First Principle Calculation of Cohesive Energy of Zirconium and Xenon Segregated Grain Boundary of UO_2

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Introduction

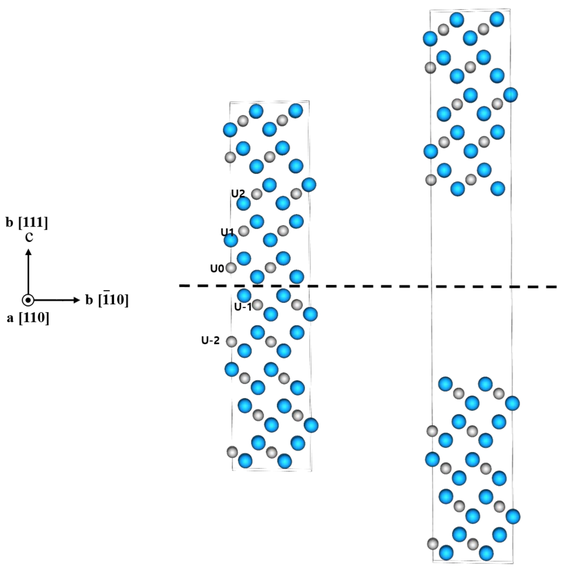
- **Grain boundary segregation** greatly affects the grain boundary properties of a materials.
- **Fission products** are generated inside UO_2 crystals during normal operation and tend to **segregate at grain boundaries**.
- The effect of segregated fission products on grain boundary cohesion has not been analyzed.
- The **segregation of zirconium and xenon** on UO_2 grain boundary and effect of segregation on **grain boundary cohesive energy** were analyzed through **DFT**.

Method

- Vienna *ab initio* simulation package (VASP) was used for first principle calculations.
- The generalized gradient approximation GGA+PBE was used for exchange correlation functional, and the project augmented wave (PAW) method were used to substitute core electron of uranium, oxygen, and fission products atoms
- Σ3(111)/[110] grain boundary was chosen for simulation.
- The most stable segregation sites for zirconium and xenon were investigated.
- The grain boundary cohesive energy of the segregated structure at the most stable segregation site was investigated.

Grain boundary structure and calculation

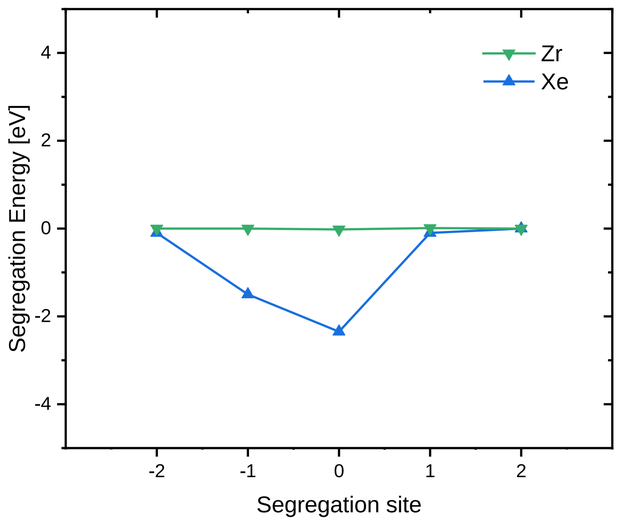
❖Structure and segregation sites of UO_2 Σ3(111)/[110] grain boundary



- For the grain boundary calculation, 40 uranium atoms and 80 oxygen atoms were used.
- Both zirconium and xenon were reported to be **most stable when placed in a cation vacancy** in UO_2. [1, 2]
- Considering periodic boundary condition, there are 5 different segregation sites and marked in picture.
- The segregation energies of zirconium and xenon for each of the five sites were calculated.
- Based on the calculated segregation energy, the grain boundary cohesive energy of the most stable structure was calculated.

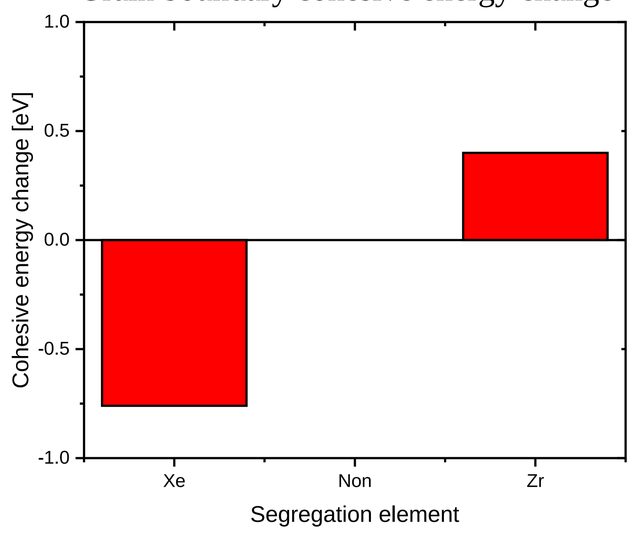
Result

❖ Segregation energy of zirconium and xenon .



- In the case of zirconium, **there was little difference** in energy depending on the segregation location.
- In the case of xenon, it was found that the result was reliably **stable at sites -1 and 0 closest to the grain boundary**.
- Xenon is stable at the **grain boundary where the atoms are the least dense** because xenon is much larger in size than U^{4+}

❖ Grain boundary cohesive energy change



Elements	Xe	U^{+4}	Zr^{+4}
Radius [pm]	216	114	80

- Based on the calculated segregation energy, the grain boundary cohesive energy of the most stable structure was calculated.
- The grain boundary cohesive energy of the structure in which the **zirconium was segregated was rather increased** when compared to the case without segregation.
- The cohesive energy was **greatly reduced** in the **structure in which Xe was segregated**.

Summary

- **The segregation of zirconium and xenon on UO_2 grain boundary and effect of segregation on grain boundary cohesive energy were analyzed through DFT Microstructure and crystal structure of alloys were investigated using SEM-EDS and XRD.**
- **It was confirmed that zirconium strengthened grain boundary cohesion, and xenon weakened it.**

[1] G. Brillant, A. Pasturel, Study of Ba and Zr stability in UO2±x by density functional calculations, Phys. Rev. B - Condens. Matter Mater. Phys. (2008)
[2] B. Dorado, G. Jomard, M. Freyss, M. Bertolus, Stability of oxygen point defects in UO2 by first-principles DFT+U calculations: Occupation matrix control and Jahn-Teller distortion, Phys. Rev. B - Condens. Matter Mater. Phys. (2010).

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