Generalized stacking fault energies, ductilities, and twinnabilities of Ni and selected Ni alloys

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The generalized stacking fault energies, Rice-criterion ductilities, and twinnabilities of selected Ni-x solid-solution alloys (x=Nb, W, Mn, Fe, Cu) are calculated using density functional theory to elucidate how alloying alters the mechanical properties of pure Ni. Relative to Ni, the alloys have smaller stacking fault energies (γsf), similar ductilities, and a greater tendency to undergo deformation twinning. The results are compared to experimental studies of the mechanical properties of nanocrystalline (nc) Ni alloys from the literature, and it is suggested that the higher strain-hardening rate recently reported for nc-Ni-Cu (relative to nc-Ni-Fe) does not arise from differences in γsf, but from a higher dislocation density caused by more facile dislocation nucleation. © 2005 American Institute of Physics. [DOI: 10.1063/1.2051793]

Over the past decade the properties of nanocrystalline (nc) metals have attracted considerable attention.1–5 This interest has been motivated by applications that exploit the high strength of these materials,4 and by the possibility that interest has been motivated by applications that exploit the thermal stability.5 Ebrahimi

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ment of $a_0/\sqrt{6}$ ($a_0 = 3.522 \text{ Å}$). The remainder of the GSF curve is generated by a similar shift on a $\{111\}$ plane adjacent to the existing fault, and contains a maximum at the unstable twinning energy ($\gamma_{ut}^{\text{us}}$). While $\gamma_{ut}$ can be measured experimentally, $\gamma_{us}$ and $\gamma_{ut}$, which represent the minimum energy barriers for partial dislocation and microtwin nucleation, respectively, can be determined only through atomistic simulation. The complex electronic interactions between elements in an alloy suggest that an $ab$ initio evaluation of GSF energies is preferable to approaches based on empirical potentials (EP). The fault energies can also be used to validate EP for use in molecular dynamics (MD) simulations of deformation.

The GSF curves were evaluated using a spin-polarized, planewave-pseudopotential method based on the generalized gradient approximation to density functional theory. The core-valence electron interaction was treated using Blochl’s projector augmented wave method with the $p$ semicore states of each element included as valence electrons. Brillouin zone sampling was performed using 10 special k-points, which was sufficient to converge $\gamma_{us}$ and $\gamma_{ut}$ to better than 10%. The planewave cut-off energy was set to 700 eV, which was sufficient to converge the total energy of a Ni unit cell to within 1 meV/atom. (This cutoff is also adequate for the alloy systems, as the Ni pseudopotential is the “hardest” of the six elements considered herein.)

The periodic supercell used here consists of a $(2 \times 2)$ slab geometry with 10 $(111)$ planes and a total of 40 atoms. An $\sim 8 \text{ Å}$ vacuum region is included along the cell’s long $(z)$ axis. For the alloy systems one Ni atom within the fifth layer was substituted with a single solute atom, resulting in a total solute concentration of 2.5%, or 12.5% in the fault planes. Following a technique used to measure the influence of H on Al plasticity, GSF energies were evaluated on the two $(111)$ fault planes bounding the solute-containing layer. The first half of each GSF curve (see Fig. 1) was evaluated by displacing layers 1–5 along $(112)$ over a distance $a_0/\sqrt{6}$. The second half was then constructed in a similar fashion by displacing only layers 1–4, resulting in the formation of a two-layer-thick twinned region. The forces on all atoms along $\{111\}$ were minimized to a tolerance of 0.05 eV/Å at each displacement.

Although nucleation of a partial dislocation or microtwin will involve shearing of the lattice, it has been demonstrated that the energy extrema encountered under shear will be the same as those obtained from the GSF surface. Partial slip along $\{112\}$ is preferred, as opposed to $\{110\}$ slip for a total dislocation, because $\gamma_{us}$ is lowest in this direction, and MD simulations suggest that deformation in nc metals is strongly dependent on the motion of partial dislocations.

Dislocation and/or twin nucleation often occurs near defects such as grain boundaries, where local solute concentrations can be enhanced by segregation. As shown by the GSF curves below, the energy barriers for nucleation are often lower in these enriched regions. Also, solute–stacking-fault interactions are known to be short ranged. These factors suggest that the present approach of evaluating the GSF curves in the vicinity of the solute-containing plane is reasonable.

**Table I.** Calculated fault energies ($\gamma$, mJ/m$^2$), ductility parameters ($D$), relative barrier heights ($\gamma_{ut}^{\text{us}} = \gamma_{us} - \gamma_{ut}$), and theoretical twinnabilities ($\tau_{\gamma}$) for pure Ni and Ni alloys.

