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Computation of Embrittling Potencies of Sulfur for a Range of Nickel Pure Tilt Grain Boundaries via Atomistic Simulation Methods

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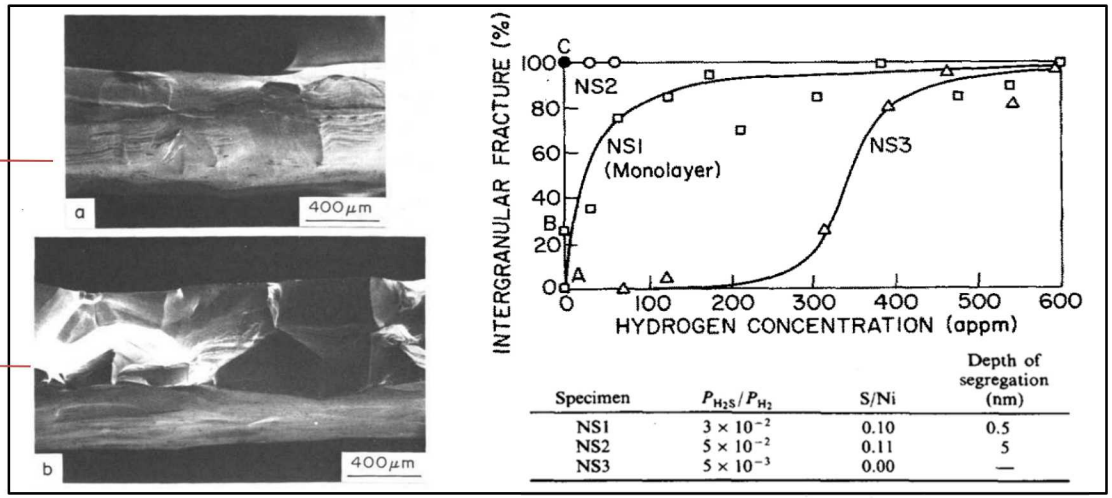
SAND Number: SAND2019- XXXX

Introduction

- **Embrittlement** is defined as the loss of ductility in metals caused by segregation of certain impurity atoms.

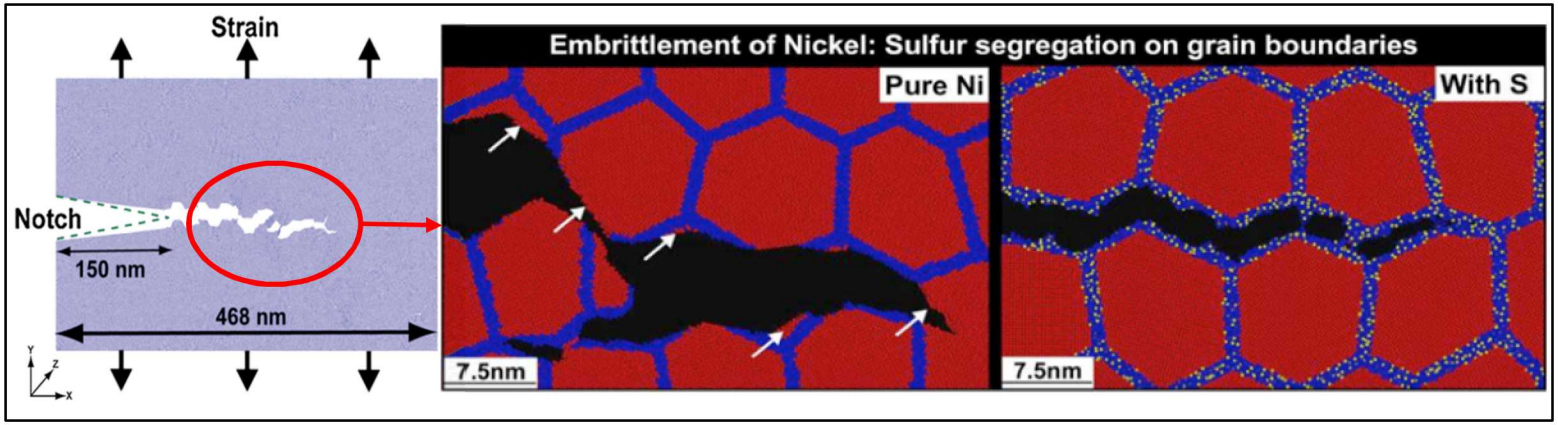
Ductile

Brittle



Specimen	P_{H_2S}/P_{H_2}	S/Ni	Depth of segregation (nm)
NS1	3×10^{-2}	0.10	0.5
NS2	5×10^{-2}	0.11	5
NS3	5×10^{-3}	0.00	—

