# Electronic Origin of Solid Solution Softening in bcc Molybdenum Alloys

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The intrinsic mechanism of solid solution softening in bcc molybdenum alloys due to $5d$ transition metal additions is investigated on the basis of *ab initio* electronic-structure calculations that model the effect of alloying elements on the generalized stacking fault (GSF) energies. We demonstrate that additions with an excess of electrons (Re, Os, Ir, and Pt) lead to a decrease in the GSF energy and those with a lack of electrons (Hf and Ta) to its sharp increase. Using the generalized Peierls-Nabarro model for a nonplanar core, we associate the local reduction of the GSF energy with an enhancement of double kink nucleation and an increase of the dislocation mobility, and we reveal the electronic reasons for the observed dependence of the solution softening on the atomic number of the addition.

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The addition of elements which improve the room temperature strength and high temperature creep resistance of materials [1,2] plays an important role in alloy design. For solute concentrations below the solubility limit, solid solution hardening (SSH) is the main reason for the increase in the strength of alloys. In some cases, besides the SSH effect the alloying can lead to the opposite phenomenon—solid solution softening (SSS)—in which the hardness decreases with additions. The SSS effect was well studied experimentally in bcc transition metal alloys [3–7] and also observed in intermetallic alloys [8] and in a ceramic spinel [9]. For the refractory VIA group bcc metals (Cr, Mo, and W), the SSS phenomenon attracts considerable attention as a possible way to improve their low temperature ductility (the so-called "rhenium" ductilizing effect [10]).

Solution softening is suggested to originate from the increase of dislocation mobility due to additions and its mechanisms may be associated with intrinsic or extrinsic factors [3,4]. In the latter case, the substitutional atoms exert an indirect influence on the dislocation mobility due to the "trapping" of the interstitial impurities (scavenging mechanism) diminishing impurity segregation on dislocations and grain boundaries. Here we focus on the intrinsic SSS mechanism connected with the direct solute-dislocation interaction which can lead to an increase of the dislocation mobility. In crystals with high Peierls relief (such as bcc transition metals), dislocation mobility is controlled by kink nucleation and propagation processes. It is commonly accepted that the intrinsic solution softening results from the enhanced double kink nucleation at point defects [4,11–13]. However, the microscopic mechanism of this phenomenon still remains a matter of discussion (see a recently published review, Ref. [14]).

Despite recent developments of powerful atomistic simulation techniques, the investigation of impurity-dislocation interactions is still a difficult problem for theoretical materials science due to the involvement of essentially different space scales—microscopic (for atoms in the dislocation core) and macroscopic (for the long-range elastic fields). As a result, current approaches have still been mostly limited to Fleischer's continuum elasticity scheme where the hardening or softening effects are described in terms of the size and shear moduli mismatch between solute and matrix atoms [1,13]. The experimental results for molybdenum alloys [4,15], however, do not support this point of view. In particular, the changes in hardening rate, $dH/dc$, for Mo alloys correlate with atomic radii differences only for W, Ta, and Hf leading to SSH and not for Pt, Ir, Os, and Re, which are softeners for low addition concentrations and low temperatures. Moreover, as shown in Ref. [15], for binary and ternary Mo alloys there is a strong correlation between the softening rates and the number of extra conduction electrons brought by the solute elements. These results indicate the importance of the "chemical" mechanism of impurity-dislocation interactions [1,16,17] in the SSS problem. However, it is not clear why SSS was observed for some additions and not for others, and what the reasons are for the variation in initial hardening rates in binary molybdenum alloys with $5d$ transition metals (TM).

Recently, a new insight into this phenomenon was stimulated by the finding [8,9,18] that solution softening in $MoSi_2$ alloys and $MgO\text{-}Al_2O_4$ spinel correlates with the decrease in stacking fault energy—one of the key parameters which control the dislocation structure. The decrease in the local value of the stacking fault energy near the solute atom was assumed to change the dislocation structure and to enhance kink nucleation. This model made it possible to explain the observable trends in SSS for a number of alloys with coplanar dissociated dislocations [18]. In bcc metals, however, the plastic deformation is realized by the motion of screw dislocations with a complex starlike nonplanar core [19–22], and thus the approach formulated in Ref. [18] cannot be applied directly in this case.

Here, we present an investigation of the microscopic mechanisms of SSS in binary Mo alloys on the basis of first-principles total energy calculations. We show that the effect of solute atoms on dislocation structure and double kink nucleation can be understood based on the generalized stacking fault (GSF) energy—a universal parameter which allows the joining of the electronic and dislocation properties. Using the generalized Peierls-Nabarro (PN) model for nonplanar cores, we demonstrate that the variations in SSS with the solute atomic number can be explained by the lowering of the energy barrier for kink nucleation due to changes in the GSF energy. Our results reveal the electronic reasons for observable correlation between the magnitude of solid solution softening and the number of solute electrons in Mo binary alloys with $5d$ TM additions.

