First-principles calculations atomic structure and elastic properties of Ti-Nb alloys

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Abstract

Elastic properties of Ti based β-alloy were studied by the method of the model structure first principle calculations. Concentrational dependence of Young modulus for the binary β-alloy Ti$_{1-x}$Nb$_x$ was discovered. It is shown that peculiarities visible at 0.15-0.18% a.u. concentrations can be related to the different Nb atoms distribution. Detailed comparison of the calculation results with the measurement results was done. Young modulus for the set of the ordered structures with different Nb atoms location, which simulate triple β-alloys Ti$_{0.518}$Zr$_{0.297}$Nb$_{0.185}$ and Ti$_{0.297}$Zr$_{0.518}$Nb$_{0.185}$ have been calculated. The results of these calculations allowed us to suggest the concentration region for single-phase ternary β-phase alloys possessing low values of Young’s modulus.

Introduction

Today the β-titanium alloys are widely used for medical applications due to their high bio-compatibility and utoxicity. The elastic moduli of these alloys have to be rather low. Elastic properties of the β-alloys of Ti$_{1-x}$Nb$_x$ system have been studied extensively. It is known that at Nb content below x=0.27 these alloys are not in a single-phase condition and contain martensite phases [1]. At higher Nb content single-phase conditions can be fixed. Martensite phases usually lead to a considerable increase in elastic constants of these alloys. Elastic moduli
of the single $\beta$-phase apparently decrease with lowering Nb content, as the $\beta$-phase turns less stable. Alloys with low elastic moduli of about 30-40 GPa are promising materials for implants. So, single-phase $\beta$-alloys with Nb content below 0.27 could be such material, however, as mentioned above they are practically impossible to obtain, and there is no experimental data on the $\beta$-phase elastic moduli dependence on Nb content in Ti$_{1-x}$Nb$_x$ alloys at $x<0.27$. It is worth to note that knowing this dependence is an important issue since it concerns changes in the elastic moduli of binary Ti$_{1-x}$Nb$_x$ alloy when Ti atoms are partially substituted by other atoms. In this regard single-phase Ti$_{1-x-y}$Zr$_y$Nb$_x$ ternary alloys with low elastic moduli are of interest. In contrast to Ti$_{1-x}$Nb$_x$ alloys, the ternary alloys can be fixed in a single-phase condition at considerably lower Nb contents (up to $x=0.14$) [2]. It is well known also that Ti$_{1-x-y}$Zr$_y$Nb$_x$ alloys have lower elastic moduli as compared to Ti$_{1-x}$Nb$_x$ alloys. Therefore, partial substitution of Ti by Zr in Ti$_{1-x}$Nb$_x$ alloy is expected to have a double effect - it will lower Nb content necessary to fix a single-phase state, and it will reduce the elastic moduli of the ternary alloy. At the first stage of search for Ti$_{1-x-y}$Zr$_y$Nb$_x$ alloy optimal compositions, the information on the elastic moduli of binary Ti$_{1-x}$Nb$_x$ $\beta$-alloy in a wide range of Nb content should be obtained. Such information is valuable also for low Nb contents at which the alloy can not be practically fixed in a single-phase condition. In this regard first-principles calculations of electronic structure and elastic properties of the alloy are useful. High-precision quantum-mechanical calculations allow to study in detail various factors affecting the elastic moduli of a material. Apparently the most important factors are Nb content and distribution of Nb atoms in the BCC lattice. Whether the elastic moduli dependence on Nb content represents a monotonic function or not is also a question of interest. The probability of an abnormal behavior of this dependence at some Nb contents should not be excluded. If so, it would be useful to elucidate the reasons of such behavior. First-principles computer simulations of electronic structure and elastic properties of alloys is an important point making much more effective experimental works on a purposeful search for ternary alloys with needed elastic properties. The present
work targeted two goals: (i) first-principles calculations of electronic structure and Young's modulus of binary Ti\(_{1-x}\)Nb\(_x\) \(\beta\)-alloy at \(x=0.07-0.25\), and (ii) determination of the partial substitution of Ti by Zr effect on electronic structure and elastic moduli of ternary Ti\(_{1-x-y}\)Zr\(_y\)Nb\(_x\) \(\beta\)-alloy.

