Invited Talk, Tuesday, May 7, 9:00 a.m. - 9:40 a.m., ICAMS² session: T1

Progress in the theory of oxide scale growth

Arthur Heuer¹,⁴, T. Nakagawa¹, David Hovis⁵, James Smialek², Brian Gleeson³, Nicholas Hine⁴,⁵, Hannes Guhl⁴,⁵, Haksung Lee⁴,⁵, Paul Tangney⁴,⁵, Matthew Foulkes⁵, and Michael Finnis⁴,⁵

¹Department of Materials Science and Engineering, Case Western Reserve University, Cleveland, Ohio 44106
²NASA Glenn Research Center, Cleveland, Ohio 44135
³Department of Mechanical Engineering and Materials Science, University of Pittsburgh, Pittsburgh, PA 15261
⁴Department of Materials, Imperial College, London, SW7 2AZ, UK
⁵Department of Physics, Imperial College, London, SW7 2AZ, UK

Our current understanding of oxide scale growth in the steady-state regime is based on the ideas of Wagner, Schottky and Kröger, reviewed by Atkinson, who wrote: “It will now be evident that a detailed application of Wagner's theory to Al₂O₃ growth is fruitless because of the uncertainties concerning the defect transport properties of the oxide in the film itself.”[1]. Nevertheless, even a qualitative application of the theory would be useful, since it would throw light on the reactive element effect, whereby small additions of e.g. Y greatly slow the growth rate and improve the coherence of alumina films on alloys; the mechanism of this useful effect remains controversial. Since this review there has been some progress on the fundamentals of defect chemistry and transport. In this presentation we review some recent progress in the theoretical models of point defects and their possible role in diffusion and corrosion. Notably, the role of the chemical potential of the electrons (loosely referred to as the Fermi energy $\varepsilon_F$) is crucial, since it makes an important contribution to the formation energy of charged defects such as $V'_O$, $V''_O$, $V'''_O$ and $V''''_O$ and hence strongly determines their equilibrium concentrations and which defect is dominant [2]. Through the thickness of a scale, according to Wagner theory, an electric field is set up that could shift $\varepsilon_F$ through the scale sufficiently to change the dominant equilibrium defects from aluminium vacancies on the outside to oxygen vacancies at the oxide-metal interface. Thus, within the thickness of a scale, the mechanism of ionic conduction and the ionic conductivity is likely to change drastically. While we know little about the electrical conductivity, except that there has to be some in order to balance the electric current carried by diffusing ions, we also expect the charged defects to supply the electron or hole carriers.

These concepts will translate to grain boundary transport; although we still know little about the possible structures of the defects, we can be confident that they will be more varied than the bulk defects. An important part in the electrical conductivity will be played by the density of states at the band edges, and our calculations of grain boundary structure, using new classical potentials of the Tangney-Scandolo type [3] together with DFT, show how this is strongly altered at a grain boundary, which is where we expect most of the conduction of all species to take place.