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An Atomistic Modeling Study of Alloying Element, Impurity Element, and Transmutation Products on the Cohesion of a Nickel $\Sigma 5$ {001} Twist Grain Boundary

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Abstract

Atomistic modeling methods were employed to investigate the effects of impurity elements on the metallurgy, irradiation embrittlement, and environmentally assisted cracking of nickel-base alloys exposed to nuclear environments. Calculations were performed via *ab initio* atomistic modeling methods to ensure the accuracy and reliability of the results. A Griffith-type fracture criterion was used to quantitatively assess the effect of elements or element pairs on the grain boundary cohesive strength. In order of most embrittling to most strengthening, the elements are ranked as: He, Li, S, H, C, Zr, P, Fe, Mn, Nb, Cr, and B. Helium is strongly embrittling (-2.04 eV/atom lowering of the Griffith energy), phosphorus has little effect on the grain boundary (0.1 eV/atom), and boron offers appreciable strengthening (1.03 eV/atom increase in the Griffith energy). Calculations for pairs of elements (H-Li, H-B, H-C, H-P, and H-S) show little interaction on the grain boundary cohesive energy, so that for the conditions studied, linear superposition of elemental effects is a good approximation. These calculations help explain metallurgical effects (*e.g.* why boron can strengthen grain boundaries), irradiation embrittlement (*e.g.* how boron transmutation results in grain boundary embrittlement), as well as how grain boundary impurity elements can affect environmentally assisted cracking (*i.e.* low temperature crack propagation and stress corrosion cracking) of nickel-base alloys.

Background

Continued advances in computing power have made increasingly complex *ab initio* atomistic calculations of structural materials viable. While empirical potential methods (*e.g.* embedded atom methods) have been used in Materials Science for some time [1-6], more computationally intensive *ab initio* methods have had limited application [7-10]. However, relative to empirical methods, *ab initio* calculations offer higher predictive power and provide more detailed quantitative information on physical and electronic structures. As summarized in Figure 1, information that can be calculated via *ab initio* calculations includes thermodynamic, structural, mechanical, electronic, chemical, and kinetic properties of material. Much of the information that *ab initio* methods can provide is difficult to determine experimentally.

Figure 1. Illustration of the information that *ab initio* methods can provide to Materials Science.

Of specific interest to the nuclear industry, are the metallurgy, embrittlement, and environmentally assisted cracking of nickel-base alloys. Understanding the factors that affect grain boundary strength, is important in assessing an alloy's fabricability (*e.g.* hot-workability and weldability), in-service lifetime (*e.g.* stress corrosion cracking), and to developing materials and processes that are resistant to intergranular cracking. While experimental methods have helped elucidate how grain boundary impurity atoms affect the intergranular fracture resistance of nickel and nickel-based alloys [11-20], fundamental understanding of why certain elements appear to strengthen or weaken grain boundaries is lacking. Moreover, gaining understanding via experimental methods is often confounded by complex changes such as simultaneous grain boundary segregation and precipitation [20], environmental interactions [14, 19, 20], or transmutation reactions [18].

As suggested by Rice and Wang [21] and shown by Briant and Mesmer, [22], Freeman *et al.* [8, 9, 23, 24], Olson [25] and others [1, 2, 7], atomistic calculations offer powerful means to assess the effect of grain boundary segregants on the cohesive strength of a boundary. Atomic modeling is especially important, given the experimental difficulties associated with determining the surface and the grain boundary segregation energies [21]. In order to better understand the effect of impurity atoms on the grain boundary cohesive strength of nickel alloys the present study utilizes *ab initio* atomistic modeling methods to quantify the effect of select impurity atoms and atom pairs on the strength of a nickel grain boundary.

