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First principles characterisation of brittle transgranular fracture of titanium hydrides

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ABSTRACT

In this work we have studied transgranular cleavage and the fracture toughness of titanium hydrides by means of quantum mechanical calculations based on density functional theory. The calculations show that the surface energy decreases and the unstable stacking fault energy increases with increasing hydrogen content. This is consistent with experimental findings of brittle behaviour of titanium hydrides at low temperatures. Based on Griffith-Irwin theory we estimate the fracture toughness of the hydrides to be of the order of 1 MPa·m$^{1/2}$, which concurs well with experimental data. To investigate the cleavage energetics, we analyse the decohesion at various crystallographic planes and determine the traction-separation laws based on the Rose's extended universal binding energy relation. The calculations predict that the peak stresses do not depend on the hydrogen content of the phases, but it is rather dependent on the crystallographic cleavage direction. However, it is found that the work of fracture decreases with increasing hydrogen content, which is an indication of hydrogen induced bond weakening in the material.

1. Introduction

Titanium (Ti) is a technologically important transition metal characterised by low density, good thermal and mechanical properties and high corrosion resistance [1,2]. An attractive weight-to-strength ratio has made Ti and its alloys important construction materials in applications where light weight poses a crucial requirement, such as in aerospace and marine applications [3–5]. However, the Ti-based materials can be susceptible to hydrogen embrittlement (HE) when subjected to hydrogen-rich environments under severe operating conditions (e.g., extreme pH levels, high temperatures and pressures).

The susceptibility of Ti alloys to HE is related to strong chemical affinity but low solid solubility of H in the hexagonal-close-packed (HCP) structure of α-Ti. When Ti is charged with H, a broad variety of hydrides with various stoichiometries and morphologies can form, depending on the hydrogen content, charging conditions and metal microstructure [6–11]. Although the titanium hydrides are mostly non-stoichiometric, three distinct hydride phases have been observed. The two most common ones are the δ- and ε-phases with face-centered-cubic (FCC) and face-centered-tetragonal (FCT) crystal structures, respectively, in which H atoms occupy the tetrahedral interstitial sites. The δ-hydride TiH_x is stable for a broad range of $1.5 < x < 1.99$ and transforms into the ε-phase when $x > 1.99$. A third phase, the so-called γ-phase, is a controversial stoichiometric phase with $x = 1$ whose thermodynamic stability is still debated in the literature [10–12].

With the exception of the ε-phase, most bulk hydride phases have been found to exhibit dislocation-driven ductility at elevated temperatures but undergo a ductile-to-brittle transition (DBT), which is manifested by a pronounced reduction of the fracture toughness and resistance to cracking [13]. The observed DBT together with a marked strain-rate sensitivity indicate that the dislocation mobility is likely strongly affected by H diffusion as well as defects associated with the hydride non-stoichiometry. Dislocation-related phenomena, such as pinning or changes of dislocation core structures due to H atoms, together with weaking of internal interfaces are the most likely factors

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contributing to the severe reduction of fracture toughness in the hydrides. Specifically, it has been observed that the fracture toughness of δ-hydride can be as low as 2 MPa·m$^{1/2}$ [14] as opposed to approximately 60 MPa·m$^{1/2}$ [15] for pure α-Ti at room temperature.

Apart from studies of bulk hydride phases, the existence of hydride precipitates at grain boundaries as well as within grains of the Ti-matrix has been confirmed by numerous experimental studies [2,7–10,16–19]. It has been reported that these precipitates can exhibit both excellent plastic deformability and brittle cleavage depending on the size, morphology, orientation and distribution of the precipitates. This fact again confirms that the mechanical behaviour of the hydrides is rather complex and affected by several factors (dislocation plasticity, properties of interfaces, H diffusion, temperature, etc.). In addition, the phase stability of the hydrides also seems to depend on external stress conditions as well as internal coherency strains in the matrix [12]. In fact, a direct link between the nucleation and growth of a continuous hydride network in the stress field of a propagating crack has been confirmed by *in situ* transmission electron microscopy [19,20].

To understand the precise role of hydride precipitates in HE of Ti-alloys it is necessary to obtain a detailed knowledge of the fundamental intrinsic mechanical properties of the hydride phases. Since hydride fracture below DBT is dominated by brittle cleavage, the fracture toughness can be assessed by using the Griffith-Irwin relation [21]. Within this approach the fracture toughness is approximated based on the elastic properties of the material and its surface energy, both of which can nowadays be computed reliably using quantum mechanical first-principles methods based on density functional theory (DFT). Such modelling has been used with great success to quantify the fracture properties of brittle materials (see, for instance, Refs. [22–25]).

