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# Elastic properties of $\beta$ , $\alpha''$ and $\omega$ metastable phases in Ti–Nb alloy from first-principles

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## Abstract

The method of pseudopotentials within the generalized gradient approximation has been employed to calculate the phase stability, electronic structure and elastic constants of  $\beta$ ,  $\alpha''$  and  $\omega$  metastable phases in the Ti–25 at.% Nb alloy. The bulk, shear and Young's moduli of those metastable phases are estimated from the theoretical elastic constants by the Voigt–Reuss–Hill averaging method. The results show that the phase stability of those different metastable phases follows the order of  $\alpha'' > \omega > \beta$  from the viewpoint of energetic and electronic structure. The bulk moduli of  $\beta$ ,  $\alpha''$  and  $\omega$  phases are close, but the shear and Young's moduli increase with  $\beta$ ,  $\alpha''$  and  $\omega$  phase in that order.

## 1. Introduction

The phase transformation in titanium metals and alloys has been investigated extensively in theory and experiment. At ambient pressure, titanium metal crystallizes in a hexagonal close packed structure ( $\alpha$ ) with space group  $P6_3/mmc$  (No. 194) at room temperature but transforms to a body centered cubic phase ( $\beta$ ) with space group  $Im\bar{3}m$  (No. 229) at high temperature. A series of reversible phase transformations ( $\alpha \rightarrow \omega, \delta, \gamma$ ) induced by high pressure were reported in titanium metals [1–3]. The electronic transfer between the broad sp-band and the narrow d-band is the driving force for the phase transformation. Alternatively, similar electronic effects on the phase transformation can be achieved by alloying with d-electron rich neighbors such as V, Nb, Mo and Ta [4]. The addition of these d-electron rich elements stabilizes the  $\beta$  phase at low temperatures. In addition, three kinds of metastable phase transformation ( $\beta \rightarrow \alpha', \alpha''$  and  $\omega$ ) have been reported in the  $\beta$  stabilized titanium-based alloys [5]. The  $\alpha'$  martensite is hexagonal as is the  $\alpha$  titanium, and  $\alpha''$  martensite has orthorhombic structure with space group  $Cmcm$  (No. 63), which forms upon rapid cooling from the  $\beta$  phase. The  $\omega$  phase with hexagonal structure and space group  $P6/mmm$  (No. 191) has been identified in titanium-based alloys slowly quenched from the  $\beta$  phase or isothermally aged at intermediate temperatures.

Because of low elastic modulus, good biocompatibility and long lifetime in the human body, the  $\beta$  stabilized titanium-based alloys containing Nb, V, Mo and Ta transition elements have been studied as load-bearing orthopaedic implants [6–8]. Recently it has also been reported that the shape memory effect and superelasticity can be achieved in those alloys [9, 10]. It is known that the elastic and other mechanical properties of the titanium-based alloys are determined by the mechanical property of their individual phase and by their phase constituents. Thus, the phase transformation can be used to optimize microstructure and to improve physical and mechanical properties of the alloys. However, to our knowledge there are few theoretical studies so far on the elastic properties of  $\beta$ ,  $\alpha''$  and  $\omega$  metastable phases in the titanium-based alloys. In this paper we use the method of pseudopotentials within the generalized gradient approximation to calculate the phase stability, electronic structure and elastic property of  $\beta$ ,  $\alpha''$  and  $\omega$  metastable phases in the Ti–25 at.% Nb alloy. Based on the equilibrium phase diagram of Ti–Nb the  $\beta$ ,  $\alpha''$  and  $\omega$  phases with the composition of Ti–25 at.% Nb are metastable. The alloys with chemical composition near Ti–25 at.% Nb have been suggested to be of low Young's modulus and promising shape memory effect and superelasticity among the Ti–Nb alloys [10, 11].

