Functional Materials 19, No.2 (2012)

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

A.N.Timoshevskii, S.O.Yablonovskii, O.M.Ivasishin[*]

Institute of Magnetism, National Academy of Sciences of Ukraine,
03142 Kyiv, Ukraine
[*]Institute for Metal Physics, National Academy of Sciences of Ukraine,
36 Vernadsky Str., 03142 Kyiv, Ukraine

Received November 29, 2011

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. Youngs 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.

Методом первопринципного моделирования на основе модельных структур исследованы упругие свойства β-сплавов на основе титана. Получена концентрационная зависимость модуля Юнга для бинарного β-сплава $Ti_{1-x}Nb_x$. Показано, что особенности этой зависимости при концентрациях 0.15–0.18 ат. могут быть связаны с разным типом распределения атомов ниобия. Проведено детальное сравнение полученных результатов с экспериментальными данными. Рассчитаны модули Юнга набора упорядоченных структур с разным типом расположения атомов ниобия, моделирующих тройные β-сплавы $Ti_{0,518}Zr_{0,297}Nb_{0,185}$ и $Ti_{0,297}Zr_{0,518}Nb_{0,185}$. Предлагается возможная область существования однофазных тройных β-сплавов с низкими значениями модулей Юнга.

1. Introduction

Today β-titanium alloys are widely used for medical applications due to their high biocompatibility and untoxicity. 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 single β-phase apparently decrease with lowering Nb content, as the β-phase turns less stable. Alloys with low elastic moduli of about 30 – 40 GPa are promising materials for implants. So, single-phase β-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 β-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 $Ti_{1-x-y}Zr_yNb_x$ ternary alloys with low elastic moduli are of inter-

est. 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 $Ti_{1-x-y}Zr_yNb_x$ 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 $Ti_{1-x-y}Zr_yNb_x$ alloy optimal compositions, the information on the elastic moduli valuse of binary $Ti_{1-x}Nb_x$ β-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 aimed at two tasks: (i) first-principles calculations of electronic structure and Young's modulus of binary $Ti_{1-x}Nb_x$ β-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 $Ti_{1-x-y}Zr_yNb_x$ β-alloy.

2. Calculation details

High-precision "ab-initio" method FLAPW realized in Wien2k package [3] was used for calculations of elastic constants C_{11}, C_{12} and Young's modulus of $Ti_{1-x}Nb_x$ β-alloy. The exchange-correlation potential was calculated in generalized gradient approximation (GGA) according to 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 $l_{max} = 12$. The electronic density and potential inside the spheres were expanded on the lattice harmonics basis up to $L_{max} = 6$. The $R_{min} \times K_{max}$ parameter which controls the number of APW functions in the basic set equaled 8.35 that corresponded to 160 APW per atom. The G_{max} value determining the number of plane waves in the interspehere 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 $3a_0 \times 3a_0 \times 3a_0$ (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 Voigt-Reuss-Hill method (VRH) [4]. For *ab-initio* simulation of elastic properties the approximation 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.

3. Results and discussion

For a more adequate simulation of real alloys, Nb atoms in the model $Ti_{54-m}Nb_m$ structures were arranged evenly as if 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 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,

Table 1. Lattice constants, elastic constants and Young's modulus (GPa) of Ti (bcc) and $Ti_{54-m}Nb_m$ (m = 2, 4, 8, 10, 12, 14) structures modeling binary Ti–Nb alloys

Alloy	Structure	a, Å	C_{11}	C_{12}	C'	B	E
$Ti_{0.962}Nb_{0.038}$	$Ti_{52}Nb_2$	3.2500	104.58	114.45	−4.93	111.16	−15.02
$Ti_{0.924}Nb_{0.076}$	$Ti_{50}Nb_4$	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
	$Ti_{44}Nb_{10}(B)$	3.2715	152.27	94.10	29.09	113.49	80.39
$Ti_{0.778}Nb_{0.222}$	$Ti_{42}Nb_{12}$	3.2553	146.67	108.47	19.10	121.20	54.43
$Ti_{0.741}Nb_{0.259}$	$Ti_{40}Nb_{14}$	3.2553	150.25	108.84	20.71	122.64	58.81

