Theoretical Strength and Onset of Yielding in Nanoindentation

M. Šob*, M. Friák*,**, and V. Vitek†

* Institute of Physics of Materials, Academy of Sciences of the Czech Republic, Žižkova 22, CZ-616 62 Brno, Czech Republic, mojmir@ipm.cz
** Institute of Condensed Matter Physics, Faculty of Science, Masaryk University, Kotlářská 2, CZ-611 37 Brno, Czech Republic, mafri@ipm.cz
† Department of Materials Science and Engineering, University of Pennsylvania, 3231 Walnut St., Philadelphia, PA 19104-6272, U.S.A., vitek@sol1.lrsm.upenn.edu

ABSTRACT

Quantum-mechanical (ab initio) approach for determining theoretical (ideal) tensile and shear strength in metals and intermetallics is briefly outlined and, as an example, tensile test for defect-free $MoSi_2$ is simulated. Theoretical values of tensile and shear strength are compared with those obtained from loading of whiskers and from nanoindentation experiments. As nanoindentation tests can sample defect-free volumes, the onset of yielding should correspond to theoretical shear strength. Possible sources of discrepancies between the measured maximum shear stress in nanoindentation experiments and theoretical values as well as corresponding corrections are discussed. The calculated or measured values of theoretical strength may subsequently serve as input parameters to a quantitative and predictive model, based on the properties of dislocation interactions, that describes the relationship between the yield behaviour and length-scale effects in the nanoscale regime.

Keywords: nanoindentation, theoretical strength, ab initio electronic structure calculations, onset of yielding

1 INTRODUCTION

Nanoindentation has emerged in recent years as the most important probe, both in basic research and industrial applications, for investigation of mechanical properties over dimensions ranging from a few nanometers to a few microns. Numerous experiments using this technique have identified a remarkable phenomenon specific to this regime, namely that the onset of yielding at the nanoscale appears to be controlled by homogeneous nucleation of dislocations in the small volume of material subject to loads approaching the theoretical strength, i.e. the strength of an ideal (defect-free) solid. This is due to the fact that the contact area under the nanoindenter is almost always dislocation-free because in well-annealed crystals the average dislocation spacing is of the order of 1 μm while the contact area is of the order of 100 nm.

The estimate most often used for this quantity is $G/2\pi$, where G is the shear modulus on the appropriate slip plane. In many materials, the shear stress at the onset of yielding differs from this estimate by a factor of 2-3. Consequently, in order to develop a quantitative theory the results of which can be directly compared with experiments, we need a more reliable estimate of the theoretical strength.

Recently, determination of theoretical strength became possible using quantum-mechanical (ab initio or first-principles) electronic structure calculations based on density functional theory. It was our group at the Institute of Physics of Materials in Brno who performed the very first fully relaxed ab initio simulation of a tensile test and obtained the theoretical tensile strength in tungsten [1]. The calculated results compared very well with the experiment performed on tungsten whiskers by Mikhailovskii et al. [2]. Further, we calculated ideal tensile strength in NiAl [3] and Cu [4]. These results found a very good response in the international community and established a basis for further calculation of ideal strength in Al [5], [6], Cu [6], and β-SiC [7]. Very recently, we have calculated the theoretical strength in transition metal disilicides $MoSi_2$ and WSi_2 [8].

For the nanoindentation experiments, the theoretical shear strength of the material is more relevant. While it cannot be easily measured experimentally, it may be also determined by means of ab initio electronic structure calculations. Here more computational effort is needed, as several independent components of the strain tensor must be relaxed to establish fully uncostrained conditions. Till now, such calculations were performed for Al and Cu [6], W [9] and Mo [10]. Non-relaxed ab initio results for numerous metals may be found in [11]; as shown in [6], [10], for Al and Cu the relaxed shear strengths are much lower than unrelaxed values. To the best of our knowledge, no ab initio calculations of theoretical shear strength were accomplished for intermetallic compounds. Our own calculations of this quantity are in progress.

