First-principles phase stability at high temperatures and pressure in Nb₉₀Zr₁₀ alloy

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Abstract

The phase stability of Nb₉₀Zr₁₀ alloy at high temperatures and compression is explored by means of first-principles electronic-structure calculations. Utilizing the self-consistent *ab initio* lattice dynamics (SCAILD) approach in conjunction with density-functional theory, we show that pressure-induced mechanical instability of the body-centered cubic phase, which results in formation of a rhombohedral phase at around 50 GPa, will prevail significant heating. The body-centered cubic structure will recover before melting at ~ 1800 K.

KEYWORDS: transition metals, phase stability, alloys, phonons, density-functional theory

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1. Introduction

In recent years much work has been invested in trying to understand the pressure and temperature behavior of Group VB (V, Nb, and Ta) metals. For vanadium metal, Ding *et al.* [1] discovered a novel low-symmetry rhombohedral (rh) phase around 63-69 GPa. Later Jenei *et al.* [2] found a dependence of the transition pressure from the body-centered cubic (bcc) to rh as a function of the hydrostatic condition of the pressure media. Non-hydrostatic conditions with no pressure medium lead to lower transition pressures (~ 30 GPa) while for quasi-hydrostatic compression in Ne pressure medium the bcc $\rightarrow$ rh phase transition occurs at much higher pressure (~ 60 GPa). In an attempt to better understand the driving forces behind the stabilization of the bcc phase in vanadium and the other members of Group VB, Landa *et al.* [3] showed that alloying them with their nearest neighbor within the same d -transition series can either destabilize or stabilize the bcc phase when alloying occurs with the neighbor with less or more d electrons, respectively. For example, alloying vanadium metal, which above 60 GPa is unstable with respect to rhombohedral distortion, with a small amount of its left neighbor, Ti, increases the instability. Adding a small fraction (~ 11 at. %) of its right neighbor, Cr, stabilizes the bcc structure of vanadium at all pressures. It was also mentioned [3] that niobium metal may undergo a transition from bcc to rh phase when alloyed with its left neighbor, (Zr, ~ 10 at. %) under compression.

Recently Landa *et al.* [4] showed that pressure-induced mechanical instability of bcc vanadium metal, which results in formation of rh phase at room temperature, will survive significant heating and compression. Destabilization of the bcc phase in Nb-Zr alloys under compression was predicted at $T = 0$ K [3] but temperature effects were not accounted for. Therefore, in the present paper, we include thermal effects and calculate the temperature dependence of stability of rh phase in Nb₉₀Zr₁₀ alloy.

One should emphasize that the Nb-rich part of the Nb-Zr phase diagram has not been studied as much as the Zr-rich Nb-Zr alloys that are widely used as medical implants in orthopedics and stomatology (see Refs. [5, 6]) and references therein). Only a few studies regarding the Nb-rich part of the Nb-Zr phase diagram can be found in the literature [7-11]. Hayez and Brotzen [7] and Walker and Peter [8] discovered that the trigonal shear elastic constant, C_{44} , of pure bcc Nb shows remarkable deviation from

normal temperature dependence: C_{44} gradually decreases as the temperature changes from 4.2 K to 300 K. Talmor *et al.* [9] and Ashkenazi *et al.* [10] found that C_{44} reaches a minimum at $T \sim 450$ K and then starts to increase monotonically with temperature up to the melting point of Nb ($T_m = 2750$ K). Walker and Peter [8], Ashkenazi *et al.* [10], and Bujard *et al.* [11] studied the temperature dependence of the shear elastic constants of Nb-Zr bcc alloys (up to 70 at. % of Zr) and found that the amplitude of this effect (anomalous temperature behavior of C_{44}) disappears progressively with increase of Zr concentration: in the low temperature range C_{44} has a minimum that drops from 450 K for pure Nb to 60 K for the Nb₇₅Zr₂₅ alloy. Further increasing Zr concentration causes the minimum to disappear completely for Nb₃₀Zr₇₀ alloy.

