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Atomistic Studies of Deformation and Fracture in Materials with Mixed Metallic and Covalent Bonding

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Poster presented at *The Search for a Sustainable Energy Future: Challenges for Basic Research*, A Mini-Symposium sponsored by the Energy Working Group at Penn, March 9, 2007.

Atomistic Studies of Deformation and Fracture in Materials with Mixed Metallic and Covalent Bonding

Abstract
Materials with high melting temperatures (over 2000°C) tend to be brittle at ambient and even relatively high temperatures. High melting temperatures originate in strong interatomic bonding arising from formation of *dd* or *dp* bonds that also affect and/or control crystal structures and properties of extended defects, such as dislocations, grain boundaries. These, in turn, govern plastic deformation and fracture.
General goal: Establish relationship between electronic structure and mechanical behavior

Comments
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MOTIVATION OF RESEARCH

Materials with high melting temperatures (over 2000°C) tend to be brittle at ambient and even relatively high temperatures.

High melting temperatures originate in strong interatomic bonding arising from formation of *dd* or *dp* bonds that also affect and/or control crystal structures and properties of extended defects, such as dislocations, grain boundaries. These, in turn, govern plastic deformation and fracture.

General goal: Establish relationship between electronic structure and mechanical behavior

Materials studied

BCC transition metals: Mo, W, Nb, Ta, V

FCC transition metal: Iridium

Intermetallic compounds: $MoSi_2$, Mo_5Si_3, Ir_3Nb, Ir_3Zr

BOND-ORDER POTENTIALS

Semi-empirical tight-binding based scheme that describes physically correctly angular dependencies of covalent bonds

Unlike commonly used tight-binding, bond-order potentials are a real-space method that includes both covalent d-d and d-p bonds and nearly free s and p electrons

$$E_{coh} = E_{pair} + E_{bond} + E_{env}$$

Electrostatic and overlap ion core repulsion represented by pair potential

Fitting: Lattice constants, elastic moduli, relative stability

Bond energy arising from formation of the valence band by *d* and *p* electrons

Contains dependence on bond angles

Fitting: Radial dependence of bond integrals and band filling to ab initio DFT based calculations

Environmentally dependent repulsive term arising from repulsion experienced by the *sp*-electrons squeezed into the interstitial volumes by the strong cohesion provided by the *d*-electrons

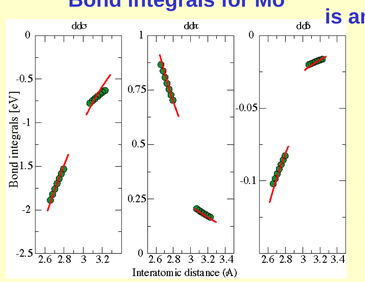
Fitting: Cauchy pressures

$$E_{\mathrm{bond}} = \sum_{i,\,j\neq i}\sum_{\alpha,\beta}\Theta_{j\beta,i\alpha}H_{i\alpha,j\beta}$$

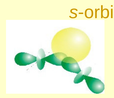
BOND ORDER $\Theta_{j\beta,i\alpha}$ is evaluated for a given Hamiltonian in real space using Lanczos recursion method and the many-body expansion for the bond-order

BOND INTEGRALS $H_{i\alpha,j\beta}$: Two-center approximation with usual Slater-Koster angular dependence. Fitted to reproduce results of ab initio calculations

Bond integrals for Mo



Environmental screening is an essential ingredient



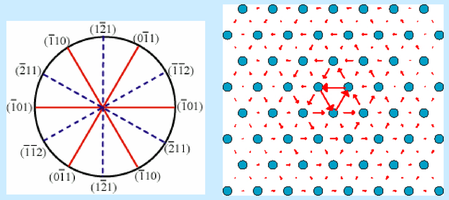
d-bond is screened by the valence *s*-orbitals of a neighboring atom.

This bond can be either weakened or strengthened.

DISLOCATION CORE STRUCTURE AND DISLOCATION GLIDE IN MOLYBDENUM AND TUNGSTEN

CORE STRUCTURE OF THE 1/2[111] SCREW DISLOCATION IN MOLYBDENUM

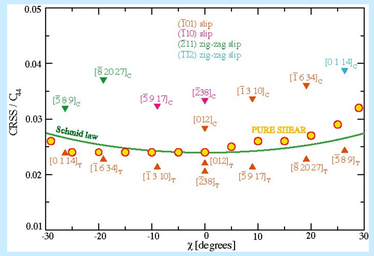
Bond-order potential and ab-initio DFT-based calculations of Woodward and Rao



