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

Donald J. Siegel[a)]
U.S. Naval Research Laboratory, Code 6390, 4555 Overlook Ave. SW, Washington, D.C. 20375 and Sandia National Laboratories, Mail Stop 9161, Livermore, California, 94551

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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 (γ_{sf}), 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 γ_{sf}, 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 novel deformation mechanisms may arise in the nanostructured limit.[3,6] From an applications perspective, electrodeposited nc metals are of interest because they can be combined with lithographic techniques[7] to fabricate elaborate microelectromechanical systems (MEMS). In the electrodeposition of single-component metals, organic precursors are often added to the plating bath to facilitate the formation of nanoscale grains.[8] However, additives can produce elevated impurity levels, resulting in embrittlement via grain boundary segregation.[9]

Recognizing that grain refinement via additives requires a compromise in purity, recent studies have focused on alloy systems, where nanoscale grains can be obtained without significant impurity incorporation.[1,2,5] In addition to their high strength, some nc alloys have favorable properties that are absent in their unalloyed counterparts, such as enhanced thermal stability.[5] Ebrahimi *et al.*[2] have reported that the strain hardening rate of nc-Ni was increased by the addition of Cu and Fe solutes, with Cu having the largest effect. The change was attributed to a reduced stacking fault energy in the alloys, which would retard dislocation cross slip.

At a fundamental level, the macroscopic mechanical properties of a material can be traced to electronic interactions (bonding) between its constituent atoms. However, an atomistic model alone cannot capture the behavior of even microscale systems because deformation is controlled by processes that act simultaneously over widely varying time and length scales. An effective way to bridge this gap is through an information passing procedure where a formulation for a macroscopic property is informed by parameters computed from first principles. This approach is adopted here by employing existing continuum mechanics models[10,11] and an *ab initio*[12,13] evaluation of generalized stacking fault[14–16] (GSF) energies to examine how alloying alters selected mechanical properties of Ni. Emphasis is placed on alloying-induced changes to dislocation nucleation barriers,[10] ductility,[10,17] and the tendency of a metal to undergo dislocation-mediated slip vs deformation twinning.[11,14] Consideration is given to transition metal solutes (Nb, W, Mn, Fe, and Cu) that are amenable to co-deposition with Ni, and that have been proposed for use in MEMS. Comparisons are made with experimental data from the literature, and an explanation for the different strain-hardening rates observed for nc-Ni-Cu vs nc-Ni-Fe[2] is proposed. While this study is motivated by the emergence of nc alloys, the present analysis does not account for the increasingly important role played by microstructure at smaller grain sizes. The results are therefore equally applicable to conventional coarse-grained systems.

The GSF surface represents the energy cost per unit area incurred by the relative displacement of two parts of a crystal through a fault vector **f**.[16] For face centered cubic (FCC) metals, **f** is conventionally taken along a ⟨112⟩ direction within a {111} slip plane (see Fig. 1).[17] The first maximum encountered along this path is the unstable stacking energy (γ_{us}), and the subsequent minimum corresponds to the intrinsic stacking fault configuration, with energy γ_{sf} at a displace-

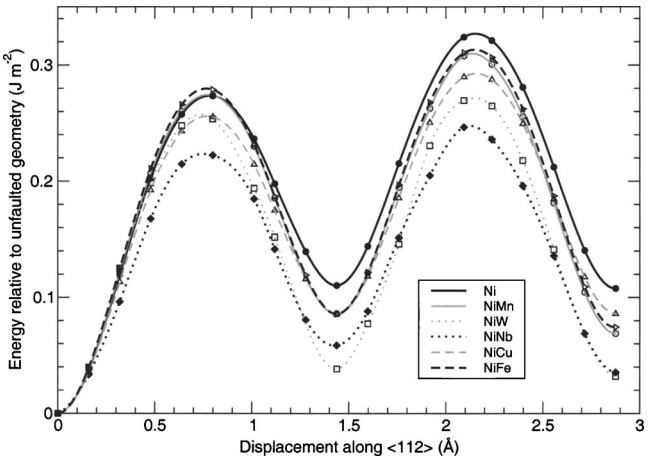

FIG. 1. Generalized stacking fault curves for Ni and Ni alloys. Cubic splines are used to connect the *ab initio* datapoints.

