JOURNAL OF MATERIALS SCIENCE 8 (1973) 349–351

Interfacial energies and chemical compound formation

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The limitations of using bulk thermochemical data to characterize the initial stages of chemical compound formation are discussed and a correction, involving the relevant interfacial energies, is proposed. Apparent anomalies in the variations of the surface energy of copper with oxygen potential are consistent with the proposed analysis.

1. Introduction

Just as the heat of solution of a solid depends on the state of subdivision or its surface-to-volume content [1], so should the heat of reaction associated with stable chemical-compound formation, such as oxidation. This implies that during the initial stages of oxidation of a solid when only a thin film is present, the relevant free energy for forming a mole of oxide should be different from that for the formation of bulk oxide. In effect, at this scale, the energies of the metal/oxide interface and the oxide/vapour interface may contribute significantly to form stable oxide at oxygen potentials below those derived from bulk oxide thermochemical data. This notion appears to have been largely ignored, at least from the point of view of direct quantitative study, although Kubaschewski and Hopkins [2] have made reference to a couple of casual observations.

In this article, we make a quantitative assessment of the significance of this notion, by examining certain apparently anomalous features in our previously published results on the variation of surface energy of copper [3] and iron [4] with oxygen potential.

Considering the typical reaction,

$$\text{Me} + \tfrac{1}{2}\text{O}_2 = \text{MeO}$$

according to standard thermochemical practice, the oxide will be energetically stable when the oxygen potential $p_{\text{O}_2} > \exp\,(2\triangle G^{\text{b}}/RT) = p_{\text{O}_2}{}^{(\text{b})}$, where $\triangle G^{\text{b}}$ is the free energy of formation of one mole of bulk oxide.

Suppose now that during initial oxidation the oxide is distributed as a thin uniform layer of thickness t (Fig. 1). The process of oxide formation liberates the surface energy of the metal substrate $\gamma_{\text{M/V}}$, but requires the free energies $\gamma_{\text{M/O}}$ and $\gamma_{\text{O/V}}$ associated with the creation of the metal/oxide interface and the oxide/vapour interface. Thus in this situation, the free energy for oxide formation is,

$$\triangle G^{t} = \triangle G^{\text{b}} + \left[\gamma_{\text{M/O}} + \gamma_{\text{O/V}} - \gamma_{\text{M/V}}\right]\frac{\Omega}{t} \quad (1)$$

where Ω is the molar volume.

For thick film oxide formation, t is very large compared with molecular dimensions and normally the second term in the above is negligible, irrespective of the magnitudes of the interfacial energies. Consider now the effect of a very small t on the oxygen potential for oxide formation. When $\gamma_{\text{M/V}} > \gamma_{\text{M/O}} + \gamma_{\text{O/V}}$, there is a net release in interfacial free-energy on oxide formation, i.e., the reaction is even more exothermic, leading to a larger total negative

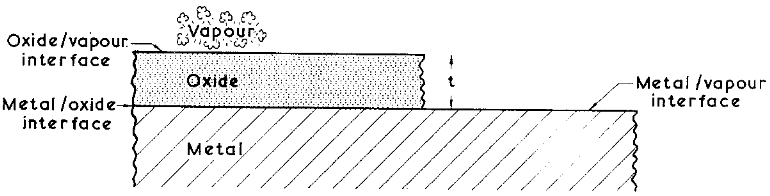

Figure 1 Schema of metal surface with a thin, uniform oxide layer.

free-energy of oxidation. (We note that for the converse situation, $\gamma_{M/V} < \gamma_{M/O} + \gamma_{O/V}$, an activation energy barrier must be overcome for the reaction to occur: this then constitutes a standard nucleation and growth phenomenon.) For the case considered here, the corresponding oxygen potential for the formation of a layer of thickness t of oxide can be shown to be

$$RT \ln p_{O_2}{}^{(t)} = RT \ln p_{O_2}{}^{(b)} - \left[\gamma_{M/V} - \gamma_{M/O} - \gamma_{O/V}\right] \frac{2\Omega}{t} \qquad (2)$$

noting that the relevant $\gamma_{M/V}$ refers to the clean metal-vapour interface and not to the metal surface with an adsorbed oxygen layer.*

2. Illustration of this effect

The above allows the interpretation of certain features of experimental results on surface energy isotherms, obtained earlier [3, 4], by use of a refined zero-creep technique on thin foils held in an atmosphere of rigidly-controlled oxygen potential. Further details of experimental technique are given in [3]. Both in the case of iron and copper, the isotherms at low partial pressures of oxygen followed the conventional form, showing a Gibbsian adsorption of oxygen, but in each case, anomalous behaviour was observed at a p_{O_2} considerably lower than that predicted for bulk oxidation.

