
THEORETICAL STRENGTH OF SOLIDS: A BRIDGE FROM INTERATOMIC BONDS TO LOCAL PLASTICITY AND FRACTURE

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INTRODUCTION

Theoretical strength (TS) of a perfect crystal of particular chemical composition, also referred to as ideal strength, represents an upper strength limit. TS was usually evaluated only for several special cases of loading, each defined by a single value of the stress tensor component: the uniaxial tension (σ_{ut}) and compression (σ_{uc}), the hydrostatic tension (σ_{ht}) and compression (σ_{hc}) and the pure shear (τ_s). Almost 100 years ago, Polanyi [1] and Frenkel [2] published first calculations of σ_{ut} and τ_s values, respectively. While the Frenkel's estimation proved to be almost accurate, those of Polanyi and Orowan [3] turned out to be several times higher when compared to recent experimental and even theoretical results [4]. It should be emphasized that theoretical and experimental data on σ_{ut} started to mutually approach only after utilization of ab initio (first principles) calculations including analyses of crystal stability [4]. The ab initio methods are based on computations of electronic structure using the density functional theory and, nowadays, they represent the most precise tool for determination of changes in the total energy of crystals during their deformation. Such obtained energy-strain characteristics are also used as benchmarks for construction of sophisticated semi-empirical interatomic potentials employed in molecular dynamics (MD) studies. In general, the ab initio calculated mechanical characteristics of perfect crystals start to be widely applied in multiscale models of fracture processes of engineering materials.

Scientific and practical significance of TS data lies in several general aspects [4, 5]. These data give us upper benchmarks when improving the strength of advanced materials. They play a decisive role in the fundamental theory of fracture: the stress necessary for both homogeneous (lattice) and heterogeneous (grain boundary) nucleation of dislocations can be well identified with τ_s and the local stress for nucleation of cleavage cracks should overcome σ_{ut} . The ratio σ_{ut}/τ_s reflects brittleness/ductility response of the crystal matrix and the difference in mechanical behavior of perfect and real crystals enables us to clearly separate the role of crystal defects from that of the perfect matrix. During the last 15 years, systematic ab

initio computations of multiaxial TS brought results important for many case studies as nanoindentation tests (e.g., [6, 7], emissions of dislocations from grain boundaries (e.g., [8]) or synergy effects in nanocomposites [9]. The fracture energy of special grain boundaries weakened by hydrogen or segregated impurity elements can also be determined using ab initio methods (e.g., [10, 11]).

RECENT CALCULATIONS OF THEORETICAL STRENGTH

When considering a perfect crystal deforming homogeneously in a nonlinear elastic way, the total internal energy of the crystal can be expanded as

$$E = E_0 + V \sum_i \sigma_i \eta_i + \frac{1}{2} V \sum_i \sum_j C_{ij} \eta_i \eta_j + O(\eta^3),$$

$$i, j = 1, 2, \dots, 6, \quad (1)$$

where σ_i are components of the stress tensor, η_i are components of the Lagrangian strain tensor, C_{ij} are the second order elastic coefficients and V is the crystal volume [12]. Here, the simple Voigt notation can be used since the tensors σ_{ij} , η_{ij} and C_{ijkl} ($i, j, k, l = 1, 2, 3$) are symmetric with respect to $(ij) \leftrightarrow (ji)$ interchange. By setting $E_0 = 0$ and using the internal energy per volume unit $E_u = E/V$, one can simply write

$$\sigma_i = \frac{\partial E_u}{\partial \eta_i}, \quad C_{ij} = \frac{\partial^2 E_u}{\partial \eta_i \partial \eta_j}. \quad (2)$$

For a prescribed deformation path, the related energy-strain curve can be determined using semi-empirical interatomic potentials or ab initio. Up to 1980, the value of TS for this path was generally assumed to correspond to the maximal stress that is associated with so called volumetric instability related to the point of inflexion on the strain-energy curve (1). However, it turned out that the volumetric instability is often preceded by phonon-induced instabilities. Particularly in the case of uniaxial tension, therefore, the values of σ_{ut} revealed to be much lower than those computed from the inflexion point. This is, however, not the case of a pure shear deformation and the value of τ_s . Therefore, the classical Frenkel's formula for τ_s can still be used for approximate assessments of τ_s [13, 14].