## 2. Computational details

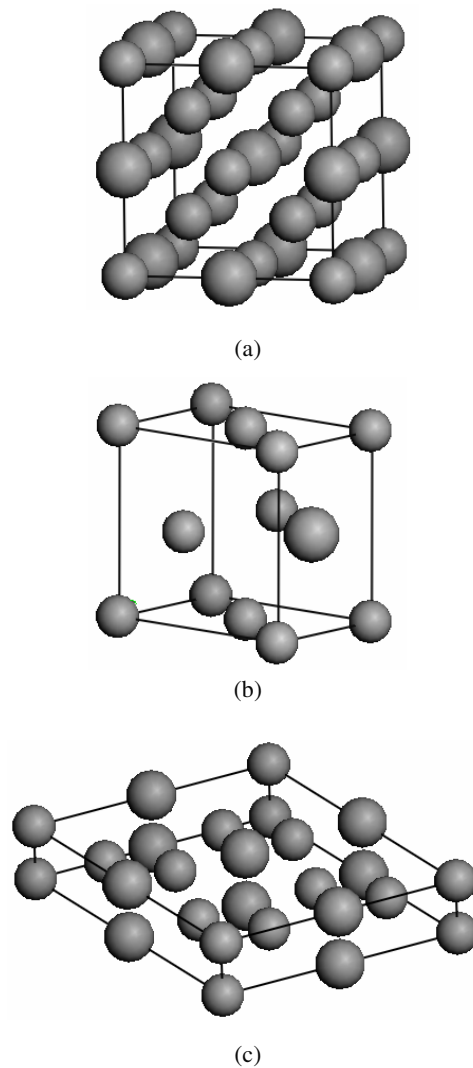
First-principles calculations of the phase stability, electronic structure and elastic properties of metastable  $\beta$ ,  $\alpha''$  and  $\omega$  phases in the Ti–25 at.% Nb alloy were performed using the method of the ultrasoft pseudopotential method [12]. Exchange and correlation effects are treated within the density functional theory (DFT) using the generalized gradient approximation (GGA) proposed by Perdew *et al* [13]. In constructing the pseudopotentials, 3s, 3p, 3d, 4s states and 4s, 4p, 4d, 5s states are chosen as the reference states for Ti and Nb atoms, respectively. A kinetic cutoff energy of 400 eV and a  $k$ -point spacing of  $0.04 \text{ \AA}^{-1}$  are chosen. The Pulay charge mixing method is adopted to accelerate the convergence [14]. The system energy is minimized using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) method to determine the equilibrated lattice constants and internal atomic coordinates [15]. Each calculation is considered to be converged when the energy difference was less than  $1 \times 10^{-6}$  eV/atom and the maximum forces on the atom were below  $2 \times 10^{-3}$  eV  $\text{\AA}^{-1}$ .

In the calculation of the  $\beta$  Ti–25 at.% Nb alloy, the  $D0_3$  structure with the space group  $Fm\bar{3}m$  (No. 225) was used, where the unit cell contains eight conventional bcc unit cells. The atomic positions are 4a(0, 0, 0) and 8c(0.25, 0.25, 0.25) sites for Ti and 4b(0.5, 0.5, 0.5) site for Nb, respectively. For the  $\alpha''$  martensite phase, the unit cell with orthorhombic structure and space group  $Pmm2$  (No. 25) was employed. The atomic positions are (0, 0, 0), (0.5, 0.5, 0), (0, 0.6, 0.5) for Ti and (0.5, 0.1, 0.5) for Nb, respectively. In the calculation of the  $\omega$  phase, a  $2 \times 2 \times 1$  supercell was used with space group  $P6/mmm$  (No. 191). The different cell structures are shown in figure 1.