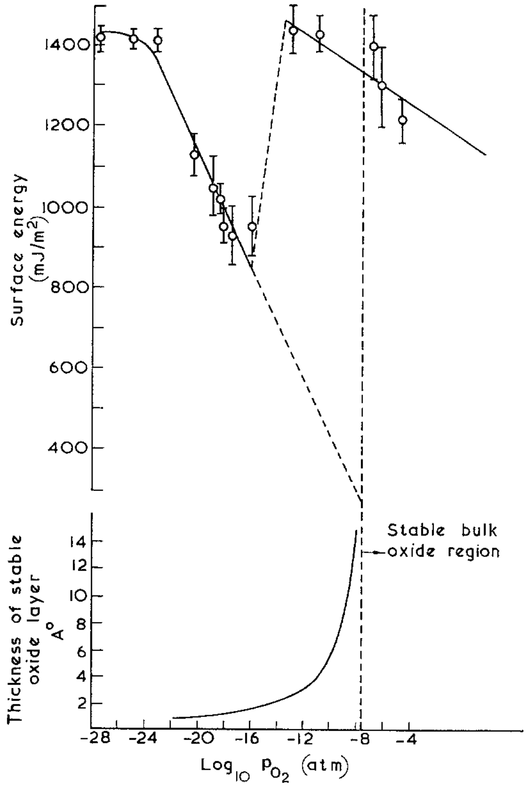

Figure 2 (Upper part): variation of surface energy of copper with oxygen potential. (Lower part): predicted variation of thickness of stabilized oxide layer with oxygen potential.

Considering for example, the Cu-O isotherm for 927°C reproduced in the top part of Fig. 2, three broad regimes can be identified: (i) at a very low p_{O_2}, the surface energy is independent of oxygen potential, indicative of clean surface: (ii) in the range $\log p_{O_2}$ between -22 and -16, the surface energy falls linearly with $\log p_{O_2}$, demonstrating Gibbs adsorption behaviour with a constant excess coverage of oxygen, which in this case corresponds to the formation of 0.26

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*The validity of this can be shown in the following way.

The condition for equilibrium between a metal surface of area A with (a) an adsorbed coverage, Γ, of oxygen; and (b) a thin layer of oxide of thickness t, can be obtained by equating the total free energies of the systems

$$\frac{At}{\Omega}\,\mu_{Me} + \tfrac{1}{2}\left(\frac{At}{\Omega} - \Gamma A\right)\mu_{O_2} + \gamma^* A = \frac{At}{\Omega}\,\mu_{MeO} + (\gamma_1 + \gamma_2)A$$

where the μ's are the chemical potentials of the various phases; and γ^*, γ_1, and γ_2 are the surface energies of the metal/adsorbed oxygen, metal/metal oxide and metal oxide/oxygen interfaces. However, we may substitute

$$\gamma^* = \gamma_O - \tfrac{1}{2}\Gamma\mu_{O_2}$$

where γ_O refers to the clean metal/vapour interface and

$$\mu_{O_2} = \mu^1 + RT \ln p_{O_2}.$$

The condition for equilibrium reduces to

$$\left(1 - \frac{2\Gamma\Omega}{t}\right) RT \ln p_{O_2}{}^{(t)} = RT \ln p_{O_2}{}^{(b)} - \left(\gamma_{M/V} - \gamma_{M/O} - \gamma_{O/V}\right)\frac{2\Omega}{t}$$

which is essentially identical to Equation 2 since $\Gamma\Omega/t \ll 1$.

of a monolayer of chemisorbed oxygen: (iii) at $\log p_{O_2} = -15$, there is a discontinuity in the isotherm, although, according to bulk thermochemical data, oxidation should not commence until $\log p_{O_2} = -7$.

The puzzling feature here is this position of the discontinuity. According to the Gibbs Adsorption Isotherm, the surface energy should fall linearly with $\log p_{O_2}$, until some other surface reaction occurs, such as compound formation.

The only reason for the discontinuity to occur at a lower p_{O_2} than that expected is that some surface compound has been formed at this p_{O_2}, probably a protoxide, Cu_2O. At this point, the surfaces are covered by a thin film of this product and it is reasonable to suggest that the measured surface energy refers to the composite quantity $(\gamma_{Cu/Cu_2O} + \gamma_{Cu_2O/V})$: the value measured here (800 mJ m^{-2}) appears reasonable.* We note that the apparently high surface energies at a p_{O_2} above the discontinuity are difficult to interpret because it is not clear what the zero-creep technique is measuring in this complex situation – further parameters, such as the grain size of the oxide are required before these surface energies can be partitioned between the relevant interfaces.

Applying the value $\gamma_{Cu/V} - (\gamma_{Cu/Cu_2O} + \gamma_{Cu_2O/V}) = 620$ to Equation 2 the thickness of oxide stable over a range of p_{O_2} can be calculated. This is shown on the lower part of Fig. 2. It indicates that the optimum thickness of stable oxide film possible in these conditions increases at first slowly with increasing p_{O_2}, and then very rapidly as the p_{O_2} approaches the value for bulk oxidation. Beyond this point, there is no energetic limit to the thickness of the oxide, which obeys normal oxidation kinetics.

3. Conclusion

We have demonstrated in the case of copper, and the same holds for iron, that there is a size effect for the thermochemical conditions for oxide formation and that a precursor oxide may exist at oxygen potentials well below those normally computed from bulk data. This should also be relevant in any chemical reaction or phase transformation in which an existing interface is replaced by two interfaces possessing a lower total interfacial free-energy. Accurate experimental values of the relevant interfacial free energies are not currently available for a broader survey of this effect.

References

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Received 14 July and accepted 29 September 1972.

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*At the lowest measured point of the first linear portion, i.e., at 800 mJ m^{-2}, there is *equilibrium* between the metal surface with adsorbed oxygen and the metal surface with an embryo oxide layer and consequently, this point measures approximately the quantity $(\gamma_{M/O} + \gamma_{O/V})$.