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First-principles study of four mechanical twins and their deformation along the ***c***-axis in pure α-titanium and in titanium in presence of oxygen and hydrogen

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ABSTRACT

Interstitial solutes such as oxygen and hydrogen have an important and complex role on the mechanical properties of titanium. With ab initio calculations, we get the atomic structures and energies of the three most common twin boundaries (TBs) observed in α-Ti (hexagonal close packed), viz. $\{10\bar{1}2\}$, $\{11\bar{2}1\}$, and $\{11\bar{2}2\}$, together with the $\{10\bar{1}1\}$ TB. The segregation energies of O and H to the four TBs are evaluated and their behaviour under deformation along the ***c***-axis is investigated, in pure Ti and in presence of segregated O or H. All TBs decrease the theoretical ultimate tensile stress of α-Ti. Remarkably, the $\{10\bar{1}2\}$ and $\{11\bar{2}2\}$ TBs are unstable for a ***c***-axis deformation as small as about 2%. O and H segregate to all four TBs except for O to the $\{11\bar{2}2\}$ TB case. As such, they slightly enhance the $\{10\bar{1}2\}$ and $\{11\bar{2}2\}$ TB limited stability under ***c***-axis deformation. They decrease the $\{10\bar{1}1\}$ TB stability under high deformation and so does O for the $\{11\bar{2}1\}$ TB.

1. Introduction

Titanium is a relatively recent light metal, by metallurgical history standard, which is very important and much used both as pure and allied in the aeronautic industry and in biomedical applications as well as for transport of some corrosive products at very low temperatures for instance [1–4]. It is much used in its hexagonal close packed (α) phase under mechanical constraints and it is therefore important to study the elementary mechanisms of its deformation behaviour which will be influenced by the presence of impurities. The two principal plastic deformation modes in hexagonal materials are dislocation gliding and deformation twinning [5,6]. Because of the insufficient number of independent slip systems in these materials, deformation twinning is also activated, all the more so for deformations along the ***c***-axis, and/or at low temperature. Deformation twinning thus has an important impact on mechanical properties such as material formability [7], texture development [8,9], strain hardening [10] and ductility [6] in titanium. The three most common twins observed in titanium, as well as in zirconium which also has a low axial c/a ratio, are the $\{10\bar{1}2\}$, $\{11\bar{2}1\}$, and $\{11\bar{2}2\}$ twins [2]. The $\{10\bar{1}1\}$ twin is observed under high compression, e.g. 25% strain at room temperature [11], and under low compression along the ***c***-axis at high temperature, above 400°C [12]. The $\{10\bar{1}2\}$ twin boundary (TB) has intensively been studied by ab initio calculations [13–15], as well as the $\{11\bar{2}1\}$ [16], the $\{11\bar{2}2\}$ [17,13], and the $\{10\bar{1}1\}$ TB [17]. The $\{10\bar{1}1\}$ TB has been correctly observed and analysed at the atomic level with high resolution transmission electron microscopy (HRTEM) in titanium in 1996, after a series of erroneous analyses [18]. Still at the HRTEM level, the $\{10\bar{1}2\}$ TB was first observed in zinc ($c/a = 1.856$) in 1994 [19], then in titanium [20], also see Ref. [11] for a review in 1999. These observations agreed with the previously established atomic models with semi-empirical interatomic potentials [21,22]. A dominant interstitial impurity in titanium such as oxygen, with a solubility limit around 3000 ppm (weight), has a clear strengthening effect [23–25], and an oxygen diffusion controlled twinning during low-temperature creep has been proposed [26]. Hydrogen, even with a solubility limit as small as about 20 wt.ppm at room temperature, has a complicated, yet important role. It softens titanium in some cases [27–29] and hardens it in other cases [30]. Because of the already mentioned importance of deformation twinning, it is worth investigating the interaction of these interstitial atoms with mechanical twins. Substitutional solute segregation to three coherent twin boundaries, accompanied by pinning and strengthening

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effects has recently been observed in magnesium [31]. The presence of oxygen in twin boundaries of α-Ti has recently been studied by ab initio calculations [15], as well as the solubility of many impurities in TBs in several hexagonal metals [13], but a complete segregation study of H or O on the three most common TBs in α-titanium has not yet been done. In view of the increasing interest for ab initio calculations of mechanical properties (see Ref. [32] for a recent review), it may also be useful to investigate at the atomistic level the behaviour of these TBs under strain along a uniquely chosen crystallographic axis, e.g. the ***c***-axis, for the sake of comparisons, without and with solutes.

In this paper, we start by studying the structures and energies of the $\{10\bar{1}2\}$, $\{11\bar{2}1\}$, $\{11\bar{2}2\}$, and $\{10\bar{1}1\}$ twin boundaries in pure titanium with a unified set of ab initio parameters. The segregation of O and H to these four TBs is investigated and their influence on the atomic and electronic structure is discussed. Then, considering one side of the TBs as the matrix part, sets of ***c***-axis deformation of these TBs in pure α-Ti and in presence of these segregated O/H are examined and compared, and tentative conclusions about the possible impacts of interstitial O/H on TBs deformation are summarised.