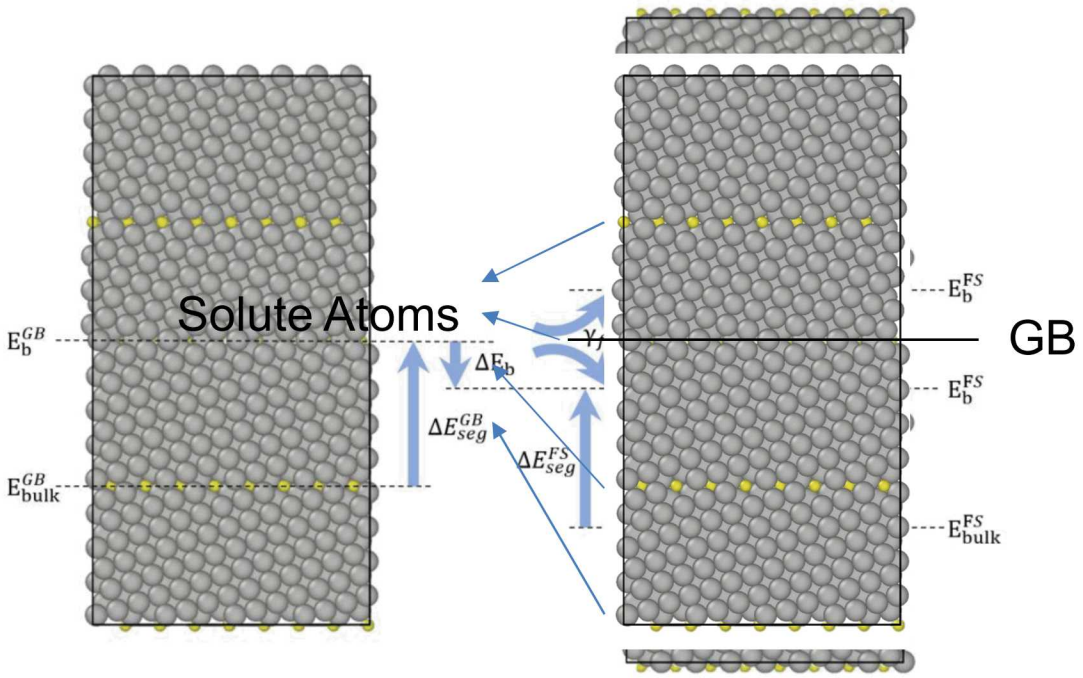
Lassila and Birnbaum (1987)



Ductile → Brittle

Chen et al. (2010)

What is Grain Boundary Segregation Induced Embrittlement?



- **Segregation energy** is defined as the binding energy difference between the bulk site and a GB/ FS site.

$$\Delta E_{seg}^{GB/FS} = E_b^{GB/FS} - E_{bulk}^{GB/FS}$$

- **Embrittling potency** is defined as the difference between the GB and FS segregation energies

$$\Delta E_b = \Delta E_{seg}^{GB} - \Delta E_{seg}^{FS}$$

Objectives

Motivation

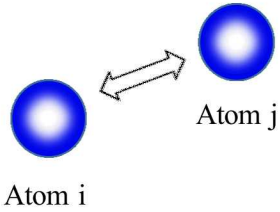
- The effect of GB structure on embrittlement behavior needs explanation.
- A computationally efficient interatomic potential for Ni-S for high-throughput simulations is lacking.

Objectives

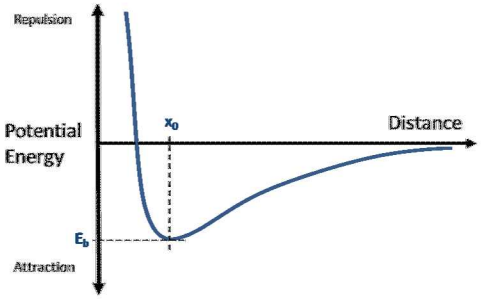
- To develop a new Embedded-Atom Method (EAM) interatomic potential **parameterized for S induced embrittlement of Ni** to perform molecular dynamics (MD) simulations
- To calculate segregation energies and embrittling potencies for various STGBs with the newly developed EAM potential

Interatomic Potential

- Interatomic potentials define the interactions between atoms in order to simulate material behaviors such as fracture, phase transformations. deformations etc.



$U(r_N)$



- One of the most computationally efficient interatomic potentials developed for modeling metals and impurities is the Embedded-Atom Method (EAM).
- In EAM, all atoms have an embedding energy which depend on the environmental effects of the host lattice.
- Total energy of the system: $E_{tot} = \sum_i F_i(\rho_i) + \frac{1}{2}\sum_{i,j} \phi_{ij}(r_{ij})$
- 3 main functions needed to fit an EAM potential:

1. Embedding Energy Function: $F(\rho)$
2. Host Electron Density Function: $\rho(r)$
3. Pair Potential Function: $\phi(r)$

Interatomic Potential Development

- In order to develop a new Ni-S EAM potential, the following functions are selected[1] for the fitting procedure:

Host Electron Density Function

$$\rho(r) = \rho_0 e^{-\frac{r-r_0}{\lambda}} \Xi(r, r_d) \quad \text{where} \quad \Xi(\chi) = -6\chi^5 + 15\chi^4 - 10\chi^3 + 1 \quad \text{and} \quad \chi(r, r_c) = \frac{r - r_c}{r_{cut} - r_c} H(r_c)$$

