

Solid solution softening and hardening by mobile solute atoms with special focus on hydrogen

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Mobile solute atoms will affect both kink formation and kink motion. Softening occurs if solute atoms segregate to kinks and if the rate determining step is the formation of kink pairs. Then double kink formation energy is reduced, which can be shown within thermodynamics. With increasing solute concentration the rate of dislocation motion will finally be determined by kink motion. Kink motion is retarded by solute drag, which increases by adding more solute. Under these circumstances hardening is observed. © 2012 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

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Usually solute atoms in alloys give rise to hardening, because higher stresses are required for plastic deformation in order to overcome the attractive forces between solutes and dislocations and/or to counteract the friction of a solute cloud dragging along with a moving dislocation. Contrary to these effects, pronounced solid solution softening has been observed for body-centered cubic (bcc) metals and interstitial solutes below room temperature [1–6]. An especially large softening has been discovered for high purity iron, where 200 atomic ppm of nitrogen reduce the flow stress at 190 K from ~200 to ~100 MPa [4]. The amount of softening depends on solute concentration, temperature, and crystal orientation and it is counteracted by solute hardening. The competition between softening and hardening leads to the effect that oxygen in a single crystal of niobium is softening the metal in one crystallographic direction and hardening it in a different direction [4]. With increasing solute concentration solute softening may turn into solute hardening [7–10]. A compilation of earlier experimental results and of various models for softening in metals is provided in Ref. [1]. Because of the absence of a generally accepted model, research in the area of alloy softening is in progress using computer simulations [11,12].

The majority of recent studies agree that hardening and softening in bcc metals at low temperatures are

based on the formation and motion of kink pairs at screw dislocations [13]. In the framework of this model, hardening is caused by the attractive interaction between solute atoms and moving kinks, whereas softening is explained by an elastic interaction between solute atoms and kink pairs during their formation and separation stage [2,4] or as a change in the dislocation core structure [5]. With the so-called defactant concept [14,15], softening can be interpreted in a general way in the framework of thermodynamics. Defactants are solutes which segregate to defects of materials like surfactants accumulate on surfaces. If defects are defined in a general way as discontinuities of materials, surfactants are a sub-group of defactants. Both solute species reduce the formation energy of these generalized defects. This is shown by introducing a new state function:

$$\Phi = F - \mu_s n_s \quad (1)$$

where F is the Helmholtz free energy, and μ_s and n_s are the chemical potential and the number of solute atoms, respectively. Then the differential of Φ becomes

$$d\Phi = pdV - SdT + V\gamma d\rho + \mu_m dn_m - n_s d\mu_s \quad (2)$$

containing the common quantities of pressure p , volume V , entropy S , temperature T , chemical potential μ_m , and the number n_m of matrix atoms. Besides the common terms, a new term, $V\gamma d\rho$, is introduced, which accounts for the work required to generate defects. Thus ρ is the defect density and γ the defect formation energy. In the

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present study kinks at dislocations are the defects of interest and ρ corresponds to the number of kinks per volume. With Eqs. (1) and (2) the following Maxwell Equation can be derived:

$$\left. \frac{\partial \gamma}{\partial \mu_s} \right|_{V, T, \rho, n_m} = - \frac{1}{V} \left. \frac{\partial n_s}{\partial \rho} \right|_{V, T, \mu_s, n_m} \quad (3)$$

The right-hand side of the last equation is defined as solute excess Γ_s at the defect:

$$\Gamma_s \equiv \frac{1}{V} \left. \frac{\partial n_s}{\partial \rho} \right|_{V, T, \mu_s, n_m} \quad (4)$$

Thus the excess solute is the number of solute atoms dn_s which have to be added from a reservoir of constant chemical potential μ_s after the formation of $Vd\rho$ kinks. Then Eq. (3) is written in a simplified form as

$$d\gamma = -\Gamma_s d\mu_s \quad (5)$$

which is equivalent to the well-known Gibbs adsorption isotherm describing the change of surface energy due to excess surfactants.

