AB INITIO CALCULATION OF THE IDEAL TENSILE STRENGTH IN COPPER AND NICKEL ALUMINIDE

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Fully self-consistent ab initio electronic structure calculation of the theoretical tensile strength of single-crystalline copper and NiAl loaded uniaxially along several crystallographic directions is performed using the full-potential LAPW method. In copper, the calculated theoretical tensile strengths are about an order of magnitude higher than the measured ones. This is in contrast with a recent similar analysis performed for tungsten where a good agreement with experimental data was attained. This indicates that another instability occurs in the material before the critical tensile stress is reached. In NiAl, the "hard" orientation [001] differs very significantly from the [111] orientation; this anisotropy may be understood in terms of higher-symmetry structures present along some deformation paths.

1. Introduction

Many structural and dynamical properties of solids can be predicted accurately from ab initio (first-principles) electronic structure (ES) calculations, i.e. from fundamental quantum theory (Schrödinger equation). Here the atomic numbers of constituent atoms and, usually, some structural information are employed as the only input data. Such calculations are routinely performed within the framework of density functional theory in which the complicated many-body interaction of all electrons is replaced by an equivalent but simpler problem of a single electron moving in an effective potential. For a given material, the calculated total energies are used to obtain equilibrium lattice parameters, elastic moduli, relative stabilities of competing crystal structures for a given material, energies associated with point and planar defects, alloy heat formations, etc. In addition, we also obtain information about electronic densities of states and charge densities that enables us to attain a deeper insight and learn which aspects of the problem are important.

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NiAl loaded along the [001] and [111] directions, discuss their anisotropy, and compare our findings with the experimental results obtained for copper whiskers.

2. Computational details

The methodology or calculation of the variation of the total energy during the tensile test has been described in detail in [1, 2, 12]. One starts with the calculation of the total energy of unloaded material. Then the crystal is elongated along the loading axis (denoted as axis 3 in the present paper) by a fixed amount ε_3, which is equivalent of applying some tensile stress $\sigma = \sigma_3$. To ensure uniaxial loading, the dimensions of the crystal in the directions perpendicular to the loading axis are relaxed by finding the minimum of the total energy as a function of these dimensions (this yields zero tensile stresses σ_1 and σ_2 along the axes 1 and 2; in elasticity this corresponds to Poisson contraction). Both directions perpendicular to the tensile axis are assumed to be changed by the same amount, ε_1. This procedure is repeated for each value of ε_3. In the case of loading along the [001] axis, the above procedure corresponds to the calculation of the Bain's path.

To obtain reliable total energies for shear deformations, the ES methods using a shape approximation of the crystal potential (e.g. spheroidization, as in the LMTO-ASA, or standard KKR, or APW approaches) are not sufficient [13, 14] and full-potential treatments must be employed. Here we use the full-potential linearized augmented plane wave (FLAPW) code described in detail in [15]. The ES calculations have been performed within the local density approximation using the exchange-correlation potential of Perdew and Wang [16]. For hydrostatic distortion, where the symmetry of the lattice is maintained during the deformation process, shape approximation methods are sufficient [17].

3. Results and discussion

The dependence of the total energy of copper vs. ε_3 for the loading along the crystallographic axes [001], [110] and [111] is shown in Fig. 1. The corresponding values of the tensile stress σ are presented in Fig. 2. The curvatures of the energy curves and the slopes of σ in the neighbourhood of $\varepsilon_3 = 0$ reflect a marked anisotropy of the Young moduli. The inflexion points of the E vs. ε_3 curves correspond to maxima of the applied forces; if some other instability of the material does not occur before reaching the inflexion point, they indicate the theoretical tensile strengths. The maxima of σ in Fig. 2 are very close to the inflexion points of the E vs. ε_3 curves.

