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Solid solution softening and hardening in the group-V and group-VI bcc transition metals alloys: First principles calculations and atomistic modeling

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The interaction of *d* transition metal additions with dislocations was studied in bcc alloys by using the atomic row model with *ab initio* parametrization of the interatomic interactions. Opposite trends were obtained for the solute-dislocation interactions in the group-V (Nb, Ta) and group-VI (Mo, W) bcc metals: while additions with extra valence electrons enhance the double-kink nucleation and result in solid solution softening in the group-VI metals, they cannot cause the intrinsic softening in the group-V metals. Oppositely, additions with fewer valence electrons should lead to an intrinsic softening in the group-V metals and a strong hardening in the group-VI metals. The effect of electronic concentration on the solute-dislocation interaction is less pronounced in the group-V alloys, and other mechanisms may be dominant in their softening and hardening behavior.

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The refractory group-V and group-VI bcc metals are of great interest as materials for high-temperature applications. Alloying with *d* transition metal (TM) elements is an important way to improve the strength and plasticity of these metals.[1] As is well known, the additions can result in an increase of the yield stress and hardness (solid solution hardening) or their decrease (solid solution softening), depending on the alloying element, temperature, and solute concentrations.[2–6] While solid solution hardening and softening in bcc metals has been a subject of intense investigations, the fundamental mechanisms of this phenomenon are still under discussion[7,8] and it is unclear why certain solutes lead to hardening, but others may cause softening.

Solid solution softening (SSS) can be observed at low solute concentration and low temperatures, while only solid solution hardening (SSH) is possible at room and higher temperatures. A small amount of 5*d* additions (1–8 at. %) with an extra number of valence $(s+d)$ electrons (Re, Os, Ir, Pt) decreases the hardness of molybdenum and tungsten below 300 K, but all these solutes produce strengthening for higher concentrations and temperature.[9,10] Softening in Mo and W is believed to be due to an intrinsic mechanism and to originate from the direct solute effect on the dislocation mobility due to the initiation of double-kink nucleation.[3,4] In contrast with the group-VI bcc metals, the scavenging of interstitials by substitutional additions is traditionally considered to control softening in the group-V metals. Such extrinsic softening mechanism is supported by the observation of the dependence of hardness on the concentration of light impurities.[11–13] However, W and Nb additions were not found to be strong removers of interstitial impurities in the Ta-W and Ta-Nb alloys[11] and some assumptions were expressed that the direct solute-dislocation interaction may also be responsible for SSS in the group-V alloys.[11,14,15]

Special attention was given to the group-VI metals alloyed with Re, which is widely used to improve their ductility and strength.[1,3,16] However, the rhenium ductilizing effect was not observed for the group-V transition metals, and vice versa, their low-temperature ductility is significantly impaired for Re alloying with more than 3 at. %.[17] No suggestions were made as to the nature of this opposite Re effect in the group-V metals.

To establish the role of intrinsic factors in softening and hardening of bcc alloys, investigation of the microscopic mechanisms of the solute-dislocation interaction appears necessary. Experimental results[3,10,18] do not support the point of view that the size and/or modulus misfits can be considered as parameters controlling SSS in bcc alloys. Moreover, the observed dependence of the initial hardening rates on the number of valence electrons in the group-VII–VIII additions clearly testifies that the softening in the Mo alloys is likely an inherent property and connected with the electronic structure.[10]

Recently, the electronic origin of SSS in bcc Mo alloys was investigated[7,8,19] by a combined approach that includes atomistic dislocation modeling with first principles parametrization of interatomic interactions. These studies demonstrated the monotonic reduction of the energy barrier for double-kink nucleation with the number of $(s+d)$ valence electrons of the additions and explained the experimental trends in the initial hardening rates in the Mo alloys. Here we employ this approach[7,19] to investigate the solute-dislocation interaction and to reveal the intrinsic mechanism of the solution softening and hardening in the refractory group-V (Nb, Ta) and group-VI (Mo, W) metals with 4*d* and 5*d* TM additions. We show that the electronic structure plays an important role in the solute-dislocation interaction and results in opposite trends for the groups-V and -VI bcc metals.