As mentioned earlier, mobile solutes, especially interstitials, give rise to hardening in most cases and softening is rare. In order to understand the interplay between softening and hardening in the framework of the defactant concept, the strain rate is expressed by the Orowan equation and its modification by Argon [11,16]:

$$\frac{d\varepsilon}{dt} = b\rho_d v = \frac{b\rho_d a}{\tau_g + \tau_m} \quad (6)$$

where ε is the plastic strain, b is the Burgers vector, ρ_d is the dislocation density, a is the distance a double kink moves the dislocation ahead (for instance the distance between two Peierls valleys), τ_g is the time constant for double kink generation and τ_m is the time necessary to move the kinks to the ends of a dislocation line. In pure metals kinks move very quickly [17] and the condition $\tau_m \ll \tau_g$ holds, leading to

$$\frac{d\varepsilon}{dt} \approx \frac{b\rho_d a}{\tau_g} \quad (7)$$

Defactants segregating to kinks reduce the kink formation energy, and therefore decrease τ_g which, via Eq. (7), leads to an increased strain rate or softening, respectively. The concomitant increase of dislocation velocity has been observed experimentally in an environmental transmission electron microscope (ETEM) for hydrogen in various metals [18]. On the other hand, increasing the solute content leads to an increasing solute drag on the moving kinks, which increases τ_m . With decreasing τ_g and increasing τ_m the condition $\tau_m \ll \tau_g$ yielding Eq. (7) no longer holds but with increasing hydrogen concentration reverses to $\tau_m \gg \tau_g$. Then hydrogen drag on kinks instead of hydrogen enhancing kink formation dominates and Eq. (6) becomes

$$\frac{d\varepsilon}{dt} \approx \frac{b\rho_d a}{\tau_m} \quad (8)$$

With increasing solute concentration τ_m increases further on, because excess solute at the kinks increases, raising the dragging forces as well. Then Eq. (8) predicts a decreasing strain rate, i.e. hardening. Thus the experimental observation of a change from softening at low carbon, nitrogen and/or oxygen concentrations in iron or niobium to hardening at higher concentrations [7–10] is explained consistently.

In summary, both softening and hardening are given by the following relations:

$$\begin{aligned} \frac{d\varepsilon}{dt} &= \frac{b\rho_d a}{\tau_g + \tau_m} \\ &= \begin{cases} \tau_g > \tau_m \Rightarrow b\rho_d a/\tau_g \text{ and } \tau_g \downarrow \text{ (solute softening)} \\ \tau_m > \tau_g \Rightarrow b\rho_d a/\tau_m \text{ and } \tau_m \uparrow \text{ (solute hardening)} \end{cases} \end{aligned} \quad (9)$$

where the vertical arrows indicate decreasing or increasing time constants with increasing solute concentration. The transition from softening to hardening is presented as a cartoon in Figure 1.

Within the generalized Gibbs adsorption theory the nucleation energy of kink pairs at dislocations is reduced due to excess defactants as explained qualitatively before. In a quantitative treatment, Eq. (5) has to be used, in order to account for the decrease of the formation en-