The inflexion points on the curves E vs. ε_3 correspond to the violation of the stability condition (with the axis 3 as a loading axis)

$$K_{33}\,(K_{11} + K_{12}) - 2K_{13}^2 > 0, \tag{1}$$

In this paper we focus on the use of ab initio electronic structure calculations to study mechanical stability of metallic materials that are deformed homogeneously under the applied external forces. We simulate an idealized tensile test in a defect--free sample, i.e. without any defects such as dislocations, cracks etc. Thus, the material does not fail at a local weak spot, but due to the fact that the whole lattice becomes unstable at a strain. This instability occurs when the system can lower its total energy by spontaneously undergoing an additional uniform deformation. The values of stress and strain at which such instability occurs may be regarded as defining the theoretical (ideal) tensile strength of the crystal [1, 2]. This represents an upper limit to the mechanical strength under given test conditions and may be approached, for example, in whiskers or dislocation-free thin films. The theoretical strength is an important concept in modern approaches to plasticity and fracture (see e.g. [3]).

Most of the calculations of the ideal strength have been based on empirical potentials adjusted to experimentally measured equilibrium quantities. However, a material close to its theoretical strength limit is in a highly non-equilibrium state and it is not guaranteed that the semiempirical descriptions adapted to the equilibrium state are applicable under those severe conditions.

Ab initio electronic structure calculations are not limited in this way since precise solutions of one-electron Kohn-Sham equation for a solid are obtained for any state of material and the total energy is accurately calculated from fundamental quantum theory. Thus, we obtain reliable results even for highly deformed states. Nevertheless, most of the ES calculations were directed towards analysis of the equilibrium state or to describe small deviations from that state. The equilibrium state corresponds, of course, to the minimum of the total energy. However, the theoretical strength is related to the maximum force which may be applied to the material without compromising its stability. It is usually connected with an inflexion point on the dependence of the total energy on deformation parameters, far from the equilibrium state.

First-principles ES calculations of the ideal strength of materials are rare. To our knowledge, the first paper dealing with the ideal tensile strength from the first principles was that of Esposito et al. [4], using unrelaxed structures of Cu. A decade later, Paxton et al. [5] calculated ideal twin strength for a number of pure metals which is analogous to the ideal tensile strength studied here [6]. Further, several calculations of the properties of some elemental metals and simple intermetallics far from equilibrium have been made, exploring their stability etc., but the corresponding inflexion points have not been interpreted in terms of the strength [7—10]. An ab initio calculation of ideal tensile strength in tungsten has been recently performed in [11].

Here we present ab initio simulations of idealized tensile tests in defect-free single-crystalline copper loaded along the [001], [110] and [111] directions and in

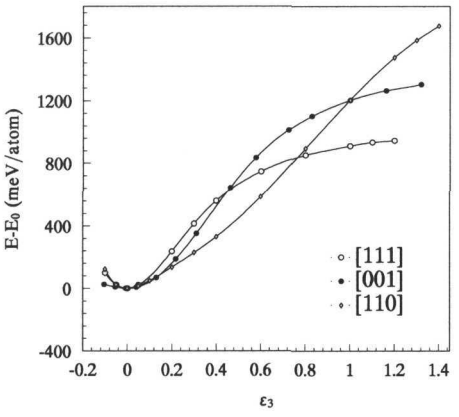

Fig. 1. Total energy, E, per atom vs. ε_3 for the uniaxial deformation of copper loaded along [001], [110] and [111] directions; E_0 is the ground-state energy of the fcc copper.

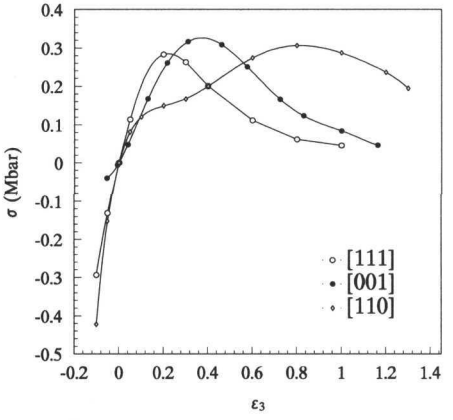

Fig. 2. Applied stress, σ, acting on the face of the face-centered cell perpendicular to the loading axis vs. ε_3 for uniaxial deformation of copper.

where $K_{ij} = \partial^2 E/\partial a_i \partial a_j$ and a_i are the dimensions of a rectangular face-centered (Cu) or body-centered (NiAl) unit cell. This condition may also be expressed via appropriately defined elastic constants [18, 19].