Despite progress in the development of powerful atomistic techniques, the effect of impurities on the structure and mobility of dislocations is still a challenging problem for direct first principles calculations. Hence, we use the combined approach which was found successful[7,19] to study the SSS mechanism in Mo alloys. Now, the plasticity of bcc metals is governed by the screw dislocations with nonplanar core[20–25] and their mobility is controlled by the kink mechanism. As result, the stacking fault energies and the planar Peierls-Nabarro model may not be reliable enough to describe the dislocation structure. In our approach, the core of screw dislocations is modeled by the displacements of the atomic rows along the dislocation line[26] with *ab initio*–determined interaction energies $\Phi(u)$ between the atomic rows which are approximated by the Fourier expansion

$$\Phi(u) = \Phi_0 \sum_{n=0}^{2} A_n \cos(2\pi n u/b), \tag{1}$$

where b is the Burgers vector, u is relative displacement, and Φ_0 and A_n are parameters.

The total energy calculations were carried out by using the full-potential linear muffin-tin orbital (FLMTO) method[27] with the generalized gradient approximation[28] (GGA) to the exchange-correlation potential. A 32-atom supercell was employed to calculate the atomic row displacement (ARD) energies

$$\Delta E_{row}(u) = 3[\Phi(u-1/3) + \Phi(u+1/3)] \tag{2}$$

for a shift along the $\langle 111 \rangle$ direction. In this supercell the shifted atomic rows with impurity are separated by four interlayer distances and the impurity concentration is about of 3 at. %. The consideration of such a solute concentration can reveal local changes near the solute within the supercell approach (the so-called "local" approximation[29]) for solute-dislocation interactions (for details of the calculations and dislocation modeling, see Ref. 19). We did not take into account the crystal relaxation caused by solute atoms. Since no correlation between the size misfit and softening behavior was observed in Mo alloys, one can believe that the relaxation is not crucial in the solute-dislocation interactions.

The calculated ARD energies show a strong dependence on the difference in the number of valence $(s+d)$ electrons, Δn, for solute and solvent atoms. For both Mo (Ref. 19) and W alloys, the values of $\Delta E_{row}(u)$ decrease gradually when Δn increases (Re, Os, Ir, Pt) and, vice versa, they increase for additions that reduce the electron concentration [Figs. 1(a) and 1(b)]. These trends in $\Delta E_{row}(u)$ strongly correlate with the experimental initial hardening rates (dH/dc at concentration c approaching to zero) at low temperatures in the Mo and W alloys.[9,10] Thus, the intrinsic mechanism of SSS is similar in the Mo and W alloys and has an electronic origin.[7,8,19]

For the Nb and Ta alloys, we obtained the opposite trend for the ARD energies [Figs. 1(c) and 1(d)]: the 4*d* and 5*d* additions with extra valence electrons increase the atomic row shift resistance and the additions with fewer electrons reduce $\Delta E_{row}(u)$. The value $\Delta E_{row}(0.5)$ gradually increases with Δn up to Re without any large change of shape. For Ir and Pt additions to both Nb and Ta, the shape of the $\Delta E_{row}(u)$ curves goes toward sinusoidal and the values of $\Delta E_{row}(0.5)$ are almost the largest among the 4*d* and 5*d* solutes, while they were the smallest in the group-VI alloys. Note that the ARD energies for unalloyed Ta and Nb are about half of those for Mo and W, in agreement with the ratio