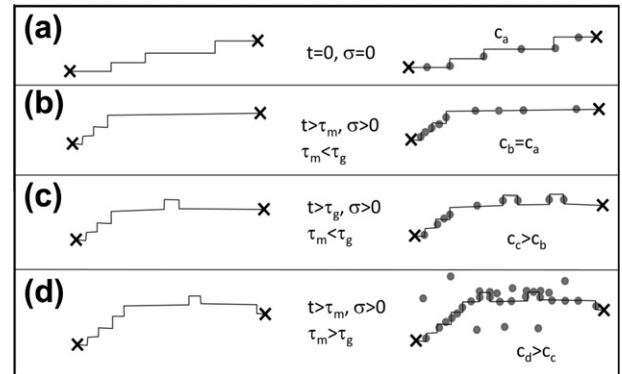


Figure 1. Movement of a slanted screw dislocation between two pinning points (crosses) as time proceeds from (a) to (d) with (right) and without (left) solute atoms of concentration c . (a) At time $t = 0$ and without shear stress ($\sigma = 0$) the slanted dislocation contains geometrically necessary kinks. The kinks have edge type character, yielding a higher coverage with solute atoms. (b) A stress is applied for $t > 0$ which exerts a force on the kinks to the left. After a time τ_m , which is larger than the average time required to move the kinks to the left pinning point, the kinks agglomerate at this point. No new kinks are formed, because the time for kink generation τ_g is larger than the time for movement τ_m . (c) New kinks are formed besides the geometrically necessary ones for $t > \tau_g$. In the presence of excess solute at the kinks the solute acts as a defactant and reduces the formation energy of kinks, i.e. their generation rate is larger (right compared to left picture) or τ_g is smaller in the presence of solutes. As the solute concentration is increased when compared to (b) the generation time is even smaller than in (c), i.e. softening occurs. (d) In the left part τ_g and τ_m are the same as in (c) but in the right part the solute concentration has been increased further on and so has the characteristic time for kink motion due to solute drag. This has become even larger now than τ_g and kink motion controls the dislocation velocity. Further increasing solute concentration leads to a steady increase of τ_m and, therefore, causes hardening.

ergy of a kink pair. Softening should be pronounced for screw dislocations as their kinks are edge type. Edge type dislocation segments are expected to have a higher solute excess as, besides the core, their long-range hydrostatic stress field interacts attractively with the strain induced by solute atoms. Interstitial solutes with their large strain tensor, especially the large trace of this tensor, interact even more strongly with edge type kinks than substitutional solutes. As screw dislocations are mainly responsible for the plastic strain during deformation of bcc metals, the reasoning provided in this paragraph explains experimental findings that softening is mainly observed in bcc metals and that interstitials give rise to the largest effect.

Besides having high chemical potentials for facilitating kink formation, it is assumed that solute atoms should be mobile enough within the lattice or dislocation core to transport and generate the necessary excess of solute atoms to a region where double kink creation occurs. Thus it is comprehensible that softening is not detected at very low temperatures, i.e. below 100 K for heavy interstitials [1,5]. In molecular dynamic simulations of nanoindentation [19,20] softening by hydrogen is not observed to the same extent as in experiments [21–28], because the time scale of the simulation does not allow H diffusion to supply sufficient excess hydrogen to the region where the dislocation loop is created. Nevertheless, in computer simulations pop-in loads during indentation are slightly smaller on average in samples containing hydrogen compared to hydrogen-free samples. This is due to fluctuations in H concentration where some regions will provide larger excess hydrogen for the creation of a dislocation loop in the simulated volume. On the atomic scale the smallest dislocation loop is one composed of two kink pairs, i.e. one screw type and one edge type kink pair. Fluctuations of concentration give also rise of a lower pop-in load for antimony in copper [12].

Fluctuations in concentrations of heavy interstitials give rise to pronounced fluctuations in strain. Thus kink creation may occur at sites of high strain, leading to heterogeneous kink nucleation with a higher rate than homogeneous nucleation. High local strains correspond to high solute concentrations which in the defactant concept lead to high excess solute at the kink and a lowering of kink formation energy. Considerations of strain fluctuations are an atomistic approach towards understanding softening, which may be just one way of fulfilling the thermodynamic requirements within the defactant concept. The alternative of interstitials moving to the site of kink creation requires some additional assumptions. In the temperature range of ~ 100 – 300 K, where softening by the heavy interstitials carbon, nitrogen and oxygen occurs [7–10], these interstitials are hardly mobile within the metal lattice. Using known diffusion coefficients [29] and their relation to the jump rate reveals that at the highest temperature of 300 K the interstitials perform about one jump in 1 s only. Thus excess solute has to be transported along the dislocation line towards a site of kink nucleation. For hydrogen in bcc metals diffusion is much faster [29] and an H-atom performs many jumps per second, even at temperatures as low as 50 K.