Computational Procedure

Calculations were performed using the Vienna *Ab initio* Simulation Package (VASP) computer code on a 40-atom model of a nickel $\Sigma 5$ {001} twist grain boundary. The 40-atom model, with a 3D periodic boundary condition was chosen as a good compromise of accuracy and computing time after investigating larger (60 atom) and smaller (20 atom) models. Both single impurity elements (He, Li, S, H, C, Zr, P, Fe, Mn, Nb, Cr, and B and selected pairs of elements (H-Li, H-B, H-C, H-P, and H-S) were investigated. A Griffith-type fracture criterion (Equation 1) was used to quantitatively assess the effect of elements or element pairs on the grain boundary cohesive strength.

$$\Delta E_{Griffith} = (E_{Surface} - E_{Surface}^{impurity}) - (E_{Grain Boundary} - E_{Grain Boundary}^{impurity}) \quad (1)$$

> 0: Weakening, < 0: Strengthening

The Griffith criterion can be expressed via Equation 2 where $\mathcal{G}$ is the critical energy release rate, σ is the stress, a is one half the crack length and E is the elastic modulus, *i.e.*:

$$Fracture Energy per Area = \mathcal{G}_c = \frac{\pi \sigma^2 a}{E} \quad (2)$$

As shown schematically in Figure 2, the computational steps in determining the fracture energy with a given impurity are as follows: (1) relax the pure nickel grain boundary, (2) determine the preferred site for the impurity and associated relaxation, (3) cleave the grain boundary, and (4) relax the free surfaces.

Figure 2. Schematic illustration of the steps involved in calculating the Griffith energies.

Results

The equilibrium positions of the interstitial impurities, substitutional impurities, and impurity pairs and the two planes adjacent to the grain boundary are shown in Figure 3. Both a top view and a cross sectional view are shown. For clarity, the nickel atoms below the grain boundary are colored green while the nickel atoms above the grain boundary are colored red. Hydrogen, boron, and carbon are interstitial impurities, while helium, phosphorus, sulfur, chromium, iron, manganese (not shown) and niobium (not shown) are substitutional impurities.

The theoretical fracture energies of nickel along a {001}-type plane and along a {001} $\Sigma 5$ -twist grain boundary are given in Table I. As expected, fracture along the grain boundary takes less energy than in the single crystal. Table I also summarizes the effects of impurity atoms on the energy to cleave the grain boundary, the grain boundary energy, and the surface energy. The results of the calculations are also presented in Figures 4 and 5. Figure 4 compares the tendency of the impurity element to segregate to the bulk, the free surface, or to the nickel {001} $\Sigma 5$ twist grain boundary while Figure 5 summarizes the effect of the impurity elements on the grain boundary fracture energy.

A Check on the Calculations

In order to check the reasonableness of the calculations, Equation (2) can be used to estimate the theoretical fracture stress of the nickel. Rearranging Equation (2) to solve for the fracture stress, σ , yields Equation (3):

$$\sigma = \sqrt{\frac{\mathcal{G} E}{\pi a}} \quad (3)$$

The value for $\mathcal{G}$ from the atomistic calculations [pure nickel {001} plane] is 4.37 J/m², E is $\approx 2.00 \times 10^{11}$ Pa, and $a = 2.76 \times 10^{-10}$ m yields a theoretical fracture stress, σ , of 3.2×10^{10} Pa. The ratio of the theoretical fracture stress to the modulus is $\sim E/6$ which is in good agreement with other estimates of theoretical strengths of metals [26].

Discussion

Effect of Single Impurity Atoms

In order of most embrittling to most strengthening, the impurity elements are ranked as: He, Li, S, H, C, P, Fe, Mn, Nb, Cr, and B as shown in Figure 5. Helium is strongly embrittling (1.07 J/m² lowering of the Griffith energy) while phosphorus has little effect on the grain boundary (-0.05 J/m²) and boron offers appreciable strengthening (-0.54 J/m² increase in the Griffith energy). These findings are consistent with experimental observations (e.g. He, S, and H are known embrittling agents and boron is a known strengthener in nickel-base alloys).