The GSF energy was calculated as a total energy variation, $\Phi(\mathbf{u})$, under the rigid shift of one part of the crystal relative to another at a fault vector $\mathbf{u}$ in the $\{110\}$ plane, which is the preferable slip plane for the low temperatures where SSS takes place [5,23]. The total energy calculations were carried out by the first-principles full-potential linear muffin-tin orbital (FLMTO) method [24] with the generalized gradient approximation for the exchange-correlation potential [25]. We used the triclinic symmetry with variable vector $\mathbf{c}$ along the fault displacement for a supercell consisting of six $\{110\}$ layers with two atoms per layer. The alloying effect was modeled by substituting one of two Mo atoms at the slip plane in the supercell, which corresponds to an average solute concentration of 8 at. %. The consideration of a high concentration allows one to reproduce the maximum changes in the GSF energy due to solutes that correspond to the "local" approximation for the solute-dislocation interaction used in Ref. [18] for explaining solution softening. The atom relaxation may reduce the stacking fault energies by over 10% [26–28], and thus we took into account the relaxation effects between the innermost two sliding layers for each displacement.

The relaxed GSF energies per unit area for sliding along $\langle 111\rangle$ (parallel to the Burgers vector) are shown in Fig. 1 for bcc Mo and Mo alloys. The reduction of the GSF energy due to atomic relaxation was found to be 18%, 8%, 3.6%, and 3% for Mo-Hf, Mo-Ta, unalloyed Mo, and Mo-Re, respectively. The unstable stacking fault energy, $\gamma_{\mathrm{us}}$ (corresponding to the maximum of the GSF energies in Fig. 1) for unalloyed Mo is close to the result of the pseudopotential density functional theory calculation [28] and larger than that obtained by the bond-order potential method [29], indicating that the last method may significantly underestimate the stacking fault energies for these systems.

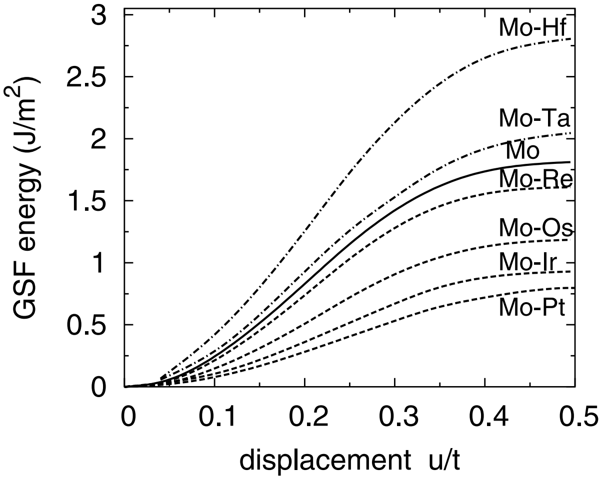

FIG. 1. GSF energies for Mo and Mo alloys for $\langle 111\rangle\{110\}$ shear. Displacement is normalized by the magnitude of the Burgers vector $1/2\langle 111\rangle$.

The value of $\gamma_{\mathrm{us}}$ is found to decrease monotonically with the atomic number of the solute atoms (cf. Table I). The additions that reduce the electron concentration (Ta and Hf), as well as an isoelectonic one (W), lead to the increase in GSF energy and the additions with excess electrons (Re, Os, Ir, and Pt) lower its value. The changes in the GSF energy obtained for the row of $5d$ TM solutes strongly correlate with the experimentally observed lowering of the initial hardening rate [15] (i.e., $dH/dc$ for concentration $c$ approaching zero) at 77 K (Table I). Thus, the calculated results point out that the SSS-SSH mechanism in Mo alloys may be connected with the decrease in GSF energy, similar to that established for fcc-based alloys [8,9].