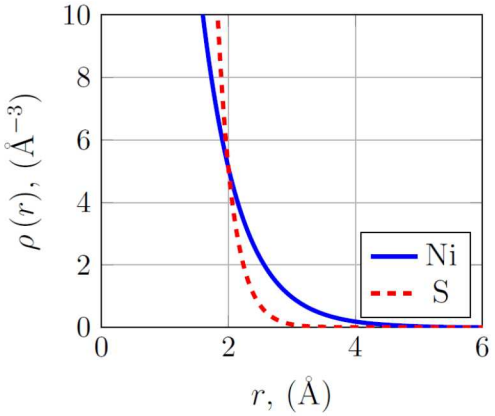
Embedding Energy Function

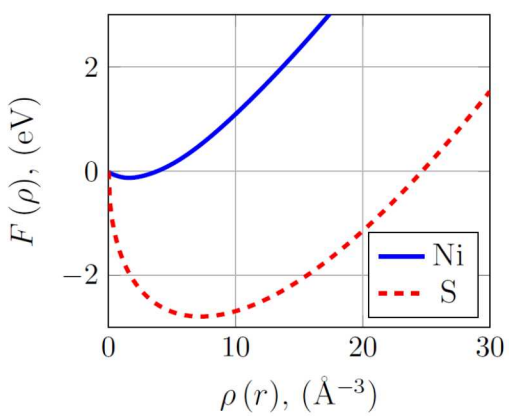
$$E_{tot} = \sum_i F_i(\rho_i) + \frac{1}{2}\sum_{i,j} \phi_{ij}(r_{ij}) \quad \text{where} \quad \rho_i = \sum_{j \neq i} \rho(r_{ij})$$

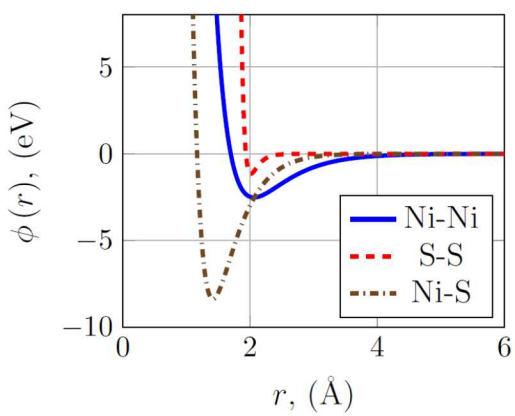
Pair Potential Function

$$\phi(r) = D_e\{\left[1 - e^{-a_m(r-r_0)}\right]^2 - 1\} \cdot \Xi(r, r_p)$$

- 3 fitting procedure needed to describe Ni-S interactions:
  - Ni-Ni ,S-S and Ni-S



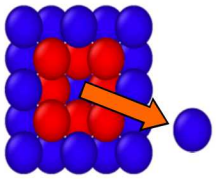




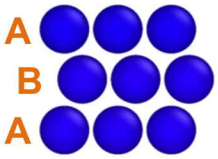
[1] O'Brien *et al.* (2018) J. Mater. Sci.

Interatomic Potential for Ni-Ni interactions

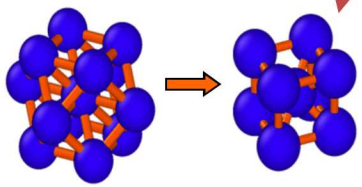
Target properties and corresponding fit results:



Vacancy formation energy



Stacking fault energy



The energy difference between FCC and BCC state of Ni

Property[a]	Target[b]	Fit	Experimental[c]
a_0	3.52	3.52	3.52
E_{coh}	-4.45	-4.45	-4.45
E_{vf} *	1.592	1.592	1.60
E_{sf} *	88.843	88.843	125
$\Delta E_{fcc-bcc}$ *	0.077	0.077	0.06
C_{11} *	2.467	2.455	2.465
C_{12} *	1.475	1.491	1.473
C_{44} *	1.250	1.343	1.247

[a] a_0 (Å) is the lattice parameter. E_{coh} (eV), E_{vf} (eV) and E_{sf} (eV) are the cohesive, vacancy formation and stacking fault energies, respectively. $\Delta E_{fcc-bcc}$ (eV) is the energy difference between FCC and BCC lattices. C_{11}, C_{12}, C_{44} are the elastic constants with units $10^{12} dyn/cm^2$.

