First Principles Calculations of Cesium Diffusion Behavior in UO_2 Fuel with Dopant Addition

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1. Introduction

After the Fukushima accident, a concept of accident tolerant nuclear fuel pellets that reduces pellet cladding mechanical interaction and the fission product release by adding additives such as Cr_2O_3 and Al_2O_3 to UO_2 nuclear fuel emerged [1]. In the case of doped UO_2 fuel, the diffusivity of hazardous fission products in UO_2 fuel will differ because the concentration of point defects in UO_2 will be significantly changed.

^{137}Cs is a radioactive isotope with a half-life of 30.1617 years, which emits beta and gamma rays through radioactive decay to stable ^{137}Ba. Because of its long half-life and radioactivity, it is necessary to investigate Cs diffusivity for the safety analysis of doped nuclear fuel.

In this study, first-principles calculations based on the density functional theory (DFT) were conducted to define the diffusion behavior of ^{137}Cs in UO_2 fuel when different types of dopants are added.

2. Methods and Results

2.1 Simulation Method

Cesium diffusivity in UO_2 can be clarified by finding its diffusion coefficient, and it can be denoted as:

$$D_{Cs} = f a^2 \nu C_v \exp\left(-\frac{G^m}{k_B T}\right) \exp\left(-\frac{G^b}{k_B T}\right)$$

To discover G^m and G^b, First-principles calculations were performed through VASP (Vienna Ab-initio Simulation Package) with 2 x 2 x 2 UO_2 unit cell, under the DFT+U framework. f is known as correlation factor, and was approximated as 1. a is lattice parameter, k_B is a Boltzmann constant, and T is a temperature.

2.2 Gibbs free energy of binding

The enthalpy term can be calculated with the combination of the total energy of each structure depicted in Fig. 1. The binding enthalpy of the vacancy and solute is defined as:

$$H^b = (H_{Cs,V} + H_{Perfect}) - (H_{Cs} + H_V)$$

The entropy of each structure can be calculated through Phonopy and phonon calculations in VASP, by describing the vibration of atoms in a solid structure. Like enthalpy calculation, the binding entropy of the vacancy and solute is defined as:

$$S^b = (S_{Cs,V} + S_{Perfect}) - (S_{Cs} + S_V)$$

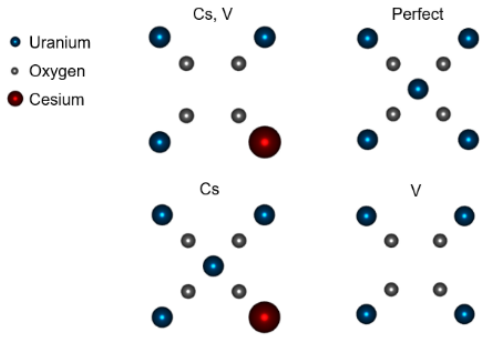

Fig. 1. Structures to calculate Gibbs free energy of binding

Through the calculation of binding enthalpy and entropy, the binding Gibbs free energy can be determined. In the temperature range between 500 K and 2500 K, which is the temperature of the nuclear fuel under normal operation and accident situations, the binding Gibbs free energy Arrhenius term of a diffusion coefficient can be expressed as shown in Fig. 2.

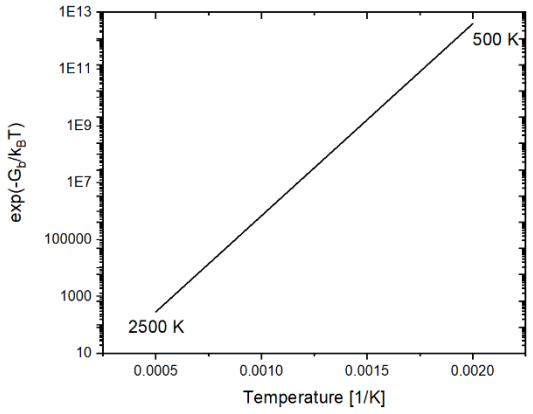

Fig. 2. Binding Gibbs free energy Arrhenius term of a diffusion coefficient

2.3 Gibbs free energy of migration

To determine the Gibbs free energy of migration, it is necessary to calculate both the enthalpy and entropy of migration, as is the case when determining the Gibbs free energy of binding. The diffusion path of cesium into the neighboring uranium vacancy can be discovered by finding the minimum energy path (MEP), and the enthalpy at the saddle point can be calculated by the CI-NEB (Climbing image - nudged elastic band) method.