If the solid is infinitesimally strained from a reference state associated with σ_{ij} by the strain tensor ε_{ij} (in the standard notation), the related Cauchy (true) stress t_{ij} can be expressed as

$$t_{ij} = \sigma_{ij} + B_{ijkl} \varepsilon_{kl} \quad (3)$$

where

$$B_{ijk} = C_{ijkl} + \frac{1}{2}(\delta_{ik}\sigma_{jl} + \delta_{jk}\sigma_{il} + \delta_{il}\sigma_{jk} + \delta_{jl}\sigma_{ik} - 2\delta_{kl}\sigma_{ij}) \quad (4)$$

is the elastic stiffness matrix ($i, j, k, l = 1, 2, 3$), generally asymmetric towards $(ij) \leftrightarrow (ji)$ interchange. Construction of this matrix is crucial for the elastic stability assessment. Namely, the system can be considered to be stable when

$$\det|\mathbf{B}| > 0 \quad (5)$$

during the loading [12, 15], i.e., the elastic stiffness matrix is positive definite. This leads to a set of so called elastic stability conditions that depend on both the crystal symmetry and the applied loading [12]. For cubic crystals under isotropic loading, e.g., the number of resulting stability conditions is reduced to the following three:

$$C_{11} + 2C_{12} > 0; \quad (6)$$

$$C_{11} - C_{12} > 0; \quad (7)$$

$$C_{44} > 0. \quad (8)$$

The first condition is equivalent to the requirement that the bulk modulus is positive (the volumetric stability). The other two conditions are related to the tetragonal and the trigonal shear moduli. The crystal becomes unstable if any of them vanishes. In eqs. (6 - 8), the values of elastic moduli must be determined for a sufficient number of points on the deformation path by introducing a given number of independent small strain deviations. Therefore, the assessment of elastic stability is very demanding and was performed only for a small number of crystals and loading modes [16 - 19]. However, one can also obtain sufficiently precise results when using a much easier method proposed in [20]. In this way, values of σ_{ut} for many fcc and bcc crystals more close to experimental ones were already obtained (see hereafter).

In fact, the elastic instability conditions represent a long wavelength limit (for vanishing wavevectors $q \rightarrow 0$) of a more general instability related to an occurrence of so called soft phonons carrying negative energy in the crystal lattice. Since the phonon energy is related to its frequency ω , the general stability criterion (in the harmonic approximation) requires

$$\omega^2(q, s) > 0 \quad (9)$$

for all wavevectors q and modes s (optical/acoustic, longitudinal/transverse) [21]. Thus,

the soft phonons with finite wave lengths ($q > 0$) may also lead to a crystal collapse. However, such instabilities can be discovered only when computing the phonon spectrum of a particular crystal during deformation and identifying the soft phonons with imaginary frequencies. Up to now, such a complete assessment of phonon-based instabilities was reported in a few works only (e.g. [22, 23]). In these works, the occurrence of some soft phonons with finite wave lengths did not reveal any dramatic reduction of σ_{ut} values with respect to those obtained by the analysis of elastic stability conditions.

