Twinnability of Ti-V Binary Alloys: Simulation and Experiment

H. Xing[a], A.P. Dong[a,*], J. Huang[b,*]

[a] Shanghai Key Lab of Advanced High-temperature Materials and Precision Forming, Shanghai Jiao Tong University, Shanghai 200240, China.

[b] State Key Laboratory of Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 201899, China

[*]jhuang@mail.sic.ac.cn, apdong@sjtu.edu.cn

Abstract

Recently metastable β titanium alloys has attracted much attention due to their important application in biomaterials. In this study, the defects and mechanical properties of bcc disordered β Ti-alloys are investigated theoretically by first-principles method. The elastic moduli, generalized stacking fault energies, twinnability in β Ti-V alloys were surveyed by calculations with virtual crystal approximation. The results show that the structural stability and generalized stacking fault energy decrease with reducing valence electron number (e/a) in the β Titanium alloys. Both twinning formation energies and twinning migration energies decrease with reducing electron valance numbers, which suggests that the energy barrier for twinning formation deceases with lower structural stability. The twins in the metastable Ti-25 at.%V alloy can form near the crack tip or triggered by the high local stress during the nucleation. As the twin is thickened, the required local stress is also greatly reduced and it can grow away from the crack tip for metastable titanium alloys. Transmission electron microscopy (TEM) shows that twins are more easily observed in Ti-V alloys with relatively low electron concentrations, which confirms the theoretical conclusion that the lower the electron concentration, the easier the twin formation.

1. Introduction

Titanium alloy is an important structural material with excellent comprehensive properties such as low density, high strength and fracture toughness, excellent corrosion resistance and heat resistance. It has been developed rapidly and widely used in the aerospace, chemical engineering, shipbuilding and other industrial application. Titanium alloys can be classified into: α type, α + β type, and β type. Compared with other titanium alloy series, β-titanium alloy has the highest strength, lowest elastic modulus, good fatigue resistance and environmental corrosion resistance, so it is widely used in biomedical fields [1-4].

The plastic deformation of the β-phase titanium alloy is very complicated and can be activated via various ways such as slip, twinning and stress-induced phase transformation. Theoretical studies based on first-principles have focused on the thermodynamic properties of β-titanium alloys, and the structure of the dislocation core has been identified by our previous calculation [5]. But there are no related theoretical simulations for the twin boundaries and stress-induced phase transitions observed in the experiments. Therefore, the understanding of the mechanism of the above plastic deformation mode is still unclear, and it is generally considered to be related to the alloying elements in the metastable β titanium alloy and the β phase stability [6]. In this study, the first-principles calculation method based on density functional theory is used to investigate the defects and mechanical properties of the disordered metastable β-Ti alloy of BCC structure. Based on the virtual crystal approximation (VCA) treatment of disordered Ti-V alloy, calculations of elastic properties and twinnability were carried out to explore of the mechanism of twinning formation in metastable β-Ti alloy, and the related experiment was also performed to illustrate the correlation between mechanical properties and microstructure of β-Ti alloy.

2. Simulation and Experiment

The first-principle software package ABINIT [7] is used for all calculations, and the local density approximation (LDA) is used to treat the exchange correlation potential [8]. Trolier-Martins type pseudopotential is generated by the Fritz-Haber-Insititute software package [9]. The disorder of the Ti-V alloy system is handled by the virtual crystal approximation (VCA) [10]. The specific pseudopotential mixing uses the method proposed by Bellaiche and Vanderbilt [11]. In order to ensure the convergence of the transition metal system, a high energy cutoff of 50Ha (1380eV) is selected, and the electronic state is treated by the Fermi-Dirac method with 0.01Ha smearing. For the calculating of the lattice constant and the elastic constant, the B2 unit cell containing two atoms is used. K point in the Brillouin zone is sampled by the Monkhorst-Pack method [12], and the K-point grid is 21×21×21. The elastic constants were determined by a function between total energies and applied strains using tetragonal or monoclinic deformation.

To calculate the energy of the twins, in order to avoid the interaction between the twin boundaries, we have built a <111>{112} slip-multilayer model, which contains a total of 24 atoms and introduces a vacuum layer equivalent to 12 layers of atomic thickness. According to the literature [13], when calculating the twin formation energy, we slip the 1~12 atomic layers on the slip plane {112} along the [111] direction by $[111]a_0/6$ vector. Each of the 12 layers of atoms is displaced by $[111]a_0/6$ vector relative to its upper layer. On this basis, we slide the 13~24 layers as a whole and then slide over half of the above displacement vector (i.e. $[111]a_0/12$ vector), which corresponds to an energy barrier of the twinning process. The difference between the total energy and the total energy of the 12 layers of twins is defined as the twin migration energy. Monkhorst-Pack scheme was used for k points sampling with 10×16×2 k-mesh. We fully relax the atoms in the direction perpendicular to the slip surface and the volume of the unit cell.

The Ti-15 at.%V, Ti-20 at.%V and Ti-50 at.%V alloys obtained by suspension smelting of water-cooled copper crucible are hot-rolled at 900 ° C, quenched in cold water, and subjected to 0.2% deformation. The TEM foils were obtained by mechanically polishing to thickness of 30 μm and then further polishing by twin-jet electrolytic in a solution of 5 vol.% sulfuric acid and 95 vol.% methanol at 50 ° C and 35 V. All microstructures were subjected to transmission electron microscopy analysis after compression deformation, and electron microscopic observation was carried out under a transmission electron microscope of JEOL JEM-2100F type with an operating voltage of 200 kV.

3. Results and Discussion

3.1 Structural stability of β-phase Ti-V alloys

The calculated tetragonal shear modulus $C'=(C_{11}-C_{12})/2$ are shown in Fig. 1. Our results are in good agreement with the calculated values of the supercell method in the literature [14]. As the electron concentration e/a decreases, C' also decreases, especially when the electron concentration approaches 4.1, C' is almost zero. According to the theory of elastic stability, cubic materials are mechanically stable only when C_{11}-C_{12} and C_{44} are both greater than zero. Our results suggest that, as the electron concentration decreases, the stability of the β phase also decreases and the transition to the α phase may occur, which is consistent with the conclusions obtained in the literature [15]. In order to further determine the correlation between the β phase stability and the electron concentration, the energy difference of the hexagonal α structure and the cubic β structure Ti-V alloy is calculated, which shows an excellent linear relationship with e/a, as shown in Fig. 2. According to the principle of energy minimum, when the electron concentration is higher than 4.1, the energy of the cubic β structure is lower than that of the hexagonal α structure, and thus β phase is more stable. As the electron concentration decreases, the stability of the β structure relative to the α structure decreases continuously. When e/a=4.1, the energy of the two structures is completely equal, corresponding to the critical point of a transition from β to α phase. It can be predicted the α phase will be more stable as the electron concentration continues to decrease.

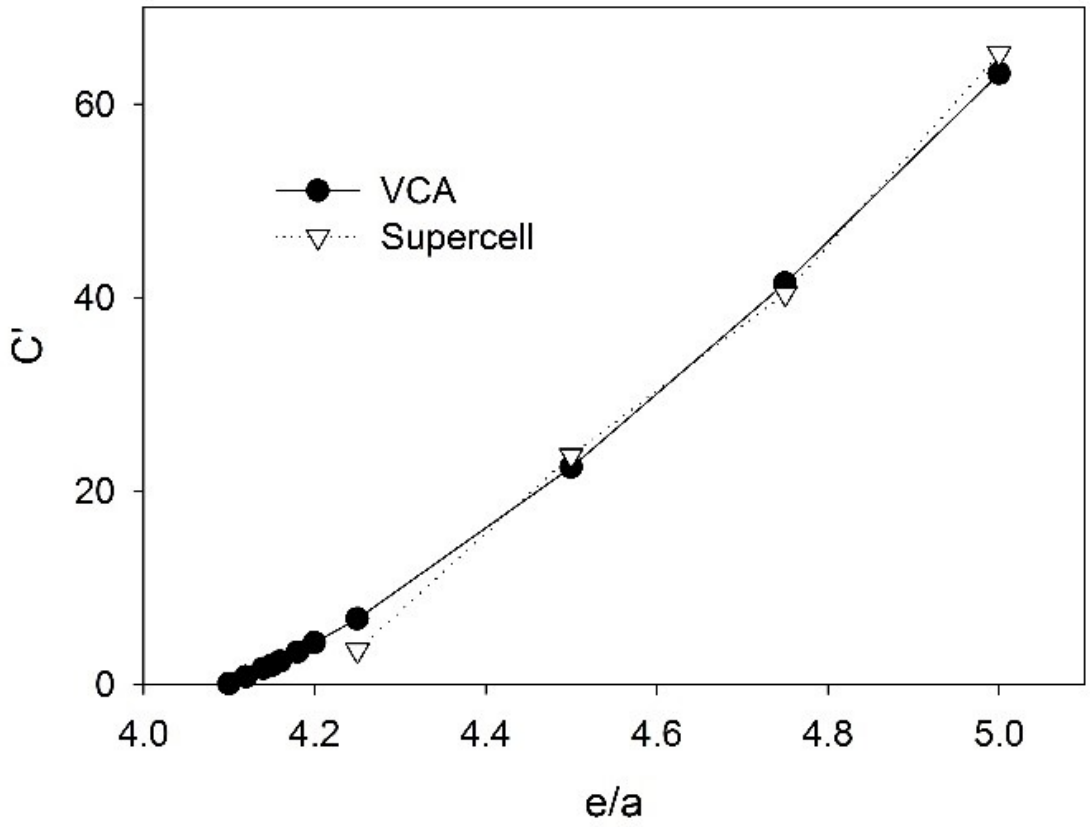

Figure 1 tetragonal shear modulus with e/a

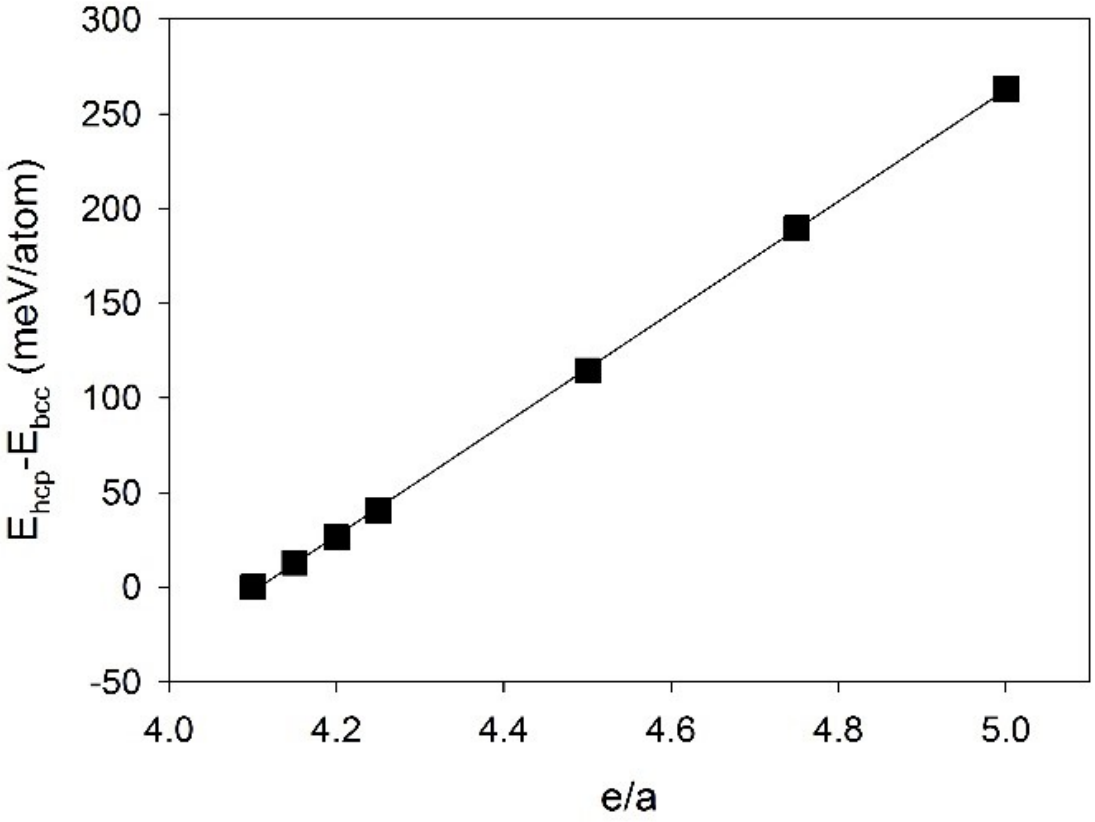

Figure 2 Energy difference between α and β phase with e/a

Further, the Young's modulus and the shear modulus of the Ti-V alloy in different directions can be calculated by the equations (1) to (6) using the obtained elastic constants, and the results are shown in Fig. 3. We can find two special values of 4.1 and 4.7 respectively. When e/a=4.1, the Young's modulus E_{001} and E_{111} and the shear moduli G_{001} and G_{111} are close to 0 at the same time, which means that the bcc structure will not be stable. It also indicates the transition from bcc structure to the hcp structure direction, which is completely consistent with the calculation of the energy difference between the different structures described above. Another special e/a value is 4.7, where the Young's modulus is exactly equal in all three directions, and the shear modulus in all three directions is also identical, indicating that the Ti-V alloy is elastic isotropic at this concentration. As the electron concentration decreases, the anisotropy of the alloy also gradually increases.

$$E_{001} = \frac{(C_{11} - C_{12})(C_{11} + 2C_{12})}{C_{11} + C_{12}} \tag{1}$$

$$E_{110} = \left\{ \frac{C_{11} + C_{12}}{(C_{11} + 2C_{12})(C_{11} - C_{12})} + \frac{1}{4}\left(\frac{1}{C_{44}} - \frac{2}{C_{11} - C_{12}} \right) \right\}^{-1} \tag{2}$$

$$E_{111} = \left\{ \frac{C_{11} + C_{12}}{(C_{11} + 2C_{12})(C_{11} - C_{12})} + \frac{1}{3}\left(\frac{1}{C_{44}} - \frac{2}{C_{11} - C_{12}} \right) \right\}^{-1} \tag{3}$$

$$G_{001} = C_{44} \tag{4}$$

$$G_{110} = (C_{11} - C_{12})/2 \tag{5}$$

$$G_{111} = \frac{3C_{44}(C_{11} - C_{12})}{4C_{44} + C_{11} - C_{12}} \tag{6}$$

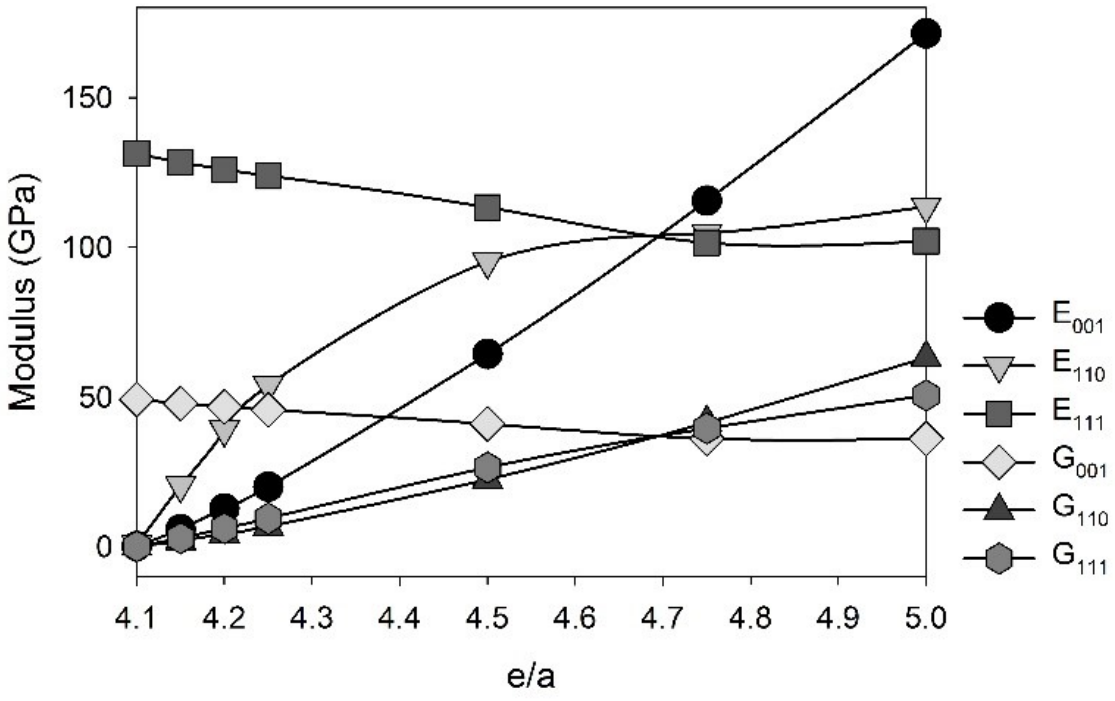

Figure 3 Young's moduli and shear moduli in Ti-V alloys

3.2 Twinning ability of β-phase Ti-V alloy

As shown in Figure 4, the convergence of the number of twin layers is first tested to ensure the sufficient reliability of calculated twin formation energy. It can be seen that when the number of layers is 1, there are no metastable single layer stacking faults, so full dislocations cannot resolve to components by means of a single layer stacking fault. When the number of twinned layers is less than 5, the energy fluctuation is large, indicating that the twins of these layers are still in an unstable state. Ogata et al. [16] also found that the number of twin layers must be greater than 5 layers to stabilize when the body-center structure Mo is studied. [16] Thereafter, the twin layer can be grown in a layer-by-layer mode. As mentioned in the previous method, the 12-layer model is used to calculate the twinning energy, which ensures sufficient convergence of the twinning energy.

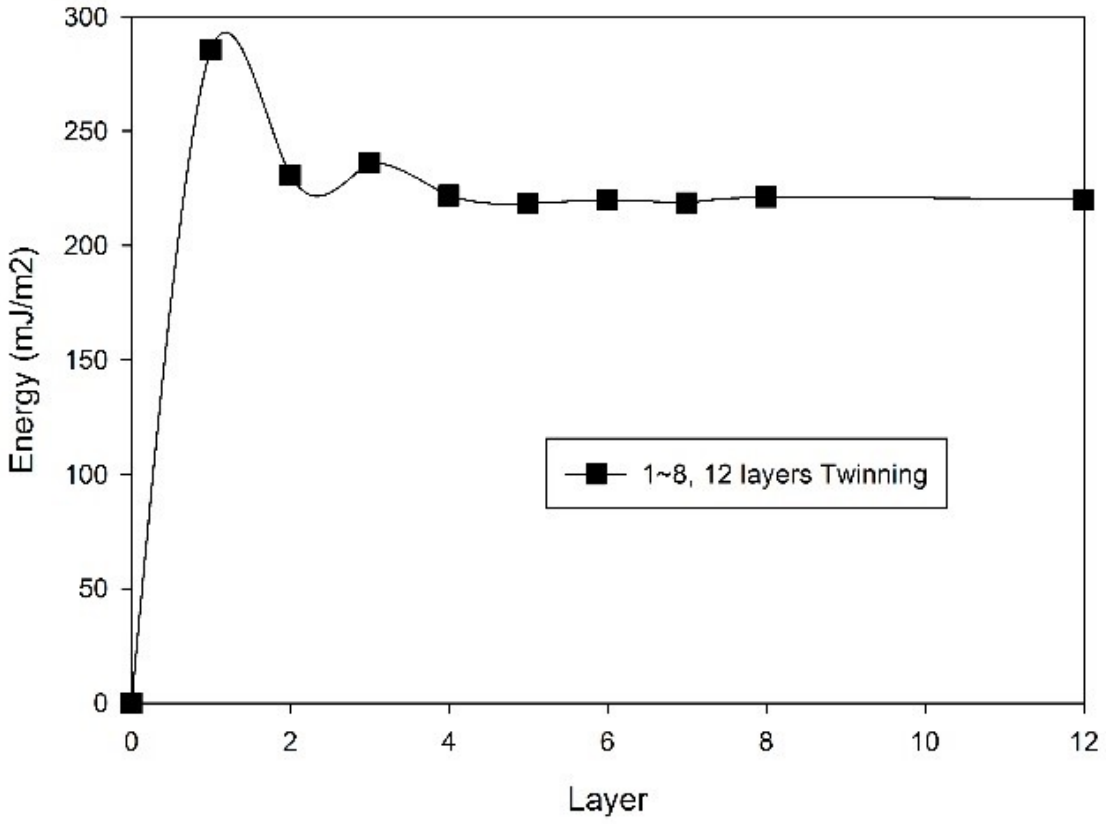

Figure 4 Convergence test of twinning layers

The calculated twin formation energy and twin migration energy of the Ti-V alloys with different e/a are shown in Figure 5. It is not difficult to find that the twin formation energy is higher than the corresponding twin migration energy. As the electron concentration e/a decreases, the twin formation energy and the twin migration energy decrease simultaneously, and the difference between the two decreases. This indicates that as the concentration of electrons decreases, the barriers needed to form twins in the system are also gradually reduced, which is easier for the formation and thickening of twins. Ogata et al. [13] calculated the nucleation stress of the twin boundary based on the twin formation energy γ_{TBF} and the twin migration energy γ_{TBM}.

$$\tau_{\max} = \frac{\pi \gamma_{TBM}}{b_p}$$

It can be seen that as the structural stability of the Ti-V alloy decreases, the nucleation stress also decreases, which means that the alloy's twinnability is also significantly improved [13].

The relationship between the thickness of the twins (expressed as the number of layers n) and the local stress can be obtained as

$$\tau_n = \frac{2\gamma_{TBF}}{nb_p}$$

Combined with the ideal shear strength of material, it can also give the distance from which the twin boundary can be far from the dislocation tip.

$$l_n \sim (\frac{\tau_{ideal}}{\tau_n})^2 a_0$$

For Ti-25 at.%V alloy, when n=6, τ_n is 816 MPa, and the ideal shear strength value calculated by Li et al. is 1.8 GPa [15]. It can be obtained that 6 layers of twins must be close as 1.5 nm to the crack tip where the stress concentration exists. When n is increased to 30, the l_{30} is increased to 38 nm. This indicates that for the Ti-25 at.%V alloy, a strong stress concentration is required when the twin is initially formed. And as the twin crystal is slowly thickened, the stress required for the twin growth is also greatly reduced, and it is also possible for twin growth to be far away stress concentrations.

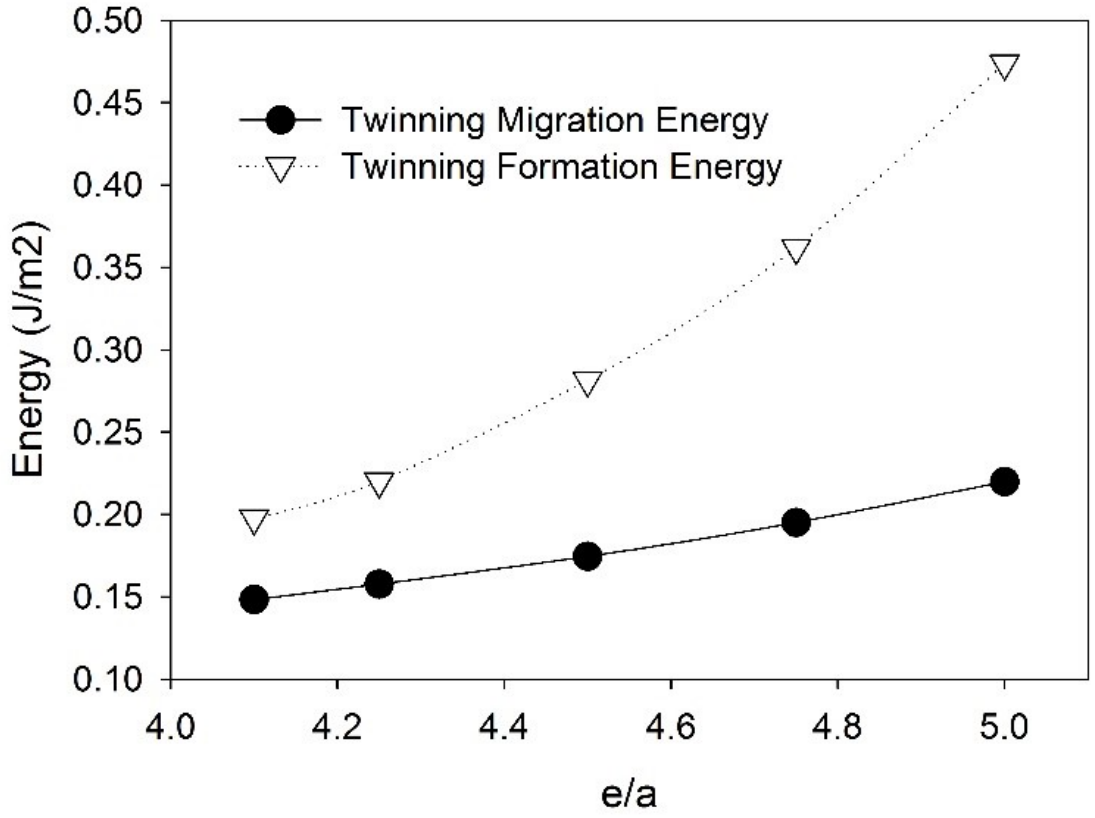

Figure 5 Twinning formation energy and twinning migration energy with e/a

3.3 Experimental verification

Above theoretical results show that as the electron concentration decreases, the structural stability of the Ti-V alloy decreases, and the formation ability of the twins gradually increases. In order to further verify the influence of electron concentration on twinning, experimental verification on alloy microstructure was carried out. Figure 6 shows the bright field of transmission electron microscopy of alloy samples with different compositions. It can be seen that as the vanadium content decreases (i.e. the electron concentration decreases), the dislocation density in the sample gradually decreases, and the striped microstructure begins to appear and gradually increases. Figure 6d shows the selected area diffraction of the fine-striped structure, indicating that it is a mechanical twin of the (211) [-111] type. Beside the twinning pattern in Figure 6d, the athermal omega phase corresponding to extra spots are also observed. Hanada et al. [17] studied a series of β-titanium alloys and pointed out that with the decrease of β-phase stability, the plastic deformation mechanism of alloys will also change from dislocation slip to twin deformation, which is consistent with the conclusions of this study.

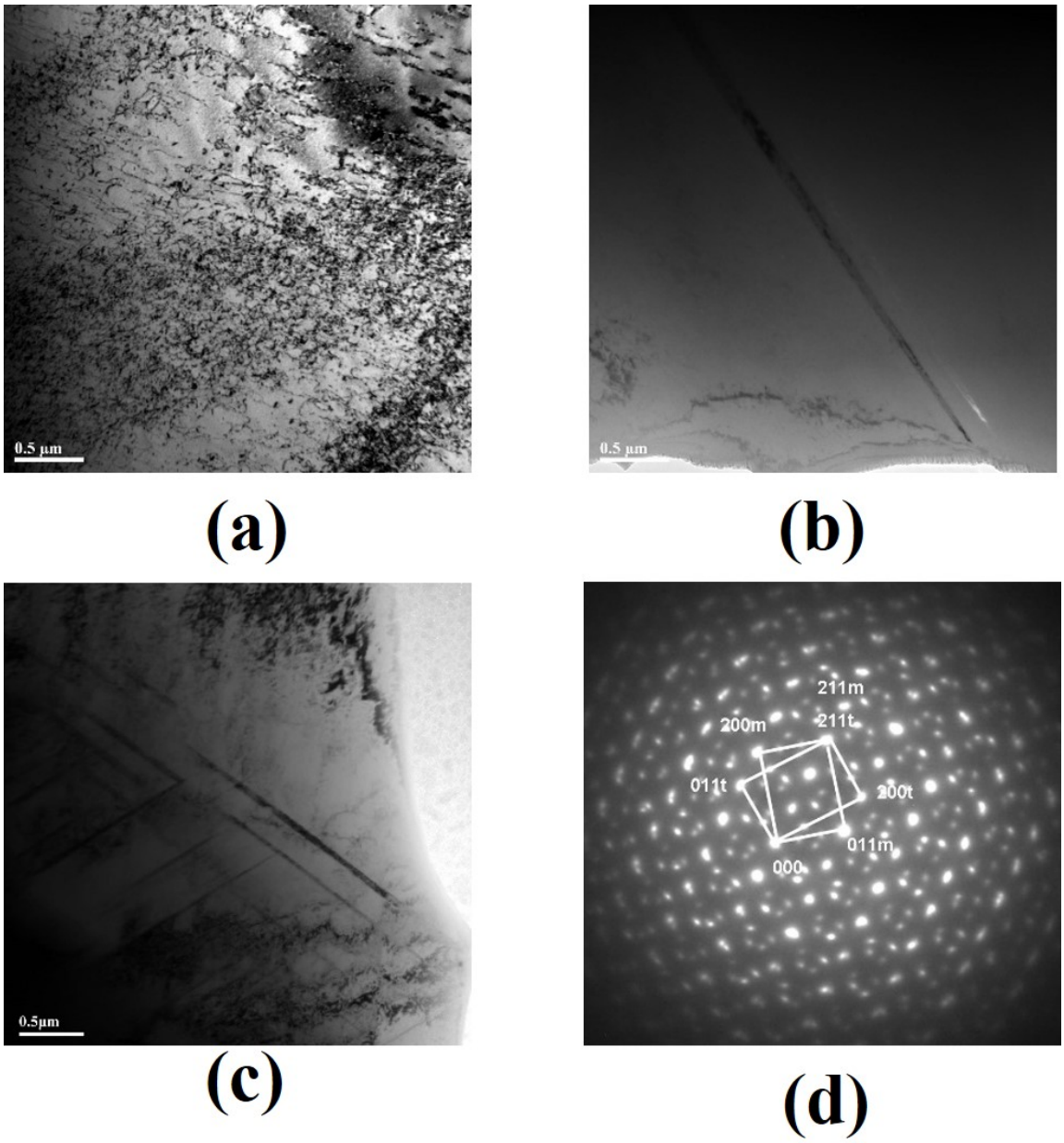

Figure 6 TEM bright field images of Ti-50 at.%V (a), Ti-20 at.%V (b) and Ti-15 at.%V (c) selected area diffraction of twinning in Ti-15 at.%V alloy

4. Conclusion

Firtst-principles calculation based on density functional theory (DFT) and generalized gradient approximation (GGA) are used to study the Ti-V disordered alloy system by virtual crystal approximation. The structural stability and the twinnability have been studied, and the conclusions are summarized as follows:

1. The calculated results of the elastic properties and the energy difference between α phase and β phase indicate that the structural stability of Ti-V alloy decreases with the decrease of the number of valence electrons.

2. The twin formation energy and the twin migration energy in Ti-V alloy decrease with the decrease of electron concentration, and the barriers needed to form twins are gradually reduced, which is easier for the formation and thickening of twins. The twins in the metastable Ti-25 at.%V alloy can only be formed by the high local stress or near the crack tip during the initial formation stage. As the twin is thickened, the required local stress is also greatly reduced and it can grow away from the crack tip.

3. TEM observation shows that twins are more easily observed in Ti-V alloys with relatively low electron concentration, which proves that the lower the electron concentration, the easier the twin formation by theoretical calculation.

Acknowledgements

The authors would like to acknowledge the financial support from the National Natural Science Foundation of China (Grant No. 51101099, 51871152 and 51831011).

Reference

[1] Zhang L.C., Zhou T., Alpay S.P., Aindow M., Wu M.H. Appl. Phys. Lett. 2005; 87: 241909.

[2] Hao Y.L., Li S.J., Sun S.Y., Zheng C.Y., Hu Q.M., Yang R. Appl.Phys. Lett. 2005; 87: 091906.

[3] Xu W., Kim K.B., Das J., Calin M., Appl. Phys. Lett. 2006; 89: 031906.

[4] Hao Y.L., Li S.J., Sun B.B., Sui M.L., Yang R. Phys. Rev. Lett. 2007; 98: 216405.

[5] Huang J., Xing H., Sun J. Scripta Mater. 2012; 66: 682-685.

[6] Hanada S., Yoshio T., Nishimura K., Izumi O. Proceedings of 6th Conference Titanium, Cannes, France. 1988.

[7] Gonze X., Beuken J.-M, Caracas R., Detraux F., Fuchs M., Rignanese G.-M., Sindic L., Verstraete M., Zerah G., Jollet F. Comput. Mater. Sci. 2002; 25: 478-492.

[8] Kohn W., Sham L.J. Phys. Rev. 1965; 140:A1133–A1138.

[9] Fuchs M., Scheffler M. Comput. Phys. Commun 1999; 119: 67-98.

[10] Schoen J.M. Phys. Rev. 1969; 184: 858-863.

[11] Bellaicha L., Vanderbilt D. Phys. Rev. B 2000; 61: 7877-7882. [9] H.J. Monkhorst, J.D. Pack, Phys. Rev. B 13 (1976) 5188-5192.

[12] Monkhorst H.J., Pack J.D. Phys. Rev. B 1976; 13: 5188-5192.

[13] Ogata S., Li J. Yip S. Phys. Rev. B 2005; 71: 224102.

[14] Ikehata H., Nagasako N., Furuta T., Fukumoto A., Miwa K., Saito T. Physical Review B. 2004; 70: 174113.

[15] Li T.S., Jr Morris J.W., Nagasako N., Kuramoto S., Chrzan D.C. Phys. Rev. Lett. 2007; 98: 105503.

[16] Ogata S., Li J., Yip S. Europhys. Lett. 2004; 68: 405.

[17] Hanada S., Ozeki M., Izumi O. Metall. Trans. A 16A 1985; 16: 789-795.