We have chosen to focus on Nb₉₀Zr₁₀ alloy for which we apply a scheme to take phonon-phonon interactions into account at elevated temperatures, namely the self-consistent *ab initio* lattice dynamics (SCAILD) method [12] that we will describe briefly in the next section. Section 2 also deals with computational parameters and methods for the density-functional-theory model that is used for the force calculations required for SCAILD. In section 3 we present our results for Nb₉₀Zr₁₀ alloy, and conclude with a discussion in section 4.

2. Computational Details

The bcc stability for the Nb₉₀Zr₁₀ alloy is studied for the fixed atomic volume $\Omega = 14.75 \text{ \AA}^3$ that corresponds to zero-temperature pressures (p) of 50 GPa. This volume is chosen because at this volume the shear elastic constant, C_{44} , for bcc Nb has a minimum [3]. The bcc stability is determined by computing the phonon dispersions as functions of temperature using the SCAILD method. This approach is described in great detail [13] and not repeated here, but the general idea is to account for thermal vibrations of the atoms and their interactions. This is accomplished by (i): calculating the forces on atoms, displaced from the ideal bcc positions according to the temperature, and (ii): computing the phonon dispersions. Because the forces, displacements, and the phonons depend on each other the scheme is set up to self-consistently determine the temperature dependence of the lattice dynamics. If the procedure converges and the bcc entropy is large enough at

the studied temperature, bcc stabilization will occur due to the phonon-phonon interaction.

SCAILD has been applied for elemental metals in the past [12, 13] showing that bcc stability takes place from excited phonons that are commensurate with the super-cell and provide the necessary entropy. However, only recently this approach has been extended to deal with phase stability in the alloy systems (V-Cr and Ti-V) [4, 14].

The forces needed for the SCAILD methodology are obtained from electronic-structure calculations performed within the framework of DFT and the necessary assumption for the unknown electron exchange and correlation functional is that of the local density approximation (LDA) [15]. Although newer varieties of this approximation have been proposed, our experience is that the calculated forces are easier to numerically converge with LDA compared to other formulations. For elemental niobium we pursued GGA [16] and found only minor numerical differences in the calculated forces ($\sim 10\%$) with very little effect on the overall phonon dispersions.

Our particular DFT implementation is founded on the full-potential linear muffin-tin orbitals (FPLMTO) method that has been outlined [17]. The basis functions are well converged, specifically, we associate a set of semi-core states $3s$ and $3p$ and valence states $4s$, $4p$, and $3d$ to two kinetic energy parameters for a so-called double basis set. For the SCAILD simulation a bcc super-cell is required and similar to previous investigations [4, 12-14] we apply a $4 \times 4 \times 4$ (64 atom) cell size. This size of the super-cell has been justified as large enough in Ref. [12, 13] for study phonon dispersion in the bcc structures.

In all present calculations the sampling of k points in the Brillouin zone (BZ) for the appropriate summations are carefully checked for convergence and 64 k points are sampled in the irreducible part of the BZ.

In order to study the Nb-Zr alloy system we conveniently apply the virtual crystal approximation (VCA) that is usually applicable and appropriate when alloying metals that are neighbors in the Periodic Table. The concept of the VCA is to replace the true alloy with an artificial metal that consists of a weighted average between the two components. For example, the VCA Nb₉₀Zr₁₀ alloy is simply a monoatomic metal with a nuclear charge of 40.9 and a total of 40.9 electrons of which 12.9 are valence electrons.

3. Stability of Nb₉₀Zr₁₀ alloy

In Fig. 1 we show the experimental Nb-Zr phase diagram at ambient pressure [18]. In the solid state Nb and Zr form a continuous series of solid solutions at sufficient high temperatures with bcc (or β) structure. At lower temperatures the Nb-Zr system exhibits a critical point ($T_c = 1250$ K at 58.8 at. % of Nb) with a corresponding miscibility gap (β -Nb-Zr $\leftrightarrow$ β -Nb + β -Zr). Pure Zr undergoes allotropic transformation, β -Zr $\rightarrow$ α -Zr (hexagonal close packed, hcp), at $T_a = 1139$ K that induces a monotectoid decomposition β -Nb-Zr $\leftrightarrow$ α -Zr + β -Nb at temperatures lower than 893 K. Using CALPHAD methodology and available experimental data, Wang *et al.* [5] showed that the tetragonal shear elastic constant, C' , of pure β -Zr becomes negative at temperatures less than 600 K and thus, according to criteria of dynamical stability of a cubic crystal [19], it is impossible to quench β -Zr to the room temperature. The critical temperature of mechanical destabilization of β -Zr appears to be about 500 K lower than the β -Zr thermodynamic destabilization temperature (1139 K), which is consistent with results from recent SCAILD calculations for β -Ti [14]: the temperature of mechanical destabilization of β -Ti is ~ 200 K lower than β -Ti thermodynamic destabilization temperature (1155 K, [20]). This makes sense because mechanical stability is necessary but not sufficient for the phase to exist and therefore the method always predicts a lower bound to the true phase boundary.