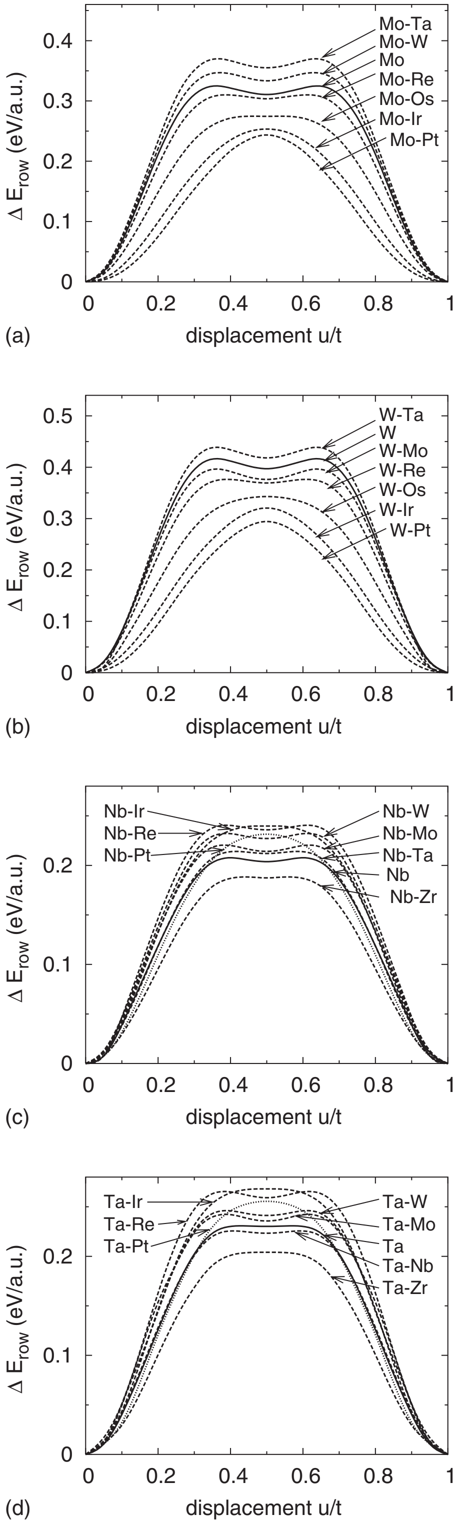

FIG. 1. ARD energies ΔE_{row} for a shift of the atomic row with solute along $\langle 111 \rangle$ versus displacement in units of the Burgers vector $1/2\langle 111 \rangle$ in (a) Mo (Ref. 19), (b) W, (c) Nb, and (d) Ta alloys.

of unstable stacking fault energies,[25] and reflects the strengthening of chemical bonding in going from the group-V to the group-VI refractory metals.

The different behavior of the ARD energies for the group-V and group-VI alloys with 4*d* and 5*d* TM additions originates from the peculiarities of their electronic structure and chemical bonding when the Fermi level is located either in the region of the bonding states (group V) or in the pseudogap between bonding and antibonding states (group VI). The Fermi level shift to lower energies reduces the bonding in the group-V alloys because some bonding states are being emptied. The increase of electron concentration leads to the occupation of antibonding states in the group-VI alloys and to additional bonding states (up to the pseudogap) in the group-V alloys, which results in the weakening and strengthening of chemical bonding, respectively. The aliovalent additions result in a small increase (W in Mo and Ta in Nb) or a decrease of the ARD energies (Mo in W and Nb in Ta), in accordance with the strengthening of metal bonding in going from Mo to W and from Nb to Ta. A similar reason leads to higher values of $\Delta E_{row}(u)$ for the W additions in comparison with those for Mo in all alloys.

Using the atomic row model with *ab initio*–determined ARD energies, we found that the screw dislocations in unalloyed Mo and W, as well as in Nb and Ta metals, have an isotropic compact core. A similar core structure was obtained previously for Mo (Refs. 19 and 22–24) and Ta (Refs. 21–23). As we showed in Ref. 19, the additions locally disturb the threefold symmetry of the dislocation core and the isotropic core of the screw dislocation tends to spread or "split" (planar core) under alloying, which decreases the ARD energy.

To illustrate the effect of additions, we calculated the energy change when the dislocation moves from the far position to the solute, ΔE_{df} (Fig. 2), which characterizes the driving force for double-kink nucleation. The softener additions which decrease the ARD energies have an attractive interaction with the dislocation ($\Delta E_{df}>0$), in contrast with the alloying elements that increase $\Delta E_{row}(u)$ and have a repulsive interaction with dislocations ($\Delta E_{df}<0$). For the W, as well as for the Mo (Ref. 19) alloys, we found an almost linear dependence of the driving forces on the difference in the number of valence electrons. The additions with $\Delta n>0$ enhance the double-kink nucleation and result in softening; the additions with $\Delta n<0$ cannot favor the kink formation. On the other hand, all additions with $\Delta n>0$ in the group-V TM alloys demonstrate a repulsive interaction with dislocations and intrinsic softening should exist only for the Zr addition, where $\Delta E_{df}>0$. Two distinguishing features are seen from a comparison of the results for the group-V and group-VI alloys. First, the dependence ΔE_{df} (Δn) for the group-V alloys is parabolic and Pt has a small effect on the dislocation structure ($\Delta E_{df}=0$); second, the values of ΔE_{df} are less in the Nb and Ta alloys because of the small values of Φ_0. This means that in these alloys the direct electronic mechanism may not play such a significant role as in the Mo and W alloys and other factors such as a scavenging of light interstitial impurities or size and modulus misfits may be predominant.