Comparison of the present work with previous atomistic calculations of impurity atoms in nickel is given in Table II. There is general agreement between the results with the exception of the results for phosphorus. The work of Geng *et al.*, suggests phosphorus is strongly embrittling in a nickel $\Sigma 5$ tilt grain boundary, [8], in contrast to the present work which indicates phosphorus to be weakly strengthening (or neutral) to the grain boundary. While the difference may be due to the different grain boundary structure (e.g. the presence of kink sites in the tilt boundary), there are two notable studies that support a weak effect of phosphorus on grain boundary strength: (1) the early work of Briant and Mesmer suggests that the nickel-phosphorus bond is more homopolar than the iron-phosphorus bond and hence, phosphorus should be much less embrittling to nickel than to iron [22], and (2) the experimental data of Bruemmer *et al.*, which indicate that phosphorus alone has little effect on the ductility of nickel but phosphorus + hydrogen is embrittling [14]. As shown in Figure 5 and discussed below, the P+H impurity pair is embrittling.

Effect of Multiple Impurity Atoms

Calculations for pairs of elements show essentially no strong attraction between H and S, P, B, and C atoms in bulk, grain boundary, and surface environments as summarized in Table III. Since there is little interaction for the concentration studied, linear superposition of elemental effects is a good approximation for the element pairs studied in the concentration investigated (i.e. one atom pair for the grain boundary). This approach can be used to help rationalize the combined effect of impurity elements on the resistance of an alloy to intergranular fracture.

The calculations are consistent with experimental work that shows sulfur and hydrogen atoms embrittle nickel grain boundaries but that phosphorus alone has little effect on intergranular fracture [16, 17, 27]. However, when hydrogen and phosphorus are both present, embrittlement of nickel [27] and nickel based alloys [15, 19, 20] has been observed experimentally. An important aspect to consider when assessing the influence of an impurity atom on hydrogen embrittlement is not just its intrinsic effect on grain boundary strength, but the possibility of its effect on hydrogen uptake. Experimental results indicate that phosphorus can poison the hydrogen recombination reaction $\{ H_{ads} + H_{ads} \rightarrow H_2(g) \}$ and promote hydrogen entry and embrittlement [14, 15, 19, 20, 28]. These experimental

findings are consistent with the calculations of the present study which show weak (~ 8 kJ/mol) binding between hydrogen and phosphorus atoms on the free surface (See Table III). This weak binding is consistent with an impurity favoring H_{ads} stability and acting as a hydrogen recombination poison.

Figure 3. Equilibrium positions of the atoms adjacent to the Ni $\Sigma 5(001)$ twist grain boundary in the presence of interstitial, impurities, substitutional impurities and impurity pairs. As reference, the structure of the pure grain boundary is given on the upper left-hand side.

Table I. Summary of the Effect of Selected Impurity Atoms on the Calculated Energies for Cleavage, the Grain Boundary, Surface, and the Change in Griffith Fracture Energy.

