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# Efficient computational search for lanthanide-binding additive dopants for advanced U-Zr based fuels

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## Abstract

A rational design strategy combining theory and experiment is highly desirable for the development of U-Zr based fuels that are resistant to lanthanide-induced fuel-cladding chemical interaction (FCCI). We performed rapid computational screening of FCCI-mitigating (via strong lanthanide-binding) elements across the periodic table by utilizing three simple criteria and density functional theory (DFT) calculated total energies of relevant elements and compounds retrieved from high-throughput DFT databases. In addition to successfully identifying previously demonstrated additives, our search leads to the discovery of Bi as a highly effective element among all 68 elements screened, and its effectiveness was experimentally confirmed in this study.

**Keywords:** Fuel additive; Density functional theory; Thermodynamics; Intermetallic compounds; Scanning electron microscopy

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The chemical reactions between fission product lanthanides and Fe-based cladding to form brittle intermetallic compounds and eutectic liquids, a phenomenon called fuel-cladding chemical interaction (FCCI), poses a notable fuel application issue that limits the lifetime and reliability of nuclear reactors utilizing U-Zr based fuels to produce energy [1]. One way to reduce detrimental FCCI effects is by doping metallic fuels with additives that can strongly bind with lanthanides and reduce their mobility and chemical reactivity. To date, the discovery of effective lanthanide-binding elements (Sb [2], Sn [3], Pd [4], and Te [5]) mostly relies on experiments guided by equilibrium phase diagrams and available thermodynamic properties, which is a costly and time-consuming process.

To greatly accelerate the design of advanced FCCI-resistant U-Zr based fuels, we developed an efficient computational strategy that can be used to rapidly identify effective lanthanide-binding elements throughout the periodic table. We consider a good lanthanide-binding element (denote by X) to be the one that simultaneously satisfies the following three criteria:

(1) The element's boiling point should be higher than 873 K. The practical experience of fuel synthesis found that fabrication is challenging if an element's boiling point is lower than or vapor pressure is very high at the casting temperature as the element would be lost due to a heavy vaporization. This criterion immediately eliminates 15 elements, as shown in Figure 1. Ideally, to avoid any uncontrollable boiling during fuel synthesis, the element's boiling point should be higher than the melting points of U and Zr, which are 1405 K and 2128 K, respectively. However, many elements do not have such a high boiling point, including the additives Sb [2] and Te [5]. Previous

experience indicates that casting an element of a relatively high vapor pressure is achievable through limiting time at elevated temperature and casting under higher positive pressure [6], though somewhat more difficult, and controlling the alloy composition is also more difficult due to vaporization.

(2) The element X must form thermodynamically stable compounds with lanthanides. Nd, Ce, Pr, and La constitute the vast majority of lanthanides present in irradiated fuels, and Nd is the most abundant [4]. The four lanthanides have similar physics and thermodynamic properties; therefore, it is reasonable to directly deal with Nd as a representative lanthanide in our screening and use the density functional theory (DFT) calculated total energy change associated with the reaction  $X + Nd = X_1Nd_1$ ,  $\Delta H_1$ , as a predictor to quantitatively measure the strength of chemical bonding between X and lanthanides. We calculate this energy change as  $\Delta H_1 = 2\Delta H_{hull}(X_1Nd_1)$ , where  $\Delta H_{hull}(X_1Nd_1)$  is the formation energy (in eV/atom) of the energetically most favorable linear combination of competing phases (i.e., the ground state convex hull) with an overall composition of  $X_1Nd_1$ , which can be calculated using grand canonical linear programming [7] and a library of DFT energies of all relevant ordered compounds retrieved from the Open Quantum Materials Database (OQMD) [8]. Note that since the convex hull can correspond to a mixture of ground state phases with different compositions, there is no requirement that a stable compound exists at the composition of  $X_1Nd_1$ . When a stable  $X_1Nd_1$  compound exists,  $\Delta H_{hull}(X_1Nd_1)$  will be equal to its formation energy. For comparison, we further calculated  $\Delta H_1$  using the Materials Project (MP) repository [9]. Currently, OQMD and MP contain more than 630,000 and 120,000 calculated structures, respectively, including all structures from ICSD (Inorganic Crystal

Structure Database) [10]. Reassuringly, the results calculated using the two high-throughput DFT databases agree well with each other. By requiring that  $\Delta H_1 < 0$  eliminates almost all elements in group IA, IIA, IIIB, IVB, VB, VIB, and VIIB, as shown in Figure 1.