2. Ab initio modelling, and the impurity concentration issue

Consideration of impurities such as H and O in a metal imposes the use of an ab initio method like the density functional theory (DFT), preferably based on unbiased plane wave bases, as already used to study twins, stacking faults or dislocation cores in hexagonal metals, specially α-Ti. We carry out these DFT calculations [33,34] with the VASP code [35,36]. The projected augmented wave method [37] is used with four 3*s*3*d* electrons explicitly taken into account for the titanium atoms. Checks with twelve 3*s*3*p*4*s*3*d* electrons have occasionally been carried out. Oxygen is modelled with its six 2*s*2*p* electrons. The GGA-PBE functional [38] is chosen for the exchange and correlation energy approximation. For α-Ti, the energy is converged to 10^{-6} eV with a plane-wave energy cutoff of 300 eV and 14 × 14 × 10 *k* points generated in a Gamma centred grid (α-Ti being hexagonal rather than cubic). The obtained crystallographic parameters are $a = 2.923$ Å and an axial ratio $c/a = 1.585$. The number of irreducible *k* points times the number of simulated atoms product is maintained as mush as possible for larger boxes. The metallic electronic partial occupancies are taken care of with the tetrahedron method with Blöchl corrections for small boxes when forces are not required, while a Methfessel-Paxton method is used for smearing with a width of 0.1 eV otherwise [36,39]. The Kohn-Sham Hamiltonian is diagonalised with the residual minimisation method direct inversion in the iterative subspace [36]. Conjugate gradient method is used to optimise the atom positions by minimising the Hellmann-Feynman forces.

As usual with atomistic simulations, and at least still today with ab initio simulations, the impurity concentrations dealt with are (far) beyond the usual experimental solubility limits. Yet, even if paradoxically at first look, this is not a problem for atomistic simulations. The reason is that a simulated system containing *N* matrix atoms plus 1 impurity atom, even with bulk periodic boundary conditions, is not equivalent to a large experimental sample with a 1/*N* impurity concentration. The simulated system only has one independent impurity atom and not an infinity of independent impurity atoms. Bulk periodic boundary conditions do not make the simulated system actually infinite, just periodically infinite. That system cannot make alloys or hydrides or oxides (unless *N* equals 1, 2 or 3 …). To put it in a nutshell, in an atomistic simulation, even with periodic boundary conditions, "1/100 ≠ 1000/100,000."

3. Deformation twin boundaries in α-Ti

The three mechanical, or deformation, twins most easily found in α-Ti, as well as in other hexagonal metals with a low axial ratio, may be simply labelled $\{10\bar{1}2\}$, $\{11\bar{2}1\}$, and $\{11\bar{2}2\}$ and will be described below, as well as for the $\{10\bar{1}1\}$ twin. The relaxed atomic structures of these four twins are shown in Fig. 1 and their twinning crystallographic elements (see Refs. [6,40–49]) are given in Table 1. K_1 is the twin plane, η_1 is the shear direction on K_1, K_2 is the reciprocal twin plane of K_1 corresponding to the choice of η_2 as the direction of K_2 which intersects the shear plane *S*, and *s* gives the magnitude of shear, here calculated in the particular case of titanium using the obtained DFT value of *c*/*a*, viz. 1.585 (see section 2). The twinning elements (K_2, η_1) can be deduced from (K_1, η_2) [41,44,46]. All these TBs can be built in the Haüy hemitropic (half-turn) way by rotating one part of a crystal by a half turn about either the axis normal to the twin plane (Mügge's type I twin) or about an axis contained in the twin plane (Mügge's type II twin, see Appendix for relevant quotations by Haüy and by Mügge). The $\{11\bar{2}1\}$ TB requires a pre-opposite direction displacement (shuffle) of $\frac{1}{12}\langle 1\bar{1}00\rangle$ on to the alternate basal planes so as to relax to its minimum energy state [21,50,51]. It eventually proves to be strictly type II. Note that if originally built as a type II twin, the atomic relaxations for the $\{11\bar{2}1\}$ TB are actually pretty small. Conversely, the relaxed $\{11\bar{2}2\}$ TB is strictly type I, because of its in depth *z* structure. Because we use bulk 3D periodic boundary conditions with a code which utilizes the Bloch theorem (VASP), there are two boundaries per simulated box, instead of one if à la Möbius periodic conditions were allowed along *z* [52].

The ninth column in Table 1 gives the TB energies γ of the four TBs obtained in this work. It is calculated with the usual equation, given just below, from the difference in energies between an optimised box containing *N* atoms with two TBs and a box containing *N* atoms with no structural defect. The normalising factor *A* is the periodic surface in the TB plane. Convergence is ensured with respect to the distance between the two TBs contained in the periodic box (i.e. the box length perpendicular to the TB planes):

$$\gamma = \frac{E_{Box+TB} - E_{Box}}{2A}$$

These TBs experience only small expansion/contraction δ values (given by the following volume difference equation), except for the highest energy one.

$$\delta = \frac{V_{Box+TB} - V_{Box}}{2A}$$

The virtual inverse coincidence lattice site (i.e. nodal site) index Σ, the Friedel's index (see Refs. [53] and [54]), is calculated with Grimmer's formula, approximating the *c*/*a* ratio for Ti to its close value $\sqrt{5/2}$ [55]. It can also be evaluated by direct inspection from the dichromatic patterns with this *c*/*a* ratio. Finally, the inverse of *A* gives the two-dimensional common nodal density at the TB plane.

These TBs can also be considered as special tilt grain boundaries (GBs) with specially low energies and simple atomic structures which do not involve any dislocation cores and can thus be called coherent twin boundaries by contrast with other more general GBs [49].

The energies of these four TBs do not seem to be correlated with any other property listed in Table 1. The $\{10\bar{1}1\}$ TB has the smallest energy and smallest shear magnitude. Yet, it is only observed under high compressive strain or at high temperature. This clearly stresses again, on the basis of a unified ab initio study of four different TBs, that neither the interface excess energy nor the shear magnitude are determinant factors for the occurrence of