Passivation in non-random solid-solution alloys

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Corrosion of solid-solution alloys must, at some level, be related to the arrangement of the metal atoms in three dimensions. For the case of a random solid solution, significant results have been obtained experimentally and by atomistic simulation, leading to hypotheses for important transitions such as the parting limit for de-alloying of a solid solution [1] and the 13% Cr criterion for passivation of stainless steel [2]. For engineering alloys used in nuclear power systems, regular solution interactions generate a non-random solid solution whose initial corrosion behaviour depends on the effective temperature at which the atomic arrangement is equilibrated. In-service ageing of such alloys will be important for the integrity of future nuclear power systems. Conventional percolation criteria for connectivity of susceptible or protective atoms in 3D are altered compared with the random case.

The Fe-Cr alloy system serves as an interesting model and has historically generated considerable interest not only in terms of the compositional dependence of corrosion/passivation, but also in terms of magnetic properties. Recent first principles-based calculations of the thermodynamic behaviour of this system shows that the enthalpy of mixing is negative to about 10 at% Cr at which point it switches sign [3, 4]. The positive heat of mixing which is of order 0.02 eV/atom at ~ 15 at% Cr causes this system to display a tendency toward clustering [3,4]. This should have the effect of lowering the site percolation threshold, whereas a tendency toward ordering should have the opposite effect. To our knowledge, effects of ordering and clustering on site percolation thresholds have never been examined. As described in earlier publications, these thresholds are important for understanding corrosion and passivation behaviour in alloy systems such as Fe-Cr. We present results from large-cell Monte Carlo renormalization group calculations [5] for the effects of ordering and clustering on site percolation thresholds in bcc alloys. Our results demonstrate that for the case of relatively small positive heats of mixing (0.01 eV/atom), the site percolation threshold is lowered from its conventional value of ~0.25 to 0.16. Conversely, for a small negative heat of mixing (-0.01 eV/atom), the threshold increases to ~0.30. We discuss the implications of these results on corrosion/passivation in the context of the integrity of materials for nuclear power systems

1. D.M. Artymowicz, R.C. Newman and J.D. Erlebacher, The relationship between the parting limit for de-alloying and a geometric high-density percolation threshold, *Philos. Mag.*, **89**, 1663-1693 (2009).
2. K. Sieradzki and R.C. Newman, A percolation model for passivation in stainless steels. *J. Electrochem. Soc*., **133**, 1979-1980 (1986).
3. P. Olsson, I.A. Abrikosov and J. Wallenius, Electronic origin of the anomalous stability of Fe-rich bcc Fe-Cr alloys, Phys. Rev. B., **73,** 104416 (2006).
4. T. P. C. Klaver, R. Drautz, and M. W. Finnis, Magnetism and thermodynamics of defect-free Fe-Cr alloys, Phys. Rev. B., **74,** 094435 (2006).
5. P.J. Reynolds, H.E. Stanley and W. Klein, Large-cell Monte Carlo renormalization group for percolation, Phys. Rev. B., 21, 1223-1245 (1980).