The purpose of the present work is to study the temperature range of existence of rh phase in the Nb-rich part of the Nb-Zr system. Fig. 2 shows calculated (FPLMTO, [3]) pressure dependence of the trigonal shear elastic constant, C_{44} , of bcc Nb. The shear elastic constant reaches a minimum close to 50 GPa before rising again. We perform SCAILD simulations for bcc Nb₉₀Zr₁₀ alloy as a function of temperatures paying particular attention to the lowest temperature that stabilizes all phonons. In Fig. 3(a) we show these phonon frequencies for Nb₉₀Zr₁₀ alloy calculated as a function of temperature in **increments** of 500 K at the atomic volume $\Omega = 14.75 \text{ \AA}^3$ ($p = 50$ GPa, see Section 2). In Fig. 3(b) we show calculations in **increments** of 100 K for the purpose of narrowing down **the interval of temperatures** at which the mechanical stabilization occurs. In this

figure we focus on the Γ to H branch noting that the Γ to N branch behaves nearly identical. Indeed for the Γ to N branch, only the T_I mode shows instability and it is weaker than for the T mode for the Γ to H branch. Notice that all phonons are predicted to be stable at $T_{tr} \sim 1800$ K. Below this transition temperature Nb₉₀Zr₁₀ alloy is mechanically unstable and bcc $\rightarrow$ rh transformation must takes place.

4. Discussion

The self-consistent *ab initio* lattice dynamics method is far more efficient than a more complete study of thermal effects using the quantum molecular dynamics simulations and it captures strong anharmonic interactions from phonon-phonon coupling but does not address electron-phonon coupling. Here we are making additional simplifications to our SCAILD treatment of the present alloy system. Namely, (i) we use VCA for the alloy treatment, (ii) we do not adjust the volume with small changes of composition in these alloys, and (iii) thermal expansion is not included. These three assumptions were also made in an earlier paper [3].

The VCA is the excellent model for an alloy between two neighboring metals. For 4d transition metals, for example, it was shown that elastic constants for neighbors could be accurately calculated within the VCA approach [21]. The fact that we ignore small volume changes due to either alloying or temperature is justified because test calculations at various volumes (± 1 -2%) resulted in insignificant changes of the phonon dispersions of Nb₉₀Zr₁₀ alloy.

The most important feature of the SCAILD method is to account for anharmonic contributions to the free energy due to the self-consistent calculation of the phonon frequencies used to calculate the harmonic entropy [13]. The success of the method include phonon stabilization of the high-temperature bcc phase of the group IVB (Ti, Zr, and Hf) and IIIB (Sc and Y) metals [12, 13], as well as La and Th [22], NiTi compound [23], Fe [24], U [25], V-Ti [14], and V-Cr [4] alloys.

By applying DFT calculations for Nb₉₀Zr₁₀ alloy and combining them with the self-consistent lattice dynamics scheme we find that at 50 GPa the rh phase remains stable under heating up to ~ 1800 K. There are no systematic studies of Nb-Zr alloys under compression [26]. According to [27], the experimental melting temperature of

pure bcc Nb at pressure 50 GPa (DAC measurements) is $T_m = 3600$ K., which is 850° higher than the melting temperature of bcc Nb at ambient pressure (2750 K). Taking into consideration that at ambient pressure, bcc Nb₉₀Zr₁₀ alloy melts at $\sim 2160^\circ$ C (2433 K) (the solidus line, [18]), we can roughly assume that, similar to bcc Nb, the melting temperature of bcc Nb₉₀Zr₁₀ alloy will also increase about 850° at 50 GPa and is approximately equal to $T_m \sim 3283$ K that is significantly higher than temperature (1800 K) of bcc Nb₉₀Zr₁₀ alloy recovery from rh phase upon heating.