To make clear the relation between the chemical bonding and the GSF energies characterizing the lattice resistance to $\langle 111\rangle\{110\}$ shear deformation, we analyzed the changes in the orbital occupations for Mo binary alloys. For the bcc structure, the $t_{2g}$ and $e_g$ orbitals are responsible for the directional bond formation between the nearest neighbor (nn) atoms (along $\langle 111\rangle$) and second (next nearest) neighbors (nnn) (along $\langle 100\rangle$), respectively. Hence, the $t_{2g}/e_g$ orbital occupation ratio shows the local bonding anisotropy. This ratio decreases for Re, Os, Ir, and Pt additions (mostly due to weakening of the nn bonds) and does not change for Hf, Ta, and W (cf. Table I). Further, we

TABLE I. The ratio of unstable stacking fault energies $\gamma_{\mathrm{us}}/\gamma_{\mathrm{us}}^0$ (where $\gamma_{\mathrm{us}}^0$ corresponds to unalloyed Mo), the ratio of the $t_{2g}/e_g$ occupations for addition atoms, the ratio of ionic radii $R_i/R_{\mathrm{Mo}}$, and the initial hardening rate [15], $dH/dc$, for binary Mo alloys (where $H$ is VHN hardness).

| | Hf | Ta | W | Re | Os | Ir | Pt |
|---|---|---|---|---|---|---|---|
| $\gamma_{\mathrm{us}}/\gamma_{\mathrm{us}}^0$ | 1.55 | 1.13 | 1.06 | 0.89 | 0.66 | 0.51 | 0.40 |
| $t_{2g}/e_g$ | 1.86 | 1.85 | 1.86 | 1.81 | 1.73 | 1.58 | 1.41 |
| $R_i/R_{\mathrm{Mo}}$ | 1.13 | 1.05 | 1.01 | 0.99 | 0.96 | 0.97 | 0.99 |
| $10^2 dH/dc$ | 10 | 5 | 0 | $-5$ | $-35$ | $-70$ | $-120$ |

also found that both the $t_{2g}/e_g$ ratio and the $t_{2g}$ occupancy gradually decrease for Mo atoms nearest to the addition in alloys with the SSS effect and increase when hardening occurs. Thus, the local changes in the occupation anisotropy correlate with the GSF energy and point out that the weakening or strengthening of the nn bonds relative to nnn near the solute atom can make the $\langle 111\rangle$ shear resistance easier or harder.

The calculated trends in the GSF energies point to the electronic nature of solution softening in Mo alloys. However, this conclusion is not evident because there is no simple relation between the GSF energy and kink formation in bcc metals, where the screw dislocations with noncoplanar core structure dominate at low temperatures. To estimate the changes in the double kink nucleation energy, we use the generalized PN model for a nonplanar dislocation core [30,31] which provides a description of the kink formation in good agreement with experiment [32]. In the framework of the PN approach, the magnitude of the barrier is determined by the energy difference between planar (twofold) and nonplanar (threefold) screw dislocation structures [32], $\Delta E_{2-3} = E_2 - E_3$. For sinusoidal restoring forces, $F = d\Phi(u)/du = \tau \sin(2\pi u/b)$, which are a good approximation to the calculated GSF curves (Fig. 1), the dislocation energy can be represented as [30]

$$E_n = \frac{\mu b^2}{4\pi} \ln\left(\frac{\alpha(n)\tau}{\mu}\right), \tag{1}$$

where $\alpha(n)$ equals 2.72 and 2.28 for two- and threefold cores, respectively, $b$ is a Burgers vector, and $\mu$ is the shear modulus. The amplitude of the restoring forces $\tau$ is proportional to the unstable stacking fault energy, $\gamma_{\rm us}$. As follows from Eq. (1), the energy difference $\Delta E_{2-3} \sim \ln[\alpha(2)/\alpha(3)]$ is positive without addition that demonstrates the preferability of the threefold core.

The solute atom locally disturbs the threefold symmetry of the dislocation structure and can cause a substantial core reconstruction [33]. The lowering of the GSF energy for one of the three $\{110\}$ planes makes favorable a planar dislocation core structure. In this case, the energy barrier may be estimated as $\Delta E_{2-3} \sim \ln[\alpha(2)\gamma_{\rm us}/\alpha(3)\gamma^0_{\rm us}]$. The values of $\Delta E_{2-3}$ calculated by using the GSF energies for different solute atoms are shown in Fig. 2. Clearly, the 5$d$ TM additions give rise to a monotonic decrease in $\Delta E_{2-3}$ with the atomic number of the addition. The solutes bringing extra electrons reduce $\Delta E_{2-3}$ in comparison with unalloyed Mo and can enhance the double kink nucleation. The additions of W, Ta, or Hf lead to an increase in $\Delta E_{2-3}$ and do not cause kink nucleation; therefore, the SSS phenomenon is absent in these alloys. Note that the suppression of kink nucleation by a solute atom may not produce SSH because in this case the double kink occurs away from the solute atoms. Nevertheless, the GSF energy gain was considered as a strict indication of solution hardening [18,34] which, together with our results, supports the suggestions [16,17] that the hardening also depends upon the changes in the electronic structure due to additions. In particular, for alloying with Hf, Ta, or W the electronic factor (ratio of stacking fault energies, $\gamma_{\rm us}/\gamma^0_{\rm us} > 1$) as well as the size misfit ($R_i/R_{\rm Mo} > 1$) correlate with the observed hardening.