<table>
<thead>
<tr>
<th>System</th>
<th>$\gamma_{ut}^{\text{us}}$</th>
<th>$\gamma_{us}$</th>
<th>$\gamma_{ut}$</th>
<th>$D$</th>
<th>$\gamma_{ut}^{\text{us}}$</th>
<th>$\tau_{\gamma}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>110</td>
<td>273</td>
<td>324</td>
<td>2.14</td>
<td>51</td>
<td>0.987</td>
</tr>
<tr>
<td>Ni-Nb</td>
<td>59</td>
<td>223</td>
<td>248</td>
<td>2.62</td>
<td>25</td>
<td>1.039</td>
</tr>
<tr>
<td>Ni-W</td>
<td>38</td>
<td>257</td>
<td>271</td>
<td>2.28</td>
<td>14</td>
<td>1.085</td>
</tr>
<tr>
<td>Ni-Mn</td>
<td>86</td>
<td>274</td>
<td>306</td>
<td>2.14</td>
<td>32</td>
<td>1.030</td>
</tr>
<tr>
<td>Ni-Fe</td>
<td>86</td>
<td>280</td>
<td>313</td>
<td>2.09</td>
<td>33</td>
<td>1.031</td>
</tr>
<tr>
<td>Ni-Cu</td>
<td>86</td>
<td>256</td>
<td>293</td>
<td>2.11</td>
<td>37</td>
<td>1.014</td>
</tr>
</tbody>
</table>

The calculated GSF curves for Ni and the five Ni-based alloys are plotted in Fig. 1; numerical values extracted from the curves’ extrema ($\gamma$s) are assembled in Table I. The curves indicate that alloying Ni at this concentration will generally reduce the size of $\gamma$. For example, in Ni a value of 110 mJ/m$^2$ was found for $\gamma_{ut}$ (experimental values fall within 125–128 mJ/m$^2$), while in the alloys $\gamma_{ut}$ ranges from 38 to 86 mJ/m$^2$. Gallagher has reviewed experimental measurements of changes to $\gamma_{ut}$ by alloying. For Ni-based alloys the data show a reduction in $\gamma_{ut}$ upon incorporation of transition-metal solutes. Furthermore, x-ray faulting probabilities suggest that Cu, Fe, and Mn additions of less than 20 at.% produce similar reductions in the Ni $\gamma_{ut}$ while alloying with W results in a larger reduction. Both of these trends are reproduced in the present calculations. Similar to $\gamma_{ut}$, the GSF curves show that $\gamma_{ut}$ is reduced in all of the alloys; $\gamma_{us}$ is reduced for Nb, W, and Cu additions, but is relatively unchanged by alloying with Mn and Fe.

To examine how alloying alters the ductility of Ni we employ Rice’s analysis of the competition between dislocation emission from a crack tip and crack cleavage. According to this model, a metal will be ductile under Mode I loading if the ductility parameter ($D$) satisfies $D = 0.3 \gamma / \gamma_{us} > 1$, where $\gamma_s$ is the (111) surface energy of pure Ni or the appropriate Ni alloy, including the effects of surface segregation. If $\gamma_s$ is small relative to $\gamma_{us}$ then the metal will tend to fail by cleavage fracture rather than shearing by dislocation-mediated slip. Calculated ductilities are listed in Table I. For pure Ni the calculated $\gamma_s = 1.95 \text{ J/m}^2$ yields $D = 2.14$, indicating that (as expected) Ni is an intrinsically ductile metal. This is consistent with Mehli’s right-binding (TB) determination of $D$ for nonmagnetic FCC metals, according to which Ni would rank as having a ductility less than Cu, Ag, and Au ($D > 3.2$), but greater than Al, Pt, Pb, etc. ($D < 1.6$). Relative to the range of ductility values predicted by TB, ductility in the alloys is found to be similar to that of pure Ni, ranging from 2.09 to 2.62. The relative insensitivity of $D$ to alloying at this concentration is a consequence of two factors. (1) With the exception of Cu, these solutes do not alter $\gamma_s$ of pure Ni as their calculated heats of segregation are positive. (2) Changes to $D$ will therefore depend only on changes to $\gamma_{us}$ and in the alloys $\gamma_{us}$ deviates from the pure Ni $\gamma_{us}$ by less than 20%.

