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THE CHEMISTRY OF DEFORMATION: HOW SOLUTES SOFTEN PURE METALS

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14. 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.

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The Chemistry of Deformation: How Solutes Soften Pure Metals

Dallas R. Trinkle* and Christopher Woodward

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 the 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.

Solutes have played a key role in producing useful materials from pure metals over the past millennia, driving technological advances in civilization—from the Bronze Age to the Iron Age to the industrial revolution. For most of human history, alloying was used to increase the strength of metals (*1*). Four decades ago, a wealth of evidence showed that for some body-centered cubic (bcc) metals, solutes could decrease material strength (*2*). This effect, known as solid-solution softening, was observed as a reduction in the stress at which a material begins to deform irreversibly (yield stress) or as a reduction in the material's ability to resist indentation (hardness). Softening is important for producing viable materials: The bcc refractory metals (Nb, W, Ta, and Mo) offer a possible new class of high-temperature materials for components used in turbine engines or nuclear power plants, but the metals have poor low-temperature behavior in elemental form. As the temperature decreases from 15% of the melting temperature (above room temperature for refractory metals) down to absolute zero, strength increases rapidly. This high strength is undesirable, because it is linked with an increase in fracture and low malleability, ultimately limiting the use of these materials as critical structural components. A classical metallurgical practice is to reduce this risk by incorporating solid-solutions or by introducing new softer phases. Models have only succeeded in qualitatively explaining the possibility of low-temperature softening (*3–5*) or in finding empirical correlations to deduce scaling trends (*6*). Moving beyond these empirical techniques requires a combination of chemistry, materials physics, and large-scale computation to investigate how solute chemistry changes deformation: the "chemistry of deformation."

Irreversible plastic deformation of metals is controlled by dislocation defects, and solute-induced softening is controlled by interactions of solutes and dislocations. Dislocations are topological line defects that move at stresses below the stress required to irreversibly deform a dislocation-free crystal (*7*). In bcc metals, low-temperature plastic deformation is controlled by moving straight screw-character dislocations. A dislocation line moves perpendicular to its length by nucleating a pair of opposite-directed "kinks." These migrate away from each other along the dislocation, moving the dislocation line forward to the next lattice site like the locomotion of a snake. Solute chemistry affects double-kink nucleation and kink migration to produce both softening and hardening.

Our model explains 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 (*8*). 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 (*9*). 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 (*10–13*) 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

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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.

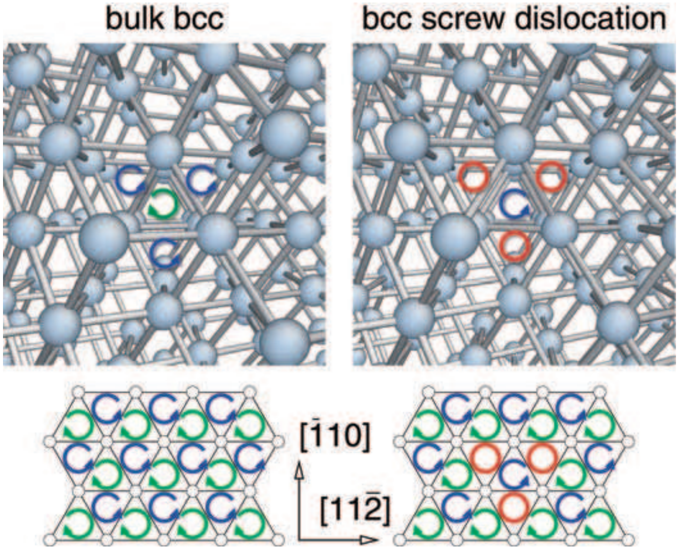

Fig. 1. Atomic nearest-neighbor geometry of a bcc 1/2[111] screw-character dislocation in Mo extending out of the page (**right**) compared with bulk bcc Mo (**left**). A bcc crystal can be viewed as atomic rows coming out of the page arranged in a triangular lattice. The upward-pointing triangles of three atomic rows spiral out of the page with clockwise chirality (CW arrow) and with counter-clockwise chirality (CCW arrow) for downward-pointing triangles. CW spirals must share edges with CCW spirals and vice versa. A screw-character dislocation is formed by changing chirality of one upward-pointing triangle. The three neighboring, downward-pointing triangle spirals flatten in the plane, removing any chirality (marked as open circles). These changes come from displacements of atomic rows out of the page. The four highly modified triangles form the "core" of the dislocation. The remaining triangles keep their initial chirality, becoming more bulklike further from the core. This figure was produced using ATOMEYE (*19*).