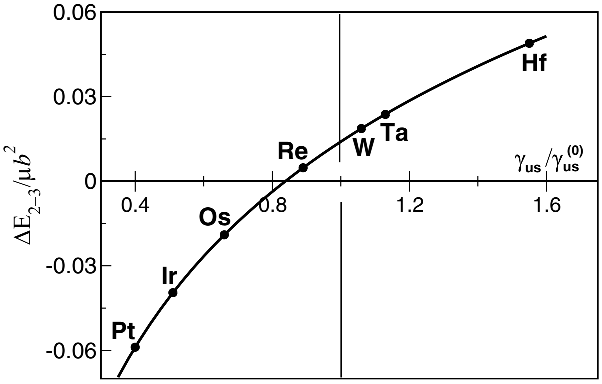

FIG. 2. The energy difference of twofold and threefold dislocation core structures $\Delta E_{2-3}$ versus $\gamma_{\rm us}/\gamma^0_{\rm us}$.

As established in recent calculations [21,22,29], the screw dislocation in Mo does not spread along the $\langle 112\rangle$ directions and has a nondegenerate isotropic core structure. In this case, being a planar defect the stacking fault does not characterize the dislocation structure quite accurately, and thus its applicability should be demonstrated. The lattice resistance to a shift of the atomic row parallel to the dislocation line seems to be a more adequate parameter for the description of the dislocaton properties in bcc alloys, where the core structure is very sensitive to the shape of the atomic row potential [35].

Hence, for Mo and some Mo alloys we performed more complicated calculations of the energy changes, $\Delta E_{\rm line}$, for a displacement of the single atomic row along $\langle 111\rangle$ using supercells with 5 layers and 8 atoms per layer; this supercell geometry corresponds to a solute concentration of 3 at. %. The variation in the dependence of $\Delta E_{\rm line}$ on the type of solute atom (Fig. 3) correlates with the tendencies obtained for the GSF energy: the resistance to a shift of atomic row decreases for the solutes with extra electrons. The decrease in $\Delta E_{\rm line}$ due to an addition should result in a significant decrease of the Peierls relief and even in a transformation from isotropic to anisotropic (degenerate) core structures [35]. Because the decrease of the Peierls relief occurs locally near the solute atoms, the double kink nucleation is made easier.

It should be noted that we considered the influence of a single solute on double kink nucleation and discussed only the initial softening or hardening effects which occur at low temperatures and solute concentrations. The observed alloying effect on hardness (softening or hardening) results from the interplay between the enhancement of kink nucleation and the deceleration of moving kinks by the

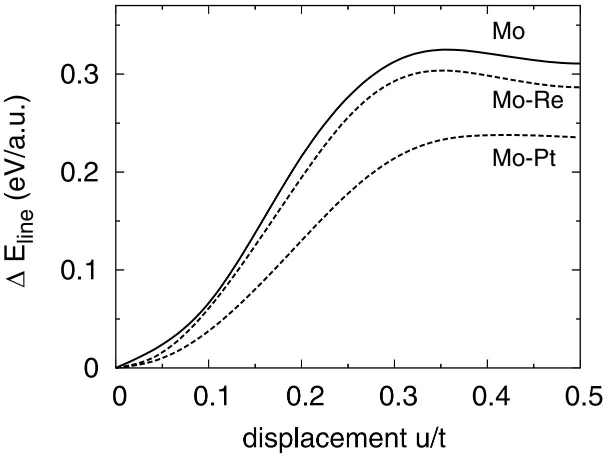

FIG. 3. The energy variation $\Delta E_{\text{line}}$ for a shift of the atomic row along $\langle 111 \rangle$.

additions. The latter contribution becomes dominant when the temperature or concentration increases and gives rise to the transition from SSS to SSH [4,15].

In summary, using the FLMTO method, we showed that the solution softening in bcc Mo alloyed with Pt, Ir, Os, or Re is intrinsic and has an electronic origin. These additions locally change the chemical bonding, decrease the GSF energy and atomic row shear resistance which reduces the barrier for double kink nucleation, and increases the dislocation mobility. As a result, the SSS effect correlates with the atomic number of the addition. This conclusion, obtained in the framework of the Peierls-Nabarro model, allows one to explain the qualitative trends in solution softening in Mo alloys with 5*d* TM additions and to emphasize an essential role of the electronic effects in the interaction between dislocations and solute atoms. Thus, one may expect that such a SSS mechanism is general and to take place also for all group VIA (Cr, Mo, and W) alloys with TM metals with extra electrons.

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