the components of elastic tensor for each structure were calculated. The calculated equilibrium lattice parameters and elastic constants of 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 Young's modulus, calculated for the binary β-alloys, is shown in Fig. 1. At low Nb contents negative values of Young's modulus were obtained, that correlates with the phase field boundaries. At those low Nb concentrations initial 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 α phase form in the real alloys. The calculations showed that the concentration dependence of 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 [6–9] and plotted in the same Figure. Up to date, Young's modulus increase in 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 electronic structure of the ordered crystal structures, modeling alloy in question. It makes a significant influence upon Young's modulus of the β 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 Young's modulus for two types of $Ti_{44}Nb_{10}$ structure A and B shown in Fig. 2. The structure A was used earlier for the calculations of Young's modulus concentration dependence, see Fig. 1. The

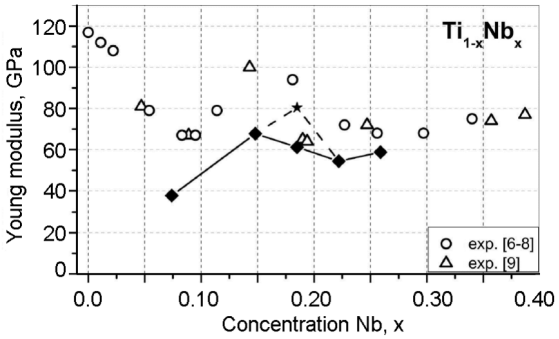

Fig. 1. Experimental and theoretical concentrational dependences of Young's modulus of $Ti_{1-x}Nb_x$.

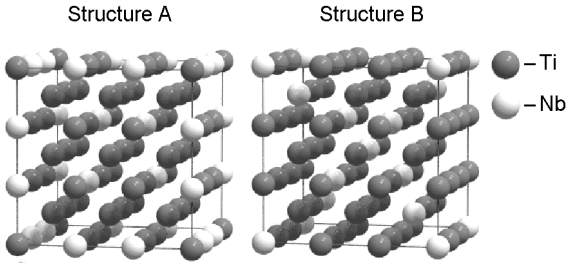

Fig. 2. Model structures $Ti_{44}Nb_{10}$.

structure 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 structure B 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 Young's modulus better correlates with experimental data if the modulus value for the structure B is considered (dashed line in Fig. 1). The calculation results allow to formulate two important conclusions. First, the concentration dependence of

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 value of 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 multiphase samples in the experimental works. Our results significantly differ from the theoretical results obtained in other works [10, 11], 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 [10, 11] 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 [10] the FLAPW method for the Young's modulus calculations was applied as well. The elastic properties were simulated by the Voigt-Reuss-Hill approximation [5] for polycrystals. In [11] the Young's modulus was calculated by the pseudo-potential method with the VASP package [15] 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 [15], 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

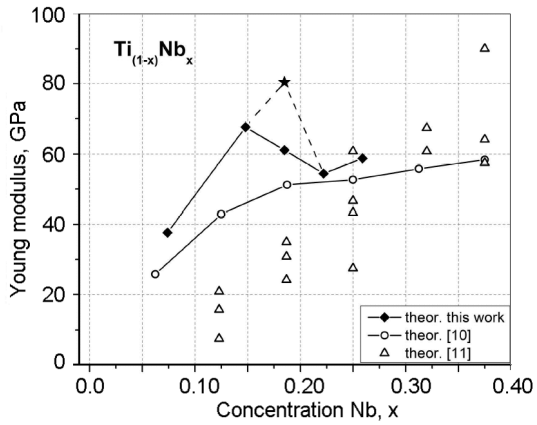

Fig. 3. Theoretical concentrational dependences of Young modulus of $Ti_{1-x}Nb_x$ alloy in [10, 11] and this work.

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 β-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, $Ti_{44-m}Zr_mNb_{10}$ ($m = 16$, 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 β-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 β-type structures. The calculations of the atomic structure and elastic constants were fulfilled for these four model structures. The results are listed

Table 2. Lattice constants, elastic constants and Young modulus (GPa) of $Ti_{44-m}Zr_mNb_{10}$ (m = 16, 28) structures modeling triple Ti–Zr–Nb alloys

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

in Table 2. The substitution of Ti by 30 % Zr atoms in the $Ti_{44}Nb_{10}(A)$ structure led to a reduction of the Young's modulus value 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 $Ti_{16}Zr_{28}Nb_{10}(A)$) structure. Therefore, our results predict a significant reduction of the Young's modulus value in the ternary alloys as compared to binary ones. However, the first-principles calculations can not 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 β-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 β field boundaries for the ternary alloys. The alloys modeled in the present work are designated by 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 the 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.

