Phase Stability and Elastic Properties of Ti-Mo-X (X=Ta, Nb, Zr) Alloys From First-principles Calculations

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The phase stability and elastic properties of Ti-Mo-X (X=Ta, Nb, Zr) alloys were investigated by the use of the first-principles method. Calculated cohesive energies suggest that Ta and Nb improve the phase stability of β phase, which shows an excellent agreement with experiment. In addition, the bulk, elastic and shear modulus, as well as tetragonal shear constant of Ti-Mo-Ta alloys were calculated by using the Voigt-Reuss-Hill averaging method. The results indicate that the lowest elastic modulus (68.94GPa) is acquired when the Ta content is 18.75 at.%. The effect of interactions between alloying atoms on elastic properties is briefly discussed.

Keywords: *First-principles, β phase stability, elastic properties*

1. Introduction

Biomaterials are used to diagnose, cure, restore or replace the tissue, organization for those who suffer from lost or disfunctioned biological structure. Titanium alloys are of special interest in the field of orthopedic implants due to their excellent corrosion resistance, good ductility, non-allergic effect and superior biocompatibility. Compared to the widely used stainless steels and Co-Cr alloys, titanium alloys exhibit much lower elastic modulus which is close to that of human bones.[1,2] However, the remained modulus mismatches between bio-titanium implants (110GPa) and human bones (10-30GPa) may cause resorption of adjacent bone tissue and premature failure of the implants.[3-5] Among all kinds of titanium alloys, β Ti alloys with lower elastic modulus are considered as promising biomaterials.[6] A number of β Ti alloys have been developed in the past few decades. Niinomi et al.[7] have developed a new β type Ti-29Nb-13Ta-4.6Zr whose elastic modulus is as small as 65GPa. More recently, Yang et al.[8] developed another outstanding β type bio-titanium alloy named Ti2448 (Ti-24Nb-4Zr-7.9Sn) with much lower elastic modulus (as low as 42GPa). It is well known that the elastic modulus of β Ti alloys correlates closely to the β phase stability. In general, the addition of VB or VIB family elements results in significant increase in β phase stability and decrease in elastic modulus[9,10].

To date there have been many investigations concentrating on the phase stability and elastic properties of Ti-X binary alloys using first-principles calculation. Yao et al.[11] indicated that once the tetragonal shear constant reaches nearly zero, the Ti-Mo and Ti-Nb alloys achieve low phase stability and low elastic modulus. Ikehata et al.[12] demonstrated that controlling the valence electron number at around 4.20-4.24 is possible to realize an extremely low Young's modulus within the β Ti alloys. At present, Ti-Mo-base alloys such as Ti-12Mo-6Zr-2Fe, Ti-15Mo, Ti-15Mo-2.8Nb-0.2Si-0.26O, Ti-15Mo-5Zr-3Al, Ti-2.5Mo-2.5Al-2.5Zr etc., have been extensively investigated, showing great potential for biomedical applications due to their superior corrosive resistance. Nevertheless, these alloys exhibit a little too high elastic modulus, which misfits that of human bones. Thus, it is of great interest to study the alloying effects of the Ti-Mo-base alloys aiming at reducing their elastic modulus.

In the present investigation, phase stability and elastic properties of Ti-Mo-X (X=Ta, Nb, Zr) ternary alloys have been studied by using first-principles methods. The lattice constants, cohesive energy and elastic properties of these alloys were presented.

2. Computational Details

CASTEP (Cambridge Serial Total Energy Package)[13] was utilized to calculate the lattice constants, cohesive energy, and elastic constants of the Ti-Mo-X (X=Nb, Ta, Zr) ternary alloys. The supercell used here contains 16 atoms, i.e., a 2×2×2 body centered cubic (bcc) unit cell, consisting one Mo atom in the center of each constructed structure. A large variety of alloy compositions were studied by replacing Ti atoms by other alloy elements systematically. We constructed a total number of 15 supercell models with chemical formula $Ti_{14}Mo_1Ta_1$, $Ti_{12}Mo_1Ta_3$, $Ti_{11}Mo_1Ta_4$, $Ti_{10}Mo_1Ta_5$, $Ti_8Mo_1Ta_7$, $Ti_{14}Mo_1Nb_1$, $Ti_{12}Mo_1Nb_3$, $Ti_{11}Mo_1Nb_4$, $Ti_{10}Mo_1Nb_5$, $Ti_8Mo_1Nb_7$, $Ti_{14}Mo_1Zr_1$, $Ti_{12}Mo_1Zr_3$, $Ti_{11}Mo_1Zr_4$, $Ti_{10}Mo_1Zr_5$, and $Ti_8Mo_1Zr_7$.

