First Principles Calculations of Cohesive Energy of Fission-Product-Segregated Grain Boundary of UO_2

Jae Joon Kim [a], Hyun Woo Seong [a], Ho Jin Ryu [a*],
[a]*Department of Nuclear and Quantum Engineering, KAIST, Daejeon, 34141, Republic of Korea*
[*]*Corresponding author: hojinryu@kaist.ac.kr*

1. Introduction

Grain boundary is the most common structural defect in UO_2 and acts for nucleation sites of fission products. There is a lot of experimental evidence that fission products weaken the cohesion of grains when they are segregated at grain boundaries. Henry et al conducted a micro-bending test on a nuclear fuel specimen with a burnup of about 35 GWd/tU and fresh fuel. It was confirmed that the grain boundary strength of the nuclear fuel specimen with a burn-up of 35 GWd/tU significantly decreased. Also, in another study by henry et al, as a result of Vicker's hardness test on the fuel surface, it was shown that indentation cracks were formed along the grain boundary in nuclear fuel with a burnup of 16 GWd/tU, unlike fresh fuel. [1][2] However, Despite experimental evidence that fission product segregation on UO_2 grain boundaries weakens grain boundary cohesion, precise studies on this have not been conducted. The grain boundary cohesive energy has been used in the fuel pulverization model, specifically in the calculation of the intergranular bubble threshold pressure for grain boundary split. In this study, the effect of grain boundary segregation of zirconium, molybdenum, cesium and xenon on the grain boundary cohesive energy of UO_2 was investigated using DFT analysis. The most stable structure where fission products can be segregated at the UO_2 grain boundary was derived, and the energy required for grain boundary separation was calculated for those structures. The calculated segregation energy of fission products elements and cohesive energy were analyzed by comparing charge density distribution and bond length.

2. Methods and Results

2.1 Computational details

DFT calculation was performed using the Vienna *ab initio* simulation package (VASP). The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) was used for the exchange correlation functional. For Hubbard *U* correction, 3.96 eV of U_{eff} value was used in this study. A plane-wave basis set with cut-off energy of 500 eV and 5x5x1 *k*-point grid were used for the calculation. Convergence of the electronic relaxation was satisfied when the total energy change was less than 10^{-7} eV/atom. Structural relaxation was continued until the Hellmann-Feynman force was less than 0.02 eV/Å.

2.2 Calculation of grain boundary segregation energy of fission products in Σ3 [110] / (111) UO_2 grain boundary

For zirconium, ,molybdenum, cesium, and xenon, the segregation energy of the Σ3 [110] / (111) UO_2 grain boundary was derived using equation (1). In Figure 1, the grain boundary segregation energy of sites 1 to 4 was obtained as the difference from the total energy when segregated at the site 5 furthest from the grain boundary. The segregation energy results are depicted in Figure 2. Cesium and xenon, which have relatively large atomic radius, were stably segregated at sites 2 and 3 close to the grain boundary, and were more stable at site 3 with a larger free volume than that of site 2. zirconium showed no segregation tendency, and molybdenum showed weak segregation at site 2. Unlike cesium and xenon, molybdenum showed the most stable appearance when segregated at site 2. Because molybdenum has a smaller size than uranium, it does not have a large preference for free volume. The crystal structure of molybdenum oxide is different from that of uranium oxide, it is most stable in the position where it can most effectively destroy the CaF_2 structure of UO_2. From the charge density distribution, it was confirmed that when molybdenum was at site 2, it broke the existing structure with 8 coordinates and effectively destroyed the crystal structure of UO_2.

$$E_{seg/X} = E_{GB/X} - E_{GB/ref} \quad (1)$$

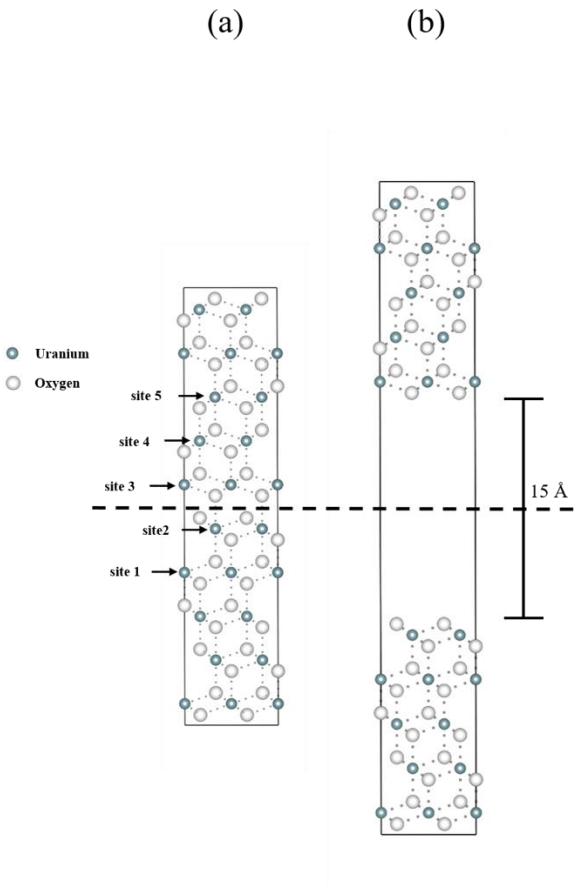

Figure 1. (a) Structure and segregation sites of UO_2 Σ3(111)/[110] grain boundary and (b) separated grain boundary structure.