For macroscopic continuum modelling of mode I cleavage, phenomenological cohesive zone models (CZM) have been commonly employed to describe the mechanics of the crack opening. This approach, originally proposed by Dugdale [26] and Barenblatt [27], is used to describe the propagation of a crack by gradual separation of two surfaces. The cohesion between the surfaces, which is one of the key material quantities in CZM, can be parametrised based on DFT calculations of the tensile behaviour [23,28–33]. Apart from providing quantitative information about the strength of chemical bonding, i.e., the cohesion, the first principles calculations can also give additional insights, for instance, how impurities and alloying elements affect the bond strength [34,35]. Previous first-principles studies of titanium hydrides have mainly been devoted to elucidating thermodynamic and elastic properties as well as the stability and transformation of the different phases [12,36–42]. Particular effort has been directed towards explaining the tetragonal distortion of ε-TiH_2, which has been found to be a consequence of multiple degenerate bands at the Fermi level in the cubic phase, promoting a tetragonal distortion based on the Jahn-Teller mechanism [40–43]. However, to the best of the authors' knowledge, DFT modelling has not been applied to analyse what causes the substantial decrease in hydrides' fracture toughness.

There are two main objectives of this paper. The first one is to investigate the theoretical fracture toughness of the δ-$TiH_{1.5}$ and ε-TiH_2 hydrides using first-principles calculations. To this end we resort to the Griffith-Irwin theory and assess the fracture toughness from DFT estimated isotropic elastic properties and surface energies of the hydride phases. The second objective is to study the traction-separation behaviour associated with the transgranular cleavage. For this purpose we carry out a series of DFT simulations mimicking computational tensile tests and fit their results using Rose's extended universal binding energy relation (UBER) [44] to obtain scalable macroscopic cohesive laws [34]. This modelling strategy allows us to extract the parameters describing the interplanar potentials and to investigate how the hydrogen content affects the peak stress and the critical interplanar separation of the hydrides. Moreover, as a part of this work we investigate how the atomic scale deformation ensues and how the electronic structure is affected by the strain.

2. Fracture mechanics of brittle materials

The first criterion for crack propagation was proposed by Griffith [45]. In this approach, the far-field critical stress, σ_f, required to propagate a crack of total length $2a$ in a brittle 2D isotropic solid is described by the relation

$$\sigma_f = \sqrt{\frac{2\gamma_S E}{\pi a}} \tag{1}$$

where E is Young's modulus and γ_S is the surface energy, which is the threshold energy that needs to be overcome to create new crack planes at the crack tip. Strictly speaking, Eq. (1) is only valid if plastic dissipation is neglected. However, in the case of brittle solids, where cleavage is the dominating fracture mechanism, this is a good approximation.

Since the prediction of crack propagation using Eq. (1) is impractical, it is common to employ an alternative but related approach based on the so-called stress intensity factor concept, as originally conceived by Irwin [21]. The stress intensity factor, K_I, is a measure of the amplitude of the stress field in front of a crack tip and can be used for an accurate prediction of initiation of crack propagation. The critical value of K_I at which the crack growth in a brittle solid becomes unstable is a material specific property commonly referred to as the fracture toughness, K_{Ic}. For an isotropic 2D solid loaded in plane deformation, the work of fracture, $G_c = 2\gamma_S$, is related to the fracture toughness through the so-called Griffith-Irwin relation

$$G_c = 2\gamma_S = \frac{1-\nu^2}{E} K_{Ic}^2 \tag{2}$$

in which ν is the Poisson's ratio of the material. For anisotropic materials, the theory becomes mathematically more complex, containing dependencies on other elastic moduli [46–48]. However, as an approximation it is possible to apply Eq. (2) to anisotropic materials with the elastic constants E and ν approximated by the components of the general anisotropic stiffness matrix [49,50]. In the present study, Young's moduli and Poisson's ratios are estimated using the Voigt-Reuss-Hill (VRH) approach [51,52].

A third way to characterise the mechanical state at a crack tip is to use the CZM concept [26,27,53–55]. In this case, a process zone of finite size is introduced, where gradual damage leads to the formation of new crack surfaces. The separation of two initially coincident points is described by the vector $\bar{\delta}_g$, and the separation of crack surfaces is governed by a traction-separation law, $\bar{\sigma}_g = \bar{\sigma}_g(\bar{\delta}_g)$, where $\bar{\sigma}_g$ is the traction vector that causes resistance to the surface separation. For symmetric loading, i.e., a pure mode I loading, the only non-vanishing components of the displacement and traction vectors are the normal components, denoted δ_g and σ_g. Thus, the total work of fracture and the surface energy are obtained by integration of the traction-separation curve as