Structural and thermodynamic properties of Zr-Nb-Co compound.

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Abstract. More advanced Zr-based alloys are being developed for the more severe operating conditions such as higher burn-up and increased operation temperature, this is due to their good resistance to corrosion and high melting point. In this work, density functional theory have been used to investigate the structural and thermodynamic properties of Zr-Nb-Co system at various concentrations. We used the virtual crystal approximation to introduce small content Co on different $Zr_{97}Nb_3$ composition. We found that the increase in Co concentration enhances the stability of the compound with the $Zr_{97}Nb_3$ being the most preferred composition, and the alloy is stable only at a small Co concentration of about 3 atomic percent (3 at. %). We also found that both binary $Zr_{97}Nb_3$ and ternary $Zr_{97}Nb_{2.5}Co_{0.5}$ structures converges at 1000K, confirming stability at high temperature.

1. Introduction

Zirconium is a very promising material for the nuclear industry and power engineering due to its excellent properties for nuclear environment that will alleviate the radiation effects [1, 2]. It is used as the structural material in a prototype core for nuclear submarines [3]. Zirconium exhibit excellent resistance to radiation in both mechanical behaviour and dimensional stability, low neutron cross-section, good corrosion resistance, high yield strength, fabricability and ductility.

Zirconium and its alloys has attracted significant attention due to its distinctive properties for extensive applications in nuclear and chemical industry [4]. The mixture of zirconium through niobium has shown to have desirable physical and thermodynamic applications [5]. Zr-Nb alloys are being developed to improve the properties of nuclear reactor plants. Most of the developing alloys are found to have higher Nb and lower Sn contents (in Zr-Sn alloys) in order to improve corrosion resistance [6]. Recently, the Nb-based binary solutions have been of much technological and academic interest as the alloys of this kind have good mechanical properties [7]. Alloys with a high percentage of Nb *(x>5)* have high capacity for hydrogenation which mainly causes poor corrosion resistance. As a consequence, alloys with small amount of Nb *(x<5)* are preferred for optimising its application in reactor metallurgy [1].

The effect of alloying elements to Zr-Nb is very important it serves as an effective strengthening element for Zr with low cytotoxicity and low magnetic susceptibility (2.2×10 cm^3 g^{-1}) which depends mostly on the composition and phase constitution [8]. In this paper, we report the effect of cobalt addition on the $Zr_{97}Nb_3$ system and deduce their elastic, electronic and thermodynamic properties at different

concentrations. Furthermore, we investigate the temperature dependence to evaluate the strength and stability of the system at higher temperature conditions.

2. Methodology

The calculations were carried out using first-principles density functional theory (DFT) [9] within the plane-wave pseudopotential method, as implemented in CASTEP code [10]. The electronic exchange-correlation potential was described within generalized gradient approximation (GGA) parameterized by Perdew, Burke, and Enzerhof (PBE) [11]. Interactions in the Brillouin zone were performed with special *k points* of 18 × 18 × 10 mesh parameter in accordance with the Monkhorst and Pack scheme [12]. The ultrasoft pseudopotentials method with a cutoff of 400 eV was used to describe the interaction between electrons and ions, and was sufficient to converge the total energy of the system [13]. The virtual crystal approximation (VCA) [14] was used to introduce a small amount of Co concentration.

3. Results and discussion

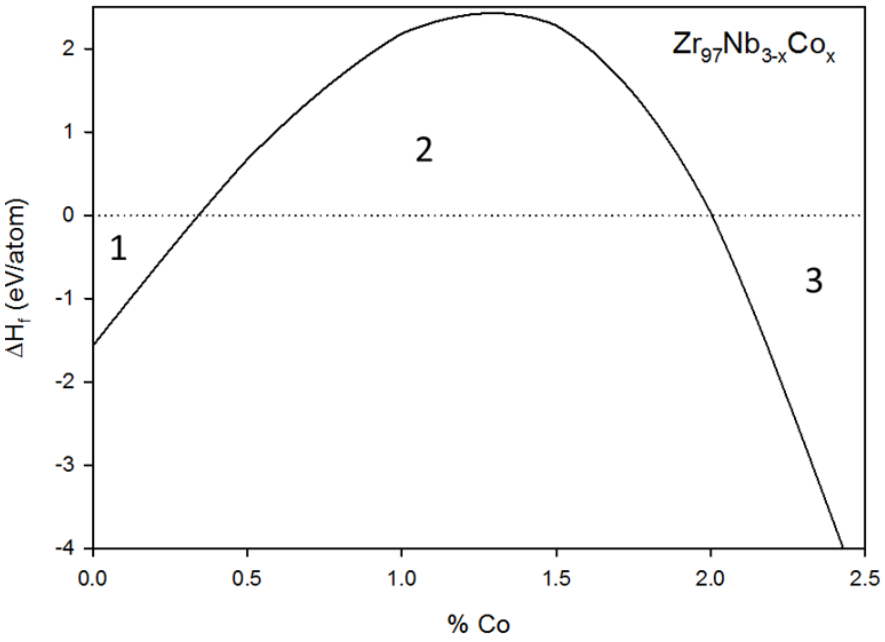

Figure 1. Calculated heats of formation against percentage Co for various $Zr_{97}Nb_3$ structures.

