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//Signature//
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//Signature//
ROLLIE DUTTON

//Signature//
GERALD J. PETRAK

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# The Chemistry of Deformation: How Solutes Soften Pure Metals

Dallas R. Trinkle and Christopher Woodward

## Abstract

Solutes have been added to strengthen elemental metals, generating usable materials for millennia; in the 1960s, solutes were found to also soften metals. Despite the empirical correlation between the "electron number" of the solute and change in strength of the material to which it is added, the mechanism responsible for softening is poorly understood. Using state-of-the-art quantum-mechanical methods, we studied the direct interaction of transition-metal solutes with dislocations in molybdenum. The interaction increases dramatically with increasing electron number and strongly influences the mechanisms responsible for plasticity in these materials. Our quantitative model explains solution softening of metals by using changes in energy and stress scales of plasticity from solutes.
The Chemistry of Deformation: How Solute Soften Pure Metals

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Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright Patterson Air Force Base, Dayton, OH 45433–7817, USA.

*To whom correspondence should be addressed. E-mail: dallas.trinkle@wpafb.af.mil

Solute chemistry affects double-kink nucleation and kink migration to produce both softening and hardening.

Our model predicts the following experimental data for a Mo-Re alloy, which is the classic solid-solution softening system. Below a temperature of 350 K, Mo-Re is softer than pure Mo for small Re concentrations. Softening continues up to 16 atomic %, where the alloy becomes harder than pure Mo. The maximum softening occurs at 8 atomic % at 77 K, and the maximum softening concentration decreases as temperature is increased. Thus, a given solute concentration can soften an alloy at one temperature and harden at another; and at a given temperature, increasing solute concentration can first soften and then harden the alloy at higher concentrations. Similar features appear for other 5d-row solutes with higher d electron numbers (Os, Ir, Pt), but the maximum softening occurs at much smaller concentrations. Metals with lower d electron numbers (Hf, Ta) harden for all concentrations and temperatures. The goal of alloy design for Mo alloys is to soften the low-temperature behavior, reducing the risk of fracture.

We show here that the prediction of strength with changing alloy concentration and temperature for Mo alloys requires calculation of the direct solute-dislocation interaction and modeling of those effects on plasticity. State-of-the-art quantum-mechanical electronic structure methods (11–13) with special dislocation boundary conditions (14) calculate the interaction energy between a single straight dislocation and a solute and the change in the resistance to the motion of the dislocation. These data enter a solid-solution softening model of plasticity by changing energy and stress scales of double-kink nucleation and kink-migration enthalpy barriers. The effect of random clustering (where more than one solute atom interacts with a kink) is crucial in modeling changes in kink migration above the dilute limit. Also, the bonding environment near a dislocation is distinct from the bulk, producing the unique chemistry of deformation. Our model quantitatively predicts strength measurements of Mo-Re and matches hardness measurements of Mo-Pt, two systems with dramatically different softening and hardening behavior. The details of the computational methods are included in (15).

As a starting point, Fig. 1 compares the nearest-neighbor geometry of bulk bcc Mo to that of a 1/2[111] screw-character dislocation. Viewed along the [111] direction, the bulk cubic structure forms a triangular lattice of atomic rows; the triangles can be viewed as spirals of alternating chirality. To form a dislocation, the chirality of a triangle is changed by displacing each row in the triangle by different amounts.
along the [111] direction (out of the page). The change of one triangle affects its neighbors, with local displacements dying off as the inverse distance from the dislocation center. Although this geometry maintains the nearest-neighbor coordination of a bcc lattice throughout, the bond states near the dislocation are distinctly different from those in bulk Mo.

Our solid-solution model is based on thermally activated motion of dislocations by double-kink nucleation and kink migration (3, 4, 15–17). Double-kink nucleation is the rate-limiting process at low temperatures, and kink migration is rate-limiting at higher temperatures. Stress \( \sigma \) (resisting force per area) is measured against applied strain \( \varepsilon \) (elongation) at a constant strain rate \( \dot{\varepsilon} \). The Orowan equation (18) connects \( \dot{\varepsilon} \) to the motion of dislocations at yield \( \dot{\varepsilon} = b \rho_m \tau_\text{ad}(\sigma) \), where \( b \) is the Burgers vector, \( \rho_m \) is the mobile dislocation density per area, and \( \tau_\text{ad} \) is the average dislocation velocity with stress. The average dislocation velocity is the distance a dislocation moves because of a kink (by geometry, 0.94b) divided by the average time to make stable double kinks and migrate the entire dislocation. Thus,

\[
\dot{\varepsilon} = 0.94b^3 \rho_m \left[ (\text{nucleation rate})^{-1} + (\text{migration rate})^{-1} \right]^{-1}
\]

where the rates are thermal activation rates, (attempt frequency) \( \times \exp(-\text{enthalpy barrier}/(k_B T)) \), where \( k_B \) is Boltzmann’s constant and \( T \) is temperature, and the enthalpy barriers decrease with stress. This equation is solved numerically for the yield stress at a given strain rate, temperature, and solute content. The enthalpy barriers have an energy and a stress scale, and solutes affect both scales.

