Linking radiation damage to solute segregation, inter-diffusion and solubility in the Zr-Nb-Cr system

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Introduction

Cr-coated Zr alloy is a promising candidate for cladding. Cr is the coating of choice as it improves the cladding’s oxidation and corrosion resistance for both normal and accident conditions. The Cr coating also inhibits the cladding’s reaction with steam.

Understanding the behaviour of Cr in Zr is also important for conventional Zr alloy cladding, as it is a major alloying element. Dissolution, segregation and clustering of solutes to microstructural features such as dislocation loops, voids and grain boundaries, severely affects the mechanical and corrosion properties of Zr alloys. This becomes even more relevant to Cr-coated Zr cladding, where the degree of intermixing between the substrate and the coating in a high-radiation environment is not yet fully understood. Ab-initio atomic-scale simulations done as part of our research has shed light on the role of vacancies on the solubility, mobility and segregation of alloying elements in HCP α-Zr (here we focus on Cr), and conversely Zr and Nb solutes in BCC-Cr.

Cr in HCP-Zr

- Cr occupies both interstitial and substitutional sites in HCP-Zr
- Diffusion of Cr in HCP-Zr is found to occur through both interstitial and vacancy-mediated mechanisms, with the former being orders of magnitude faster than the latter
- Cr is an ultra fast diffuser under equilibrium vacancy concentration
- Against common assumptions, excess vacancies (e.g. from radiation damage) may slow down the diffusivity of Cr
- Cr is dragged (see Fig. 8) by vacancies at all temperatures and expected to decorate vacancy sinks

Fig. 5: Cr atoms are found to bind strongly with Zr vacancies, which may accommodate as many as 3 Cr per vacancy

Zr/Nb in BCC-Cr

- Zr and Nb only occupy substitutional sites in BCC-Cr
- The diffusion mechanism for Zr and Nb in BCC-Cr is confirmed to be vacancy-mediated, and therefore strongly susceptible to vacancy concentration, and consequently neutron fluences
- Both Zr and Nb exhibit slow diffusion in BCC-Cr
- Zr is strongly dragged by vacancies at all temperatures towards vacancy sinks
- Drag ratio for Nb is low and becomes negative slightly above conventional PWR operating temperature

Fig. 6: Zr and Nb are found to be strongly bound to vacancy in the 1st nearest neighbour position.

Fig. 7: Diffusivity coefficient of Zr and Nb in BCC-Cr

Conclusion

- Both Cr in alpha-Zr and Zr in BCC-Cr are dragged by vacancy wind → predicted enrichment of vacancy sinks (Potentially detrimental)
- Cr ultra-fast diffusion is slowed down by excess vacancies as the vacancies trap Cr (up to 3 Cr per vacancy)

Methodology

- DFT simulation: VASP, PBE. Supercell size- Zr: 150 atoms, Cr: 128
- Transition state energy calculated using cNEB
- Diffusivity calculated using Onsager code by Dallas Trinkle

References

Solute Segregation