Softening by hydrogen was observed in pure iron [30–35], but effects are small compared to nanoindentation experiments. Softening has also been detected in α -Ti [35]. However, the measuring temperatures were in the range of 500 to 800 °C. Compared to bcc metals like iron the H diffusivity in hexagonal close packed (hcp) Ti is much lower and, therefore, higher temperatures may be necessary to reach a sufficient mobility for the solute atoms to cause softening in a dynamic strain rate test.

In a fatigue experiment Murakami et al. [36] observed with increasing hydrogen concentration in stainless steel an increasing crack velocity followed by a decreasing velocity when compared with the hydrogen-free sample. If the crack velocity is determined by plastic flow, the faster crack growth at low H content is due to an increase of dislocation velocity by a decreased double kink formation energy with the condition $\tau_m < \tau_g$ still being valid. For larger H contents the chemical potential is larger and the kink formation should be even easier, i.e. τ_g decreases. In addition, with increasing H content the excess hydrogen at the kinks becomes larger too, and so does the characteristic time τ_m for kink motion. Thus the condition $\tau_m > \tau_g$ is reached with increasing H content and the behavior changes from softening to hardening.

Kink nucleation and motion can be observed within internal friction experiments [17]. For kinks on screw dislocations of pure bcc metals this leads to a pronounced peak at ~ 300 K, labeled γ -peak. Dissolving heavy interstitials gives rise to an additional peak at much higher temperatures, which is called the cold-work or Snoek–Köster peak [17]. According to an analysis by Seeger [17] the activation energy of the corresponding relaxation process is the sum of four energies: (i) the formation energy of a kink pair, (ii) the migration energy of a kink, (iii) the energy for solute segregation to dislocations, and (iv) the activation energy of solute diffusion. The theory is in agreement with experimental findings for the heavy interstitials but discrepancies have been noted for hydrogen by Seeger [17]. Seeger assumes that the hydrogen Snoek–Köster peak is related to the α -peak, which occurs at much lower temperatures (~ 50 K) and which is attributed to kinks on 71° dislocations [17]. This is consistent with the Snoek–Köster peak of heavy interstitials occurring at temperatures well above the γ -relaxation. Hirth hypothesized instead [37] that the hydrogen Snoek–Köster peak in iron is related to the γ -relaxation, i.e. the kink formation at screw dislocation, and that the fact that it shows up at temperatures below the γ -peak has to be attributed to a decrease of the kink formation energy due to the presence of hydrogen. Within the defactant concept, Hirth's assumption becomes a thermodynamic fact. Then hydrogen decreases the kink formation energy via Eq. (5) and it saturates the trap sites at the dislocation immediately at low concentration due to its high mobility and, therefore, the segregation energy does not play a role [17]. In addition, the high hydrogen diffusivity is due to a small activation energy of diffusion, which also leads to a slight increase of the activation energy for kink motion only. Thus the decrease of kink formation energy has the largest effect, the sum of the four energies

which is the activation energy of the Snoek–Köster peak is reduced, and the peak temperature is below the γ -peak. For the heavy interstitials carbon, nitrogen and oxygen, the activation energy for diffusion is much larger compared to hydrogen with a concomitant larger solute drag on the moving kinks. Both contributions to the activation energy of the Snoek–Köster peak will not be compensated by the reduction of kink formation energies by excess interstitials and the Snoek–Köster peak appears at temperatures above the γ -peak.

In summary, the defactant concept with its predictions about kink formation at dislocations provides a consistent description of solid solution softening and hardening where the latter is determined by the modified Orowan equation (Eq. (6)). The transition from softening to hardening with increasing concentration can be explained by a change of the rate determining step from kink nucleation rate to kink migration rate. In addition, a discrepancy regarding the Snoek–Köster peak of hydrogen in niobium and iron [17,37] when compared to heavy interstitials is overcome.

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