(3) The third and the most critical criterion is that element X must have a higher preference to form compounds with Nd over other fuel constituents, e.g. Zr. The strength of this preference can be measured by the energy change for the reaction  $Zr_4X_1 + Nd = Zr_4X_1Nd_1$ ,  $\Delta H_2$ .  $Zr_4X_1$  is a composition, simply reflecting the fact that there is much more Zr in the fuel than additive X, instead of referring to an intermetallic compound. Previous experimental investigations have revealed that roughly 6-7 at. % X can stabilize all the lanthanides at approximately 20 % burnup of a U-23Zr at. % fuel, and the investigated fuel alloys were in the compositions of U-22Zr-6X or -7X at. % [2,3,5,11]. The irradiated tests on the Pd-additive fuels [12] indicate the additional Zr added to combine with Pd (e.g. the fuel comprised of U-27Zr-7Pd at. %) have helped improve fuel performance in comparison with the fuel comprised of U-22Zr-7Pd at. %. Accordingly, the ratio of Zr-to-X, in a fresh fuel prior to irradiation, is approximated to 4 in this study. Such an energy change can be readily calculated as  $\Delta H_2 = 6\Delta H_{hull}(Zr_4X_1Nd_1) - 5\Delta H_{hull}(Zr_4X_1)$ . Here,  $\Delta H_{hull}(Zr_4X_1Nd_1)$  and  $\Delta H_{hull}(Zr_4X_1)$  are the convex hull formation energies (in eV/atom) at compositions  $Zr_4X_1Nd_1$  and  $Zr_4X_1$ , respectively. By requiring that  $\Delta H_2 < 0$ , 14 elements are eliminated as shown in Figure 1.

The DFT calculated values for  $\Delta H_1$  and  $\Delta H_2$  for the remaining 16 elements that pass our initial screening are shown in Figure 2. Except As, calculations using OQMD and MP databases exhibit very similar results. Remarkably, the experimentally

investigated lanthanide-binding elements (Sb [2], Sn [3], Pd [4], Te [5], In [13]) all satisfy our search criteria ( $\Delta H_1 < 0$  and  $\Delta H_2 < 0$ ). A very negative  $\Delta H_2$  value is beneficial since this indicates a strong thermodynamic driving force for the dissociation of X-Zr compounds so that X can bind with lanthanides and release Zr back to the fuel matrix. A very negative  $\Delta H_1$  value is also favorable as this suggests a strong bonding between X and lanthanides. Among the 16 remaining elements, Mg, Zn, Ag, Cd, In and Tl exhibit less-negative values for both  $\Delta H_1$  and  $\Delta H_2$ , and therefore may not be effective lanthanide-binding additives. For In and Tl, such a conclusion is consistent with a previous theoretical study by Bozzolo et al. [14]. Conversely, Bi and Se exhibit the most negative  $\Delta H_2$  and  $\Delta H_1$  values, respectively, and they represent the two best Pareto-optimal solutions. However, since the boiling point of Se is 958 K, which is much less than the melting point of U, selecting Se as an additive may arise the difficulty of fuel casting. The boiling point of Bi is significantly higher (1837 K); therefore, Bi is more advantageous than Se in terms of synthesizability.

An implicit assumption of using  $\Delta H_2$  as a predictor is that the additive element X prefers to form compounds with Zr rather than with U in a U-Zr fuel. To test this hypothesis, we further calculated the energy change for the reaction  $\text{Zr}_4\text{X}_1 + \text{U} = \text{Zr}_4\text{X}_1\text{U}_1$ ,  $\Delta H_3$ , using both OQMD and MP databases. Since the stable  $\delta\text{-UZr}_2$  phase is not included in either database, any negative value for  $\Delta H_3$  would suggest some reactivity between  $\text{Zr}_4\text{X}_1$  alloy and U matrix. Reassuringly, we obtain  $\Delta H_3 = 0$  for all 16 elements shown in Figure 2, supporting the validity of our hypothesis.

The screening results depend on the quality of the DFT-calculated convex hulls. For example, the  $\Delta H_2$  value for As is calculated to be -0.27 and -0.034 eV using OQMD



and MP database, respectively. The underlying reason for this discrepancy is the non-inclusion of stable  $\text{Zr}_3\text{As}$  phase (space group  $\text{P4}_2/\text{n}$  [15]) in the OQMD. Overlooking this ground-state structure modifies the convex hull, and therefore the value of  $\Delta H_2$ . For Bi and Se, to consider the possibility that there may exist thermodynamically stable structures in Bi-Zr, Bi-Nd, Se-Zr and Se-Nd systems that have not been included in the high-throughput DFT databases, we performed *ab initio* evolutionary search [16] to uncover these “missing” structures. The searches are performed using the variable-composition mode of the USPEX code [17]. Due to constrained computing resources, this ground-state search is limited to structures with less than 16 atoms per cell. The first generation of structures are randomly created, and the following are produced through heredity, permutation, mutation, and transmutation. DFT calculations are performed using the projector augmented wave potentials [18] and generalized gradient approximation of Perdew-Burke-Ernzerhof [19], as implemented in VASP code [20]. The plane-wave basis cutoff energy is set at 400 eV. Dense Monkhorst-Pack k-point meshes are used to ensure high numerical accuracy. All structures are fully relaxed with respect to unit cell volume, shape, and internal atomic positions using a conjugate-gradient scheme.