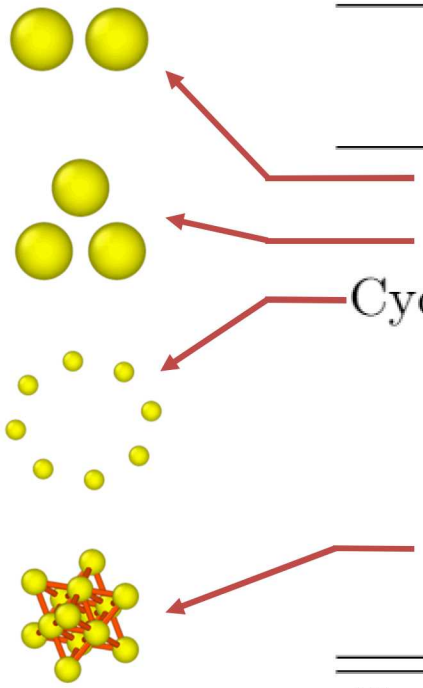
[b] Values obtained from MD simulations using Ni-Al-H EAM potential Angelo and Baskes (1995,1997).

[c] Experimental values taken from Angelo and Baskes (1995,1997).

Target energies for Ni-Ni interactions are matched exactly

Interatomic Potential for S-S interactions

Target properties and corresponding fit results:



Structure	Target[a] a_0 (Å)[b]	Target[a] E_0 (eV)[b]	Fit a_0 (Å)[b]	Fit E_0 (eV)[b]
Dimer *	1.91	-3.28	2.00	-3.28
Trimer *	2.03	-3.86	2.03	-3.86
Cyclo-octasulfur *	2.04	-4.06	2.03	-3.86
Hexagonal	2.32	-3.30	2.15	-3.45
Diamond	5.79	-3.13	5.24	-3.22
SC	2.59	-3.51	2.35	-3.11
FCC *	4.00	-2.84	3.66	-2.84
BCC	3.18	-3.01	2.89	-2.88

[a] Target values are taken from the DFT database[1].
[b] a_0 (Å) is the lattice parameter and E_0 (eV) is the energy per atom.

Target energies for S-S structures are in good agreement

[1] T. Liang *et al.* (2009) Phys. Rev. B

Interatomic Potential for Ni-S interactions

Target properties and corresponding fit results:

∑5 [100]/(210) 36.87°

Property[a]	Target[b]	Fit	ReaxFF[c]
ΔE_{seg}^{GB} *	-1.40	-1.40	-1.34
ΔE_{seg}^{FS} *	-2.39	-2.69	-2.96
E_{bulk}^{GB} *	-3.22	-3.22	-3.37
E_{bulk}^{FS}	-	-3.22	-3.35
E_{b}^{GB}	-	-4.62	-4.71
E_{b}^{FS}	-	-5.91	-6.31
ΔE_b	0.99	1.29	1.62

[a] All energies are in (eV). $\Delta E_{seg}^{GB/FS}$ is the segregation energy associated with a GB/FS cell, $E_{bulk}^{GB/FS}$ is the bulk energy associated with a GB/FS cell, $E_{b}^{GB/FS}$ is the binding energy associated with a GB/FS cell and ΔE_b is the embrittling potency.

[b] Target values are taken from Všianská *et al.* (2011).

Pair interactions for Ni-S is more favorable than S-S interactions, causing the attraction between S-S to diminish

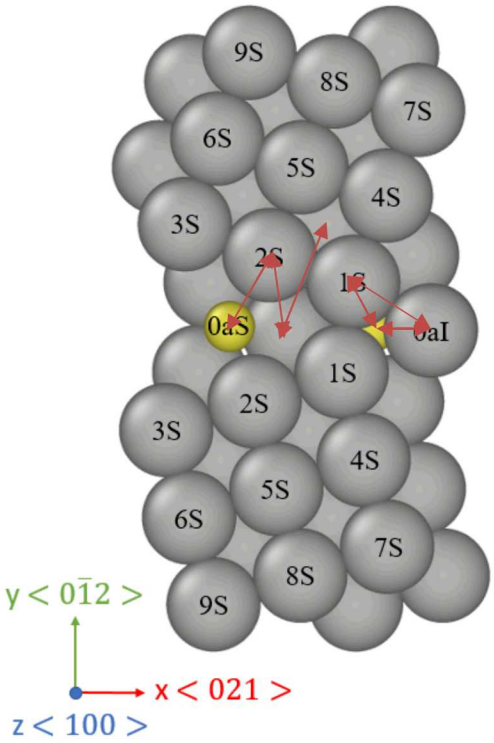
Results not Included in the Fitting Database

- Ni-S bond lengths less than 3 Å are computed for a ∑5 STGB with S atoms at the substitutional GB site: “0aS”

∑5 [100]/(210) 36.87°

	Present Work		Yamaguchi *et al.* (2015) DFT calculations	
	0aS (S)	**0aI (Ni)**	**0aS (S)**	**0aI (Ni)**
0aS (S)	-	2.28	-	2.25
1S (Ni)	2.26	2.64	2.27	2.65
2S (Ni)	2.18	2.74	2.17	2.76
3S (Ni)	-	2.84	-	2.87

* All lengths are in Angstroms.

