



# Segregation-induced changes in grain boundary cohesion and embrittlement in binary alloys



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## ABSTRACT

Grain boundary embrittlement occurs when a solute enriches at a grain boundary and lowers its cohesive energy. While grain boundary enrichment is often attributed to equilibrium segregation effects, most models of embrittlement consider either the energetics of decohesion or the equilibrium adsorption at the boundary, but not both phenomena together. We develop a model for the change in cohesive energy of a grain boundary of a pure metal upon introduction of solute under conditions of equilibrium segregation prior to fracture. A heuristic grain boundary cohesion map is presented to delineate whether a given solute–solvent pair will exhibit weakening or strengthening of grain boundaries. The analysis helps to clarify that grain boundary embrittlement requires a solute that will both lower the cohesive energy of the boundary and segregate in the first place. The map reasonably captures known metal–metal embrittling pairs.

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## 1. Introduction

Phenomenologically, metal–metal embrittlement occurs when an otherwise tough metal loses its ability to plastically dissipate large amounts of energy during crack propagation, owing to the presence of a second, metallic embrittling species [1]. Fractographic analyses reveal that such failures often occur along grain boundaries [2,3], where embrittlement via segregation or wetting of tramp elements has occurred. Such impurity-induced embrittlement has been shown to commonly occur in most metallic base metals of interest, such as Cu- [4], Ni- [5], Fe- [6], and Al-based [7–11] systems. A grain boundary is considered embrittled when boundary cleavage (i.e. breaking the bonds across a grain boundary) becomes energetically favorable to blunting mechanisms (i.e. dislocation emission) [12]. The energetic barrier to cleavage is the grain boundary cohesive energy [13], which is given by:

$$E_{\text{GBC}} = 2\gamma_{\text{S}} - \gamma_{\text{GB}} \quad (1)$$

where  $E_{\text{GBC}}$  is the energy of grain boundary cohesion,  $\gamma_{\text{S}}$  is the surface energy and  $\gamma_{\text{GB}}$  is the grain boundary energy. The surface and

grain boundary energies are both a strong function of alloy chemistry, as solute atoms reduce the energy of the boundary according to the Gibbs adsorption isotherm [14]:

$$d\gamma = -\sum_i \Gamma_i d\mu_i \quad (2)$$

where  $d\gamma$  is a differential change in interfacial energy,  $\Gamma_i$  is the specific excess of solute  $i$  at the interface, and  $d\mu_i$  is a differential change in the chemical potential of the solute. The strong dependencies of  $\gamma_{\text{S}}$  and  $\gamma_{\text{GB}}$  on the chemical potential of solutes imply that  $E_{\text{GBC}}$  is also a strong function of solution chemistry at equilibrium. As the plastic work needed to extend a crack has been shown to be proportional to  $E_{\text{GBC}}^{2-5}$  [15,16], adsorption-based effects on material toughness can be unintuitively large.

Hirth et al. presented a thermodynamic framework for describing the changes in the cohesive energy of a grain boundary due to solute adsorption by integration of the Gibbs adsorption isotherm under various constraints, formalizing the concept of interfacial cohesive energies under constrained equilibrium [17–20]. Under the constraint of no diffusion of solute to or from the grain boundary during cleavage (i.e. during fast crack growth relative to diffusion), the following expression was derived for the non-equilibrium work of separation for a given amount of enrichment:

$$E_{\text{GBC}}(\Gamma) = E_{\text{GBC}}(\Gamma = 0) - \int_0^{\Gamma} [\mu_{\text{GB}}(\Gamma) - \mu_{\text{S}}(\Gamma/2)] d\Gamma \quad (3)$$

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where  $E_{\text{GBC}}(\Gamma = 0)$  is the reversible work of separation of the pure material and  $\mu_{\text{GB}}$  and  $\mu_{\text{S}}$  describe the chemical potentials of the solute at the grain boundary and surface before and after cleavage respectively at the given enrichment,  $\Gamma$ . The integral in (3) defines the change in grain boundary cohesive energy of the pure material upon addition of solute to the system. In this general treatment, the change in grain boundary cohesion is governed by two quantities: the amount of segregant at the interface,  $\Gamma$ , and the difference in the chemical potentials at the interface/surfaces before and after segregation,  $\mu_{\text{GB}}(\Gamma) - \mu_{\text{S}}(\Gamma/2)$ . Proper prediction of changes in grain boundary cohesion in specific alloy systems amounts to the simultaneous analysis of these two terms.

Previous modeling work on intergranular embrittlement has mostly explored these two terms independently. The  $\mu_{\text{GB}}(\Gamma) - \mu_{\text{S}}(\Gamma/2)$  term defines the energetics of embrittlement and was explored first parametrically [21–25], and more recently computationally [22,26,27]. Seah used a quasichemical bond-breaking model to describe the embrittling tendency of different solutes in iron [21]. More recently, Geng et al. described embrittling potency in Fe and Ni via a modified bond-breaking model with an added elastic mismatch term, and correlated the predictions with ab initio results for grain boundary cohesive energies [22,23]. Additional ab initio studies have been performed for many other alloy systems; see for example [22,26,27]. A recent study by Lejcek and Sob reviewed the existing literature on changes in grain boundary cohesion for Fe-based systems [28]. Their systematic review suggested that changes in grain boundary cohesive energies upon alloying can be quantitatively predicted by the difference between the enthalpies of sublimation of the solute and solvent, in accord with the analytical work of Seah [21].

While these models consider the energetics of the solute at the grain boundary versus the surface (essentially the  $(\mu_{\text{GB}}(\Gamma) - \mu_{\text{S}}(\Gamma/2))$  term in Hirth, Rice and Wang's treatment), they include limited or no treatment of whether the solute will enrich at the grain boundary to begin with. Grain boundary segregation can be described with surface adsorption analogs [29], as first conceptualized by McLean [13], with one of the most successful theories describing co-segregation and temper embrittlement in multinary iron alloys via the use of multinary interaction parameters [30,31]. Segregation to grain boundaries can also be studied computationally through Monte Carlo simulations [32–34], but such studies are relatively infrequent and, to the authors' knowledge, have not been explicitly linked to changes in cohesion.

Hence, the problem of equilibrium interfacial cohesion is still relatively un-explored. Several groups have treated the problem in the thermodynamic abstract [17–20,35,36], while other groups have done so parametrically [36–38]. Recently, Lejcek has applied the Fowler isotherm to a quasichemical, bond-breaking model to simultaneously study the embrittling tendency and equilibrium segregation in both binary [37] and higher order [38] alloy systems. To the authors' knowledge, this is the only study to provide a framework for the quantitative treatment of embrittlement in the presence of equilibrium segregation using readily measureable materials parameters. However, the developments of Lejcek are analytical and parametric, and use only equilibrium properties of interfaces, and are thus not readily applicable to changes in interfacial cohesion due to non-equilibrium segregation [5,6], or to the chemically-constrained equilibrium of fast fracture. