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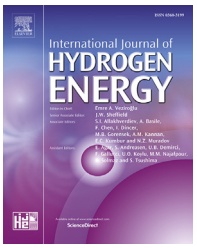

Improving the mechanical processing of titanium by hydrogen doping: A first-principles study

Lu Sun, Wei Xiao, Shuhui Huang, Jianwei Wang, Ligen Wang *

Institute for Engineering and Technology, General Research Institute for Nonferrous Metals, Beijing, 100088, China

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ABSTRACT

Solute H in Ti alloys has an important effect on their deformation and ductility, therefore changing the mechanical properties and improving the mechanical processing. We have performed first-principles calculations to investigate the effects of H on the mechanical properties of the hexagonal close packed α-Ti and the body centered cubic β-Ti, and make an attempt to understand how the solute H improves the mechanical processing. We compute the structural parameters, elastic properties, and the generalized stacking fault energies for α- and β-Ti with and without the H addition. We find H decreases the shear moduli and the unstable stacking fault energies of α-Ti, enhancing the deformation tendency, while these quantities are increased by H in β-Ti. We predict the H effect on the ductility using different criteria, and find H makes α-Ti more ductile, but raises the brittleness of β-Ti. Our results indicate H may have a favorable effect on improving the mechanical processing of Ti alloys.

Introduction

Titanium and its alloys are broadly developed for structural applications, especially in automotive and aerospace industries due to their great strength-to-weight ratio and corrosion resistance [1–4]. However, Ti alloys have poor plastic formability at room temperature, limiting the thermo-mechanical processing [5]. Solute alloying and interstitial impurity atoms are found to have an important effect on the plasticity and ductility of Ti alloys [6–10]. Hydrogen, as a temporary alloying element, interacts with Ti in the applications such as hydrogen storage and thermo-hydrogen processing [11,12]. The addition of H decreases the deformation resistance and temperature, improving the plasticity of Ti alloys as a result [11–15]. Therefore, to further develop an understanding of the hydrogen-improved mechanical processing of Ti alloys, it is very crucial to systematically investigate the effects of H alloying on the mechanical properties of Ti systems.

Ti is normally stabilized in the hexagonal close packed (hcp) α phase at room temperature. Upon heating, the α phase transforms to the body center cubic (bcc) β phase at high temperature above 1155 K [16]. The microstructure evolution between the α and β phase is believed to be closely related to the mechanical processing of Ti alloys [11–16]. Alloying with H can effectively modify the phase compositions of Ti alloys. Many experimental studies have demonstrated the low temperature α phase is destabilized when increasing the H concentration, while the high temperature β phase is stabilized along with a created α+β phase [11,12,16]. Moreover, the H-induced softening effect of α-Ti which results in a decrease of the deformation temperature and the flow stress, and the hardening effect of β-Ti due to H addition were discovered

* *Corresponding author.*
E-mail address: lg_wang1@yahoo.com (L. Wang).

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[11–15]. One mechanism for such effects is that the addition of H decreases the shear and Young's moduli of the α phase, weakening the atomic bonds between Ti atoms, while increases these of the β phase [11,12,17–19]. On the other hand, experimental reports in the literatures indicated that H would decrease the dislocation density and promote the dislocation motion of α-Ti alloys, therefore, improves the plasticity [12–15].

Theoretical studies on the mechanical properties of Ti alloys have also appeared [20–32]. Liang et al. [20,21] found the elastic moduli of α-Ti were overall decreased with increasing H concentrations, but those of β-Ti were increased based on density functional theory (DFT) calculations. They also reported H facilitates the α-β phase transformation under the Burger's mechanism [33], i.e., the transition between α {0001} planes and β {110} planes through shearing, in the light of elastic constants. Regarding the mechanism of the dislocation glide, the generalized stacking fault energy (GSFE), also known as the γ-energy, is introduced to quantify the energy required for shearing a crystal in DFT calculations [34]. In current literatures, the stacking fault energies for independent slip systems such as the basal, prismatic, and pyramidal slip in pure α-Ti were intensely studied [6–10,23–32], and the contribution of each slip system to the plasticity was discussed. However, the stacking fault energies and the elastic properties in pure β-Ti have scarcely been reported so far. Most importantly, there is still a serious lack of studies of H effects on the elastic constants and the stacking fault energies in both α- and β-Ti, therefore, the dominant mechanism of H effects on the deformation behavior of Ti alloys is still unclear.