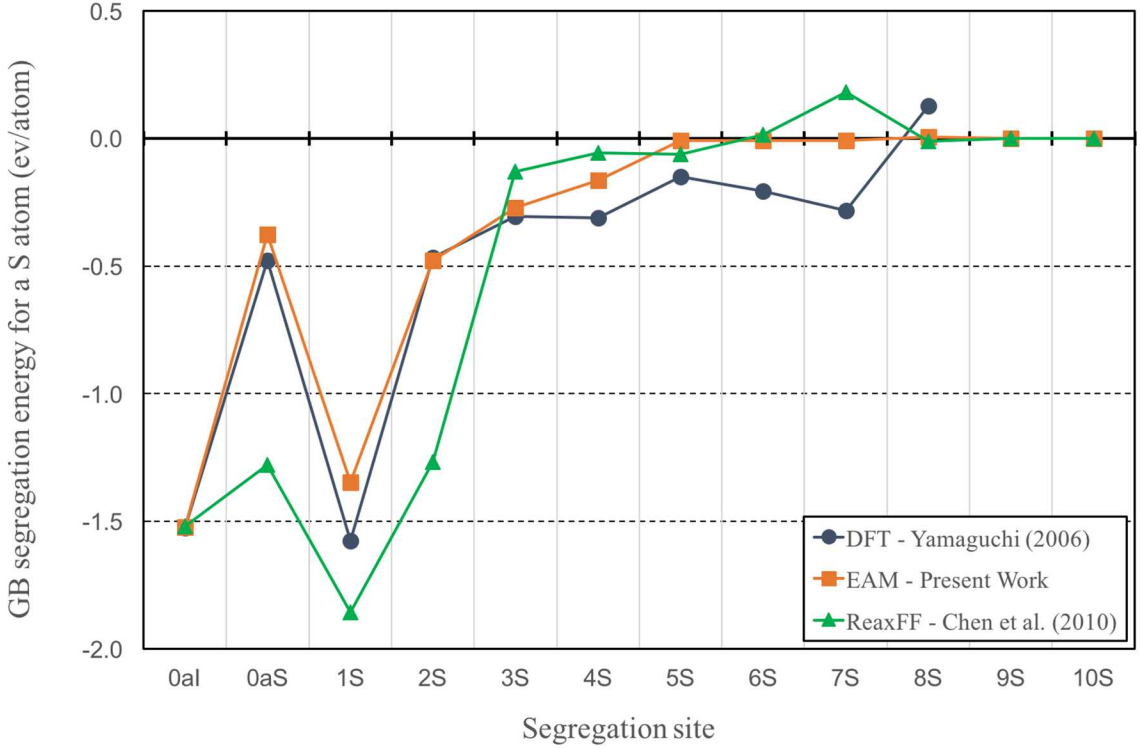


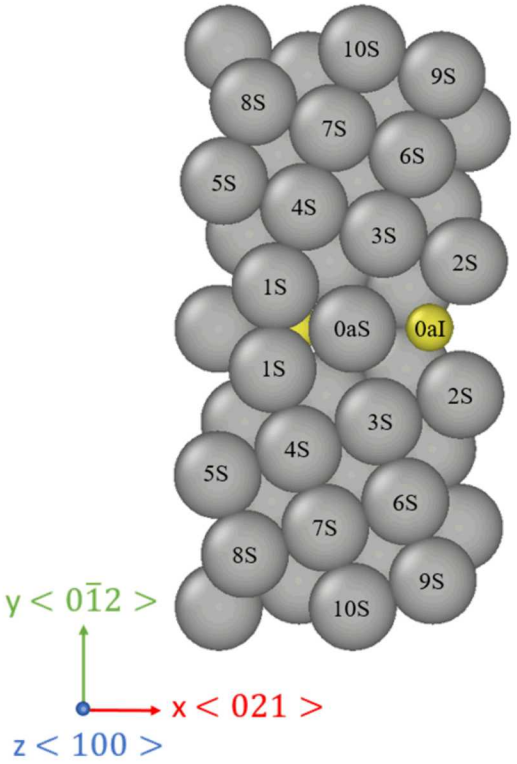
Ni-S bond lengths calculated by our EAM potential are in good agreement with DFT results.

Results not Included in the Fitting Database

- **Assumption:** S prefers interstitial sites at GB/FS region and substitutional sites at bulk region