## 3. Results and discussion

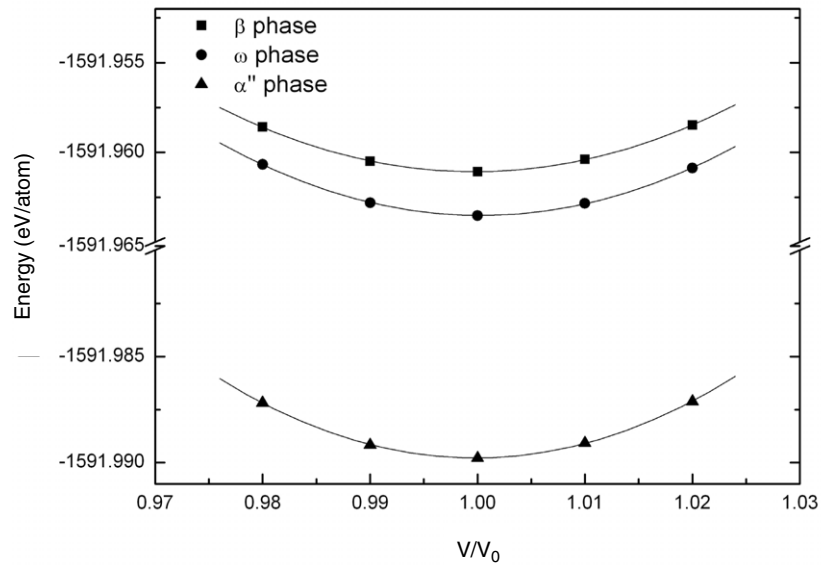
The structures were firstly optimized to determine the equilibrium lattice constants and internal atomic coordinates for  $\beta$ ,  $\alpha''$  and  $\omega$  metastable phases. The fits to the calculated total energy as a function of volume for the different phases are presented in figure 2, in which the Birch–Murnaghan equation of state is expressed as

$$E = a + bV^{-\frac{2}{3}} + cV^{-\frac{4}{3}} + dV^{-2}, \quad (1)$$



**Figure 1.** The cell structures for the  $\beta$  phase (a),  $\alpha''$  phase (b) and  $\omega$  phase (c), where small spheres represent Ti atoms and larger spheres represent Nb atoms.

where  $E$  and  $V$  are the total energy and the volume under pressure, respectively. It is seen from figure 2 that the phase ordering at the equilibrium volume is  $\alpha''$ ,  $\omega$  and  $\beta$  phase with increasing total energy. The calculated equilibrium lattice constants of  $\beta$ ,  $\alpha''$  and  $\omega$  phases in the Ti–25 at.% Nb alloy are summarized in table 1. It can be seen from table 1 that the equilibrium lattice constant of the  $\beta$  phase is 3.260 Å, which agrees well with the experimental one of 3.287 Å [10]. This value is also very close to the other theoretical calculation of 3.273 Å [11]. The lattice constants of the  $\alpha''$  martensite phase ( $a$ ,  $b$ ,  $c$ ) are calculated to be 3.307, 4.761 and 4.438 Å, respectively. On the other hand, the lattice constants of the  $\alpha''$  martensite phase of the Ti–25 at.% Nb alloy were recently determined experimentally to be 3.19, 4.80 and 4.64 Å by Kim *et al* [10]. Their studies also showed that the lattice constants of the  $\alpha''$  martensite phase strongly depend on the Nb content of the alloys. The theoretical



