeed a satisfactory index, as shown by Stone [1].

The purpose of the present note is to show that the relative ease (or difficulty) of *thermal* oxidation of various metals is related to their relative ease (or difficulty) of *anodic* oxide growth; the oxide formed in the latter process results from the electrochemical processes occurring on the anode dipped in an electrolyte solution and placed in an electrolysis configuration [2].

In the thermal oxide growth, the overall process is:

$$\text{M} + \text{O}_x \rightarrow \text{MO}_x \qquad (1)$$

where M is the metal. In the anodic oxide growth, the corresponding reaction in acidic or neutral solutions is:

$$\text{M} + x\,\text{H}_2\text{O} \rightarrow \text{MO}_x + 2x\text{H}^+ + 2xe. \qquad (2)$$

In the alkaline solutions, the anodic oxide growth occurs by the reaction:

$$\text{M} + 2x\,\text{OH}^- \rightarrow \text{MO}_x + x\,\text{H}_2\text{O} + 2xe. \qquad (3)$$

The driving force for oxide growth during the thermal oxidation is the temperature. When one adopts T_p as the parameter denoting ease of oxidation, after Stone [1], higher T_p values indicate that larger driving force (i.e., temperature) is needed to force the oxidation; alternatively, lower T_p values show that the thermal driving force needed is rather low.

In the anodic growth, the driving force (corresponding to the T_p of thermal growth) is

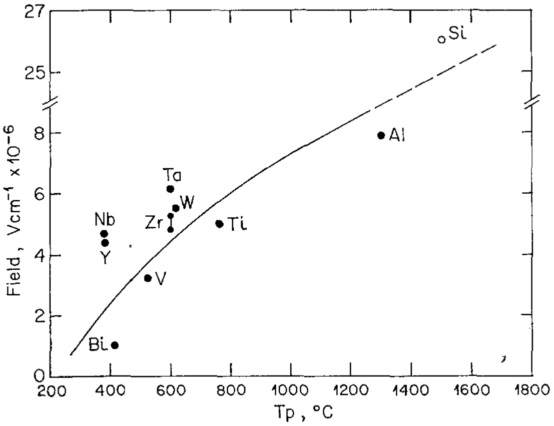

Figure 1 A plot of T_p, in °C, for the thermal oxidation of the shown metals versus the field required to sustain a typical ionic current density (1×10^{-3} A cm^{-2} in the present case) during anodic oxide growth. The T_p values are defined in the text and are from [1]; the values of the anodic field are taken from a previous paper [5].

the *field* needed to sustain a given value of the ionic current density, the latter being responsible for the conversion of the metal to the corresponding oxide in accordance with the well-known Faraday's laws of electrolysis. For the metals for which the data are available in the literature, the driving force needed for the thermal oxidation (T_p) and that for the anodic oxidation (field at a given current density) appear to be roughly correlated (Fig. 1). It is clear that higher T_p values herald higher fields, notwithstanding the broken scale in Fig. 1, which was necessary to accommodate Si. Very high T_p values tend to be associated with very high fields as for the case of Al and Si; conversely, low fields tend to be associated with low T_p values as in the case of Bi. The purpose of this correlation (Fig. 1) is only to show that roughly similar trends are followed by metals with regard to thermal and anodic oxidation. This is, of course, not entirely unexpected since in Equations 1 to 3 the same reaction is always carried out, namely, conversion of M to MO_x, although the means of negotiating the activation energy barriers involved in these reactions are different in the two cases, namely, temperature in the thermal oxidation and applied field in the anodic oxidation.

It should be mentioned that reliable data on the fields required during anodic oxide growth on metals other than those in Fig. 1 are not reliable. In fact, it is not possible to sustain appreciable *anodic* oxide growth on many other metals simply because anodization in electrolyte solutions can lead to other parallel reactions, occurring preferentially to oxide growth; e.g., oxidation of the electrolyte components, oxygen evolution and anodic dissolution of the metal, etc [3, 4].

References

1. H. E. N. STONE, *J. Mater. Sci.* **7** (1972) 1147.
2. J. W. DIGGLE, T. C. DOWNIE and C. W. GOULDING, *Chem. Rev.* **69** (1969) 365.
3. A. K. VIJH, *Corrosion Sci.* **11** (1971) 411.
4. *Idem*, "Electrochemistry of Metals and Semiconductors" (Marcel Dekker, New York, 1973).
5. *Idem*, *J. Electrochem. Soc.* **116** (1969) 972.

Received 21 May
and accepted 11 June 1973

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

A metallic replica technique for scanning electron microscopy

The scanning electron microscope (SEM) is a very useful tool for observing the surface topography of materials. For most metals, it is unnecessary to give the sample any treatment before observation. For non-conductive materials, such as polymers, the usual method to prepare the surface for observation in the SEM is to deposit a thin metal layer on the sample surface. This treatment is usually found to be satisfactory for low magnification (×100 to 1000). For higher magnification, where higher time-average electron beam densities are required, the sample will distort, degrade and often crack in the region of scanning. In an electron beam, polymers do not merely distort owing to differential expansion of different crystalline regions but also undergo irreversible structural changes. For crystalline polymers, such as polyethylene, the electron beam can influence