The highest energy value in the calculation is the enthalpy of migration, which is shown in Fig. 3.

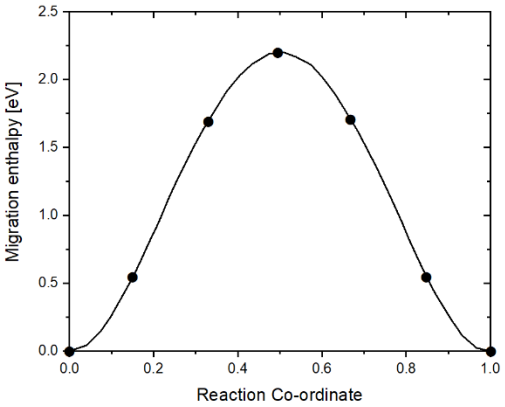

Fig. 3. CI-NEB calculation result and the enthalpy of migration

Similar to the calculation of binding entropy, the calculation of migration entropy should also be performed through phonon calculations. The entropy of each structure at the point of maximum enthalpy can be determined to find the migration entropy.

In the temperature range between 500 K and 2500 K, the Arrhenius term of the migration Gibbs free energy of a diffusion coefficient can be expressed as shown in Fig. 4.

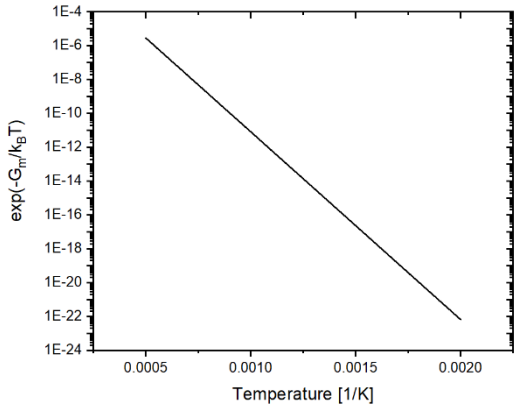

Fig. 4. Migration Gibbs free energy Arrhenius term of a diffusion coefficient

2.4 Calculation result

Through first-principles calculations, G^b and G^m with temperature changes were obtained. In addition, the vacancy concentration of uranium for different dopants has been studied [2], [3]. Based on our findings, it was able to conduct a comprehensive analysis of the diffusion behavior of cesium in UO_2 fuel with various types of dopants.

Up to about 1650 K, the uranium vacancy concentration is constant regardless of dopant type. Above 1650 K, the uranium vacancy decreases with vanadium, manganese, and chromium additions, as shown in Fig. 5.

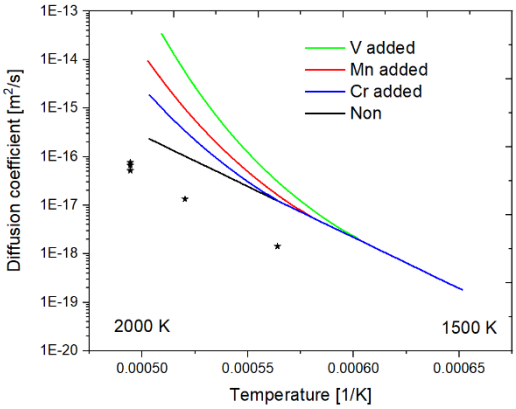

Fig. 5. Difference in diffusion coefficient for different type of dopant

3. Conclusion

This study revealed that the addition of small quantities of oxide to UO_2 fuel significantly alters the concentration of uranium vacancies, leading to a change in the diffusion coefficient of cesium. Moreover, our results indicate that the type of dopant is one of the critical factors that plays a significant role in the diffusion behavior of cesium in UO_2 fuel.

ACKNOWLEDGMENT

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