**Figure 2.** The total energy as a function of volume for the different phases in the Ti–25 at.% Nb alloy.

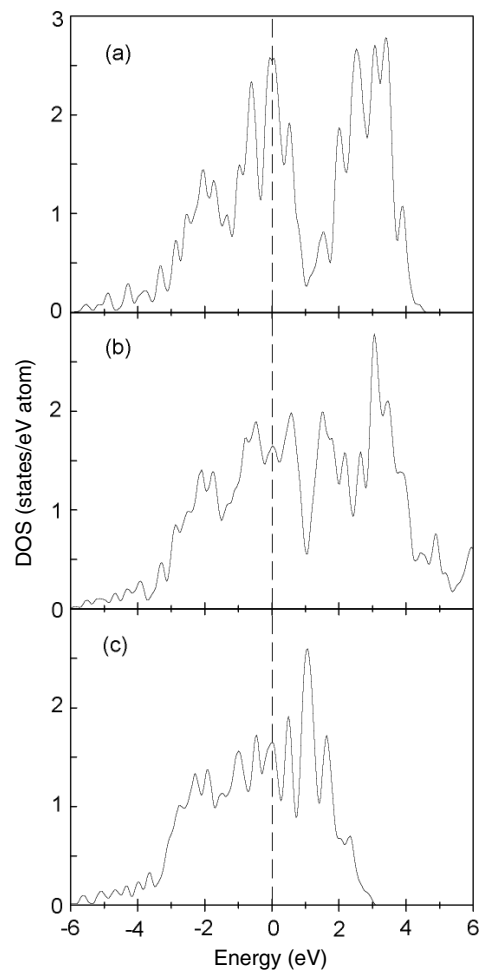
**Table 1.** Equilibrium lattice constants ( $\text{\AA}$ ) and cohesive energies (eV/atom) of the  $\beta$ ,  $\alpha''$  and  $\omega$  phases in the Ti–25 at.% Nb alloy.

Phase	Lattice constants			Cohesive energy
	$a$	$b$	$c$	
$\beta$	3.260			7.240
	3.273 <sup>a</sup>			
$\alpha''$	3.287 <sup>b</sup>			7.236
	3.307	4.761	4.438	7.269
$\omega$	3.19 <sup>b</sup>	4.80 <sup>b</sup>	4.64 <sup>b</sup>	7.253
	4.658		2.790	7.243

<sup>a</sup> Reference [11].

<sup>b</sup> Reference [10].

$a$  axis in this work is longer and the  $c$  axis shorter compared with the experimental results. The discrepancy between theoretical and experimental lattice constants is probably related to the strain constraints of the  $\beta$  matrix to the  $\alpha''$  metastable phase during the process of the  $\beta \rightarrow \alpha''$  martensite transformation. The theoretical lattice constants of the  $\omega$  phase ( $a$ ,  $c$ ) are 4.658 and 2.790  $\text{\AA}$ , respectively. The cohesive energies of  $\beta$ ,  $\alpha''$  and  $\omega$  phases were also calculated in this work and are shown in table 1. It is shown that the cohesive energies of  $\beta$  and  $\alpha''$  phases calculated using theoretical lattice constants are slightly larger than those calculated using experimental lattice constants. The calculated cohesive energies are close among  $\beta$ ,  $\alpha''$  and  $\omega$  metastable phases, and follow the order of  $\alpha'' > \omega > \beta$ . This implies that the phase stability follows the same order of  $\alpha'' > \omega > \beta$  from the viewpoint of energetics. These calculations of the ground state are consistent with the experimental observations on the phase transformations. For example, the  $\beta \rightarrow \alpha''$  martensite transformation and  $\beta \rightarrow \omega$  phase transformation have already been reported in the Ti–Nb alloys [5, 10]. In the following calculations, experimental



**Figure 3.** The electronic structures of the  $\beta$  phase (a),  $\alpha''$  phase (b) and  $\omega$  phase (c) in the Ti-25 at.% Nb alloy.

lattice constants were used for  $\beta$  and  $\alpha''$  phases, while theoretical lattice constants for the  $\omega$  phase were used due to lack of experimental ones for the  $\omega$  phase in the Ti-25 at.% Nb alloy.

The electronic structures of  $\beta$ ,  $\alpha''$  and  $\omega$  metastable phases in the Ti-25 at.% Nb alloy were calculated additionally. The densities of states (DOS) of those different phases are shown in figure 3. The DOS curve of the  $\beta$  phase is almost the same as that reported by Ikehata *et al* [11]. Clearly, there is a pronounced pseudogap between the low-energy bonding and high-energy anti-bonding regions for the  $\beta$  phase. However, the Fermi level is located in the bonding region of the DOS spectrum, resulting in a high value of the DOS at the Fermi level of 2.44 states per eV and atom. This means that the phase stability of the  $\beta$  structure is relatively low in the Ti-25 at.% Nb alloy. In contrast, although there is no clear pseudogap in the DOS spectra for  $\alpha''$  and  $\omega$  phases, the DOSs at the Fermi level for both structures are 1.64 and 1.65 states per eV and atom, respectively. These values of the DOS at the Fermi level are much lower than that of the  $\beta$  structure, which implies the  $\alpha''$  and  $\omega$  phases are more stable than the  $\beta$  phase in the Ti-25 at.% Nb alloy.

