

Computational modelling of Zr-Nb alloys by solid solution approach

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Abstract. We use density functional theory to investigate the structural, elastic properties and energetic stabilities of Zr, Nb and its alloys in the alpha and beta phases, employing pseudopotential plane wave methods within the Perdew-Burke-Ernzerhof Generalized Gradient Approximation (PBE-GGA). The structures were fully optimized in a non-magnetic state, allowing atomic positions, cell volume and shape to change. Lattice parameters for the pure phases gave excellent agreement with the available experimental data. We also found that the phonon dispersions curves display soft-modes for the metastable beta-Zr phase which is lacking on the alpha-Zr and beta-Nb, condition of mechanical stability. The solid solution calculations show that an increase in the Nb contents destabilizes the structures in both the alpha and beta phases. Interestingly, the calculated elastic moduli for Zr-2.3%Nb are in good agreement to the experimental results of Zr-2.5%Nb.

1. Introduction

Recently, zirconium has attracted lot of attention due to its high resistant to corrosion and high melting point 1855 °C. It is soft, ductile and a malleable metal, solid at room temperature, though it becomes hard and brittle at lower purities. However, its mixture with niobium (high melting point of 2,468 °C) has desired physical and thermodynamic applications; it exhibits superelasticity properties, superconductivity properties and forms dielectric oxide layers [1].

Zirconium alloys are extensively used in various types of fission reactors both light and heavy water types for different applications, since 1960 zirconium alloys were the principle cladding material due to the good irradiation stability, high mechanical strength, the superior neutron economy and corrosion resistance etc. These zirconium alloys are available to designers of high level nuclear waste disposal containers as internal components or external cladding [2].

There are different compositions of zirconium alloys, the most common alloys that has been used in the nuclear technology are zrcaloy-2 which is composed of Zr-1.5%Sn-0.15%Fe-0.1%Cr-0.05%Ni and has been predominantly used as fuel cladding in Boiling Water Reactors (BWR), the other is zrcaloy-4 which is composed of Zr-1.5%Sn-0.2%Fe-0.1%Cr and is typically used as fuel cladding in Pressurized Water Reactors (PWR) and Canadian Deuterium Uranium (CANDU) reactors and Zr-2.5%Nb which has been of interest as the pressure tube material in CANDU and RBMK reactors [3,4,5]. Zr-2.5%Nb alloy plays a significant role in structural material for pressure tubes of channel nuclear power reactors, and have been widely investigated for various mechanical properties such as tensile and creep resistance, resistance to plastic flow and rapture to reactor pressure types [6,7,8].

However more advanced Zr-based alloys are required for the more severe operating conditions such as higher burn-up, increased operation temperature, and high pH operation. Most new Zr alloys that are being developed contain the Nb element, for example Zirlo (Zr-1.0Nb-1.0Sn-0.1Fe) [3], M5 (Zr-1Nb-O) [4] and NDA (Zr-0.1Nb-1.0Sn-0.27Fe-0.16Cr) [5]. The tendency to select Nb as the major alloying element in such alloys is a common characteristics for the newly developed fuel cladding material [9]. Other research findings on Nb-Zr alloys, revealed that the microstructural and corrosion test with variation of cooling rate and Nb content in alpha matrix plays important role to enhance the corrosion resistance than the supersaturated Nb, the beta phase and the precipitates [3], on the other hand Kim et.al found that the Nb-Zr alloys showed a good corrosion resistance which was not affected by the annealing temperature [10].

In this paper, we carry out DFT calculations to investigate the structural, electronic, energetic and mechanical properties of Zr, Nb and Zr-Nb alloys using solid solutions approach. Firstly, their energy of formation and elastic constants will be calculated for pure Zr and Nb phases. Secondly, we will find that the α -Zr is vibrationally stable while β -Zr is mechanically unstable due to presence of imaginary frequency in the phonon dispersion spectrum. Lastly, the elastic constants and bulk properties of Zr-Nb solid solutions will be determine.

2. Methodology

In the present study, we use density functional theory [11, 12] employed two plane wave pseudopotential codes that are CASTEP [13] and VASP [14], to study the structural, electronic and mechanical properties of pure Nb, Zr structures and their alloys. All calculations have been performed using the same gradient-corrected functional, namely, that of Perdew, Burke, and Ernzerhof (PBE) [15]. The phonon spectra were calculated using PHONON code [16] as implemented by Materials Design within their MedeA software platform [17] in which the DFT force constants are obtained via the VASP program [14,18]. The structures were optimized allowing atom positions to relax, cell volume and cell shape to change and calculations were performed using non-magnetic magnetism, a cutoff energy of 400eV and Monkhorst-Pack special k-point mesh of 18x18x10 for alpha Zr and 20x20x20 for beta Nb was used [19]. Equivalent number of k-points was used for Nb-Zr solid solution, and the elastic constants were calculated for small strain of 0.004, for all structures.