The present contribution gives an account of applications of quantum-mechanical electronic structure calculations to the problem of theoretical strength in metals and intermetallics. First, we briefly describe the way of simulating the tensile test, the calculation of shear strength, and the electronic structure calculational method. Then we shortly discuss the theoretical strength values in a number of elemental metals and intermetallics and compare them with available experimental data, both from measurements on whiskers and from nanoindentation experiments.

2 TENSILE TEST SIMULATION AND CALCULATION OF SHEAR STRENGTH

The tensile strength of materials is usually limited by presence of internal defects, mostly dislocations. In a defect-free crystal, the tensile strength is several orders of magnitude higher and is comparable with elastic moduli. Most of the calculations of theoretical strength is based on empirical potentials with the parameters adjusted to experimental data. However, these experimental data usually correspond to the equilibrium ground state. Therefore, the semiempirical approaches adapted to the equilibrium state may not be valid for materials loaded close to their theoretical strength limits.

In the first-principles (ab initio) electronic structure calculations, we start from the fundamental quantum theory. The only input is atomic numbers of the constituent atoms and, usually, some structural information. This approach is reliable even for highly non-equilibrium states.

To simulate the tensile test, we first calculate the total energy of the material in the ground state. Then, in the second step, we apply some elongation of the crystal along the loading axis (in the [001] direction, for example; the loading axis is denoted as axis 3) by a fixed amount ε_3 that is equivalent to the application of a tensile stress σ_3. Subsequently, we fully relax both the stresses σ_1 and σ_2 in the directions perpendicular to the axis 3 as well as the internal structure parameters, if any. In this way, we find the contractions ε_1 and ε_2 which correspond to zero tensile stresses σ_1 and σ_2 and the new values of internal parameters.

Let us dicuss the case of transition metal disilicides $MoSi_2$ and WSi_2 loaded along the [001] axis in more detail. Their $C11_b$ structure is tetragonal and keeps its tetragonal symmetry during this uniaxial loading. Therefore, $\sigma_1 = \sigma_2$, and we minimize the total energy as a function of lattice parameter a and internal structure parameter Δ (defined e.g. in [12], [13]).

The tensile stress σ_3 is then given by [14]

$$\sigma_3 = \frac{c}{\Omega}\frac{\partial E}{\partial c} = \frac{1}{Ac_0}\frac{\partial E}{\partial \varepsilon_3}, \qquad (1)$$

where E is the total energy per repeat cell, Ω is the volume of the repeat cell, c is a dimension of the repeat cell in the direction of loading, $A = \Omega/c$ is the area of the basis of the repeat cell in the plane perpendicular to the loading axis, and c_0 is the value of c in the undeformed state. The inflexion point in the total energy dependence yields the maximum of the tensile stress; if some other instability does not occur before reaching the inflexion point, it also corresponds to the theoretical tensile strength.

The theoretical shear strength is calculated analogously. A shear deformation is applied along a chosen direction and plane (e.g. along a $\langle 112 \rangle$ in a $\{111\}$ plane in fcc metals) and the total energy is calculated as a function of the magnitude of this deformation. The maximum slope of this curve then determines the theoretical shear strength for the chosen mode of shearing. It is again important to allow relaxation of five strain components other than imposed shear and of internal structure parameters, if any.

