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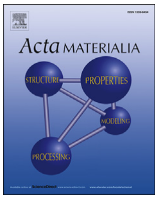

Solid solution strengthening of hexagonal titanium alloys: Restoring forces and stacking faults calculated from first principles

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The solid solution strengthening of α-Ti was investigated in respect of dislocation nucleation and dissociation in all four active glide modes. A series of Ti+X alloys (X = Al, Sn, V, Zr and O) was selected to analyze the impact of solute valence structure (Al, Sn – *p* type elements, V, Zr – *d* type elements) and lattice site (interstitial O) on the mechanisms responsible for variation of mechanical properties. The computational procedure relied on the generalized stacking fault energy (GSFE) concept combined with the nudged elastic band method that enables full atomic relaxation and determination of the true, minimum energy GSFE path. Additionally, various concentrations of solutes and their distance to the glide plane were considered as well. Our study revealed a strong, nonlinear influence of X position on GSFE and migration of O atoms during the crystal slip. These new phenomena allowed one to determine three solution strengthening mechanisms: (I) hindrance of <*a*> prismatic dislocation emission and reconfiguration of 1/3 $<11\bar{2}0>$ screw dislocation cores (*p* type solutes), (II) hindrance of <*a*> prismatic dislocation emission (V) and SFE reduction in other modes (both *d* type solutes) and (III) suppression of dislocation nucleation in all modes caused by O. We found that the stacking faults formed by the single partial dislocations have a thickness of few atomic layers and exhibit a highly non-uniform structure. Their ability to accommodate the lattice deformation introduced by solute elements greatly affects the stacking fault energies of the α-Ti alloys.

1. Introduction

The high strength-to-density ratio of hcp Ti and Mg makes them valuable for all spheres of industry in which reduction of energy consumption and weight play a major role. The development of metallurgy, processing and solid state physics related with their properties are of particular interest. One of the method for improvement of mechanical properties of Mg and Ti is solution strengthening. Further investigation of solution effects in these metals is motivated by the enormous ductility enhancement in Mg–Y alloys [1] and high strength with balanced malleability in Ti–O systems [2] both occurring in single phase alloys.

Plastic deformation in α-Ti can be realized by four types of slip systems on three glide planes [3]: $<11\bar{2}0>$ (0001) – <*a*> on the basal plane, I $<11\bar{2}0>$ $\{10\bar{1}0\}$ – <*a*> on prismatic plane, II $<11\bar{2}0>$ $\{10\bar{1}1\}$ – <*a*> on pyramidal plane, I $<11\bar{2}3>$ $\{10\bar{1}1\}$ – <*c*+*a*> on pyramidal plane (I and II symbols indicate larger and smaller interplanar distance, respectively [4]). The fifth deformation mode is twinning. The activity of these systems has been studied for decades, resulting in the description of several solution strengthening concepts. A strong chemical impact of alloying elements on deformation modes was postulated by Conrad, Collings and co-workers [5,6] who categorized the alloying elements into two groups: B-type, with *p* valence structure radically improving strength, and T2 group consisting of transition metals with a markedly weaker strengthening effect. Distinct mechanical properties of Ti–B and Ti-T2 alloys were explained by large perturbation of the electronic wave functions caused by *p* elements resulting in strong bonds character similar to those occurring in intermetallic TiAl phase. It is worth noting that interstitial elements like C, H, N and O which have the most prominent impact on α-Ti properties [6] were classified as B solutes and their different lattice positions were not analyzed. Separate interstitials effect was investigated by the measurements of critical resolved shear stresses (CRSS) in α-Ti. Churchman [7] observed that O and N change relative activity of glide modes and proposed simple lattice model, denoting dependency between particular slip systems and the number of

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Ti–O(N) bonds broken during the slip. Further, the selective impact of substitutional solutes on deformation modes was also confirmed by Zaeffer [8] who showed a conspicuous increase in the amount of basal dislocations and reduction of the CRSS <*c*+*a*> pyramidal/<*a*> prism ratio in TiAl6V4 alloy relative to pure Ti.

Progress in our understanding of the generalized stacking fault energy (GSFE or γ) [9–15] and development of the computational methods like density functional theory (DFT) [16] allowed for detailed analysis of titanium plasticity. Complex calculation of the α-Ti GSFE [4] revealed the existence of stable stacking fault (SF) configurations in all slip systems. The interplay of interstitial O with some of these faults was examined in Refs. [17,18] with the conclusion that O stabilizes/destabilizes basal/prismatic faults, respectively. The next important feature of the planar defects – twin boundaries (TB) reported lately [19], show better solubility of many Ti alloying atoms in TB than in bulk. This unique phenomenon was correlated with the excess TB volume delocalized within 4–5 atomic planes, implying relatively large TB – solute interaction distance. It should also be noted that appropriate modification of the γ curve calculation procedure [4] makes it possible to precisely determine the restoring forces of dislocations nucleation in all α-Ti slip systems. However, comprehensive GSFE studies of Ti based alloys are still unavailable.