Calculation detail

The high-precision "ab-initio" FLAPW method realized in Wien2k package \[3\] was used for calculations of elastic constants \(C_{11}\), \(C_{12}\) and Young’s modulus of Ti\(_{1-x}\)Nb\(_x\) \(\beta\)-alloy. The exchange-correlation potential was calculated in generalized gradient approximation (GGA) according to the Perdew-Burke-Ernzerhof model \[3\]. Atomic sphere radii both for Ti and Nb atoms were 2.2 a.u. The calculations were performed for 2,000 k-points in the first Brillouin zone. Inside the atomic spheres the wave function was expanded up to \(l_{\text{max}}=12\). The electronic density and potential inside the spheres were expanded on the lattice harmonics basis up to \(L_{\text{max}}=6\). The \(R_{\text{min}}\times K_{\text{max}}\) parameter which controls the number of APW functions in the basic set equaled 8.35 that corresponded to 160 APW per atom. The \(G_{\text{max}}\) value determining the number of plane waves in the inter-sphere potential expansion equaled 12. These parameters allowed to calculate the total energy of model ordered structures with accuracy of 0.001 eV. The calculations were carried out under conditions of a complete structural optimization considering both homogeneous and inhomogeneous deformations, i.e. the lattice parameters and atom locations were optimized. The model volumes were \(3a_0\times3a_0\times3a_0\) (54 atoms), where \(a_0\) is the BCC lattice parameter of titanium. The elastic moduli were calculated for ordered structures Ti\(_{54-m}\)Nb\(_m\) (\(m=2,8,10,12,14\)) which corresponded to Ti\(_{1-x}\)Nb\(_x\) (\(x=0.037, 0.148, 0.185, 0.222, 0.26\)) alloys. The large model volume used provides comparatively high accuracy in calculations of the atomic structure and deformations caused by substitution of Ti by Nb atoms in the alloys. The bulk compression, shear, and Young’s moduli were calculated by the Voigt-Reuss-Hill method (VRH) \[4\]. For ab-initio simulation of elastic properties the approxima-
tion of an elastically isotropic material with $C' = C_{44}$, where $C' = (C_{11} - C_{12})/2$, was applied. It should be noted that all calculations realized in the present work correspond to 0 K.

Results and discussion

For a more adequate simulation of real alloys, Nb atoms in the model Ti$_{54-m}$Nb$_m$ structures were arranged as uniformly as was possible. Each Nb atom did not have any Nb atom adjoining. As mentioned above, the calculations of total energies for these structures were performed with a complete structural optimization. The components of elastic tensor for the cubic symmetry were found using the CubicElast package (Wien2k [3]). The structures with tetragonal symmetry were generated from the model cubic structures for various Nb contents. Then appropriate deformations with lattice parameters changes not higher than 3% were applied to these structures. The total energies were calculated by the FLAPW method for all generated structures. Using the total energies of initial and deformed structures, the components of elastic tensor for each structure were calculated. The calculated equilibrium lattice parameters and elastic constants of the β-titanium and model Ti$_{54-n}$Nb$_n$ ($n = 2, 4, 8, 10, 12, 14$) are listed in Table 1 The concentration dependence of the Young’s modulus, calculated for the binary β-alloys, is shown in Fig. 1 At low Nb contents negative values of the Young’s modulus were obtained, that correlates with the phase field boundaries. At those low Nb concentrations initial

