

# Ab Initio Thermodynamic and Kinetic Model of Hydrogen Segregation in Zirconium Grain Boundaries

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Zirconium alloys (zircalloys) are used as fuel cladding in nuclear reactors and as getter materials for tritium in tritium-producing burnable absorber rods (TPBARs). For fuel cladding application, the accumulation of hydrogen causes embrittlement of the cladding. As hydrogen solubility in zircalloys decreases rapidly with temperature, from 50 at.% at 500 °C to 0.0001 at.% at room temperature, zirconium hydrides precipitate at lower temperatures upon hydrogen accumulation, which further enhances the embrittlement. Conversely, for TPBARs, maximum accumulation of tritium is preferred. In both applications, the formation of hydrides and/or tritides changes the zircaloy microstructures. Furthermore, hydrides have been observed to form predominantly at grain boundaries (GBs). Therefore, it is important to consider the thermodynamics and kinetics of hydrogen segregation at the GBs to predict the microstructure evolution and the performance of irradiated zircalloys.

In this talk, we will present the results of ab initio studies of 1) hydrogen segregation for several GBs as a function of hydrogen concentration and 2) hydrogen migration energy barriers within the GBs. The GBs that are investigated include a  $\Sigma 7$  coherent basal-basal twist GB, a semi-coherent basal/prismatic GB, and a coherent  $\langle 1\bar{2}10 \rangle \{ \bar{1}011 \}$  tilt GB. The studies are performed within the density functional theory (DFT) method using the VASP software. The calculations show that individual hydrogen strongly segregates to the GBs with a segregation energy ranging from approximately -0.1 to -0.2 eV per atom. The segregation data as a function of concentration is subsequently used to construct the partition function of the system, from which a thermodynamic model of free energy is derived as a function of hydrogen concentration, temperature, and grain size. Furthermore, extensive DFT calculations are performed within the climbing nudged elastic band (cNEB) method to explore the energy landscape of H migration within the GBs as well as across the GBs (i.e. the migration from one grain to another). The results show that, in general, H migrates more readily within the GBs compared to within the crystalline bulk, however the migration barriers across the GBs are higher than the bulk values.