**Table 2.** Calculated elastic constants (GPa) of the  $\beta$ ,  $\alpha''$  and  $\omega$  phases in the Ti–25 at.% Nb alloy.

Phase	$C_{11}$	$C_{12}$	$C_{13}$	$C_{22}$	$C_{23}$	$C_{33}$	$C_{44}$	$C_{55}$	$C_{66}$
$\beta$	117.29	105.62					19.90		
	128.5 <sup>a</sup>	115.5 <sup>a</sup>					14.9 <sup>a</sup>		
$\alpha''$	129.89	91.12	126.81	148.22	69.32	135.59	28.38	23.13	39.65
$\omega$	162.15	124.94	84.78			234.29	22.28		18.61

<sup>a</sup> Reference [11].

Elastic constants are determined by calculating the stress tensors on applying strains to the equilibrium structure. In order to calculate the elastic constants of the cubic structure, the strain mode of  $\varepsilon_{11}$  and  $\varepsilon_{23}$  is used. For the orthorhombic structure, the unit cell is deformed by three different strain modes, whose nonzero strains are as follows: (1)  $\varepsilon_{11}$  and  $\varepsilon_{23}$ , (2)  $\varepsilon_{22}$  and  $\varepsilon_{31}$ , and (3)  $\varepsilon_{33}$  and  $\varepsilon_{12}$ . For the hexagonal structure, two different strain modes are used, whose nonzero strains are as follows: (1)  $\varepsilon_{33}$ , (2)  $\varepsilon_{11}$  and  $\varepsilon_{23}$ . Table 2 shows the calculated results of the elastic constants of  $\beta$ ,  $\alpha''$  and  $\omega$  phases in the Ti–25 at.% Nb alloy. It can be seen from table 2 that the elastic constants of  $C_{11}$  and  $C_{12}$  of the  $\beta$  phase are in good agreement with the theoretical result in the literature [11]. However,  $C_{44}$  shows little difference from that calculated by Ikehata *et al* [11]. The experimental and/or theoretical values of the elastic constants for the  $\alpha''$  and  $\omega$  phases could not be found for a comparison with the present calculated results. Moreover, the elastic stability of  $\beta$ ,  $\alpha''$  and  $\omega$  phases can be analyzed by the elastic constants. For the cubic, orthorhombic and hexagonal structure, the elastic stability requires the elastic constants to satisfy the following conditions, respectively [16].

$$\begin{aligned} C_{44} &> 0, \\ C_{11} + 2C_{12} &> 0, \\ C_{11} - |C_{12}| &> 0 \end{aligned} \quad (2)$$

$$\begin{aligned} C_{ii} &> 0 \quad (i = 1-6), \\ C_{22}C_{33} - C_{23}^2 &> 0, \\ 2C_{12}C_{13}C_{23} - C_{12}^2C_{33} - C_{13}^2C_{22} &> 0, \end{aligned} \quad (3)$$

$$\begin{aligned} C_{44} &> 0, \\ (C_{11} + C_{12})C_{33} - 2C_{13}^2 &> 0, \\ C_{11} - |C_{12}| &> 0. \end{aligned} \quad (4)$$

From the elastic constants shown in table 2, it is known that all of the  $\beta$ ,  $\alpha''$  and  $\omega$  metastable phases are elastically stable.