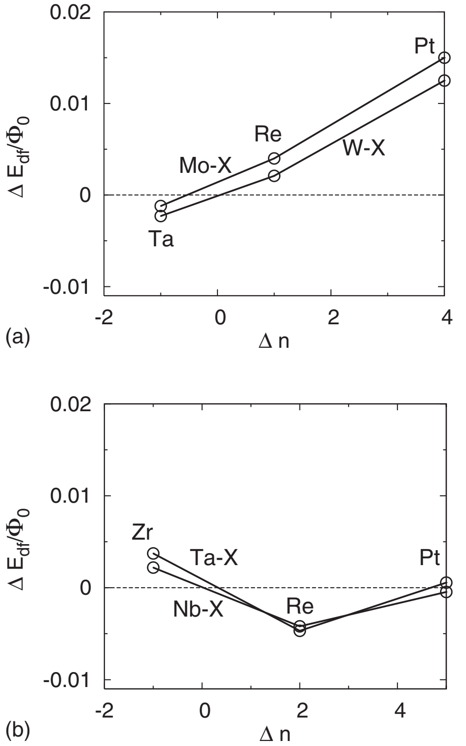

FIG. 2. Dependence of the driving force for kink nucleation (in units of Φ_0 for corresponding metals) on the difference in the number of valence electrons for the (a) group-VI and (b) group-V bcc alloys.

It should be noted that for the group-VI alloys, the observable hardening rates follow the trends in the ARD energies, which correlate with the atomic size only for the hardener solutes, but not for softeners. So the contribution due to misfit strain can arise only for additions [Ta, W, and Hf (Ref. 19)], which increase the ARD energies. No correlation exists between the atomic size of solute and the ARD energies in the Nb and Ta alloys. In these alloys, all additions with smaller atomic radii lead to an increase of $\Delta E_{row}(u)$ and ΔE_{df}, while Zr (the largest radius) decreases these energies. This finding clearly points out that the electronic factor may be competitive with the elastic contribution caused by the size misfit. In particular, the intrinsic softening effect may not appear for alloys with Zr due to the hardening from size misfit, as was mentioned, for example, for $MoSi_2$ with W additions.[29]

The changes in $\Delta E_{row}(u)$ and ΔE_{df} obtained for the 5*d* solutes from Ta to Pt strongly correlate with the experimentally observed lowering of the initial hardening rate in the Mo and W alloys.[9,10] For the group-V alloys, we predict the intrinsic SSS only for the Zr addition and indeed Zr was cited as a softener in Nb and Ta.[3] Other 4*d* and 5*d* additions cannot enhance the double-kink nucleation and will contribute to hardening as obstacles for kink propagation. A distinct solid solution hardening was observed in the Nb-*X* (*X*=Ta, Mo, W, Ir) binary alloys, where Ta has the smallest hardening effect,[30,31] which corresponds to the trends found in our calculations. In contrast with the group-VI alloys, where Re, Ir, and Pt result in softening, we found a sharp increase of the ARD energies and a repulsive interaction with dislocation for the Re and Ir additions in Nb and Ta, which indicates an intrinsic strengthening effect. This result is in agreement with a recent experiment,[17,31] where both thermal and athermal components of the flow stress were found to increase with solute content in these alloys.

In summary, based on *ab initio* calculations, we found opposite trends in the lattice resistance and solute-dislocation interaction in the group-V (Nb, Ta) and the group-VI (Mo, W) alloys. The solution softening in Mo and W alloys with additions with excess electrons (Re, Os, Ir, Pt) appears to be due to the decrease of the ARD energies, which results in an enhancement of kink nucleation and an increase of dislocation mobility. Additions with the fewer numbers of valence electrons lead to an increase of the ARD energies and have repulsive interactions with dislocations; they do not favor kink formation and contribute to hardening.

By contrast, in the group-V metals only Zr causes an attractive interaction with dislocations and may favor the dislocation mobility by the initiation of kink nucleation. Additions with excess electrons (Mo, W, Re, Os, Ir, Pt) in the Nb and Ta alloys increase the ARD energies, lead to the repulsive interaction with dislocations, and cannot be intrinsic softeners. Thus, the solution softening in these alloys should be connected with an extrinsic origin, as was found in Ta-Re-N.[3] This difference in the softening mechanisms correlates with the solubility of light interstitial impurities, which is much higher in the group-V metals. Finally, our results demonstrate that the intrinsic mechanism plays an important role in the softening in the group-VI (Mo, W) alloys, but the changes in dislocation behavior are less pronounced in the group-V alloys and may be masked by other factors such as the solute-interstitial interaction or size and modulus misfits.

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