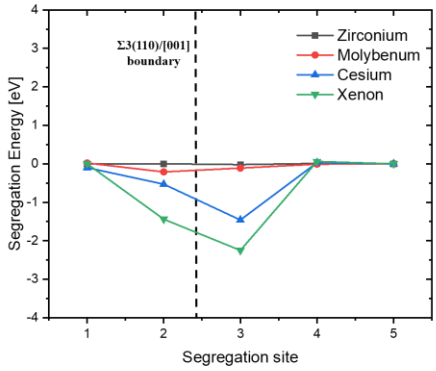

Figure 4. Segregation energy of fission product atoms at each segregation site.

2.3 Cohesive energy calculation of fission-product-segregated Σ3[110]/(111) UO_2 grain boundary

The grain boundary cohesive energy was calculated for the structure in which fission product atoms were segregated at the most stable positions. The grain boundary cohesive energy was derived by adding a slab of 15 Å between the grain boundary and comparing the energy difference before and after by equation 2.

$$E_{coh/X} = \frac{E_{seperated\ GB/X} - E_{GB/X}}{A_{GB}} \quad (2)$$

The calculation results in Figure 3 show that segregation of zirconium and molybdenum increases the grain boundary cohesive energy, and that of cesium and xenon decreases the grain boundary cohesive energy. For grain boundary separation, it is necessary to break the bond between the metal ions present at site 2 and the oxygen cations of the upper crystal crossing the grain boundary. In the case of the structure in which zirconium and molybdenum were segregated, the length of the corresponding bonds was shortened. This means that the bonds are stronger, which is consistent with the cohesive energy result. The cesium and xenon segregated structures show structural distortion due to the large radius of the segregated elements. It was shown that this structural distortion was resolved when the grain boundary was separated. It is thought that the grain boundary cohesive energy decreased because the structural distortion was resolved when the grain boundary was separated.

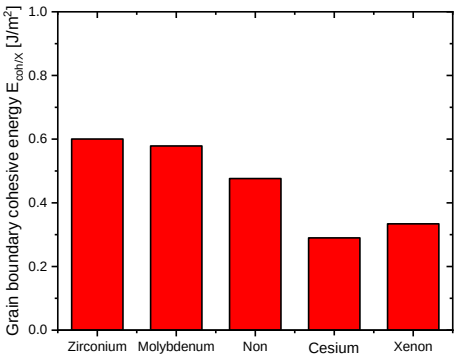

Figure 3. Calculated grain boundary cohesive energy of fission-product-atom-segregated grain boundary.

3. Conclusions

The segregation energy of zirconium, molybdenum, cesium, and xenon at Σ3 [110] / (111) UO_2 grain boundary was investigated. Xenon and cesium showed a large segregation tendency, molybdenum showed a small segregation tendency, and zirconium showed no segregation tendency. The grain boundary cohesive energy was investigated based on the grain boundary structure in which each fission product element was segregated at the most stable position. As a result of the calculation, it was confirmed that zirconium and

molybdenum increased the grain boundary cohesive energy, and cesium and xenon weakened the grain boundary cohesive energy. Because cesium and xenon, which have a relatively large tendency for grain boundary segregation, effectively lower the grain boundary cohesive energy, grain boundary cohesion will be weakened as fuel burnup increases during the normal operation of nuclear power reactors.

Acknowledgments

This study is supported by NRF ROK-UAE Nuclear Cooperation Project funded by MSIT, Korea

REFERENCES

[1] R. Henry, I. Zacharie-Aubrun, T. Blay, N. Tarisien, S. Chalal, X. Iltis, J.M. Gatt, C. Langlois, S. Meille, Irradiation effects on the fracture properties of UO2 fuels studied by micro-mechanical testing, J. Nucl. Mater. (2020). https://doi.org/10.1016/j.jnucmat.2020.152179.

[2] R. Henry, I. Zacharie-Aubrun, T. Blay, S. Chalal, J.M. Gatt, C. Langlois, S. Meille, Fracture properties of an irradiated PWR UO2 fuel evaluated by micro-cantilever bending tests, J. Nucl. Mater. (2020). https://doi.org/10.1016/j.jnucmat.2020.152209.