It is seen from Table 1 that the experimental ideal strengths of copper are much lower than the calculated maximum stresses. The maxima of σ correspond to relatively high values of strain, ε_3. Of course, in real samples some residual defects are present and, therefore, one can expect that the experimental values should be somewhat lower than the calculated ones. But in Table 1 we face an order of magnitude differences. Let us note that this situation is very different from that in tungsten, where the experimentally measured ideal strength was very close to the calculated values [11]. This may be related to the fact that when deforming an fcc crystal in uniaxial tension, there are no higher-symmetry structures on the deformation path. As a result, the E vs. ε_3 curves do not have to bend towards symmetry-dictated extrema [7, 14] and the inflexion points appear at very high values of strain and stress. (This is not the case of bcc tungsten in [001] and [111] loading directions [11] or B2 NiAl loaded in the [111] direction, as discussed below.) In the case of copper, therefore, some stability condition may be violated before such an inflexion point is reached. For example, after some uniaxial deformation has been performed, it may be energetically more favorable for the crystal to undergo a transformation $\delta a_1 = -\delta a_2$, if the stability condition

$$K_{11} - K_{12} > 0 \tag{2}$$

Table 1. Tensile stresses of copper subjected to uniaxial loading along the [001], [110] and [111] directions corresponding to inflexion points of the energy E vs. ε_3 and to maxima σ_{max} of the stress vs. ε_3 curves. The calculated values of σ_{max} are compared with experimental ideal strengths σ_{exp}

Direction	ε_3	σ_{max} [Mbar]	σ^a_{exp} [Mbar]
[001]	0.36	0.33	0.0123
[110]	0.79	0.31	0.0138
[111]	0.22	0.29	0.0306

[a] experimental values from Ref. [20] obtained from tensile stress measurement in copper whiskers

is violated, or to change the angle between the crystallographic axes [2, 18]. In addition, imaginary frequency phonon modes may appear in deformed structures before reaching the inflexion point.

Indeed, for the [001] loading direction, there is an indication that the condition (2) is violated before the inflexion point at the E vs. ε_3 curve is reached. Semiempirical calculations based on a Morse-function lattice model of a Cu crystal have shown that $K_{11} = K_{12}$ at $\varepsilon_3 = 0.069$ and $\sigma = 0.07$ Mbar [18], which is somewhat closer to the experimental value of 0.0123 Mbar. It may be expected that similar instabilities will occur for the [110] and [111] orientations, as well. Determination of these instabilities and thus of more realistic values of ideal tensile strength in single-crystalline copper from the first principles will be the subject of future investigations.

The E vs. ε_3 curves and the corresponding σ values for NiAl loaded along the [001] and [111] directions are seen in Figs. 3 and 4. For the loading direction [001], known as the "hard" single crystal orientation, there is no higher-symmetry structure on the deformation path except the ground-state B2 structure [14] and, therefore, no other symmetry-dictated extremum may be expected. The E vs. ε_3 curve increases quite steeply and its inflexion point occurs at relatively high values of strain. For the [111] direction, the B1 (NaCl) structure occurs as a higher-symmetry structure at the deformation path and, therefore, the E vs. ε_3 curve reaches a symmetry-dictated maximum at $\varepsilon_3 \approx 0.7$. The inflexion of the E vs. ε_3 curve (corresponding to the maximum of the applied force and, very closely, to the maximum of the applied stress σ_{max}) occurs at $\varepsilon_3 = 0.21$. The results are summarized in Table 2. As there are, to the best of our knowledge, no NiAl whiskers or other measurements of strength of the defect-free material, we could not compare our results with any experimental values. Again, the stresses corresponding to the