The stress scales are connected to the Peierls stress, which is the critical applied stress where a dislocation moves, producing plastic deformation and relieving stress. The Peierls stress of pure Mo at 0 K has been previously calculated by applying a stress and monitoring the motion of atomic rows of the dislocation (14). A screw-character dislocation moves to the right (i.e., the \([112]\) direction) by displacing atomic rows along \([111]\) to change chirality (Fig. 1). The atomic row at the bottom right of the core upward-pointing triangle moves out of the page by \(1/6[111]\) to change its spiral from counter-clockwise (CCW) back to clockwise (CW), and the remaining two rows of the core upward-pointing triangle to the right change chirality from CW to CCW. Thus, the Peierls stress is correlated to the stiffness for moving a single atomic row in the dislocation core, and changes in this stiffness from solutes change the stress scale in the enthalpy barriers in our solid-solution model.

Different solutes change the energy to displace an atomic row in the core of a \(1/2[111]\) screw-character dislocation (Fig. 2). Solutes having lower d electron numbers (Hf and Ta) increase the stiffness (the curvature at zero displacement, table S1) (15), which we infer strengthens the Mo alloy, whereas those having higher d electron numbers (Re, Os, and Ir) decrease the stiffness, leading to softening. The exception to this trend is Pt, which shows a small change in stiffness relative to pure Mo. However, Mo-Pt is known experimentally to be softer than pure Mo for small Pt concentrations. The inability of the change in stiffness (which we define as the Peierls misfit) to explain softening implies an additional solute-dislocation interaction is responsible.

The energy scales are connected to the direct solute-dislocation core interaction (Fig. 3). The energy profile is defined relative to a widely separated dislocation-solute pair, and \( E_\text{int} \) is defined as the maximum interaction energy (table S2 shows all solutes) (15). Re shows a weak, short-range interaction, but it has a larger Peierls misfit than does Pt. The weaker interaction and larger Peierls misfit of Re produces a small softening effect; but these effects increase at high concentrations, where multiple solutes interact with the dislocation. The large attractive interaction of Pt produces a substantial change in the energy scale and strong initial softening, but leads quickly to hardening at higher concentrations.

Solutes modify double-kink nucleation by changing the nucleation barrier along
the entire length of dislocation and by locally modifying the barrier at solute sites. Solute changes the stiffness for dislocation motion, producing a global change in the stress scale for double-kink nucleation. Locally, an average c possible nucleation sites are occupied by a solute, whereas (1 – c) are not. The change in the nucleation energy scale from the solute is the solute-dislocation interaction energy $E_{\text{int}}$. Attractive solute interactions and negative Peierls misfits (Re, Os, Ir, and Pt) increase nucleation of double kinks and provide more favorable nucleation sites, which leads to softening at low temperatures.

The rate-limiting step in kink migration is the time to overcome the largest solute cluster on the dislocation line (16). The size of the largest clustered encountered (assuming a random distribution of solutes) is $2\sqrt{c}$, where the prefactor depends weakly on the dislocation density and kink width (fig. S2) (15). This gives a cluster size of 1 solute for $c = 0.16$ atomic %, and 8 solutes for $c = 10$ atomic %. Kinks in pure bcc metals are very mobile, so any solute interaction impedes the motion of kinks. Thus, we write the solute barrier energy scale as $2\sqrt{c(E_{\text{int}})}$, slowing kink migration and producing hardening at higher temperatures and concentrations.

The predicted strength for Mo-Re and Mo-Pt with changing solute concentration for several temperatures compared with experiment is shown in Fig. 4. The predicted value of flow stress and hardness for pure Mo was fit to the experimental data (figs. S1 and S3) (15). The attractive interaction of Re leads to softening for low solute concentrations because of increased double-kink nucleation. As the concentration increases, there is a crossover to kink-migration–limited flow stress, which hardens with additional solute. The crossover happens at lower concentrations for higher temperatures, because kink migration becomes more important than double-kink nucleation at higher temperatures. Qualitatively, the same softening behavior is seen for Pt as for Re: softening initially for low concentrations and crossing over to hardening at higher concentrations. The crossover concentration decreases with increasing temperature. However, the concentration scales differ by an order of magnitude. Even though Mo-Re and Mo-Pt differ dramatically in range of concentrations and temperatures. Our model for solid-solution softening and the computation of interaction parameters requires careful treatment of the dislocation geometry and chemistry, as well as the statistics of clustering. The geometry and the dislocation core creates a bonding environment that is distinct from the bulk. In fact, using classical bulk approximations can produce erroneous results (hardening versus softening) or mechanisms (interaction energy versus Peierls misfit). Statistical modeling of the solute distribution is needed to produce the clustering effect important for the hardening of Mo-Re at high solute concentrations. Without clustering, the Re-dislocation interaction is too small to produce hardening effects.

Our model and calculation of the interaction parameters explains the softening and hardening of Mo by Re and Pt over a range of concentrations and temperatures. Direct solute-induced changes to energy and stress scales of double-kink nucleation and kink migration are sufficient, when coupled with the correct interaction parameters, to quantitatively predict experimental observations. The calculation of the interaction uncovers underlying electronic effects that we are now able to access by using current tools and computational resources. Our approach connects ab initio atomic-level interactions and mesoscopic mechanical behavior to explain the chemistry of deformation. Such an approach can also be applied to solute-induced softening in other technologically important materials, such as Fe and Nb.

**References and Notes**

1. G. Agricola, De Re Metallica (1556) [H. Hoover, Transl. (Dover, New York, 1950)].
15. Materials and methods are available as supporting material on Science Online.
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**Supporting Online Material**

www.sciencemag.org/cgi/content/full/310/5754/1665/DC1

Materials and Methods

Figs. S1 to S3

Tables S1 and S2

References and Notes

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