Values of σ_{ht} , σ_{ut} and τ_s computed for selected crystals of elements from first principles [4, 24-29] are collected in Tab. 1 along with available experimental data [7, 30-32] obtained on whiskers, nanopillars or from nanoindentation tests. The bold print highlights values for σ_{ut} and σ_{ht} that were achieved by taking the stability conditions into account and those for τ_s obtained by a full relaxation of atomic positions during deformation. All these values agree with experimental ones within a factor of two. Note that, especially for σ_{ut} , one cannot expect a full agreement between theory and experiment since one can hardly avoid some imperfections of specimens (surface roughness, defects) as well as of the loading path. The fcc crystals exhibit the lowest values of σ_{ut} for $\langle 110 \rangle$ loading direction and the highest ones for $\langle 100 \rangle$ direction. On the other hand, the highest tensile strength of bcc crystals corresponds to $\langle 110 \rangle$ and the lowest one to $\langle 100 \rangle$ directions. This behavior can be understood in terms of displacive phase transformations [33]. For example, the bcc structure of crystals deformed in the trigonal $\langle 111 \rangle$ direction transforms to the simple cubic structure of a relatively high energy. On the other hand, the deformation along the $\langle 100 \rangle$ direction leads to the fcc structure of much lower energy that induces the low $\langle 100 \rangle$ value of σ_{ut} . This is the intrinsic reason why, at low temperatures, the real bcc polycrystals exhibit brittle (cleavage) fracture along $\{100\}$ planes perpendicular to $\langle 100 \rangle$ direction.

Table 1. Calculated and experimental values of theoretical strength for isotropic, uniaxial and shear loading

Crystal	σ_{ht} [GPa]	σ_{ut} [GPa]		τ_s [GPa]	
	theory	theory	experiment	theory	experiment
C (dia)	88.5	95<111> 130<100>	20.7 (graphite) 19.6 (graphite)	96.6 <112>	
W (bcc)	57.4	32.4 <110> 37.5 <111> 28.9 <100>	28.3 <110>	17.5 {110} 17.1 {112}	
Mo (bcc)	42.7	31.9 <110> 28.4 <111> 28.3 <100>	19.8 <110>	15.1 {110} 14.8 {112}	
Ni (fcc)	29.0	18.3 <100> 15.4 <111> 9.1 <110>		5.05 <112>	5.4 <112>
Fe (bcc)	26.7	27.7 <111> 33.0 <110> 14.2 <100>	13.1 <111>	6.0 {112}	3.56 <111>
Cu (fcc)	20.2	4.6 <110> 9.3 <100> 7.5 <111>	1.59 <110> 1.74 <100> 2.94 <111>	2.16 <112>	1.65 <112>
Si (dia)	15.5	26.3 <100>	4.14	8.6 <112>	
Ag (fcc)	11.4	12.3 <100>	3.80<100>	1.65 <112>	0.71 <011>
Al (fcc)	11.0 10.2	4.5 <110> 9.0 <100> 8.8 <111>	2.3 (bending)	3.77 <110> 2.84 <112>	
Na (bcc)	2.2	0.90 <111> 0.04 <100> 0.20 <110>		0.20 <111>	

After 2000, the influence of coupling of various stress tensor components on TS started to be systematically studied. Tensile and compressive tests of many cubic crystals were simulated in the <100>, <110> and <111> loading directions under superimposed biaxial transverse stresses [33-35]. The maximum tensile stresses were found to be almost linearly increasing (decreasing) functions of tensile (compressive) biaxial stresses for most of the studied crystals. This means that, as a rule, the highest strength of perfect crystals can usually be achieved under the isotropic tensile loading. Results concerning the dependence of the ultimate strain ϵ_u (at the inflection point) on the applied biaxial transverse stress revealed that, in general, the ultimate strain of fcc metals decreased with increasing biaxial stress whereas the opposite trend referred to bcc metals. The average ductility of

fcc metals was higher than that of bcc crystals but, rather surprisingly, it was comparable to that of diamond crystals. Such a response of perfect crystals to the triaxial stress state is qualitatively different from that of engineering materials. In the latter case, an increase in the tensile traxiality always leads to a decrease of ultimate strain which can be attributed to a plasticity driven growth and coalescence of microvoids initiated by secondary phase particles [4]. On the other hand, an assessment of brittleness/ductility behavior of perfect crystals on the basis of the ratio σ_{ht} / τ_s qualitatively corresponds to behavior of both single crystals and polycrystals containing defects. Consequently, this kind of behavior is, at least partially, predetermined by intrinsic properties of the crystal lattice [4].