Combining the structures reported in OQMD and MP databases with those newly discovered by our evolutionary search allows to construct the state-of-the-art convex hulls for Zr-Bi-Nd and Zr-Se-Nd systems, as shown in Figure 3a and 3b, respectively. It is evident that  $\Delta H_1$  values for Bi and Se correspond to two times the formation energies (in eV/atom) of BiNd and SeNd, respectively. Both databases include these two compounds and therefore correctly predict the  $\Delta H_1$  values for Bi and Se. Since the

ground state of  $Zr_4Se$  ( $Zr_4SeNd$ ) corresponds to a mixture of  $Zr$  and  $Zr_2Se$  ( $SeNd$ ), the  $\Delta H_2$  value for  $Se$  can be calculated from their formation energies as  $\Delta H_2 = 2\Delta H_{hull}(SeNd) - 3\Delta H_{hull}(Zr_2Se)$ . Both databases predict the correct  $\Delta H_2$  value for  $Se$  since they contain  $Zr_2Se$  and  $SeNd$  phases. Finally, our calculated convex hull for  $Zr$ - $Bi$ - $Nd$  indicates the ground state of  $Zr_4Bi$  ( $Zr_4BiNd$ ) to be a mixture of  $Zr$  with  $Zr_3Bi$  ( $BiNd$ ).  $\Delta H_2$  for  $Bi$  can therefore be calculated from the formation energies of these two compounds as  $\Delta H_2 = 2\Delta H_{hull}(BiNd) - 4\Delta H_{hull}(Zr_3Bi)$ . Our calculated  $\Delta H_2$  value for  $Bi$  (-0.889 eV) is less negative than those predicted by OQMD (-1.044 eV) and MP (-1.138 eV), which is due to their non-inclusion of  $Zr_3Bi$  phase. Nevertheless,  $Bi$  remains the element with the most negative  $\Delta H_2$  even after refinement of the convex hull.

$Bi$  has been experimentally confirmed in this work. Table 1 provides the compositions of three  $U$ -10 $Zr$  alloys prepared with  $Bi$  as the additive. The casting operation is carried out in an arc-melter within an argon-filled glovebox. After adding each element, the resulting cast button is flipped and re-melted three times to ensure homogeneity. To prepare  $U_{10}Zr_7Bi_4Nd$  and  $U_{10}Zr_3Bi_4Nd$  alloys, pre-alloy buttons of  $U$ - $Zr$ - $Bi$  were prepared, followed by the addition of  $Nd$ . The buttons are cast into 5-mm diameter pins. Approximately 3 mm from each pin is cut for annealing, wrapped in tantalum ( $Ta$ ) foil, sealed in quartz tubes under vacuum, and placed in a furnace at 923 K for 504 hours. The samples are quenched in water after heating and cut to expose a fresh surface for analysis. Samples are mounted with epoxy and polished by grinding surfaces flat with  $SiC$  grinding papers followed by polycrystalline diamond suspensions to 1  $\mu m$ .

Scanning electron microscopy (SEM) is performed on the as-cast and annealed samples using JEOL JSM-IT500HR SEM equipped with an Oxford Instruments X-Max

20 silicon drift energy dispersive X-ray spectrometer (EDS). The EDS is controlled by Oxford Aztec software, which also provides image acquisition capabilities. The SEM is operated at an accelerating voltage of 20 keV and a nominal beam current of approximately 14 nA. All X-ray spectra are accumulated for 45 live seconds, collected over an energy range of 0-20 keV.