The method of supercell and pseudopotential plane waves within generalized gradient approximation (GGA)[14,15] was adopted. The construction of the pseudopotentials, 3s, 3p, 3d and 4s states were chosen as the reference states for Ti atoms. For Mo, Nb and Zr atoms, 4s, 4p, 4d and 5s states were chosen as the reference states, respectively. 5d and 6s states were chosen as the reference states for Ta atoms. The cut-off energy was carefully tested to be 400eV and an 8×8×8 Monkhorst-Pack mesh was used to sample the Brillouin zone. Self-consistent field tolerance was 2.0e-6 eV/atom. The convergence tolerance of maximum stress and maximum force were 0. 1 GPa and 0. 05 eV/Å, respectively. During the optimization process, BFGS was adopted.

3. Results and Discussion

The equilibrium lattice constants of Ti-Mo-Ta, Ti-Mo-Nb and Ti-Mo-Zr alloys are plotted in Figure 1. It can be seen that the lattice constants of Ti-Mo-Zr alloys increase monotonously with increasing content of Zr, which may result from that the atomic radium of Zr is larger than that of Ti. With increasing content of Ta or Nb, the lattice constants changes slightly, implying that the chemical bonding and bond distance between Ta or Nb and other atoms become stronger and shorter, respectively. Note that there is an abrupt change at 25 at. % for all systems considered, which calls for further exploration.

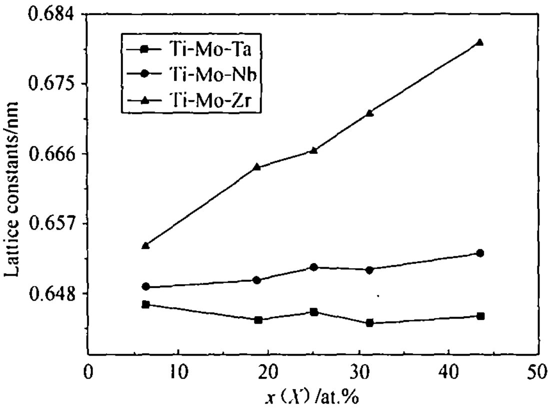

Figure 1. Relationship between lattice constants and X content

The cohesive energy reflects the binding ability of atoms, which correlates with the phase stability. In order to obtain the contribution of components to β phase stability, we calculated the cohesive energy of $Ti_{15-x}Mo_1X_x$ alloys as

$$E_{coh}=\frac{(15-x)E_{Ti}+E_{Mo}+xE_X-E_{Ti_{15-x}Mo_1X_x}}{16} \qquad (1)$$

where$E_{Ti_{15-x}Mo_1X_x}$ is total energy of Ti-Mo-X alloys, while E_{Ti}, E_{Mo} and E_X are the monatomic energy of Ti, Mo and X, respectively.

Figure 2 shows the calculated cohesive energy of Ti-Mo-X alloys. It can be seen that the cohesive energy of Ti-Mo-X increases significantly and linearly with increasing content of Ta or Nb, indicating that increasing content of Ta or Nb makes a contribution to improving β phase stability. This implies that Ta and Nb are indeed β stabilizers, which is completely consistent with experiment. For Ti alloys, Zr is a neutral element, whose α-stabilization effect and β-stabilization effect are both unapparent. As shown in Figure 2, the cohesive energy of Ti-Mo-Zr changes slightly with Zr concentration, implying that the stabilization effect of Zr is much weaker than that of Ta or Nb, which is also in perfect agreement with the experiments.

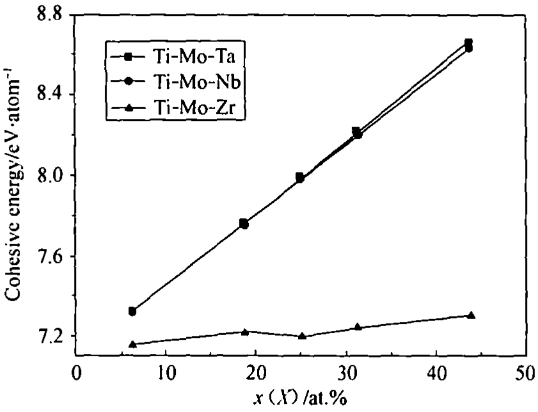

Figure 2. Relationship between cohesive energies and X content

The calculation of elastic modulus was performed by Voigt-Reuss-Hill averaging method[16]. For the cubic structure, $C_{11}=C_{22}=C_{33}$, $C_{12}=C_{13}=C_{23}$, $C_{44}=C_{55}=C_{66}$, and $S_{11}=S_{22}=S_{33}$, $S_{12}=S_{13}=S_{23}$, $S_{44}=S_{55}=S_{66}$ (C_{ij} and S_{ij} are the elastic constants and elastic compliances, respectively). Only three elastic constants are independent, viz., C_{11}, C_{12} and C_{44}. With these relations, within the Voigt approach, the expression for the shear modulus is

