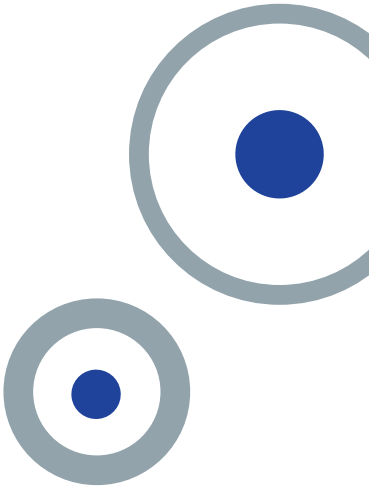
ICAMS 2
INTERDISCIPLINARY COLLOQUIUM ON ADVANCED MATERIALS SIMULATION
COLLOQUIUM



Invited Talk, Tuesday, May 7, 9:00 a.m. - 9:40 a.m., ICAMS^2 session: **T1**

Progress in the theory of oxide scale growth

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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 Al_2O_3 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 ε_F) is crucial, since it makes an important contribution to the formation energy of charged defects such as $V_O^{\bullet\bullet}$, $V_O^{\bullet}$, $V_{Al}^{'''}$ and $V_{Al}^{''}$ 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 ε_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.

[1] Atkinson, A., Transport processes during the growth of oxide films at elevated temperature. *Reviews of Modern Physics* **1985,***57*, 437-470.
[2] Hine, N. D. M.; Frensch, K.; Foulkes, W. M. C.; Finnis, M. W., Supercell size scaling of density functional theory formation energies of charged defects. *Physical Review B* **2009,***79*, 024112 -1-13.
[3] Tangney, P.; Scandolo, S., An ab initio parametrized interatomic force field for silica. *Journal of Chemical Physics* **2002,***117* (19), 8898-8904.