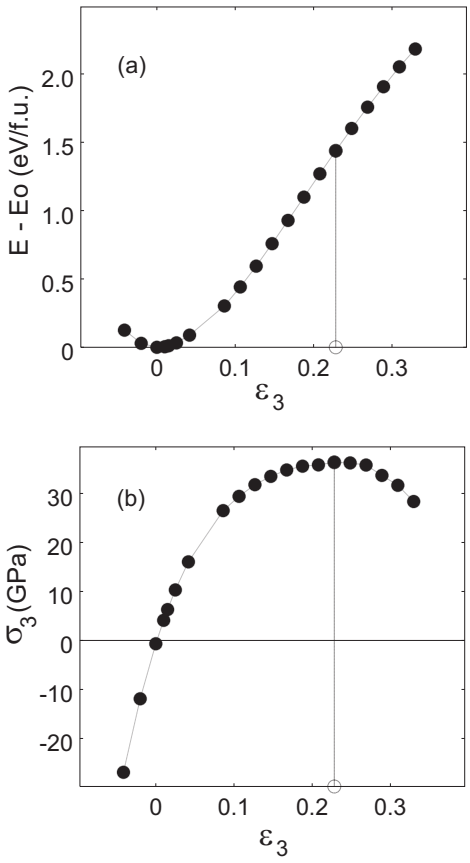

Figure 1: Variations of (a) total energy, E, per formula unit (f.u.), and (b) tensile stress σ_3 during the simulation of the tensile test along the [001] direction in $MoSi_2$. Here E_0 is the ground-state energy and ε_3 is the strain. The position of the inflexion point in the energy dependence and the maximum of the tensile stress are denoted by a thin vertical line.

3 DETAILS OF THE CALCULATIONS

In order to obtain reliable ab initio total energies of materials during tensile test simulations and calculations of shear strength, the methods using a shape approximation of the crystal potential (for example spheroidization, as in the LMTO-ASA method or in standard KKR and APW approaches) are not adequate [1]. Instead, full-potential treatments must be employed. In this study we utilized the full-potential linearized augmented plane waves (FLAPW) code described in detail in [15]. The electronic structure calculations were performed self-consistently within the local density approximation (LDA).

Table 1: Theoretical tensile strengths σ_{th} calculated ab initio

material	structure	orientation of the of the loading axis	σ_{th} (GPa)	reference
W	A2	[001]	28.9	[1]
		[001]	29.5	[9]
		[111]	40.1	[1]
		[110]	54.3	[1]
Al	A1	[001]	12.1[a]	[5]
		[111]	11.05	[5]
Cu	A1	[001]	33	[4]
		[110]	31	
		[111]	29	
NiAl	B2	[001]	46	[3], [4]
		[111]	25	[3], [4]
β-SiC	B3 (3C)	[001]	101	[7]
		[111]	50.8	[7]
$MoSi_2$	$C11_b$	[001]	37	[8]
WSi_2	$C11_b$	[001]	38	[8]

[a] A value of 12.54 GPa would be obtained from the slope of the strain dependence of total energy at the inflexion point [5].

In our calculations, crystal lattices are severely distorted and some atoms may move very close together. Therefore, the muffin-tin radii must be sufficiently small to guarantee non-overlapping of the muffin-tin spheres at every stage of the test. For example, in transition metal disilicides, we use the muffin-tin radii equal to 2.3 a.u. for transition metal atoms and 2.1 a.u. for silicon. These are kept constant in all calculations presented here. The product of muffin-tin radius and the maximum reciprocal space vector, $R_{MT}k_{max}$, is equal to 10, the maximum l value for the waves inside the atomic sphere, l_{max}, and the largest reciprocal vector $\mathbf{G}$ in the Fourier expansion of the charge, G_{max}, are set to 12 and 15, respectively, and the number of $\mathbf{k}$-points in the first Brillouin zone is equal to 2000.

4 RESULTS AND DISCUSSION

In Fig. 1, we display, as an example, the dependences of total energy E and tensile stress σ_3 on the strain ε_3 in the [001] direction in $MoSi_2$. The total energy has a parabolic shape around the minimum; it becomes almost flat in the neighborhood of the inflexion point corresponding to the maximum of the tensile stress. The variations of the internal parameter Δ and of bond lengths may be found in [8], [16].