$$G_V=\frac{C_{11}-C_{12}+3C_{44}}{5} \qquad (2)$$

and within the Reuss approach, the shear modulus is

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

The shear modulus in Voigt-Reuss-Hill averaging can be obtained by

$$G=\frac{1}{2}(G_V+G_R) \qquad (4)$$

The calculated elastic modulus is completely described by the bulk modulus B and the shear modulus G

$$E=\frac{9GB}{G+3B} \qquad (5)$$

The elastic constants of Ti-Mo-Ta alloys are listed in Table 1. C_{11} increases monotonously with increasing content of Ta, and C_{44} remains almost unchanged, while the tendency of C_{12} is not evident.

With the results listed in Table 1, the bulk modulus (B), shear modulus (G), elastic modulus (E) and tetragonal shear constant ($C'=(C_{11}-C_{12})/2$) of Ti-Mo-Ta alloys were calculated and shown in Figure 3. The tetragonal shear constant (C') is used to evaluate the elastic stability of cubic crystal and its value is inversely proportional to that of elastic stability[11]. The tetragonal shear constants of the crystals considered here are all positive, suggesting that they are all mechanically stable. The trends of G, E, and C' with Ta content are similar and reach the minimum at about 18. 75 at. % Ta, where the lowest elastic modulus (68. 94 GPa) is obtained.

Table 1. Elastic constants of Ti-Mo-Ta alloys

Nominal formula	C_{11}/GPa	C_{12}/GPa	C_{44}/GPa
$Ti_{14}Mo_1Ta_1$	137.4395	98.0514	38.3372
$Ti_{12}Mo_1Ta_3$	166.0872	131.4621	30.4610
$Ti_{11}Mo_1Ta_4$	175.0882	100.7869	37.2664
$Ti_{10}Mo_1Ta_5$	188.9843	127.9097	39.2057
$Ti_8Mo_1Ta_7$	210.2694	138.5436	39.7924

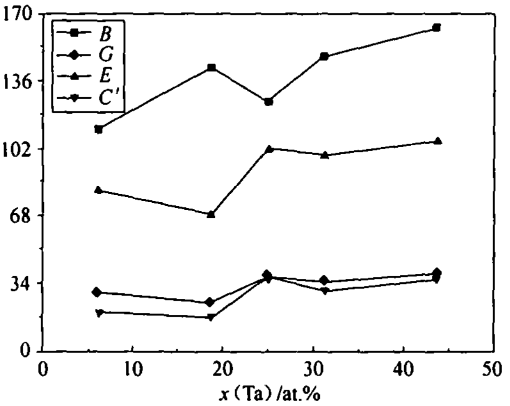

Figure 3. Calculated bulk modulus (B), shear modulus (G), elastic modulus (E) and tetragonal shear constant (C') of Ti-Mo-Ta alloys

The B, G and E of $Ti_{14}Mo_1X_1$ (X=Ta, Nb, Zr) and $Ti_{12}Mo_1X_3$(X=Ta, Nb, Zr) are displayed in Figure 4(a) and 4(b), respectively. It can be seen that the bulk modulus increases while the elastic modulus decreases with increasing X content. Furthermore, the variation is more significant for Ta in comparison with Nb and Zr. It demonstrates that the addition of Ta plays a more important role on reducing the elastic modulus of Ti-Mo-X alloys.