	E_{Cleavage}		$\Delta E_{\text{Grain Boundary}}$ ($E_{GB} - E_{GB}^{\text{impurity}}$)		$\Delta E_{\text{Surface}}$ ($E_{\text{Surface}} - E_{\text{Surface}}^{\text{impurity}}$)		$\Delta E_{\text{Griffith}}$ ($E_{\text{Surface}} - E_{GB}$)	
	(eV/atom)	(J/m ²)	(eV/atom)	(kJ/mol)	(eV/atom)	(kJ/mol)	(eV/atom)	(J/m ²)
Cleavage of pure Ni along {001} plane	8.34/8.21	4.37/4.30	---	---	---	---	---	---
Cleavage of pure Ni along $\Sigma 5$ {001} twist grain boundary	6.51/6.35	3.41/3.33	---	---	---	---	---	---
Impurity Element at $\Sigma 5$ {001} twist grain boundary	(eV/atom)	(J/m ²)	(eV/atom)	(kJ/mol)	(eV/atom)	(kJ/mol)	(eV/atom)	(J/m ²)
He	4.47	2.35	0.51	49	2.55	246	2.04	1.07
Li	5.85	3.07	0.14	14	0.80	77	0.66	0.35
S	5.99	3.14	1.37	132	1.89	182	0.52	0.27
H	6.09	3.19	0.16	15	0.58	56	0.42	0.22
C	6.14	3.22	0.66	64	1.03	99	0.37	0.19
Zr	6.43	3.37	1.02	98	1.10	106	0.08	0.04
P	6.61	3.47	1.01	97	0.91	88	-0.10	-0.05
<i>Fe</i>	<i>6.90 / 6.51</i>	<i>3.41</i>	<i>-0.03</i>	<i>-3.0</i>	<i>-0.42</i>	<i>-41</i>	<i>-0.17</i>	<i>-0.09</i>
<i>Mn</i>	<i>6.54</i>	<i>3.43</i>	<i>-0.19</i>	<i>-18</i>	<i>-0.39</i>	<i>-38</i>	<i>-0.20</i>	<i>-0.10</i>
Nb	6.98	3.66	0.49	47	0.03	3.0	-0.46	-0.24
<i>Cr</i>	<i>7.10 / 6.87</i>	<i>3.60</i>	<i>-0.02</i>	<i>-2.0</i>	<i>-0.61</i>	<i>-59</i>	<i>-0.53</i>	<i>-0.28</i>
B	7.54	3.95	1.70	164	0.67	65	-1.03	-0.54
Impurity Element Pair at $\Sigma 5$ {001} twist grain boundary	($\frac{\text{eV}}{\text{atom pair}}$)	(J/m ²)	($\frac{\text{eV}}{\text{atom pair}}$)	(kJ/mol)	($\frac{\text{eV}}{\text{atom pair}}$)	(kJ/mol)	($\frac{\text{eV}}{\text{atom pair}}$)	(J/m ²)
H+Li	2.85	1.50	0.36	34.7	1.44	138.9	1.08	0.57
H+S	2.98	1.56	1.54	148.6	2.37	228.7	0.83	0.43
H+C	3.02	1.58	0.86	83.0	1.63	157.3	0.77	0.40
H+P	3.22	1.69	1.19	114.8	1.57	151.5	0.38	0.20
H+B	3.73	1.96	1.88	181.4	1.27	122.5	-0.61	-0.32

Italics indicate that magnetic effects were included in the calculation

Table II. Comparison of the Results of the Present Work with the Calculations of Geng et al., on a Nickel $\Sigma 5$ -tilt Grain Boundary. The Results are in General Agreement with the Exception of Geng et al.'s result on phosphorous.

Energy	Impurity Element				Boundary Type	Reference
	Hydrogen	Phosphorus	Sulfur	Boron		
$\Delta E_{\text{Grain Boundary}}$ (eV/atom)	0.42	-0.10	0.52	-1.03	$\Sigma 5$ Twist (001)	Present Work
	0.27	0.70	---	-0.49	$\Sigma 5$ Tilt (210)	[8]
	---	---	(+) weakening	(-) strengthening	$\Sigma 11$ (11 $\bar{3}$)/[110]	[29]

Figure 4. Comparison of the tendency of selected impurity elements to segregate to the free surface or to the Ni {001} $\Sigma 5$ twist grain boundary.

Figure 5. Comparison of the effect of selected impurity elements and pairs of impurities on the cohesive strength of a nickel $\Sigma 5$ {001} twist grain boundary. The cleavage energy of the pure nickel grain boundary is 3.41 J/m².

Table III. Comparison of Pair Formation Energies in the Bulk, Grain Boundary, and Free Surface. Negative Numbers Indicate Attraction, Positive Numbers Repulsion. The Attraction Between H and P at the Surface Suggest P Can Act as a Hydrogen Recombination Poison.

System	Pair Formation Energy (kJ/mol)		
	Bulk	Grain Boundary	Surface
H-P	0	-3	-8
H-B	5	3	3
H-C	4	-1	3
H-S	-1	-2	10

Metallurgy, Irradiation Embrittlement, and Environmentally Assisted Cracking

Metallurgy

It is well established empirically, that small additions of boron can increase the grain boundary strength of nickel-based alloys [11, 12]. However, fundamental understanding of why boron is beneficial is lacking. Postulated mechanisms include: (1) alteration of the grain boundary precipitate structure, (2) an interaction with a deleterious element, and (3) a reduction in grain boundary diffusivity [12]. Atomistic calculations show that boron is strengthening, in agreement with empirical results, and give insight into why strengthening is observed. The present study predicts B s-to-p electron transfer and hybridization of boron 'p' and nickel 'd' electrons as shown in Figure 6. This hybridization is believed to be a general effect and not specific to this grain boundary type. Unlike boron, the lower energy of carbon 's' electrons relative to the p electrons inhibits s-to-p electron promotion and subsequent hybridization with Ni d electrons as shown in Figure 6. These findings suggests that hybridization of impurity electronic states with the Ni d states can be associated with strengthening, while lack of hybridization (as in the case of carbon) results in embrittlement.