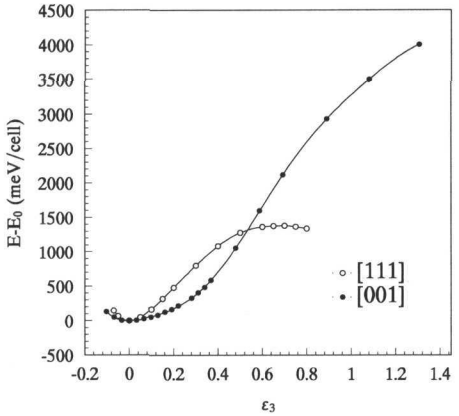

Fig. 3. Total energy, E, per cell vs. ε_3 for the uniaxial deformation of NiAl loaded along [001] and [111] directions; E_0 is the ground-state energy of the B2 NiAl. The maximum of the [111] curve corresponds to the B1 (NaCl) structure.

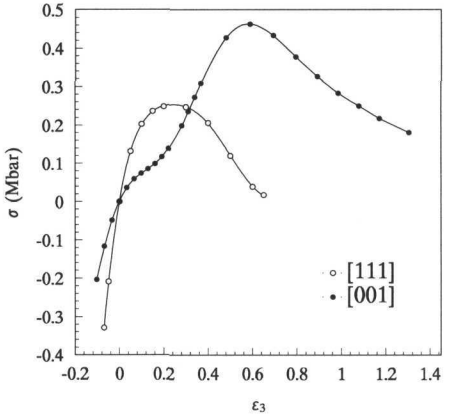

Fig. 4. Applied stress, σ, acting on the face of the body-centered cell perpendicular to the loading axis vs. ε_3 for uniaxial deformation of NiAl.

Table 2. Tensile stresses in NiAl subject to uniaxial loading along [001] and [111] directions corresponding to inflexion points of the energy vs. ε_3 and to maxima σ_{max} of the stress vs. ε_3 curves

Direction	ε_3	σ_{max} (Mbar)
[001]	0.59	0.46
[111]	0.21	0.25

inflexion point would correspond to the theoretical tensile strengths provided no other instability before this inflexion point has been reached. This will be the subject of a future study.

Let us note here that the concept of the "hard" orientation has nothing to do with the behaviour of our ideal tensile curves (Fig. 3) but is connected with the slip behaviour of real (non-ideal) NiAl single crystals containing dislocations and other defects. The primary Burgers vector in NiAl is ⟨001⟩, and if the loading direction is along [001] the ⟨001⟩ dislocations have a zero resolved shear stress and do not move. As a result, deformation occurs primarily by non-⟨001⟩ dislocation processes

which are more difficult. This gives rise to a high yield stress at low temperatures as well as enhanced creep strength at elevated temperatures for [001] orientations compared with the other crystal orientations [21].

4. Conclusions

We have shown that using the first-principles electronic structure calculations, theoretical tensile strength of single crystals may be reliably calculated. No adjustable parameters or interatomic potentials are introduced – the calculation is based on fundamental quantum theory in the local density approximation. In this paper, we analyzed ideal tensile strength of copper and NiAl loaded uniaxially along the main crystallographic directions. In the case of copper, an order of magnitude difference between the theoretical results and available experimental data indicates that some other instabilities occur on the deformation paths before the calculated maximum tensile stresses can be reached. In NiAl, the anisotropy of energy vs. strain curves may be understood in terms of existence or absence of higher-symmetry structures along the deformation paths considered.

The approach presented here may be used to calculate the behavior of various (defect-free) materials under extreme loading conditions. It is especially important for materials for which the empirical interatomic potentials need not be sufficiently reliable far from equilibrium, such as for various intermetallic compounds.

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