3. Summary of results and conclusion

We show the results of equilibrium lattice parameters and volume, the elastic constants and bulk moduli in table 1. Our predicted parameters for the pure zirconium structure agree very well to the experimental data to within 0.4%, while the Zr-Nb alloys show reasonable values. It should be noted that the α -Zr (P63/mmc) phase was found to be the most structurally stable since it had the lowest heats of formation value, in agreement to the experimental phase diagram [20]. The solid solution calculations of the Zr-Nb alloys shows that an increase in the Nb contents destabilizes the Zr-Nb structures since the energy increases, both in the alpha and beta phase. However, addition of 1 to 1.26 atomic percent niobium content on the P6/mmm zirconium gives desirable results. The current observations suggest that the Zr-2.6%Nb is more energetically favorable.

The mechanical stability of these systems was evaluated using the elastic constants, C_{ij} , and the phonon dispersion curves. Firstly, all the independent elastic constants (C_{ij}) in the Zr, α -Zr and β -Zr pure structures as well as the solid solutions (Zr-Nb alloys) are positive satisfy the stability conditions as described elsewhere [21-23]. However, the β -Zr phase is elastically unstable since it gives a negative tetragonal shear modulus, C' . The predicted C_{ij} for the Zr-Nb alloy give good agreement to the experimental results of Zr-2.5%Nb [24]. Lastly, the phonon dispersion curves are shown in figure1, α -Zr spectrum show real frequency phonon modes (positive frequency) along high symmetry direction in the Brillouin zone, indicating that the structure is mechanically stable. On the other hand the β -Zr phase display negative frequency phonon modes, condition of mechanically instability, in

agreement with the predicted tetragonal elastic modulus. In contrast to β -Zr phase, the β -Nb phonon spectra display real frequency in agreement to the experimental observations.

Table 1. Lattice parameters and elastic properties of pure Zr and Z-Nb alloys.

	Zr	α -Zr	β -Zr	Zr- 1.6%Nb	Zr- 2.3%Nb	Zr- 2.6%Nb	Zr-2.5%Nb Exp. [23]
Symmetry	P6/mmm	P6 ₃ /mmc	Im-3m				
Lattice parameters(Å)							
a	5.061	3.231	3.095	5.057	5.055	5.056	-
b	5.061	3.231	3.095	5.057	5.055	5.056	-
c	3.156	5.171	3.095	3.148	3.143	3.148	-
Angles							
α	90	90	109.47	90	90	90	-
β	90	90	109.47	90	90	90	-
γ	120	120	109.47	120	120	120	-
Volume (Å³/atom)	70.020	46.733	22.822	63.756	69.549	69.697	
Elastic constants (GPa)							
C11	149.56	151.99	72.168	153.87	153.48	152.79	147.08
C12	62.693	56.10	90.423	70.746	65.12	63.206	74.46
C13	45.867	-	-	45.975	45.364	46.257	75.38
C33	177.04	-	-	171.51	182.71	184.64	145.33
C44	30.740	26.09	28.248	30.539	32.091	31.436	33.81
C'	43.433	47.95	-9.127	41.562	44.188	44.792	-
Bulk modulus, B (GPa)	87.16	93.06	84.34	89.37	88.99	88.95	98.7

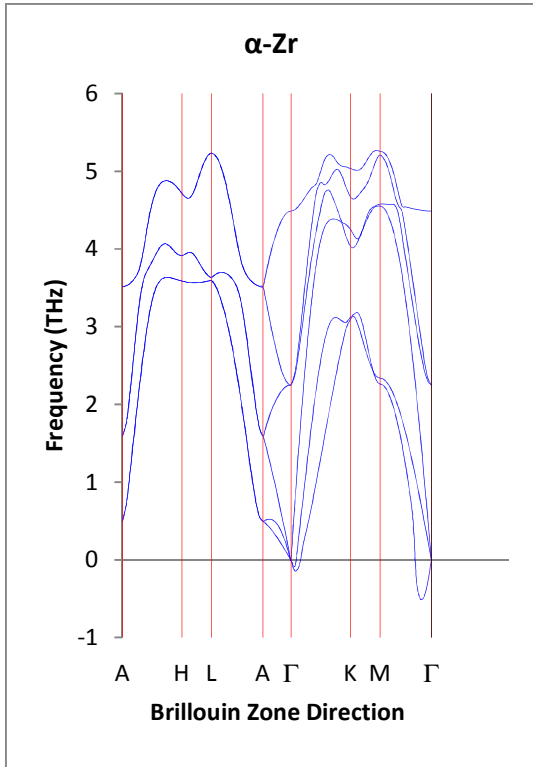


Figure 1(a). Phonon dispersion spectra of α -Zr structure.