In addition to its effect on ductility, we have also investigated whether alloying can alter the mode of plastic deformation. Based on a derivation by Tadmor and Hai, Van Swygenhoven et al. have discussed how the relative sizes of $\gamma_{us}$ and $\gamma_{ut}$ provide a qualitative gauge of whether dislocation-mediated slip or deformation twinning will be the preferred deformation mechanism. According to this analy-
sis, once a leading partial has been nucleated, whether a subsequent nucleation event will consist of a trailing partial (i.e., a full dislocation) or of a second leading partial on an adjacent slip plane (twinning) will be influenced by the difference $\gamma_{us} - \gamma_{ts} = \delta_{ts}$. Within this framework, the GSF data show (Table I) that the barrier for nucleation of the trailing partial is in all cases less than for formation of a microtwin, $\delta_{ts} > 0$, suggesting that alloying will not switch the dominant deformation mechanism from dislocation-mediated slip to twinning. However, it is clear that alloying will make twinning more likely, since $\delta_{ts}$ is reduced when solutes are present. Whether twinning would ever be observed in a real system will therefore depend sensitively upon the stress intensity at the point of nucleation.

A more thorough treatment of the balance between dislocation-mediated slip and deformation twinning has been derived by Bernstein and Tadmor in the form of their “twinnability measure” ($\tau_a$):

$$\tau_a = \left[ 1.136 - 0.151 \frac{\gamma_{sf}}{\gamma_{us}} \right] \sqrt{\frac{\gamma_{us}}{\gamma_{ts}}}.$$  (1)

$\tau_a$ is a relative measure of the tendency of a polycrystalline FCC metal to undergo deformation twinning based on the number and strength of active twinning systems: A larger $\tau_a$ indicates a greater propensity for twinning. The twinnability of pure Ni has not been previously calculated. The present value (0.987, Table I) is in very good agreement with the value expected from a synthesis of experimental data and TB calculations on nonmagnetic FCC metals. Calculated twinnability measures for the alloy systems show that solute incorporation should enhance the twinnability of pure Ni, in qualitative agreement with reports of higher twin densities in incorporation measures for the alloy systems show that solute incorporation should enhance the twinnability of pure Ni, in qualitative agreement with reports of higher twin densities in electrodeposited nc-Ni-Mn films relative to Ni-sulfamate. Relative to the TB calculations in Ref. 11, the ab initio data suggest Ni-Cu will twin comparably to Pd; Ni-Nb, Ni-Mn, and Ni-Fe similar to Pb; and Ni-W should twin more readily than Ag. The fact that $\tau_a$ is inversely proportional to $\delta_{ts}$ (Table I) suggests that the qualitative picture based on relative unstable barrier heights is reasonable, at least for FCC metals.

Finally, the GSF data can be used to clarify the mechanisms underlying the differing effects of Cu and Fe additions on the strain-hardening rate ($\Theta$) of nc-Ni recently reported by Ebrahimi et al. These authors suggested that the increase in $\Theta$ observed for the alloys may be a result of their lower stacking fault energies. This hypothesis would also imply that Cu, which produced a greater increase in $\Theta$ than did Fe, will lower $\gamma_{sf}$ more than Fe. However, the present calculations and experimental data show that Cu and Fe additions of less than $\sim 10$ at. % produce similar reductions in the Ni $\gamma_{sf}$. Hence $\gamma_{sf}$ alone cannot account for the higher $\Theta$ observed in nc-Ni-Cu. The higher $\Theta$ in Ni-Cu may instead result from a reduction in $\gamma_{us}$ (Table I), which would facilitate dislocation nucleation. It is well-known that strain-hardening arises from increasing dislocation-dislocation interactions as a function of deformation; a smaller $\gamma_{us}$ would increase the dislocation density in the metal, the quantity upon which strain-hardening directly depends.

In conclusion, this study has applied an information-passing approach to examine how alloying with transition metals alters selected mechanical properties of Ni; ab initio generalized stacking fault curves have been calculated and used to parametrize continuum mechanics models of dislocation nucleation, brittle-ductile behavior, and deformation twinning. The results indicate that alloying will generally lower the fault energies of Ni, and calculated intrinsic stacking fault energies were found to be consistent with experimental measurements from the literature. Evaluation of the Rice criterion for ductility revealed that alloying at the present concentration should not significantly alter the inherent ductility of Ni. On the other hand, alloying should increase the likelihood that plastic deformation will occur via twinning. Finally, the GSF and experimental data suggest that the higher strain-hardening rate reported in nc-Ni-Cu relative to nc-Ni-Fe is not due to differences in $\gamma_{sf}$, but rather to an increased dislocation density resulting from more facile dislocation nucleation.

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29. While the values of $\tau_a$ in Table I vary by only $\sim 10\%$, differences of this magnitude are significant in the context of the values obtained for nonmagnetic metals in Ref. 11.