∑5 [100]/(210) 36.87°

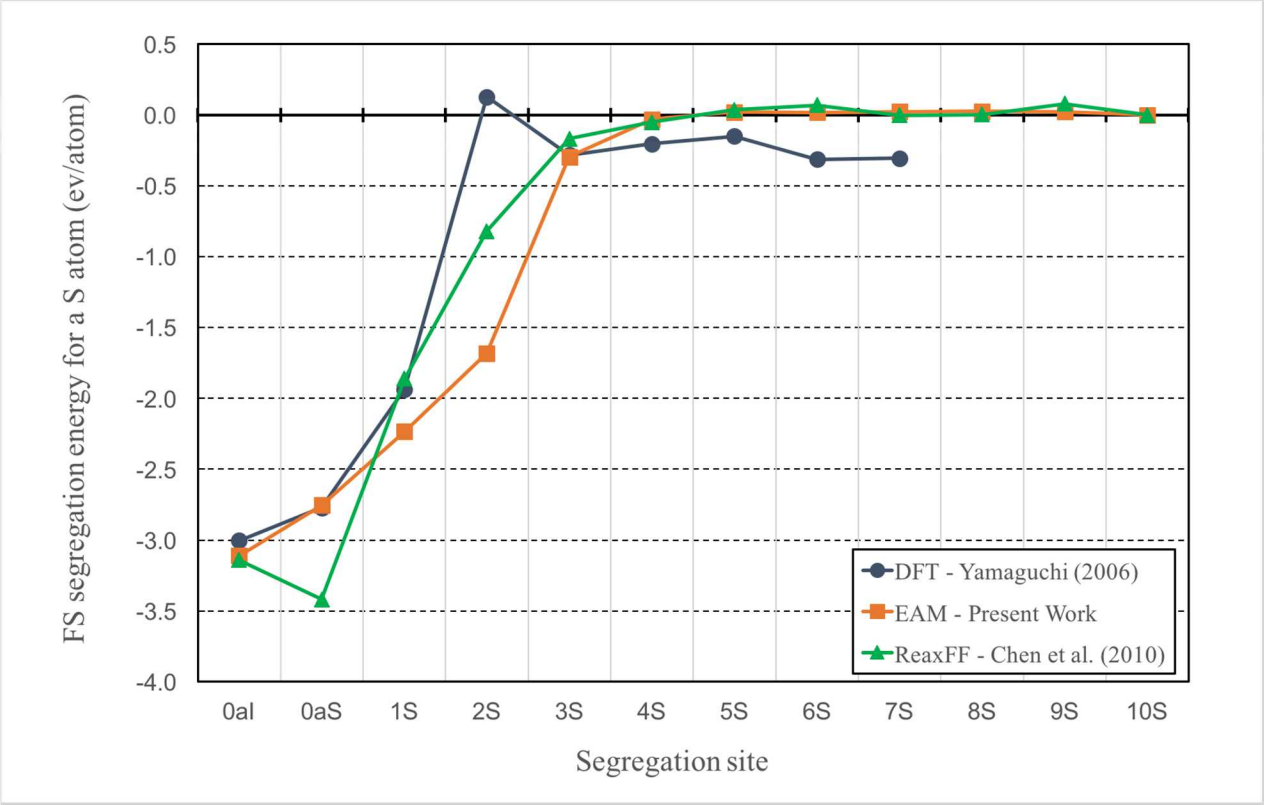


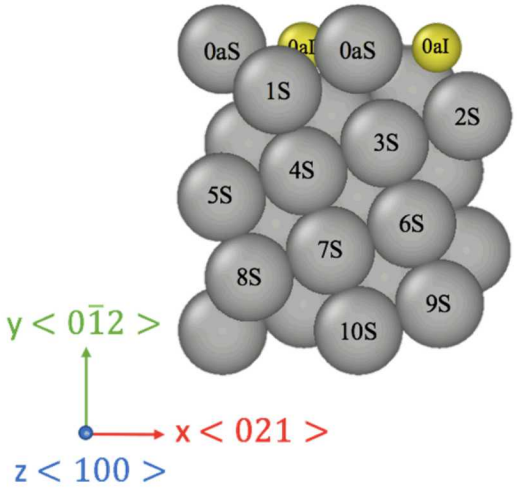


The segregation energies associated with different segregation sites are matching the DFT results