Values of τ_s were evaluated as a function of the resolved normal stress σ_n on the shear plane while all other stress tensor components were relaxed [36-40]. It was found that the function $\tau_s(\sigma_n)$ increases (decreases) with the applied compressive (tensile) stress practically for all studied fcc and bcc metallic crystals. This is, most probably related to the related variation of friction on shear planes as also discussed in terms of a distribution of valence electron density [39]. However, the ceramic crystals often exhibit an opposite behaviour [41] which means that the strength of interatomic bonds in the shear plane also plays an important role.

Since the results of ab initio calculations stand only for zero absolute temperature, let us briefly mention the influence of temperature on TS. Historically, two relevant methods were applied to predict the temperature influence: the Einstein model of harmonic oscillators combined with the elastic instability criterion and the model of dislocation nucleation supported by phonon fluctuations [7]. These approaches predicted a small drop in σ_{ut} (less than ten of percent) when increasing the temperature from zero to 300K. More recently, both MD simulations of shear TS in Cu and Al [10] and ab initio calculations, corrected for soft phonons with vanishing wavevectors [42], also confirmed the less than 10% difference between the TS values corresponding to 0K and 300K. However, the most physically justified approach to the temperature problem would be so called ab-initio based correlated electron-ion dynamics that is currently under development [43].

FROM INTERATOMIC BONDS TO LOCAL PLASTICITY AND FRACTURE

Nanoindentation tests became a very promising experimental method for identification of ideal shear strength. Due to a very small penetration depth, the stressed volume beneath the sharp nanoindenter is usually constricted to one grain and may be free of pre-existing dislocations. During the nanoindentation, therefore, the increasing local shear stress can reach the value of ideal shear strength to nucleate dislocations in a perfect crystal lattice. Such an onset of local plastic deformation could be detected as a pop-in on the load-displacement curve (e.g., [44]). During the last 10 years, several physically plausible models of the nanoindentation test were published and applied to Mo, W, Cu and Ni crystals (e.g., [6, 7, 31, 45]). These models utilized multiscale "bottom-up" approaches, starting from ab initio calculations of the dependence of ideal shear strength on superimposed normal stress components. The values of indentation forces and penetration depths corresponding to pop-ins could be predicted in a reasonable agreement ($\pm 20\%$) with experimental data for all investigated crystals.

The close relation of the function $\tau_s(\sigma_n)$ to dislocation nucleation processes in copper and aluminium was also confirmed by MD simulations [8, 46]. Indeed, the shear stress required for dislocation nucleation in single crystals increased as the resolved normal stress σ_n decreased in the same manner as determined for τ_s . The tensile stress σ_{GB} required to dislocation nucleation at grain boundaries must be linked to both the grain boundary structure and the inclination angle Φ that refers to the degree of rotation of the boundary plane from the coherent twin about the $\langle 110 \rangle$ tilt axis. For $\Sigma 3$ boundaries with $\Phi \sim 45^\circ$ in Cu and $\Phi \sim 30^\circ$ in Al, the dislocations are nucleated and emitted under a relatively low nucleation stresses $\sigma_{GB,Cu} \approx 5$ GPa and $\sigma_{GB,Al} \approx 4$ GPa, respectively. This nearly corresponds to the nucleation resolved shear stress $\tau_{GB} \sim 3$ GPa very close to τ_s of both Al and Cu crystals.

Uniaxial tensile tests of perfect nanocomposites with Mo and V matrixes as function of atomic fraction of reinforced W-fibres was simulated by ab initio methods [9]. The values of σ_{ut} for composites containing about 75% of W were found to be comparable to (or even slightly higher than) that of the 100% W fibre. This synergy effect, significantly beyond the linear mixture rule, could basically be explained by an influence of internal stresses developing in both composite constituents during deformation. In particular, the strength of Mo and V matrixes increased under increasing transverse tensile stresses. Most probably, a redistribution of valence electrons along W-Mo and W-V interfaces also contributed to this effect.