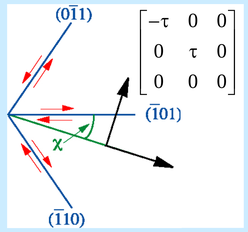
MOLYBDENUM

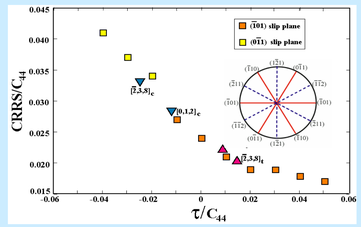
Tension and compression compared with corresponding pure shear in the direction of the Burgers vector

If only the shear stress parallel to the Burgers vector controled glide the CRSS would be the same for pure shear, tension and compression



EFFECT OF SHEAR STRESSES PERPENDICULAR TO THE BURGERS VECTOR

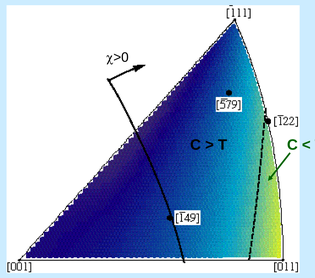




COMPRESSION **TENSION**

Tension-compression asymmetry based on the theory

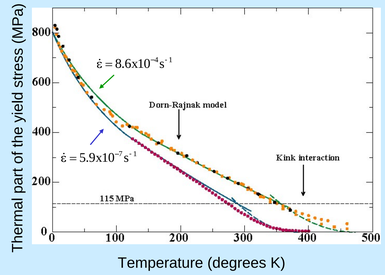
Temperature dependence introduced $\dot{\varepsilon} = \dot{\varepsilon}_0 \exp(-\Delta H/kT)$

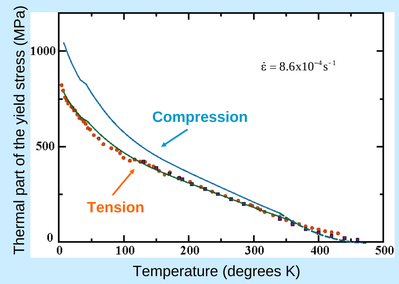


FULL AGREEMENT WITH EXPERIMENTS

Hollang, Hommel and Seeger, *Phys. Stat. Sol.* 160, 329, 1997

Hollang and Seeger, *Materials Transactions, JIM* 40, 141, 2000

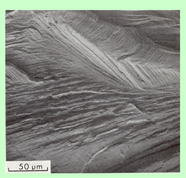




IRIDIUM

Transgranular cleavage up to 500°C

Cleavage is preceded by extensive neck-free plastic deformation

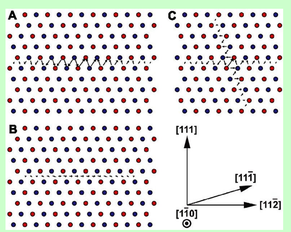


Fracture surface of Ir single crystal

Two core configurations of the screw 1/2<110> dislocation

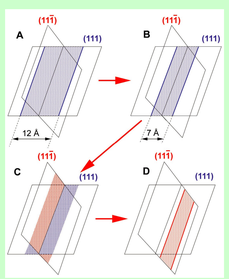
Screw component

Edge component



Spreading into Two {111} planes

Metastable structure unstable in other fcc metals



ATHERMAL CROSS-SLIP IN FCC IRIDIUM

Non-planar core serves as an intermediary for athermal cross slip along long segments of screw dislocations

Unusually high density of Frank-Read sources generated by double cross-slip. These sources are distributed homogeneously throughout the sample.

Rapid increase of dislocation density with strain but no strain localization and no necking occurs.

Unusually rapid work-hardening limiting relaxation of stress concentrations.

Fracture results as a consequence of hardening.

FUTURE RESEARCH

SHORT TERM

Properties of special and general grain boundaries in iridium and comparison with other fcc metals to clarify the propensity for intergranular brittleness in polycrystalline iridium.

Studies of stacking faults and dislocations in molybdenum silicides: $MoSi_2$ (tetragonal $C11_b$, hexagonal C40, orthorhombic C54) and Mo_5Si_3 ($D8_m$).

LONG TERM

Transition bcc metals (Mo, W, Ta, Nb, V)

Establish general rules of the dependence of their plastic behavior on electronic structure, in particular filling of the *d*-band. Investigate effects of point defects, in particular interstitials produced by irradiation, impurities and alloying elements on dislocation glide and thus deformation and fracture of these materials.

Ferromagnetic iron

Development and testing of BOP that includes ferromagnetism. Using this BOP to investigate dislocations, interstitials, grain boundaries, alloying elements and their interactions in bcc iron with emphasis on effects of ferromagnetism and comparison with non-magnetic bcc metals.