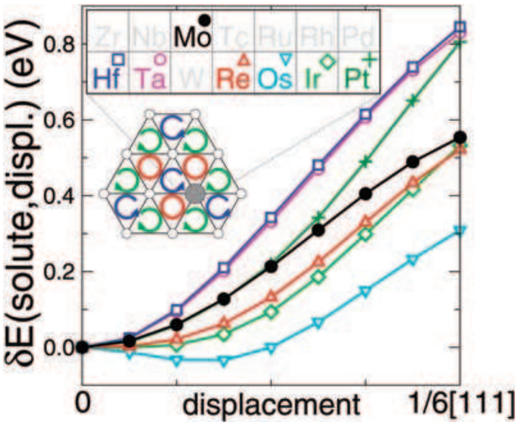

Fig. 2. The change in energy from displacement of an atomic row in the core of a Mo dislocation for different solutes substituted into that row. The inset dislocation core schematic identifies the displaced row in gray. The solid circles indicate the energy for a row of pure Mo; the remaining curves give the energy for a row in the core containing a solute atom. Energies are relative to the relaxed core with the respective solute. The curvature at zero displacement is the stiffness for moving a row in the dislocation core; differences in stiffness change the Peierls stress.

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 σ (resisting force per area) is measured against applied strain ε (elongation) at a constant strain rate $\dot{\varepsilon}$. The Orowan equation (*18*) connects $\dot{\varepsilon}$ to the motion of dislocations at yield $\dot{\varepsilon} = b\rho_m\bar{v}_{\mathrm{disl}}(\sigma)$, where b is the Burgers vector length, ρ_m is the mobile dislocation density per area, and $\bar{v}_{\mathrm{disl}}$ 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,

$$\dot{\varepsilon} = 0.94b^2\rho_m \times\left[(\text{nucleation rate})^{-1} + (\text{migration rate})^{-1}\right]^{-1}$$

where the rates are thermal activation rates, (attempt frequency) × exp[−(enthalpy barrier)/(k_BT)], 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 [11$\bar{2}$] 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 new 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_{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

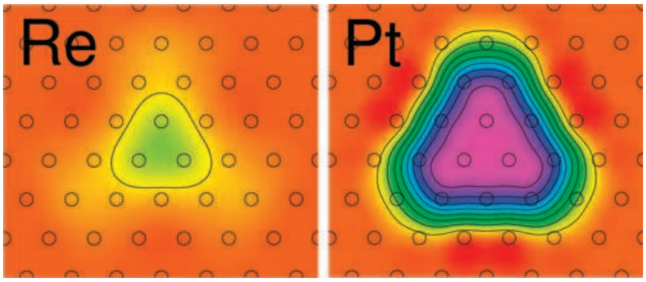

Fig. 3. Solute-dislocation interaction-energy profile for Re (**left**) and Pt (**right**) in Mo. The contours are at 0.1-eV intervals, and the interaction is attractive for all sites. Each circle is a possible lattice site for a solute atom in an atomic row; the dislocation is located in the center of the profile. The Pt dislocation interaction is stronger and has a longer range than Re. The interaction energy E_{int} is the maximum value in the profile.

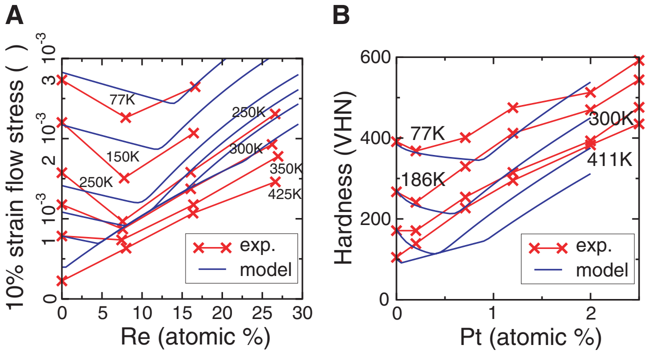

Fig. 4. Predicted strength for Mo-Re and Mo-Pt as a function of solute concentration for different temperatures, compared with experiments. (**A**) Flow stress at 10% strain for Mo-Re and experiments (exp.) of (*8*). The flow stress is scaled to the shear modulus μ = 139 GPa. (**B**) Vickers hardness number (VHN) for Mo-Pt and experiments of (*9*).

the entire length of dislocation and by locally modifying the barrier at solute sites. Solutes change 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_{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 cluster encountered (assuming a random distribution of solutes) is $25\sqrt{c}$, 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 $25\sqrt{c|E_{\mathrm{int}}|}$, 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 scale, a single model can capture the key physics of both systems.

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 of 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.

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