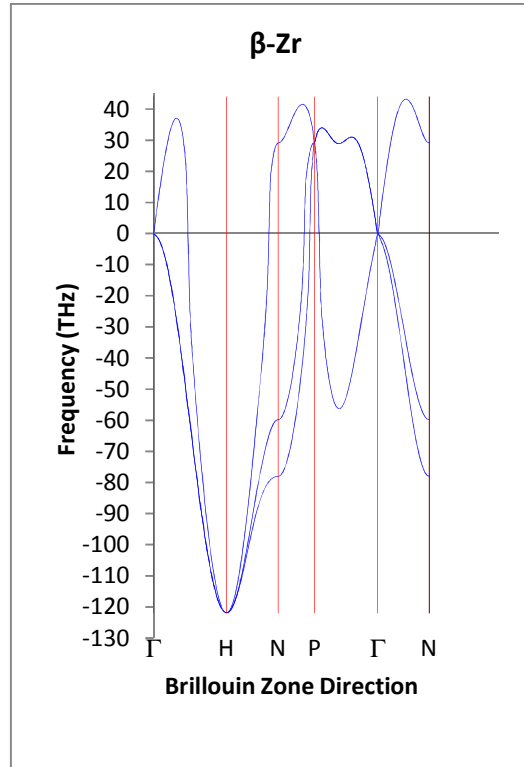


Figure 1(b). Phonon dispersion spectra of β -Zr structure.

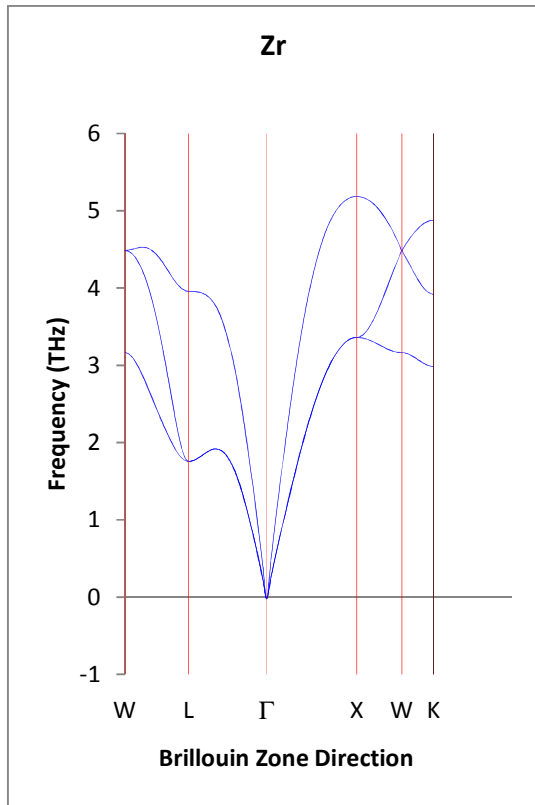


Figure 1(c). Phonon dispersion spectra of Zr structure.

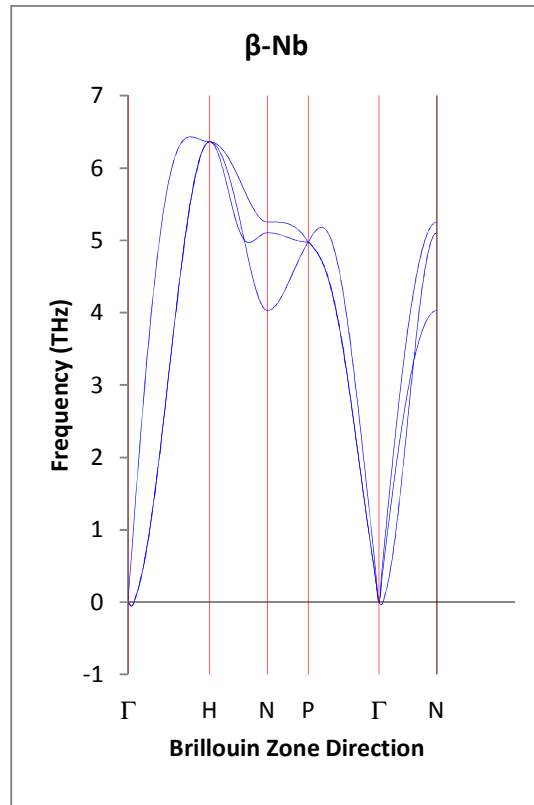


Figure 1(d). Phonon dispersion spectra of β -Nb structure.

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