| Alloy         | Structure  | $a$, Å  | $C_{11}$ | $C_{12}$ | $C'$   | $B$     | $E$    |
|--------------|------------|---------|----------|----------|--------|---------|--------|
| Ti           | Ti         | 3.2553  | 79.80    | 122.38   | -21.29 | 108.19  | -68.35 |
| Ti$_{0.962}$Nb$_{0.038}$ | Ti$_{52}$Nb$_{2}$ | 3.2500  | 104.58   | 114.45   | -4.93  | 111.16  | -15.02 |
| Ti$_{0.923}$Nb$_{0.076}$ | Ti$_{50}$Nb$_{4}$ | 3.2513  | 138.31   | 122.29   | 16.02  | 127.63  | 37.68  |
| Ti$_{0.852}$Nb$_{0.148}$ | Ti$_{46}$Nb$_{8}$ | 3.2662  | 145.71   | 97.34    | 24.19  | 113.46  | 67.74  |
| Ti$_{0.815}$Nb$_{0.185}$ | Ti$_{44}$Nb$_{10}(A)$ | 3.2586  | 140.57   | 97.16    | 21.70  | 111.63  | 61.15  |
| Ti$_{0.776}$Nb$_{0.222}$ | Ti$_{42}$Nb$_{12}$ | 3.2715  | 152.27   | 94.10    | 29.09  | 113.49  | 80.39  |
| Ti$_{0.741}$Nb$_{0.259}$ | Ti$_{40}$Nb$_{14}$ | 3.2553  | 150.25   | 108.84   | 20.71  | 122.64  | 58.81  |
stresses extensively deform the BCC lattice, allowing atoms to occupy energetically more favorable sites proper for the HCP phase. At higher Nb contents metastable martensite phases energetically more favorable than the \( \alpha \) phase form in the real alloys. The calculations showed that the concentration dependence of the Young’s modulus of the binary Ti\(_{1-x}\)Nb\(_x\) alloys is not a monotonic function. This dependence has certain peculiar features at Nb contents of \( x=0.15-0.18 \) (Fig. 1). These results correlate well with the experimental data obtained in [5, 6, 7, 8] and plotted in the same Figure. Up to date, the Young’s modulus increase in the Nb concentration range mentioned above has been attributed to the presence of martensite phases. However, our results allow to suggest that the increase in Nb concentration leads to considerable changes in the electronic structure of the ordered crystal structures, modeling alloy in question. It makes a significant influence upon the Young’s modulus of the \( \beta \) phase. Another important factor affecting the Young’s modulus is the distribution of Nb atoms in the model lattice. This can be demonstrated by calculating the Young’s modulus for two types of \( Ti_{44}Nb_{10} \) structure A and B shown in Fig. 2. The A was used earlier for the calculations of the Young’s modulus concentration dependence, see Fig. 1.

The B was constructed from the A by changing the Nb atom sites. In the B
each Nb atom has one or several Nb atom neighbors. The B structure appeared to be energetically more favorable and had higher Young’s modulus as compared to the A, see the asterisk in Fig. 1. It should be noted that the calculated concentration dependence of the Young’s modulus better correlates with experimental data if the modulus value for the B structure is considered (dashed line in Fig. 1). The calculation results allow to formulate two important conclusions. First, the concentration dependence of the Young’s modulus of the binary single-phase β-alloy is apparently not a monotonic function. So, the peculiar behavior of the experimental concentration dependence at certain Nb contents can be explained not only by a multi-phase state. Second, the distribution of Nb atoms in ordered structure modeling β-titanium significantly affects the Young’s modulus. The structures with a short range ordering, when each Nb atom has one or several Nb neighbors, have higher Young’s modulus values as compared to the structures without such ordering. To clarify the reasons of this effect, a detailed investigation on the nature of the chemical bonds in Ti-Nb system and the mechanism of the β-phase stabilization by Nb is needed. Unfortunately, these problems are beyond the scope of present paper. The discrepancy between the calculated and experimental Young’s modulus values can be explained by using polycrystalline and multi-phase samples in the experimental works. Our results significantly differ from the theoretical results obtained in other works [9, 10], see Fig. 3 for comparison. Our theoretical values
have the best correlation with experimental data, see Fig. 1. The peak on the theoretical concentration dependence at $x=0.185$ is a peculiar feature of our results. The better correlation with experiment is reached for the absolute values of the Young's modulus as well. The values obtained in [9, 10] are significantly lower than both ours and experimental ones. The main reason of the better correlation of our results with experiment is possibly a larger model volume used (54 atoms), while in the works mentioned above model volume comprised 16 atoms ($2a_0 \times 2a_0 \times 2a_0$, where $a_0$ is the BCC lattice parameter). In [9] the FLAPW method for the Young's modulus calculations was applied as well. The elastic properties were simulated by the Voigt-Reuss-Hill approximation (VRH) [4] for polycrystals. In [10] the Young's modulus was calculated by the pseudo-potential method with the VASP package [11] in the elastically isotropic approximation. The Young's modulus of several model structures for fixed Nb contents but different atom distributions were also calculated in [11], the results are included in fig. 3. Unfortunately, the authors
did not describe the principles of structure selection used. The insufficient model volumes used in the two earlier works, in our opinion, is one of the reasons of a considerable discrepancy between the theoretical and experimental values. The three-fold larger model volume used in the present work apparently allowed a more adequate modeling the real atomic structure, and a more accurate calculation of deformation effects caused by substitution of Ti by Nb atoms. The concentration dependence of the Young’s modulus of the binary Ti-Nb $\beta$-alloy makes possible modeling the elastic properties of ternary alloys. Our aim is to predict the compositions providing single-phase state and Young’s modulus values lower as compared to the binary alloy. As mentioned in the Introduction, Zr as the third element is promising. Model ordered structures of ternary alloy were formed from the A and B structures shown in Fig. \[2\] The Nb content in these structures was constant, $x=0.185$. The Young’s modulus calculated for this concentration was quite high, Table \[1\] So, it is of interest to substitute some Ti by Zr atoms in proportions that would result both in a further reduction of the Young’s modulus as compared to the binary alloy, and in single-phase state. Two model structures of the A type with differing Zr content, Ti$_{44-m}$Zr$_{m}$Nb$_{10}(m = 16, 28)$, were chosen. These structures correspond to Ti$_{0.519}$Zr$_{0.296}$Nb$_{0.185}$ and Ti$_{0.296}$Zr$_{0.519}$Nb$_{0.185}$ alloys. As earlier for the binary alloys, the $\beta$-type structures with a peculiar Nb distribution were constructed from the A structures. In the B structures Nb atoms had one or several Nb neighbors. As for the binary alloys, the calculations showed high energetic favorability of the $\beta$-type structures. The calculations of the atomic structure and elastic constants were fulfilled for these four model structures. The results are listed in Table \[2\] The substitution of Ti by 30% Zr atoms in the Ti$_{44}$Nb$_{10}$ (A)