Figure 6. Partial density of states of B and C in their equilibrium sites at the Ni $\Sigma 5(001)$ twist grain boundary. The solid yellow and red areas correspond to the B and C, s and p partial densities of states, respectively. The blue lines are a superposition of the Ni-3d partial densities of states of all 40 Ni atoms of the simulation cell. Note the significantly lower 2s energy for C compared with B. For the grain boundary with boron, there is a strong hybridization peak near -2.5 eV (indicated by an arrow). A similar peak is absent for carbon.

Irradiation Embrittlement

In contrast to its beneficial metallurgical effect in most environments, when irradiated, the transmutation of boron $^{10}\text{B}(n,\alpha)^7\text{Li}$ (Equation 4) is known to produce embrittlement in stainless steels and in nickel based alloys [18, 27].

However, the mechanism of embrittlement is poorly understood. If given post-irradiation heat treatments at high temperature ($\sim 1500^\circ\text{F}/1\text{ hr}$) grain boundary, He-rich bubbles have been observed [18] but embrittlement is not due to bubble formation since it occurs well before helium bubbles are observed experimentally [18, 27]. Atomistic modeling helps us postulate an embrittlement scenario that does not depend on helium-rich, grain boundary bubble formation.

The first consideration is that the loss of boron, in itself, reduces grain boundary strength. Additionally, as shown by the modeling, He and Li are strongly embrittling to the nickel grain boundary. Since boron is likely present at the grain boundary initially, and the particles emitted by the transmutation are relatively energetic, helium and lithium may be injected some distance away from the grain boundary. The α particle emitted from the boron decay (1472 keV) [30] has been estimated to be injected up to $\sim 3\text{ }\mu\text{m}$ from the grain boundary [27], while lithium is estimated to be with $\sim 1\text{ }\mu\text{m}$ of the grain boundary.

If helium and lithium are ejected away from the grain boundary, the second step in embrittlement occurs as they collect at the grain boundary over time. As shown by the atomistic modeling (Figure 4), helium and lithium can lower the energy of the system by migrating to the grain boundary (or free surface) from the bulk grain. The kinetics of He and Li collection at the grain boundary are poorly understood, so the relative contribution of this embrittlement is difficult to assess. However, the lithium ($\sim 0.85\text{ MeV}$) is not as energetic as the helium ($\sim 1.49\text{ MeV}$), and the Li is ejected on the order of $\sim 1\text{ }\mu\text{m}$ compared to $\sim 3\text{ }\mu\text{m}$ for the helium. If the kinetics of helium and lithium diffusion are similar, then Li, not He, may play a greater role in grain boundary embrittlement. However, it should be emphasized that the kinetics of helium and lithium transport in an irradiated material are poorly understood.

If the transport of helium and lithium is similar to nickel self-diffusion, then at intermediate temperatures ($500\text{--}700^\circ\text{F}$) the time required for appreciable diffusion ($\sim 1\text{ }\mu\text{m}$) are unrealistically long. In contrast, at 1500°F , simple diffusion can support transport over micron-scale distances, which is consistent with the observation of grain boundary, helium-rich bubbles [18]. Alternately, simple diffusion may not apply to an irradiated material, where vacancy damage may facilitate transport kinetics. Although the kinetics of helium and lithium collection at a grain boundary are poorly understood, the key point is that grain boundary bubble formation is not required to produce embrittlement, helium and lithium atoms are intrinsically embrittling and after transmutation, lithium atoms are, on average, closer to the grain boundary than helium atoms. Possible steps in the embrittlement process are shown schematically in Figure 7.

Figure 7. Schematic illustration of boron transmutation process showing helium and lithium injection into the bulk grain and their transport back to the grain boundary. The loss of boron atoms, and the presence of helium and lithium atoms all act to weaken the nickel grain boundary.