Results not Included in the Fitting Database

∑5 [100]/(210) 36.87°



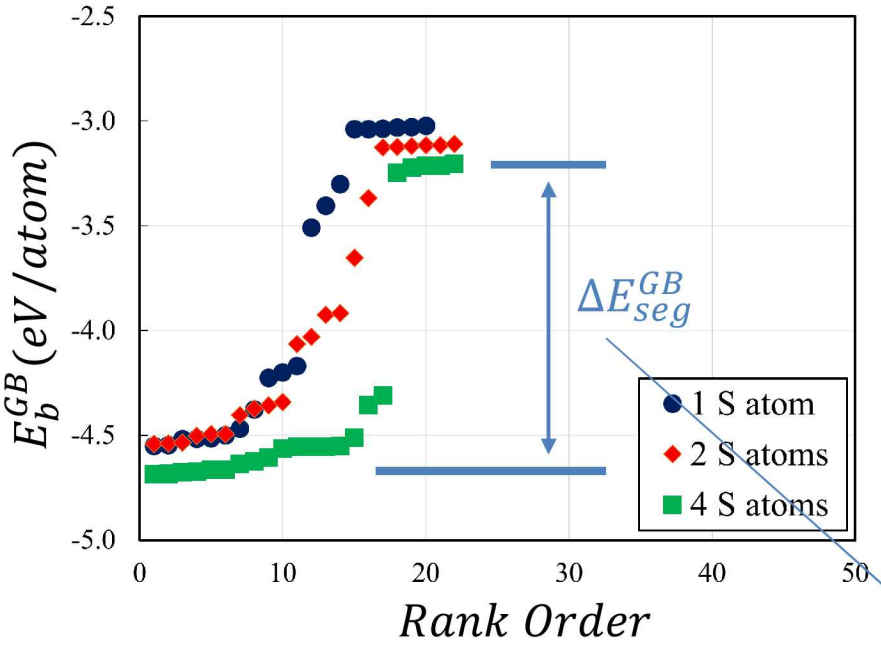


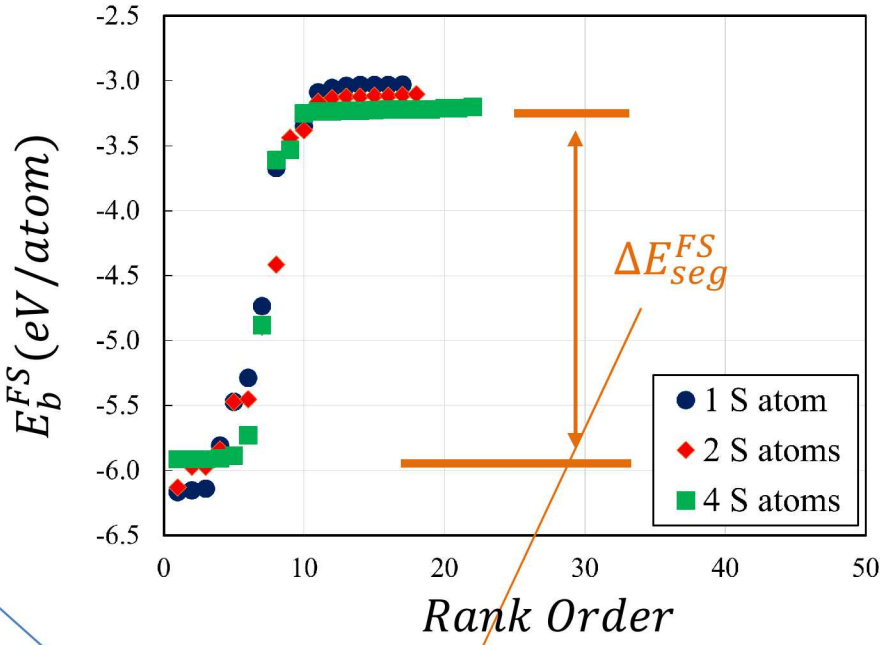
The segregation energies associated with different segregation sites are matching the DFT results

Effect of S Coverage

- Rank ordered binding and segregation energies obtained from the newly developed EAM potential shows the effect of S coverage in the system.