Another valuable approach to α-Ti ductility relies on full dislocations modeling using DFT and molecular dynamic (MD) techniques. Low temperature deformation of titanium is controlled by the motion of 1/3<11$\bar{2}$0> prism screw dislocations [8,20–22]. The privileged activity of these dislocations compared to basal glide in IV B elements (Ti, Zr, Hf) originates from the low prism SF energy [23,24]. The 1/3<11$\bar{2}$0> core structure is still a matter of debate [25–28], but its five distinct geometries have been distinguished. Different cores are identified as strain spreading into various atomic planes, leading to local SF configurations. The lowest energy 1/3<11$\bar{2}$0> core is planar and predominantly spread on the prism plane [26,27]. However, other configurations are partially spread on the prism, basal and pyramidal planes with only ~0.004–0.006 eV/*b* energy excess [27]. These results are consistent with the polymorphism of dislocation cores confirmed experimentally in MgO [29]. The calculations made for other materials indicate that dislocation core geometry and Peierls potential can be altered by alloying elements [30]. Direct interaction of the solute atoms with dislocation cores (rather than its elastic interaction at a finite distance) has been also proposed as a main strengthening mechanism in α-Ti [20,21].

Summarizing, it has been shown that α-Ti solution strengthening is deeply related with the solute valence structure, its position in the crystal lattice and interaction with structural defects. While deformation by twining is relatively well described, knowledge about dislocation nucleation and motion in Ti alloys is still very limited. The available reports show great capabilities of DFT in terms of dislocation nucleation prediction [4] and the substantial impact of alloying elements on SF stability [17,18], which in turn control the structure and mobility of dislocation cores [23,26,27]. Both restoring forces and SF energies of Ti alloys can be accurately determined by the GSFE calculations, and their changes are fundamental for understanding the solution strengthening mechanism.

In this paper we present a systematic study of the GSFE calculated by the first principle approach for all active slip systems in a series of hexagonal Ti+X alloys. X = Al, Sn, V, Zr and O were selected to determine the effect of the valence structure and lattice position of solutes on the characteristics of γ curves. Additionally, two concentrations of alloying elements and their interaction were analyzed. The results obtained demonstrate unexpected oxygen migration forced by the crystal slip and significant, nonlinear variations of the γ curves as a function of the slip plane – solute atom distance for all studied elements in most slip modes. These new effects together with other results and available experimental data were discussed in terms of dislocation nucleation and possible dislocation core structure modification in the studied alloys.

2. Computational method

Ab initio calculations were performed using Vienna *Ab initio* Simulation Package (VASP) code [31,32], with the projector augmented wave (PAW) method for core-valence electron interaction [33]. Our previous studies [34,35] showed that Perdew-Burke-Ernzerhof (PBE) [36] generalized gradient functional properly reproduce properties of Ti and Ti-based alloys, and therefore was utilized in this study. The number of valence electrons for pseudopotentials used in computations are as follows: 3 for Al ($3s^2$, $3p^1$), 4 for Sn ($5s^2$, $5p^2$), 6 for O ($2s^2$, $2p^4$), 4 for Ti ($3d^2$, $4s^2$), 5 for V ($3d^3$, $4s^2$) and 12 for Zr ($4s^2$, $4p^6$, $4d^2$, $5s^2$).

Fermi smearing of the electronic occupancy with 0.2 eV and plane-wave cutoff energy of 425 eV was used. The Brillouin zone was sampled in accordance with the Monkhorst-Pack scheme [37]. The suitable 16 × 16 × 12 k-point mesh for α-Ti unit cell was initially established and subsequently adjusted to the investigated slab models. The relaxation of ions was stopped when 1 and 20 meV/Å force (for equilibrium and distorted structures, respectively) and 1 meV energy convergences were reached. These parameters allowed one to obtain very good agreement of lattice constants $a = 2.94$ Å and $c/a = 1.583$ with experiments $a = 2.95$ Å and $c/a = 1.587$ [38]. According to the slip planes available in α-Ti (prismatic, basal and pyramidal) three types of supercells were built. Preliminary γ curve computations were performed to establish the correct geometry of the models with respect to the number of atomic planes, their size and vacuum height.[1] Finally, 18 atomic layer models (4 atoms in each plane – 2 × 2 in-plane unit cell) with 8, 12, and 10 Å of free space, respectively, for basal, prism, and pyramidal slip modes were chosen for full GSFE calculations. In the alloyed systems one solute atom (substitutional or interstitial) was placed in each supercell. The selected models ensure GSFE errors less than 5% relative to twice as high reference structures (36 planes). Two types of larger structures were also adopted:

(I) 3 × 3 in-plane unit cell, 18 atomic layers supercells used when alloying element concentration was analyzed,

(II) 2 × 2 in-plane unit cell, 26 atomic layers structures utilized for calculations of X–SF effective range interaction. The results obtained for larger models are explicitly marked in the text.

The GSFE reproduces the interplanar potential energy for sliding one-half of a rigid crystal over the other half along the glide plane. According to this definition the output energy variation is equal to a pure misfit energy of particular slip planes. Since, the atomic relaxation in conventional γ curve computations is allowed only in direction perpendicular to the glide plane the measured misfit energy is not precise. It is expected that the additional “in-plane” atomic shuffling should reduce GSFE by varying slip amplitude and

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[1] Our tests showed no differences of pure Ti GSFEs when atomic plane areas are equal to or higher than 2 × 2 unit cell (the SFE, USFE and maximum gradients of γ curve reach errors up to 3% between 1 × 1, 2 × 2, 3 × 3 and 4 × 4 plane size). However, we found energy gradient errors of up to 10% for the single unit cell plane size at the onset of the slip. To eliminate this issue, further improvement of k-points density and NEB force convergence criterion for the smallest structures are required. This modification substantially increases calculation time without any significant γ corrections observed in the larger supercells.