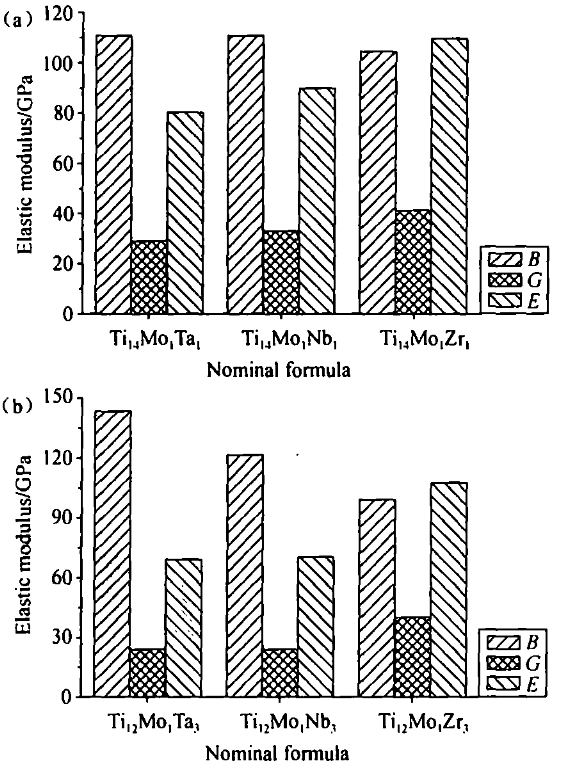

Figure 4. B, G and E of $Ti_{14}Mo_1X_1$ alloys (a) and $Ti_{12}Mo_1X_3$alloys (b) (X=Ta, Nb, Zr)

We have also discussed the effect of interactions between alloying elements on elastic properties. The elastic properties of Ti-Mo binary alloys have been well documented in literature[17], indicating that the addition of Mo may enhance the elastic modulus significantly, which is unexpected in the design of low-modulus bio-titanium alloys. As shown in Figure 5, the addition of Ta or Nb reduces the elastic modulus of Ti-Mo alloys, which may be due to the interactions between Mo and Ta or Nb. The effect of Mo-Nb is weaker than that of Mo-Ta, which demonstrates the effect of Ta for reducing the elastic modulus is better than Nb in Ti-Mo-X alloys. This is consistent with that shown in Figure 4.

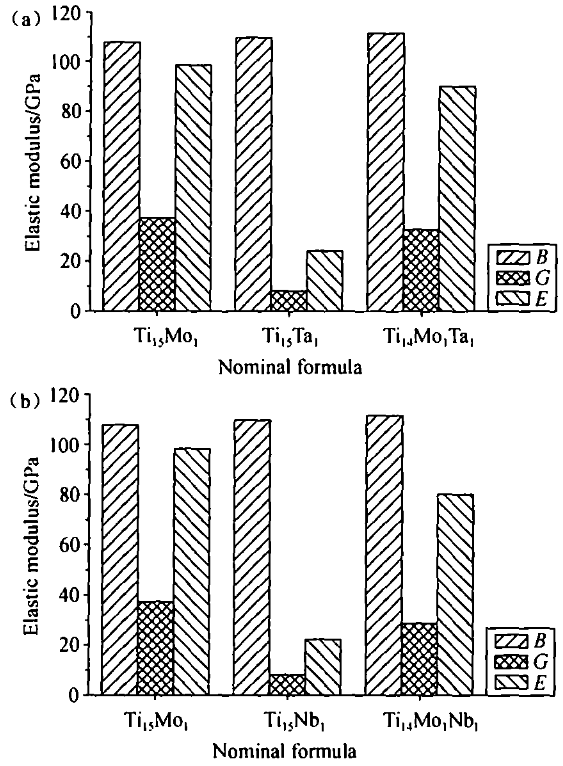

Figure 5. The effect of interactions between Mo and Ta (a) or Nb (b) on elastic properties

4. Conclusions

In order to investigate the phase stability and elastic properties of Ti-Mo-X (X=Ta, Nb, Zr) alloys, the lattice constants, cohesive energy and elastic constants of these alloys were calculated by using the method of supercell and pseudopotential plane waves within generalized gradient approximation. The main results are summarized as follows:

(1) The lattice constants of Ti-Mo-Zr alloys increase monotonously with increasing content of Zr. With increasing content of Ta or Nb, the lattice constants changes slightly, implying that the chemical bonding and bond distance between Ta or Nb and other atoms become stronger and shorter, respectively.

(2) Increasing content of Ta or Nb makes a contribution to improved β phase stability, and the stabili-

zation effect of Zr is much weaker than that of Ta or Nb.

(3) The trends of G, E, and C' with Ta content are similar and reach the minimum at about 18.75 at.% Ta, where very low elastic modulus (68.94 GPa) is obtained.

(4) The addition of Ta or Nb reduces the elastic modulus of Ti-Mo alloys, which may be due to the interactions between Mo and Ta or Nb. The effect of Mo-Nb is weaker than that of Mo-Ta, which demonstrates the effect of Ta for reducing the elastic modulus is better than Nb in Ti-Mo-X alloys.

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