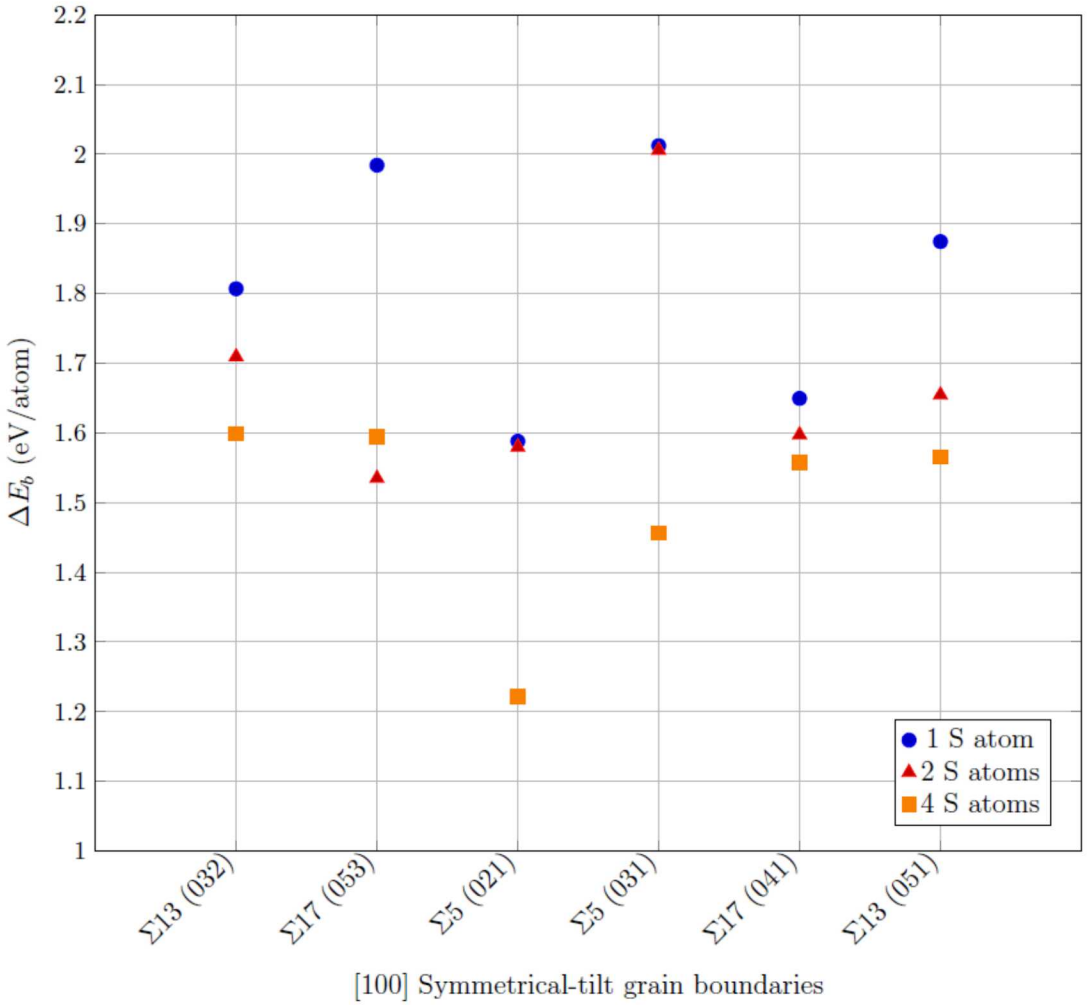
∑5 [100]/(210) 36.87°





Embrittling potency: $\Delta E_b = \Delta E_{seg}^{GB} - \Delta E_{seg}^{FS}$

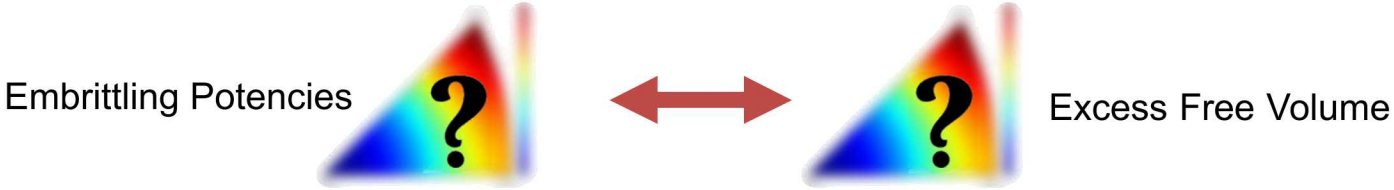
Embrittling Potencies for six [100] STGBs



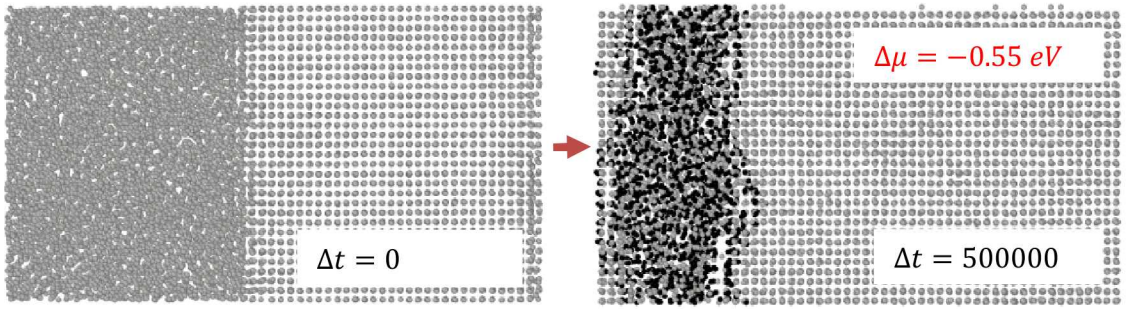
The embrittling potency of S varies for different GBs as well as different S coverages.

Systematic Comparison and Future Directions

- Same type of approach can be used to plot embrittling potencies for a wide range of GBs, and visualized using stereographic projection.



- Impurity atoms can be introduced to the system by using a hybrid semi-grand canonical Monte Carlo/Molecular Dynamics approach. This hybrid approach requires some properties to be calculated.
  - ➢ Properties calculated with the new EAM potential:
    - Melting Temperature of Ni: $T_m = 1760\ K$(compared to 1728 K) [1]
    - Equilibrium chemical potential difference: $\Delta\mu = \sim -0.55eV$ of a supercooled system. (965 K) [1]



[1] Hu *et al.* (2018) Nature Comm.

Summary and Conclusions

- A new embedded-atom method (EAM) interatomic potential parametrized for segregation induced embrittlement behavior of S in Ni is developed
  - The resulting fit is compared to literature with satisfactory results achieved
  - Allows simulation of a larger number of atoms or longer simulation times than DFT methods or atomistic simulation with the ReaxFF potential

- Segregation energies and embrittling potencies are calculated for six [100] STGBs using molecular statics calculations with the newly developed EAM potential
  - These results indicate the importance of the GB structure and S coverage on the embrittlement behavior

- Selection of GB sets by matching the embrittling potencies of different interfaces to isolate the role of grain boundary structure could provide insights on the embrittlement mechanisms[1]

[1] Dingreville, R., Aksoy, D., Spearot, D.E. (2017) Scientific Reports, 7, 8332