Environmentally Assisted Cracking

Low temperature crack propagation (LTCP) resistance of nickel based alloys has been correlated to the intergranular segregation of metalloid-type impurity atoms (S, P) [15, 19, 20]. However, the correlation between fracture toughness and grain boundary concentration of these elements exhibits large scatter as shown previously [15, 19, 20]. Atomistic modeling can help explain why the data are not well correlated. At least for the $\Sigma 5$ -twist boundary investigated, there appears to be a fundamental difference between S and P. Sulfur is intrinsically embrittling while phosphorus is not. However, the weak binding between hydrogen and P on the free surface is consistent with P acting as a hydrogen recombination poison [28]. The implication of this is that P promotes embrittlement by facilitating hydrogen uptake while S is intrinsically embrittling. While both elements are detrimental to grain boundary toughness, the dependencies between grain boundary concentration, hydrogen uptake, and grain boundary cohesion must be better understood in order to develop accurate correlations between grain boundary composition and the occurrence of LTCP.

In addition to LTCP, the grain boundary composition may also affect the resistance of nickel-based alloys to primary water stress corrosion cracking. One notable observation is a difference in crack growth rate (Table V) and failure rate (Figure 8) between compositionally similar heats of X-750 HTH. Testing of both fasteners and compact tension specimens shows that Heat B exhibits more susceptibility to SCC (*i.e.* faster crack growth rates and more failures) than Heat A. TEM examination of these heats shows that Heat B contains an unusually high number of boron-rich grain boundary precipitates (Ni_{23}B_6 -type), as shown in Figure 8. Boron rich precipitates may be promoted by grain boundary segregation and by higher aging temperatures. The presence of nickel-borides vs. chromium-carbides would (1) mitigate the strengthening effect of *free* boron on the grain boundary cohesion, (2) not produce beneficial Cr depletion of the grain boundary region as a Cr_{23}C_6 carbide does, and (3) result in additional free carbon on the grain boundary, which modeling indicates is embrittling.

Table IV. Comparison of the Bulk Composition of Two Heats of Alloy X-750 HTH. While Heat B has Lower Bulk Boron it Displayed Grain Boundary Boride Particles

Heat #	Ni	Cr	Fe	Ti	Al	Mn	C	B	P	S	Nb+Ta
A	72.43	15.54	7.93	2.60	0.79	0.07	0.039	0.0037	0.007	0.001	0.86
B	71.47	15.25	8.15	2.66	0.73	0.15	0.043	0.0022	0.002	0.002	0.97

Table V. Comparison of the Selected Mechanical Properties and the Stress Corrosion Crack Growth Rate of Two Heats of Alloy X-750 HTH. While the Mechanical Properties are Similar, Heat B (Which Displayed Grain Boundary Boride Particles) Exhibits a Faster SCC Rate.

Heat #	YS (ksi)	UTS (ksi)	% El	%RA	SCCGR at 680°F and 35 ksi√in in high purity water (mils/day)
A	118	172	27	32	1.1
B	117	176	26	36	1.8

Figure 8. Illustration of the SCC performance (left) and the grain boundary structure (right) of two heats of X-750 condition HTH. The more susceptible Heat (B) contains significantly more grain boundary boride particles than the less susceptible Heat (A).

Conclusions

- In order of decreasing strength: He, S, H, and C embrittle Ni $\Sigma 5$ {001} twist grain boundaries
- Zirconium and phosphorus have little effect on grain boundary cohesion. However, the weak binding between hydrogen and phosphorus on the nickel surface is consistent with phosphorus acting as a hydrogen recombination poison.
- In order of increasing strength: Fe, Mn, Nb, Cr, and B would strengthen Ni $\Sigma 5$ {001} twist grain boundaries if present, but note that calculations show Fe, Mn and Cr prefer the bulk rather than the grain boundary. The ability of boron 2p electrons to hybridize with nickel 3d electrons helps explain its known effect as a grain boundary strengthener.
- For the concentration investigated, linear superposition of the effect of single elements is a good approximation for the pairs of elements investigated (H-S, H-C, H-P, and H-B).

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