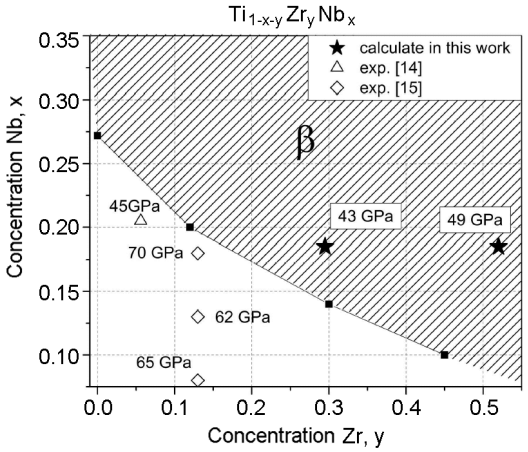

Fig. 4. Region of existence of single phase and multi phase triple β-phases Ti–Zr–Nb.

4. 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.

References

1. M.Abdel-Hady, K.Hinoshita, M.Morinaga, *Scripta Mater.*, **55**, 477 (2006).
2. S.Banerjee, P.Mukhopadhyay, *Pergamon Mater. Ser.*, **12**, 259 (2007).
3. P.Blaha, WIEN2K, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties, Technische Universitat, Wien, Austria (2001).
4. J.P.Perdew, M.Burke, K.Ernzerhof, *Phys. Rev. Lett.*, **77**, 3865 (1990).
5. R.Hill, *Proc. Phys. Soc. A*, **65**, 349 (1952).
6. S.G.Fedotov, O.K.Belousov, *Sov. Phys. Dokl.*, **8**, 496 (1963).
7. S.G.Fedotov, O.K.Belousov, *Phys. Met. Metallorg.*, **17**, 83 (1964).

8. S.G.Fedotov, *Transl. Israel Program for Scientific Translations Ltd., IPST. Cat.*, **1454**, 199 (1966).
9. H.M.Ledbetter, *J. Phys. D: Appl. Phys.*, **13**, 1879 (1980).
10. Q.Yao, J.Sun, H.Xing, W.Guo, *Trans. Nonferrous Met. Soc. China*, **17**, 1417 (2007).
11. D.Raabe, B.Sander, M.Friaoverset'k et al., *Acta Mater.*, **55**, 4475 (2007).
12. M.Abdel-Hady, H.Fuwa, K.Hinoshita et al., *Scripta Mater.*, **57**, 1000 (2007).
13. V.Brailovski, S.Prokoshkin, M.Gauthier et al., *Mater. Sci.Engin. :C*, **31**, 643 (2011).
14. S.Schneidera, S.G.Schneidera, H.M.da Silvab et al., *Mater. Res.*, **8**, 435 (2005).
15. G.Kresse, J.Furthmuller, *Phys. Rev. B*, **54**, 1169 (1996).

Першопринципне моделювання атомної структури і пружних властивостей сплавів Ti–Nb

А.М.Тимошевський, С.О.Яблоновський, О.М.Івасишин

Методом першопринципного моделювання на основі модельних структур досліджено пружні властивості β-сплавів на основі титану. Отримано концентраційну залежність модуля Юнга для бінарного β-сплаву $Ti_{1-x}Nb_x$. Показано, що особливості залежності для концентрацій 0,15–0,18 ат. можуть бути зв'язані з різним типом розподілу атомів ніобію. Проведено детальне порівняння отриманих результатів з експериментальними даними. Розраховано модулі Юнга набору упорядкованих структур з різним типом розміщення атомів ніобію, моделюючих потрійні β-сплави $Ti_{0,518}Zr_{0,297}Nb_{0,185}$ і $Ti_{0,297}Zr_{0,518}Nb_{0,185}$. Пропонується можлива область існування однофазних потрійних β-сплавів з низькими значеннями модулів Юнга.