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Revisiting thermodynamics and kinetic diffusivities of uranium–niobium with Bayesian uncertainty analysis

Thien C. Duong^{a,*}, Robert E. Hackenberg^c, Alex Landa^d, Pejman Honarmandi^a, Anjana Talapatra^a, Heather M. Volz^c, Anna Llobet^c, Alice I. Smith^c, Graham King^c, Saurabh Bajaj^b, Andrei Ruban^e, Levente Vitos^e, Patrice E.A. Turchi^d, Raymundo Arróyave^a

^a Materials Science and Engineering, Texas A & M University, College Station, TX 77843, USA

^b Environmental Energy & Technologies Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

^c Los Alamos National Laboratory, P.O. Box 1663, Los Alamos, NM 87545, USA

^d Lawrence Livermore National Laboratory, Livermore, CA 94550, USA

^e Royal Institute of Technology, Valhallavägen 79, Stockholm, Sweden

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ABSTRACT

In this work, thermodynamic and kinetic diffusivities of uranium–niobium (U–Nb) are re-assessed by means of the CALPHAD (CALculation of PHase Diagram) methodology. In order to improve the consistency and reliability of the assessments, first-principles calculations are coupled with CALPHAD. In particular, heats of formation of γ -U–Nb are estimated and verified using various density-functional theory (DFT) approaches. These thermochemistry data are then used as constraints to guide the thermodynamic optimization process in such a way that the mutual-consistency between first-principles calculations and CALPHAD assessment is satisfactory. In addition, long-term aging experiments are conducted in order to generate new phase equilibria data at the $\gamma_2/\alpha + \gamma_2$ boundary. These data are meant to verify the thermodynamic model. Assessment results are generally in good agreement with experiments and previous calculations, without showing the artifacts that were observed in previous modeling. The mutual-consistent thermodynamic description is then used to evaluate atomic mobility and diffusivity of γ -U–Nb. Finally, Bayesian analysis is conducted to evaluate the uncertainty of the thermodynamic model and its impact on the system's phase stability.

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1. Introduction

Over the years, U–Nb has been known to be a promising nuclear fuel for Gen-IV fast breeder reactors. The material exhibits a high melting point, good corrosion resistance, good conductivity and a continuous bcc region at high temperatures. This, in principle, would introduce thermal and mechanical stability during the thermal operation of the reactor, given that the desired fuel exists in the form of pure-bcc single- or polycrystals. In reality, depending on its heat treatment conditions, various forms of metastable phases exist as different microstructures within the bcc matrix, among which some lead to the fuel's enhancements while others to its degradation. For example, during the monotectoid decomposition of U–Nb, a quenched γ_1 (U-rich bcc) does not decompose continuously into the end equilibria of α (orth) and γ_2 (U-depleted bcc). Instead, it tends to transform into different

intermediate states depending on its heat treatment condition. Aging at ~ 300 °C and lower results in significant age-hardening accompanied by subtle microstructural changes (e.g., [1–4]). Under these conditions, the system remains distant from thermodynamic equilibrium even after long-term (~ 5 years) aging and the specific transformation mechanisms remain unresolved. The microstructural evolution upon aging at higher temperatures (300–647 °C) has been more definitively characterized. In particular, the system accesses a mixture of α phase plus a metastable phase of an intermediate Nb composition with the same bcc crystal structure as the stable γ_2 phase [5]. This mixture has a lamellar structure and is associated with the so-called cellular reaction [6]. After further prolonged annealing, the metastable γ_{1-2} transforms into the final mixture of α and γ_2 when stable γ_2 nucleates inside the system, and the lamellar structure coarsens. Under these structural changes, the material is known to undergo considerable degradations in terms of strength, ductility, and corrosion resistance [2].

Understanding the origins and mechanisms of these microstructure evolutions is key to the evaluation and, in an ambitious

* Corresponding author.

E-mail address: terryduong84@tamu.edu (T.C. Duong).

and optimistic vision, engineering of the fuel's macroscopic properties and performance. Given that U–Nb is a promising fuel candidate, such an understanding is found to be relevant to the national interest in the research and development of nuclear energy as a promising clean and sustainable energy resource for social development. In order to build up such an understanding of the microstructure evolutions, the essential first step is to establish a sound background of fundamental thermodynamics and kinetic diffusivities of the material. This background, in the long run, can also serve as prerequisite to understanding the Nb-based fuel—cladding interactions, or assessing the properties and performance of advanced multi-component metallic fuels, built upon the binary fuel (e.g. U–Zr–Nb), hence benefiting further the national interest. The present work, as such, seeks to contribute to the establishment of the background of fundamental thermodynamics and kinetic diffusivities of U–Nb by means of first-principles calculations, CALPHAD assessments, XRD experiments, and Bayesian uncertainty analysis.

