

Ab-initio Calculation of the Metallic Fuels

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1. Introduction

The sodium-cooled fast reactor (SFR) is one of the Generation IV reactors and metallic fuels have many advantages such as a high density of fissile and fertile materials, a high thermal conductivity, a high breeding performance, a simple fabrication procedure, and a good compatibility with sodium coolant. Therefore, metallic fuels are ideal for SFR. Especially uranium-zirconium (U-Zr) and uranium-plutonium-zirconium (U-Pu-Zr) alloys are considered as excellent metallic fuels because of the high melting point, reduced fuel swelling, and reliable fuel performance [1–5]. In Korea, resource of metallic fuels is obtained by using the pyroprocessing of pressurized water reactor (PWR) spent nuclear fuels. In spent nuclear fuels, there are many fission product elements. Rare earth element (REE) such as lanthanum (La), cerium (Ce), praseodymium (Pr), and neodymium (Nd) is one of the fission product elements. Since the chemical properties of REEs and trans-uranium element (TRU) are similar, separation of REEs and TRU by using pyro-processing is difficult [6,7]. Therefore, the lower the concentration of the REEs component in the metallic fuel, the more expensive it is. Therefore, the metallic fuels might contain rare earth elements. However, there is a lack of information about metallic fuel with rare earth elements because experiments with uranium and plutonium have many limitations.

To overcome the lack of experimental data, ab-initio calculations based on density functional theory (DFT) are used to predict structural, thermodynamic properties, and physical properties in this paper. DFT is a computational quantum mechanical modeling [8]. DFT is already applied to study the phase equilibria in the U–Zr system [9–15]. In this paper, we use ab-initio calculations for the U, Zr, and δ -UZr₂ and then compare the thermodynamic properties from previous experiments [5, 16–20] and ab-initio calculation data.

2. Methodology

Ab-initio calculations based on DFT are carried out using the Vienna ab-initio Simulation Package (VASP) [21]. VASP employs the plane wave basis set, the periodic boundary conditions, the projector augmented wave (PAW) method [22] and the generalized gradient approximation (GGA) as implemented by Perdew, Burke, and Erzenfest (PBE) [23]. A plane wave energy cutoff of 229.9 eV is used for all calculations. For total energy calculations of the pure elements and δ -UZr₂, all degrees of freedom for the structures are allowed to relax. The pure U, pure Zr, and δ -UZr₂ calculations are performed with a gamma k-point mesh 6 × 3 × 3, 6 × 6 × 3, and 4 × 4 × 5, respectively. The structure of δ -UZr₂ phase is a C32 (AIB2) type structure. The C32 (AIB2) structure has two non-equivalent types of sublattice; ‘A1’ (one site) and ‘B’ (two sites) types. Zr atoms occupy the A1-type position (0, 0, 0) and a random mixture of U and Zr atoms occupies the B-type positions (2/3, 1/3, 1/2) and (1/3, 2/3, 1/2) [11,13]. The structure was made by Visualization for Electronic and Structural Analysis (VESTA) [24]. DFT is to obtain the 0 K ground state energy. So, the enthalpy of mixing for δ -UZr₂ is calculated by the following equation:

$$\Delta_f H_{UZr_2} = E_{UZr_2} - \frac{1}{3}E_U - \frac{2}{3}E_{Zr} \quad (1)$$

where the $\Delta_f H$ term is the enthalpy of formation and the E terms are the total energies per atom.

3. Result and Discussion

The validity of the ab-initio calculations is examined by comparing the lattice parameters of experimental and ab-initio results. In Table I, the lattice parameters of U and Zr are compared to experimental and calculated data. Difference errors are about 1%.

Table I: Lattice parameters and %error for U and Zr with experiment and ab-initio calculation

		a, Å	% Error	c, Å	% Error
U	Exp.	2.854	-	4.955	-
	Calc.	2.809	1.577	4.910	0.908
Zr	Exp.	3.232	-	5.147	-
	Calc.	3.239	0.217	5.172	0.486

In Table II, the total energy of U, Zr, and δ -UZr₂ is calculated by ab-initio. From equation.(1), we have also calculated the enthalpy of formation of the δ -UZr₂. Our ab-initio calculations reveal $\Delta_f H_{UZr_2} = -23.1 \text{ kJ/mol}$ that is significantly different from the experimental measurements of $\Delta_f H_{UZr_2} = -4.0 \text{ kJ/mol}$ at T = 298 K.

Table II: Total energy of U, Zr, and δ -UZr₂ by ab-initio calculation.

	U	Zr	δ -UZr ₂
E(eV/atom)	-11.293.	-8.496	-9.189

4. Conclusion and Future work

Ab-initio calculations based on density functional theory can compensate for the lack of experimental thermochemical data. And for the U-Zr system, the ab-initio calculation data about pure material by using VASP software is similar to experimental data. However, there are some errors in δ -UZr₂. These errors seem to occur by initial setting such as energy cutoff, k-points, potential assumption method, random alloy method, etc. After optimizing the initial settings, the ab-initio calculations are reliable for applying to the U-Zr-REEs and U-TRU-REEs system. And by using ab-initio calculation data, thermodynamic modeling of the metallic fuels can be made.

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