| Alloy                | Structure          | $a$, Å  | $C_{11}$ | $C_{12}$ | $C'$  | $B$   | $E$   |
|----------------------|--------------------|---------|----------|----------|-------|-------|-------|
| Ti$_{0.519}$Zr$_{0.296}$Nb$_{0.185}$ | Ti$_{28}$Zr$_{16}$Nb$_{10}$(A) | 3.3520  | 130.00   | 100.00   | 15.00 | 110.00 | 43.04 |
|                      | Ti$_{28}$Zr$_{16}$Nb$_{10}$(B) | 3.3820  | 144.22   | 94.66    | 24.78 | 111.18 | 69.19 |
| Ti$_{0.296}$Zr$_{0.519}$Nb$_{0.185}$ | Ti$_{16}$Zr$_{28}$Nb$_{10}$(A) | 3.4253  | 129.01   | 94.67    | 17.5  | 105.67 | 49.75 |
|                      | Ti$_{16}$Zr$_{28}$Nb$_{10}$(B) | 3.4315  | 137.12   | 89.70    | 23.71 | 105.5  | 66.18 |
structure led to a reduction of the Young’s modulus from 61.15 to 43.04 GPa in the Ti$_{28}$Zr$_{16}$Nb$_{10}$ (A) structure. Further increase in Zr content up to 52 at.% resulted in the Young’s modulus of 49.75 GPa in the Ti$_{16}$Zr$_{28}$Nb$_{10}$ (A) structure. Therefore, our results predict a significant reduction of the Young’s modulus in the ternary alloys as compared to binary ones. However, the first-principles calculations cannot predict whether the ternary alloys will be single-phase or not. To clarify this question we used experimental results of [12]. In this work the influence of Zr on the phase composition of ternary Ti-Zr-Nb alloys in a wide concentration range was investigated. The authors showed that partial substitution of Ti by Zr in binary Ti-Nb alloy led to the $\beta$-phase stabilization. The samples annealed at 1173 K were investigated. Based on the results of [12], we plotted the dependence of the lowest Nb content providing single-phase state on Zr concentration, see Fig. 4. This allowed to estimate the single-phase $\beta$ field boundaries for the ternary alloys. The alloys modeled in the present work are designated by an asterisk. The Young’s modulus values calculated for the A-type structures are indicated. Apparently, the search for compositions providing low Young’s modulus values is most effective.
in the hatched area at moderate Nb contents. Experimental results of [13, 14] are also included for comparison. The samples studied in those works comprised several phases, that resulted in comparatively high Young’s modulus values.

Conclusions

The concentration dependence of the Young’s modulus of several ordered Ti$_{54-m}$Nb$_m$ structures, modeling binary Ti$_{1-x}$Nb$_x$ alloys, was calculated by first-principles methods. It was shown that the features of this dependence at 0.15-0.18 at.% Nb can be attributed to the types of Nb atoms distribution. A detailed comparison of the theoretical results with experimental data was fulfilled. The Young’s modulus values were calculated for a set of ordered structures with different Nb atoms distribution, modeling ternary alloys Ti$_{0.518}$Zr$_{0.297}$Nb$_{0.185}$ and Ti$_{0.297}$Zr$_{0.518}$Nb$_{0.185}$. The results of these calculations allowed us to suggest the concentration region for single-phase ternary β-phase alloys possessing low values of Young’s modulus.

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