Brittle fracture induced by segregation of impurity elements to grain boundaries is a very important practical problem. Although direct ab initio computations of strength of embrittled boundaries are still in an embryonic state, concepts based on the ideal fracture (surface) energy γ or ideal binding (cohesive) energy U are well in progress. Let us first mention a relationship between the binding energy of a perfectly brittle crystal and its fracture toughness:

$$K_{Ic} \approx \left(\frac{EU}{2S} \right)^{1/2}, \quad (10)$$

where E is the Young's modulus and S is the area per atom on the fracture surface [4]. This relation directly connects quantities related to atomistic and macroscopic scales and provides, under the assumption of ideal cleavage fracture, a physical lower-bound benchmark for fracture toughness of engineering materials: $K_{Ic} \in (0.5, 1)$ MPa.m^{1/2}. Indeed, for most metallic and ceramic crystals, the values of U and S are in units of eV/atom and 10^{-19} m²/atom, respectively.

There are basically four different atomistic models of impurity embrittlement mechanisms that can work in various impurity-metal systems: drawing of charges from metal-metal bonds [47], difference between impurity segregation enthalpy at the grain boundary and the free surface [48], change of non-directional metallic bonds to more directional (less flexible) ones [49, 50] and, more recently, also an opposite transition from directional *s-d* bonds to more metallic (less strong) ones [11]. Using a combined theoretical (ab initio calculations) and experimental (electron energy loss spectroscopy) approach, the latter mechanism was proved to operate in the case of bismuth-induced embrittlement of copper grain boundaries [11, 51]. The copper atoms surrounding the segregated Bi exhibit a closed 3*d* shell, reduced *s-d* hybridization and an overfull *s* band. All these changes of electronic structure weaken the bonds between the copper atoms.

Hydrogen-induced embrittlement is believed to be caused by two basic mechanisms [52]: the hydrogen enhanced localized plasticity (HELP) and the hydrogen induced decohesion (HID). While HELP seems to predominantly underlie the intergranular fracture, HID was usually considered to be associated with the transgranular one. The latter consideration was supported by ab initio calculations of ideal fracture energy of Al {111} and Fe {110} surfaces as functions of hydrogen coverage θ [53]. These calculations revealed a steep linear decrease of both γ_{Al} and γ_{Fe} with increasing θ . However, more recent ab initio calculations [10] of binding energies of H with the grain boundary and the free surface in Ni indicate that, by virtue of the Rice-Wang theory [48], the HID mechanism can also work at grain boundaries. For bcc Fe, the predicted strong tendency to creation of both the linear hydrogen-vacancy complexes $VaCH_2$ - $VaCH_2$ along the $\langle 111 \rangle$ direction and the planar clusters on {100} planes [10] deepens our understanding of both HELP and HID mechanisms in steels. Indeed, the vacancy rows along $\langle 111 \rangle$ slip direction may promote dislocation motions and the {100} clusters can lead to crack nucleation and cleavage on these planes.

Conclusion

Ab initio methods for calculation of uniaxial theoretical strength combined with stability analyses already give data that agree with experimental ones within a factor of two. This is already a plausible result owing to unavoidable imperfections of experimental tests. Values of both ideal shear strength and ideal binding energy are even more accurate and, therefore, they can be utilized as physical upper and lower bounds of shear strength and fracture toughness, respectively. Values of fracture

energy of grain boundaries computed from first principles significantly help us to understand embrittlement mechanisms induced by hydrogen and impurity atoms. Thus, the superstructure of the bridge from interatomic bonds to local plasticity and fracture is quickly building and starts to carry a rising traffic on roads connecting these different scales.

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