Prediction of Alloy Component Oxidation Order from a Kinetic Model using Free Energies of Oxide Formation

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Described is a method based on the modified Cabrera–Mott model to predict the order of oxidation of alloy components under conditions of varying temperature and oxygen pressure.

Alloys are increasing in complexity with multiple components and manufacturing treatments.[1] The complexity of the chemistry of oxidation has also increased accordingly, such that complex oxide overlayers provide the ultimate corrosion protection for the metal. Through extensive surface studies of the oxidation of the following bulk alloys and their thin films prepared in vacuum: Cu–Mn,[2] Ag–Mn,[3] Ni–Zr,[4–6] Ni–Ti,[7] Ni–Hf,[8] Ti–Cu[9] and Ti–Al,[9–11] Cocke and coworkers have found an amazing compliance, on a qualitative level, between the Grimley[12] modified Cabrera–Mott model and the thin layer structure and order of alloy component oxidation. The centrepiece of this model is based on the free energies of formation of the oxides calculated on a per mole of O^{2-} in the oxide. This model not only predicts which alloy component will oxidize preferentially but also successfully predicts which particular oxide for a given metal will actually form and the ultimate oxide overlayer structure. We have demonstrated that the modified Cabrera–Mott model (after Atkinson[13]), eqn. (1),

$$\Delta\Phi = \frac{-\Delta G^0_f}{2e} + \frac{kT}{2e}\ln\left[\frac{4e^2 N_s a_{O_2}^{1/2}x}{kT\varepsilon\varepsilon_0}\right]\tag{1}$$

where $\Delta\Phi$ is the potential across the growing oxide that drives the oxidation process, provides a qualitative guide to understanding alloy oxidation. This potential is described as the sum of two terms. The first term involves the free energy of formation of oxygen anions at the surface, $-\Delta G^0_f$, and can be approximated by the free energy of formation of the oxide per mole of O^{2-}. The second term includes the temperature, T, and the oxygen activity (relative fugacity), a_{O_2}, which are experimentally controllable parameters. The other terms in the Cabrera–Mott equation are the total number of surface O^{2-} per unit area of surface, N_s; the film thickness, x; the electronic charge, e; the relative electron permittivity (the dielectric constant), ε; the electron permittivity in vacuum, ε_0; and the Boltzmann constant, k. The model was originally derived by considering only a single metal component system and only the electron transfer and oxygen adsorption reaction at the metal gas interface: $[1/2\ O_2 + 2e^- + \text{Surface} \rightarrow O^{2-}_{(\text{surface})}]$. the model provides a qualitative framework for the discussion of chemistry of alloy oxidation. Eqn (1) identifies the parameters that control alloy oxidation. The first term in eqn. (1) dominates the potential at low oxygen fugacity and low temperature. Therefore, the oxide that forms first under these conditions is the one that has the largest negative free energy of formation. In an earlier publication (ref. 9) the correlation was not recognized because the free energies of formation were compared on the mole of metal cation basis. However, a comparison based on the free energies of formation per mole of oxygen anions produced (Table 1) has provided an agreement with the C–M model for the alloys studied.

A simple case, such as the thermal oxidation of Ti, XPS spectra, Fig. 1, demonstrates the stepwise growth of the higher oxidation state oxides at progressively higher temperatures while maintaining a constant oxygen fugacity. As Table 1 and eqn. (1) suggest, TiO forms at lower temperatures than Ti_2O_3 and TiO_2, and Ti_2O_3 forms at a lower temperature than TiO_2.

The model cannot distinguish between the polymorphs such as rutile and anatase because the closeness of their ΔG's of formation (Table 1). In the case of alloys, similar results are observed considering the $-\Delta G^0_f$ (kJ mol^{-1} O^{2-}) for both alloy components. For Ti–Cu alloys, as the alloy is exposed to progressively higher temperature at a fixed low oxygen fugacity, the titanium component oxidizes preferentially in the same fashion as the metal. Only at higher temperatures, does the Cu oxidize with Cu^+ (i.e. Cu_2O) forming preferentially to

Table 1 Free energies of formation for selected oxides[14]

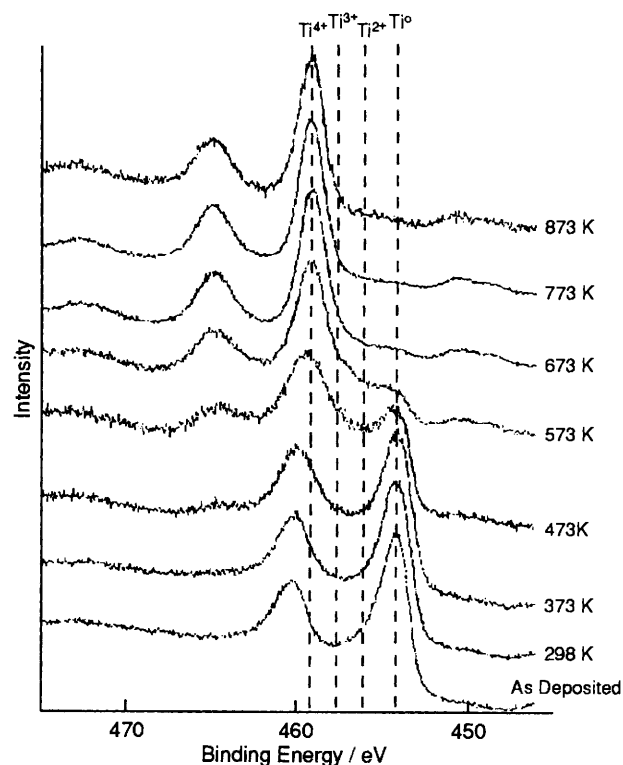| Oxide	$-\Delta G^0_f$ (kJ mol^{-1}) $T = 298$ K [700 K]	$-\Delta G^0_f$ (kJ mol^{-1} O^{2-}) $T = 298$ K [700 K]
γ-Al$_2$O$_3$	1589.0 [1455.7]	529.7 [479.8]
Cu$_2$O	147.7 [117.9]	147.7 [117.9]
CuO	128.1 [92.0]	128.1 [92.0]
α-TiO	495.1 [462.8]	495.1 [462.8]
Ti$_2$O$_3$	1434.4 [1322.1]	478.1 [440.7]
TiO$_2$ (anatase)	877.3 [804.2]	438.7 [402.1]
TiO$_2$ (rutile)	877.6 [804.2]	438.8 [402.1]

Fig. 1 Ti(2p) XPS spectra of a Ti film (1000 Å) deposited on a Cu sample mount. XPS data was collected after the film was deposited and after successive heat treatments (15 min) in 5 × 10^{-3} Torr of oxygen.

Cu^{2+} (*i.e.* CuO) (Table 1) and segregating to the surface forming a stable Cu_2O overlayer on the preformed Ti oxide structure. Reasons for the layer structure are currently not confirmed and are being researched. Thermal oxidation studies of Cu–Mn alloys[2] involving variations of oxygen fugacity as well as temperature have shown that the model is followed. However, the model does not account for the formation of mixed-metal oxide compounds such as $CuMn_2O_4$.

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