[a)]Electronic mail: dsiegel@dave.nrl.navy.mil

ment of $a_0/\sqrt{6}$ (a_0=3.522 Å).[18] 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 (γ_{ut}).[19] While γ_{sf} can be measured experimentally, γ_{us} and γ_{ut}, which represent the minimum energy barriers for partial dislocation[10] and microtwin nucleation,[11] 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.[3,20]

The GSF curves were evaluated using a spin-polarized, planewave-pseudopotential method[21] based on the generalized gradient approximation[22] to density functional theory[12,13] (VASP). The core-valence electron interaction was treated using Blöchl's projector augmented wave method,[23,24] 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 γ_{us} and γ_{sf} to better than 10%. The planewave cutoff 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 (2×2) slab geometry with 10 (111) planes and a total of 40 atoms. An ~8 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,[25] 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 $[11\bar{2}]$ 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.[15]

Although nucleation of a partial dislocation or microtwin will involve shearing of the lattice, it has been demonstrated[10] 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 γ_{us} is lowest in this direction, and MD simulations suggest that deformation in nc metals is strongly dependent on the motion of partial dislocations.[20]

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.[26] These factors suggest that the present approach of evaluating the GSF curves in the vicinity of the solute-containing plane is reasonable.[25]

TABLE I. Calculated fault energies (γ_i, mJ/m^2), ductility parameters (D), relative barrier heights ($\delta_{us}^{ut} \equiv \gamma_{ut} - \gamma_{us}$), and theoretical twinnabilities (τ_a) for pure Ni and Ni alloys.

System	γ_{sf}	γ_{us}	γ_{ut}	D	δ_{us}^{ut}	τ_a
Ni	110	273	324	2.14	51	0.987
Ni-Nb	59	223	248	2.62	25	1.039
Ni-W	38	257	271	2.28	14	1.085
Ni-Mn	86	274	306	2.14	32	1.030
Ni-Fe	86	280	313	2.09	33	1.031
Ni-Cu	86	256	293	2.11	37	1.014

The calculated GSF curves for Ni and the five Ni-based alloys are plotted in Fig. 1; numerical values extracted from the curves' extrema (γ_i) are assembled in Table I. The curves indicate that alloying Ni at this concentration will generally reduce the size of γ_i. For example, in Ni a value of 110 mJ/m^2 was found for γ_{sf} (experimental values fall within 125–128 mJ/m^2),[11] while in the alloys γ_{sf} ranges from 38 to 86 mJ/m^2. Gallagher[27] has reviewed experimental measurements of changes to γ_{sf} by alloying. For Ni-based alloys the data show a reduction in γ_{sf} upon incorporation of transition-metal solutes. Furthermore, x-ray faulting probabilities[27] suggest that Cu, Fe, and Mn additions of less than 20 at.% produce similar reductions in the Ni γ_{sf}, while alloying with W results in a larger reduction. Both of these trends are reproduced in the present calculations. Similar to γ_{sf}, the GSF curves show that γ_{ut} is reduced in all of the alloys; γ_{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[10] 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 $D=0.3\gamma_s/\gamma_{us}>1$, where γ_s is the (111) surface energy of pure Ni or the appropriate Ni alloy, including the effects of surface segregation. If γ_s is small relative to γ_{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 γ_s=1.95 J/m^2 yields D=2.14, indicating that (as expected) Ni is an intrinsically ductile metal. This is consistent with Mehl's[17] tight-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 γ_s of pure Ni as their calculated heats of segregation are positive. (2) Changes to D will therefore depend only on changes to γ_{us}, and in the alloys γ_{us} deviates from the pure Ni γ_{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,[19] Van Swygenhoven *et al.*[14] have discussed how the relative sizes of γ_{us} and γ_{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 $\gamma_{ut}-\gamma_{us}\equiv\delta_{us}^{ut}$.[10] 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, $\delta_{us}^{ut}>0$, 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 δ_{us}^{ut} 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[11] in the form of their "twinnability measure" (τ_a):

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

τ_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 τ_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.[11] Calculated twinnability measures for the alloy systems[29] 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.[5] 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 τ_a is inversely proportional to δ_{us}^{ut} (Table I) suggests that the qualitative picture[14] 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 ~6 wt.% Cu and Fe additions on the strain-hardening rate (Θ) of nc-Ni recently reported by Ebrahimi *et al.*[2] These authors suggested that the increase in Θ 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 Θ than did Fe, will lower γ_{sf} more than Fe. However, the present calculations and experimental data[27] show that Cu and Fe additions of less than ~10 at.% produce similar reductions in the Ni γ_{sf}. Hence γ_{sf} alone cannot account for the higher Θ observed in nc-Ni-Cu. The higher Θ in Ni-Cu may instead result from a reduction in γ_{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;[28] a smaller γ_{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[2] in nc-Ni-Cu relative to nc-Ni-Fe is not due to differences in γ_{sf}, but rather to an increased dislocation density resulting from more facile dislocation nucleation.

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