The DFT calculations were performed using VCA to investigate the effect of cobalt addition for various $Zr_{97}Nb_3$ structures. Note that the structures were obtained by alloying the α–Zr *(a = 3.231 Å, c = 5.171 Å)* with Nb. It has been ascertain that the α–phase is in its equilibrium state, the lattice parameters were in good agreement to within 1% of the experimental values. The $Zr_{97}Nb_{3-x}Co_x$ structure was geometrically optimized by allowing both atomic positions and volume to relax until a ground state energy was achieved. However, when Co is added to the system, the lattice parameter increases slightly; the volume increases as the Co content is increased. The thermodynamic stability was evaluated for small Co concentration deduced from the heats of formation:

$$\Delta \boldsymbol{H_f} = \boldsymbol{E_{Zr_{97}Nb_{3-x}Co_x}} - \mathbf{0.97}\boldsymbol{E_{Zr}} - (\mathbf{0.03} - \boldsymbol{x})\boldsymbol{E_{Nb}} - \boldsymbol{xE_{Co}} \qquad (1)$$

Where, E_{Zr}, E_{Nb}, and E_{Co} are the individual elemental energies in the hcp, bcc, and hcp ground state structures, respectively. At lower Co content we found that the structures yielded lower energies (H_f), suggesting thermodynamic stability. However, as Co was increased, the structure reaches maximum above zero at region 2 in Figure 1 (becomes positive thermodynamically unstable) and drops back to negative. The structure is thermodynamically stable to within 0.4 at. % Co content (region 1) and $2 \leq x \geq 3$ (region 3; the structure show transition in region 2 (unstable alloy). This observation support previous report that Zr_xNb alloys with a high percentage of niobium *(x > 5)* causes the deterioration of corrosion properties.

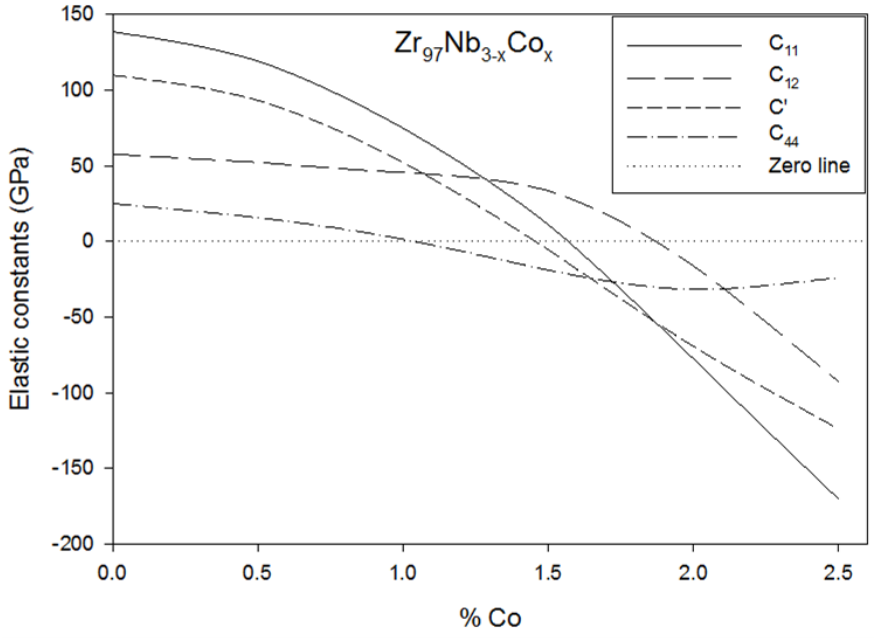

Figure 2. Displaying elastic constants against percentage Co for various $Zr_{97}Nb_3$ structures.