In this paper, we perform first-principles calculations to systematically investigate the effects of H on the mechanical properties of both α- and β-Ti. We calculate the structural parameters, the elastic moduli, and the generalized stacking fault energies of α-Ti-H and β-Ti-H systems. Finally, we discuss the ductile/brittle behavior of the α- and β-Ti-H systems using different criteria. Based on the calculated results, we give a deep understanding of the mechanism of the H-improved mechanical processing of different phases of Ti alloys.

Computational methods

We performed our calculations in the framework of DFT with projector-augmented wave (PAW) potentials [35] as implemented in the VASP code [36,37]. PAW potentials with the valence electrons $3d^3 4s^1$ for Ti and $1s^1$ for H atoms were used. The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional for the generalized gradient approximation (GGA) [38] was employed. The energy cutoff for the plane wave basis was set to be 400 eV. Tests for the solution energy of the interstitial H using a cutoff of 500 eV indicate that the total-energy differences are converged within less than 0.05 eV. In order to simulate different H concentration cases, the supercell models containing 16 Ti atoms and 4 Ti atoms were adopted. Integrations over the Brillouin zone of the supercell were performed using a $7 \times 7 \times 5$ k-points mesh for α-Ti and $15 \times 15 \times 7$ for β-Ti by the Monkhorst-Pack scheme [39]. We also performed tests using $9 \times 9 \times 7$ and $17 \times 17 \times 9$ meshes to ensure convergence. The structure and volume of the supercells were relaxed during atomic relaxations until the force on each atom was lower than 0.01 eV/Å.

Elastic constants C_{ij} were derived from the strain-stress relationship [40] by performing six finite distortions of the lattice and fully relaxing the lattice to determine the elastic tensor. For a hexagonal crystal, there are five independent elastic constants, namely, C_{11}, C_{12}, C_{13}, C_{33} and C_{44}. Starting from the elastic constants C_{ij}, the bulk modulus (B), shear modulus (G), and Young's modulus (E) were obtained within the Voigt-Reuss-Hill (VRH) approximations [41–43]. Within the Voigt's approximation [41], the expressions for the bulk and shear moduli are as follows,

$$B_V = \frac{2}{9}\left(C_{11} + C_{12} + \frac{C_{33}}{2} + 2C_{13}\right), \tag{1a}$$

$$G_V = \frac{1}{30}(C_{11} + C_{12} + 2C_{33} - 4C_{13} + 12C_{44} + 12C_{66}). \tag{1b}$$

The Reuss's approximation [42] gives the following formula,

$$B_R = \frac{(C_{11} + C_{12})C_{33} - 2C_{13}^2}{C_{11} + C_{12} + 2C_{33} - 4C_{13}}, \tag{2a}$$

$$G_R = \frac{5}{2}\left(\frac{\left[(C_{11} + C_{12})C_{33} - 2C_{13}^2\right]C_{44}C_{66}}{3B_V C_{44}C_{66} + \left[(C_{11} + C_{12})C_{33} - 2C_{13}^2\right](C_{44} + C_{66})}\right). \tag{2b}$$

For a cubic crystal, there are three independent elastic constants, i.e., C_{11}, C_{12} and C_{44}. The corresponding bulk and shear moduli are given by

$$B_V = \frac{C_{11} + 2C_{12}}{3}, \tag{3a}$$

$$G_V = \frac{C_{11} - C_{12} + 3C_{44}}{5}, \tag{3b}$$

and

$$B_R = B_V, \tag{4a}$$

$$G_R = \frac{5[C_{44}(C_{11} - C_{12})]}{4C_{44} + 3(C_{11} - C_{12})}. \tag{4b}$$

The elastic moduli within the VRH approximations [43] are thus calculated by substituting the above expressions (1–4) into the following formula,

$$B = \frac{B_V + B_R}{2}, \tag{5a}$$

$$G = \frac{G_V + G_R}{2}, \tag{5b}$$

$$E = \frac{9BG}{3B + G}. \tag{5c}$$

To calculate the generalized stacking fault energy curves for the slip systems in Ti, a slab supercell consisting of several atomic layers was constructed based on the theoretical lattice parameters. The lattice vectors ($\boldsymbol{\alpha}_1$, $\boldsymbol{\alpha}_2$) of the slab atomic layer were taken to lie in the slip plane with $\boldsymbol{\alpha}_1$ parallel to the slip direction and $\boldsymbol{\alpha}_2$ normal to the slip direction. The deformation

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