The values of the theoretical tensile strength of $MoSi_2$ and WSi_2 are presented in Table 1 which also shows all ab initio values of the theoretical tensile strength calculated up to now. All these calculations included relaxations of perpendicular dimensions of the crystal and, if applicable, of internal structure parameters. Most of these values correspond to the inflexion point at the strain dependence of total energy. The σ_{th} value of about 29 GPa for [001] orientation of tungsten (Table 1) is in a very good agreement with the experimental result of (24.7±3.6) GPa obtained for a whisker grown along the [110] axis [2]. Our theoretical strength for [110] loading is, however, too high (54.3 GPa). This suggests that the material probably breaks down due to some other instability before reaching the inflexion point and, therefore, the theoretical tensile strength will be lower than that given in Table 1. It is nearly certain that this is also the case of Cu where the experimental ideal strengths are about an order of magnitude lower than the calculated results [4], [17]. Semiempirical calculations [18] suggest indeed that, for the [001] direction, the tetragonal shear modulus becomes zero far before reaching the inflexion point. It may be expected that similar instabilities will occur in the [110] and [111] orientations as well. This will be a subject of further investigations.

Theoretical shear strengths under fully relaxed conditions were calculated for Al, Cu, W and Mo (the results are summarized in [10]). Krenn et al. [19] performed an analysis of tensile and shear strengths in bcc metals. They argue that there are nearly identical shear strengths on the shear systems $\langle 111\rangle\{110\}$, $\langle 111\rangle\{112\}$, and $\langle 111\rangle\{123\}$. This is in agreement with the ab initio values of theoretical shear strengths in W which are within the interval $\langle 17.6; 18.2\rangle$ GPa [9].

Although the values of the measured maximum shear stress in nanoindentation experiments depend, to a certain extent, on the tip radius, it is remarkable how well they sometimes agree with the simple estimate of $G/2\pi$. For example, Bahr et al. [20] report the measured maximum shear stress in W to be 28.6 GPa, whereas $G/2\pi$ equals to 26 GPa. Further examples include Cu, c-BN, Mo_5SiB_2, Ti_3Al, and NiAl [21], where the differences between the measured maximum shear stress and $G/2\pi$ are not very large.

However, the ab initio values of shear strength should be more reliable than $G/2\pi$. Nevertheless, in tungsten, the experimental value of 28.6 GPa does not fit into the interval of $\langle 17.6;\ 18.2\rangle$ GPa found in the calculations. Roundy et al. [9] explain this disagreement by means of triaxiality of the load at yield and by a limited applicability of the Hertz solution for the elastic strain field used in the analysis of the experimental data. Including the effect of non-linearity of stress-strain relation at high strains, they introduce a simple correction of experimental data (multiplication by a factor of $2/\pi = 0.64$), which improves the agreement of experimental and calculated values. Krenn et al. [22] performed a computer simulation including both triaxiality of the load and non-linearity of stress-strain relation, arriving at nearly perfect agreement of experimental and theoretical shear strength in W and Mo.

The calculated or measured values of theoretical (ideal) strength may subsequently serve as input parameters to a quantitative and predictive model, based on the properties of dislocation interactions, that describes the relationship between the yield behaviour and length-scale effects in the nanoscale regime. This approach will complement and enhance the strain gradient models of continuum mechanics that are currently state-of-the-art when dealing with deformation of materials subject to inhomogeneous loads on nano- and microscale. It will contribute to a deeper understanding of the onset of yield in nanoindentation and, in general, of some other aspects of deformation in materials subject to large inhomogeneous loads. This work is in progress.

5 CONCLUSIONS

We have demonstrated that, using the first-principles electronic structure calculations, theoretical tensile and shear strengths of single crystals may reliably be calculated. No adjustable parameters or interatomic potentials are introduced – the calculations are based on fundamental quantum theory in the local density approximation. In this paper, we have shown the results of ab initio simulation of tensile test in $MoSi_2$, reviewed the values of ideal tensile and shear strengths calculated ab initio under fully relaxed conditions up to now and discussed their applicability in explaining of nanoindentation experiments.

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