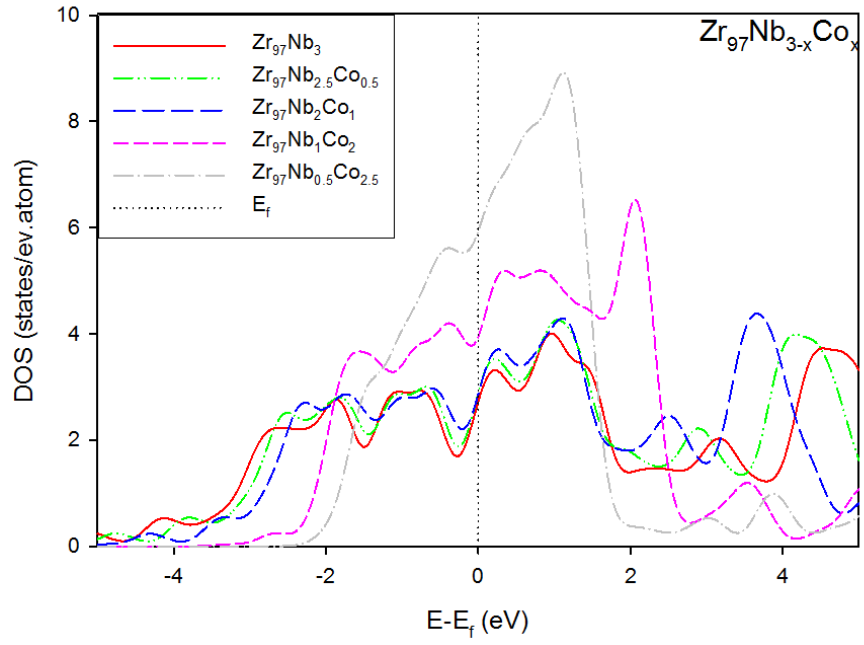

Figure 3. Comparison of the total density of states (tDOS) for the $Zr_{97}Nb_3$ structure at various at. % Co content. The Fermi energy is taken as the energy zero (E-Ef = 0).

The effect of small Co addition on the elastic constants (Cij) were also evaluated. The results are shown in Figure 2. At lower concentrations it is shown that all elastic moduli are positive, the increase in Co content indicates there is softening of elastic moduli above 1.5 at. % Co ($C'<0$, elastically unstable). This findings suggest that the system is mechanically stable at lower concentrations. We also performed the density of states (DOS) calculations to verify the electronic stability of the $Zr_{97}Nb_{3-x}Co_x$ as shown in Figure 3, it is noted that structures without Co content have the lowest peaks at the Fermi energy (electronically stable), the stability trend is observed from the peaks at Fermi energy with respect to the pseudogap. The small amount of Co content show significance effect. We note that the structures with lowest DOS at Fermi correspond to those with low Co content. It was also observed that 0.5 at. % Co content is electronically stable.

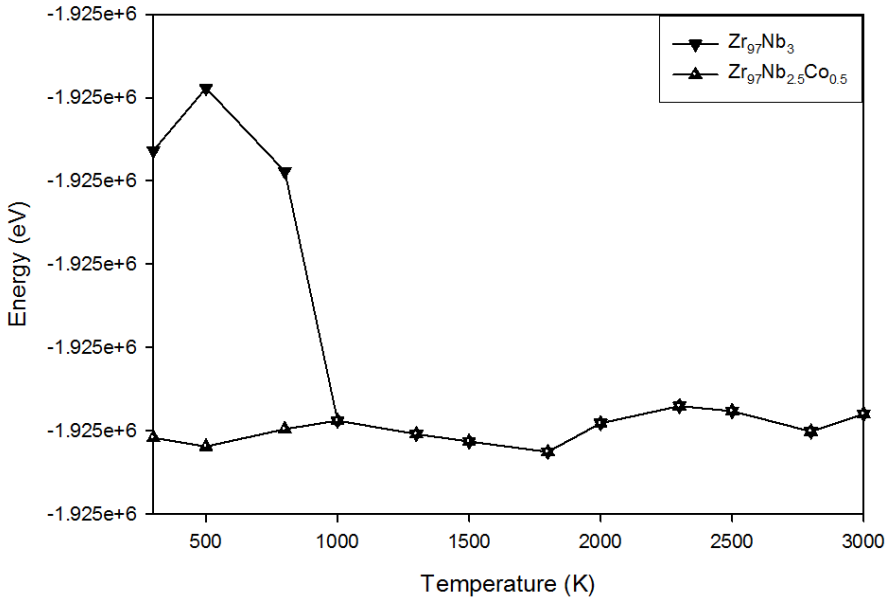

Figure 4. Indicating the temperature dependence of $Zr_{97}Nb_3$ structures at 0.5 at. % Co content.

In Figure 4, we observe that the system is stable at temperatures above 1 000K up to 1 800K since the system energy is minimal at that temperature. This findings suggest that the small addition amount of Co may be crucial in the development of better fuel cladding material, as this may enhance the stability of the system.

4. Conclusion

The equilibrium lattice parameter, heats of formation, elastic properties and electronic structures of the $Zr_{97}Nb_{3-x}Co_x$ alloy were determined using ab initio calculations. It was shown graphically in Figure 2 that the shear modulus is positive ($C' > 0$) for alloys with less amount of Co and becomes unfavourable above 1.5 at. % Co. The DFT results are in agreement with the experimental findings. It was found that the $Zr_{97}Nb_{2.5}Co_{0.5}$ structure is more stable (lowest heats of formation); whereby the VCA showed preference of doping on Co on Nb sublattices at small concentrations. Finally the DOS show that structures with high Co are high in energy while those with small concentration are lowered at Fermi level which confirms condition of stability.

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