From these theoretical results of the elastic constants, the bulk modulus  $B$ , shear modulus  $G$  and Young's modulus  $E$  of  $\beta$ ,  $\alpha''$  and  $\omega$  metastable phases in the Ti–25 at.% Nb alloy can be estimated. The elastic moduli in table 3 are Hill's averages, which is the arithmetic mean of the Voigt average and the Reuss average [17]. In the Voigt average, the shear modulus is given by

$$G_v = \frac{C_{11} - C_{12} + 3C_{44}}{5}, \quad (5)$$

while in the Reuss average it is given by

$$G_R = \frac{5}{4S_{11} - 4S_{12} + 3S_{44}}, \quad (6)$$

**Table 3.** Calculated elastic moduli (GPa) of  $\beta$ ,  $\alpha''$  and  $\omega$  phases in the Ti–25 at.% Nb alloy.

Phase	$B$	$G$	$E$
$\beta$	109.51	12.20	35.29
	119.8 <sup>a</sup>	10.69 <sup>a</sup>	31.14 <sup>a</sup>
$\alpha''$	105.10	16.46	46.93
$\omega$	127.24	26.99	75.62

<sup>a</sup> Reference [11].

where  $S_{ij}$  is the inverse matrix of  $C_{ij}$  with the relations  $C_{44} = S_{44}^{-1}$ ,  $C_{11} - C_{12} = (S_{11} - S_{12})^{-1}$  and  $C_{11} + 2C_{12} = (S_{11} + 2S_{12})^{-1}$ . The Young's modulus is given by

$$E = \frac{9GB}{G + 3B}, \quad (7)$$

From table 3, it is seen that the bulk modulus of the  $\beta$  phase is very close to the theoretical result achieved by Ikehata *et al* [11]. But the shear and Young's moduli are slightly higher than those calculated by Ikehata *et al* [11]. It is also seen that the bulk moduli are close for  $\beta$ ,  $\alpha''$  and  $\omega$  phases in the Ti–25 at.% Nb alloy. Thus, it can be deduced that the bulk modulus is not a dominant factor in the reduction of the elastic moduli of Ti–Nb alloys. However, the shear and Young's moduli of  $\beta$ ,  $\alpha''$  and  $\omega$  phases are very different. The shear and Young's moduli increase with the  $\beta$ ,  $\alpha''$  and  $\omega$  phase in order in the Ti–25 at.% Nb alloy.

It has been widely accepted that the  $\omega$  phase has the highest Young's modulus in the titanium-based alloys with different alloying elements [5]. However, there is a discrepancy for the elastic modulus of the  $\beta$  phase and  $\alpha''$  martensite phase in those alloys [18–22]. The present calculations theoretically confirmed that the  $\omega$  phase has the highest Young's modulus among  $\beta$ ,  $\alpha''$  and  $\omega$  metastable phases, and the  $\alpha''$  martensite has higher Young's modulus than the  $\beta$  phase in the Ti–25 at.% Nb alloy. Therefore, in titanium alloy design for low elastic modulus, the addition of several atomic percentage of alloying elements is required to suppress the occurrence of the  $\alpha''$  and  $\omega$  phases. On the other hand, the precipitation hardening effect of the  $\omega$  phase can be used to increase the critical stress of the slip deformation of the Ti–Nb alloys because of its high elastic modulus, and thus large recovery strain and stable superelasticity can be achieved in the Ti–Nb alloys with fine  $\omega$  precipitates.

#### 4. Conclusions

In summary, the phase stability, electronic structure and elastic constants of the  $\beta$ ,  $\alpha''$  and  $\omega$  metastable phases in the Ti–25 at.% Nb alloy have been calculated by first-principles calculations based on the ultrasoft pseudopotential method within GGA. The bulk, shear and Young's modulus of those metastable phases were estimated from the theoretical elastic constants by the VRH method. The calculated results of the energetics and electronic structures showed that the phase stability follows the order of  $\alpha'' > \omega > \beta$ . The bulk moduli of  $\beta$ ,  $\alpha''$  and  $\omega$  phases are close, but the shear and Young's moduli of  $\beta$ ,  $\alpha''$  and  $\omega$  phases are very different. The shear and Young's moduli increase with the  $\beta$ ,  $\alpha''$  and  $\omega$  phase in order in the Ti–25 at.% Nb alloy.

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