Before moving on to details, it is noted that the CALPHAD thermodynamic assessment of U–Nb has already been conducted by Liu et al. [7], and its result was later used by Liu et al. [8] to estimate the atomic mobilities of γ also within the CALPHAD framework. Even though the thermodynamic study [7], on which the kinetic work [8] is based, shows good phase equilibria under the liquidus line, consistent with previous evaluations and experiments [9–12], extrapolation of γ -free energy to temperatures above 5000 °C results in an inverse miscibility gap, manifested in the metastable diagram of the bcc phase. As indicated by Bajaj et al. [13], although this phenomenon is thermodynamically possible and such features are found in various polymer systems, it is likely an assessment artifact in simple metallic alloys. They have pointed out that CALPHAD's parameter optimization is an inverse problem that has many possible solutions among which some may contain unreasonable "hidden" phase stabilities. The use of ab initio energetic data can impose a restriction on the CALPHAD optimization and hence reduce the probability of encountering artifacts. This is in accordance with the spirit of the Ringberg workshops on the relations between first-principles calculations and CALPHAD modeling during the years from 1996 to 1999 [14–16].

In the present work, we practice the mutual-consistent assessment strategy, coupling first-principles calculations with CALPHAD methodology, as suggested in [13]. In particular, first-principles calculations are conducted within the framework of Density Functional Theory (DFT) to estimate for the ground-state heats of formation of γ . The ab initio energies are then combined with experimental equilibria to re-assess the fundamental thermodynamics of U–Nb via CALPHAD. Assessment results are overall in reasonable agreement with the work of Liu et al. [7] without producing the inverse miscibility gap. Their reliability is further checked against our supplementary equilibria of the $\gamma_2/\alpha + \gamma_2$ phase boundary measured by sufficient long-term aging experiments (up to 5 years). The achieved thermodynamic data is then used to re-evaluate the kinetic diffusivities of γ described in terms of atomic mobilities [17] also within the framework of CALPHAD. Finally, model uncertainty is analyzed via Bayesian Monte-Carlo simulation. The detailed discussions are presented in the following.

2. First-principles calculations of γ 's formation energies

2.1. Computational details

For the first-principles investigations in the present work, we utilize two different Green's function approaches, namely

Korringa–Kohn–Rostoker (KKR) multiple scattering formalism and exact muffin-tin orbital (EMTO) method. The self-consistent calculations are performed within the scalar-relativistic regime for a basis set of *spdf* valence orbitals. The core states are recalculated at every ionic step according to the soft-core approximation. Generalized gradient approximation (GGA) is adopted for the exchange-correlation functional [59]. The integration over the Brillouin zone is done using a $31 \times 31 \times 31$ grid of k-points determined according to the Monkhorst–Pack scheme [18]. Integration of the Green function is carried out over a complex energy contour with a 2.6Ry diameter using a Gaussian integration technique with 40 points on a semi-circle enclosing the occupied states. The substitutional disorder of the alloys is treated by using the coherent potential approximation (CPA) [19]. The applicability of CPA is checked in supercell calculations realized by the locally self-consistent Green function (LSGF) method within the EMTO formalism [20,21]. The screening constants α and β are found to be 0.725 and 1.088, respectively.

In addition to Green's function approaches, we also use a different DFT approach for the self-consistent energetic calculations to strengthen our first-principles investigation. Namely, the full potential projector augmented wave (PAW) method [22,23] as implemented in the Vienna ab initio simulation package (VASP) [24–26] is considered. Here, the disordered structures of U – 12.5 at.% Nb, U – 25 at.% Nb, U – 50 at.% Nb, U – 72.5 at.% Nb and U – 87.5 at.% Nb are modeled by the special quasirandom structure (SQS) technique [27] generated by Monte-Carlo algorithm using 64-atom supercells [28]. A Monkhorst–Pack mesh of $7 \times 7 \times 7$ points (including Γ) and cut-off energy of 478 eV are considered for the integration over the Brillouin zone. It is believed that the used cell size, number of k-points and cut-off energy are reasonably chosen for good accuracy of self-consistent energetic calculations. Indeed, a verification calculation, carried out for the case of U–50 at.% Nb using a 128-atom SQS supercell with a $9 \times 9 \times 9$ grid of k-points and a cut-off energy of 550 eV, demonstrates a small energetic difference (in the order of $\frac{1}{10}$ meV/atom) w.r.t to the previous calculation. For better results, the value of 10^{-7} eV is chosen for the convergence criterion. The GGA is again used to approximate for the exchange-correlation interactions.

2.2. Results and discussions

To verify our first-principles approaches, concentration-dependent lattice parameters of γ were calculated and compared with experimental data [9]. Results, shown in Fig. 1, indicate that the proposed Green's function techniques reasonably reproduce the structural characteristics of the materials (with maximum error less than 3% after taking into account the correction from thermal expansion using the linear coefficients of thermal expansion of $20 \times 10^{-6}K^{-1}$ and $7.88 \times 10^{-6}K^{-1}$ around 1000 °C for pure γ uranium and niobium, respectively [29]). Note that for these results we did not treat the uranium's 5f-electrons as strongly correlated electrons. It has been shown in the recent work of Söderlind et al. [30] that uranium when alloyed with metals possesses weakly correlated electrons which can be adequately described within the context of DFT–GGA.

In order to reduce the computational expense, PAW were only considered for the static calculations of ground-state formation energies with lattice constants interpolated from the EMTO's verified results. Within the framework of PAW and the Green's function approaches, isostructural formation energies are evaluated according to the following formula:

$$\Delta H^\phi = {}^0E_{U_{1-x}Nb_x}^\phi - (1-x){}^0E_U^\phi - x{}^0E_{Nb}^\phi \quad (1)$$

where, ${}^0E^\phi$ are the ground-state energies of phase ϕ and x is

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