The as-cast and annealed microstructures of U10Zr7Bi alloy are shown in Figure 4a, with a representative EDS spectrum of the granular precipitates. The only change between as-cast and annealed structures is the separation of fuel matrix, i.e.,  $\alpha$ -U and  $\delta$ -UZr<sub>2</sub> or  $\gamma$ -(U,Zr) phases. The precipitates, roughly 100-400  $\mu$ m, have essentially identical structures before and after the heat treatment. Given the high melting temperatures for the precipitates, no change is expected in the precipitates. This assumption also proves to be correct for U10Zr7Bi4Nd and U10Zr3Bi4Nd alloys. The relatively large precipitates do not appear to be homogeneous, with different contrast areas of grey and dark grey, and with U precipitates trapped in the precipitate in the white contrast. Roughly, the dark grey regions in the precipitates are comprised of 34Bi-56Zr-10U at. %, and the grey regions are comprised of 27Bi-58Zr-15U at. %, based on the EDS analysis. These compositions indicate the precipitates are mixtures of Zr<sub>3</sub>Bi<sub>2</sub> and Zr<sub>2</sub>Bi compounds, which are two reported compounds in the Zr-Bi binary system [21] with the highest and second-highest melting points, respectively. It is interesting to point out that the experimentally observed Zr<sub>3</sub>Bi<sub>2</sub> phase is actually predicted to be metastable at T = 0 K with respect to a mixture of ZrBi and Zr<sub>5</sub>Bi<sub>3</sub> by DFT calculations, although it only lies 2 meV/atom above the convex hull (Figure 3c). It is likely that the ground state crystal structure of Zr<sub>3</sub>Bi<sub>2</sub>, which is yet experimentally unknown, was not found by our evolutionary search under the constraint

of limited computing resources. Future experimental and theoretical studies of  $\text{Zr}_3\text{Bi}_2$  structure will be of interest. We also note that as much as 15 at. % U was observed in the precipitates. It is not known if this is due to the solubility of U or trapped U precipitates. In addition, there is no indicator of free additive Bi present in the alloy. Bi has a melting temperature (545 K) significantly below the experiment temperature. If any precipitates of Bi were present, a melt region within the annealed alloy would be an obvious indicator. The obvious advantage of Bi binding with Zr is to prevent Bi from melting prior to lanthanides burning into the fuel during irradiation.

In the  $\text{U}_{10}\text{Zr}_7\text{Bi}_4\text{Nd}$  and  $\text{U}_{10}\text{Zr}_3\text{Bi}_4\text{Nd}$  alloys, since the pre-alloys of U-Zr-Bi have a similar microstructure as  $\text{U}_{10}\text{Zr}_7\text{Bi}$ , to form Bi-Nd compounds, Zr-Bi compounds must first decompose. Similar approaches to immobilize lanthanides with the dopant Pd have been conducted in Advanced Test Reactor (ATR) but the microstructural analysis is needed to ultimately confirm the possibility [12]. In the as-cast and annealed microstructures for  $\text{U}_{10}\text{Zr}_7\text{Bi}_4\text{Nd}$  and  $\text{U}_{10}\text{Zr}_3\text{Bi}_4\text{Nd}$  alloys, as shown in Figure 4b and 4c, the Bi-Nd precipitates are not homogeneous based on the different contrast regions that are grey or dark grey, and are much smaller than the Zr-Bi precipitates in the  $\text{U}_{10}\text{Zr}_7\text{Bi}$  alloy. The precipitates have essentially identical structures before or after the heat treatment. The compositions of the compounds present in the two alloys are not the same due to different ratios of Bi-to-Nd added into the alloys. In the  $\text{U}_{10}\text{Zr}_7\text{Bi}_4\text{Nd}$  alloy, the precipitates are roughly comprised of 44Nd-45Bi-6U-5Zr at. % based on the EDS analysis. In the  $\text{U}_{10}\text{Zr}_3\text{Bi}_4\text{Nd}$  alloy, the precipitates approximately contain 62Nd-35Bi-3U at. %. The EDS results correspond to compounds  $\text{NdBi}$  and  $\text{Nd}_5\text{Bi}_3$ , respectively, which are known compounds on the Bi-Nd binary phase diagram [22]. Both  $\text{NdBi}$  and

Nd<sub>5</sub>Bi<sub>3</sub> are confirmed to be stable compounds by DFT calculations (Figure 3d). A few at. % U and Zr in the precipitates are due to the EDS analysis interaction volume with the fuel matrix surrounding the precipitates, or solubility of U or Zr in the precipitates. The dark grey regions contain more oxygen than the grey regions due to oxidation of Nd, while there is no distinct difference of ratios of Bi-to-Nd between the two regions.

To summarize, we performed a rapid computational search across the periodic table for effective lanthanide-binding and FCCI-mitigating additives for advanced U-Zr fuels using three simple screening criteria in combination with high-throughput DFT databases. Our search successfully finds four experimentally shown effective lanthanide-binding additives, Sb, Sn, Pd, and Te. In addition, we judge Mg, Zn, Ag, Cd, In, and Tl to be non-effective lanthanide-binding additives in view of their relatively weak binding with lanthanides. Importantly, we predict Bi and Se as two highly effective lanthanide-binding elements, and the effectiveness of the former has been corroborated by our experiments showing strong preference of Bi to bind with Nd over Zr.

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#### **Declaration of Interest**

None

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