The differential form of the Lindemann law of melting is [28]

$$\frac{d \ln T_m}{d \ln \rho} = 2 \left(\gamma - \frac{1}{3} \right),$$

where ρ is density and $\gamma(\rho)$ is the density dependent Grüneisen parameter. Using a general relation [28]

$$\frac{\gamma}{\gamma_0} = \left(\frac{\rho}{\rho_0} \right)^{-q},$$

where q is an arbitrary positive constant, the above equation for $T_m(\rho)$ can be integrated to yield [28]

$$T_m(\rho) = T_m(\rho_0) \left(\frac{\rho_0}{\rho} \right)^{2/3} \exp \left\{ \frac{2\gamma_0}{q} \left[1 - \left(\frac{\rho_0}{\rho} \right)^q \right] \right\}.$$

Here ρ_0 is the reference density, which is usually taken to be the density of the solid state at the ambient melting point, and $\gamma_0 = \gamma(\rho_0)$. Approximating these values for bcc Nb₉₀Zr₁₀ alloy by the corresponding values for pure bcc Nb, $\rho_0 = 8.25$ g/cm³ and $\gamma(\rho_0) = 1.6$ [29], and taking the ambient melting point of the bcc Nb₉₀Zr₁₀ alloy to be, $T_m(\rho_0) = 2433$ K [18], a very reasonable choice of $q = 4.7$ leads to the melting point of bcc Nb₉₀Zr₁₀ alloy $T_m(10.44 \text{ g/cm}^3) = 3280$ K at pressure of 50 GPa (the density of $\rho = 10.44$ g/cm³ corresponds to the atomic volume $\Omega = 14.75$ Å³ used in calculations.). Hence, a very simple theoretical approach supports our assumption that the melting point of bcc Nb₉₀Zr₁₀ alloy at 50 GPa is ~ 3280 K.

Even though our calculations show that Nb₉₀Zr₁₀ alloy remains in the rh phase up to high temperatures, it will be very difficult to detect this phase experimentally. As we mentioned in the previous sections, the miscibility gap ($\beta\text{-Nb-Zr} \leftrightarrow \beta\text{-Nb} + \beta\text{-Zr}$) exists in the Nb-Zr phase diagram with maximum critical temperature, $T_c = 1250$ K, at 58.8

at. % of Nb. For Nb₉₀Zr₁₀ alloy at ambient pressure, the bcc phase starts to decompose into two bcc solid solutions at temperatures below 953 K (see Nb-Zr phase diagram [18]) and below 893 K a monotectoid decomposition $\beta\text{-Nb-Zr} \leftrightarrow \alpha\text{-Zr} + \beta\text{-Nb}$ starts. Using DFT and cluster expansion method, Widom [30] showed that at low temperatures the energy and configurational entropy favors a bcc solid solution over hcp at all but the most Zr-rich compositions. Thus it may be possible to create the metastable bcc Nb₉₀Zr₁₀ solid solution at moderate temperatures and then stabilize it by heating just above 953 K and then compress in the diamond-anvil cell up to 50 GPa looking for formation of a rh phase.

Acknowledgements

This work performed under the auspices of the U.S. DOE by LLNL under Contract DE-AC52-07NA27344.

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Figure Captions

1. Experimental phase diagram for the Zr-Nb system at ambient pressure [18]. The plot is taken from the ASM Alloy Phase Diagram Database.
2. Calculated (FPLMTO, [3]) pressure dependence of the trigonal shear elastic constant of Nb.
3. Calculated phonon dispersions for $\text{Nb}_{90}\text{Zr}_{10}$ bcc alloys at different temperatures at the atomic volume $\Omega = 14.75 \text{ \AA}^3$. (a) $T = 500 \text{ K}, 1000\text{K}, 1500 \text{ K}, 2000 \text{ K}$; (b) $T = 1500 \text{ K}, 1600\text{K}, 1700 \text{ K}, 1800 \text{ K}$ (only part of Γ to H is shown).

Figure 1

Figure 2

Figure 3 (a)

Figure 3 (b)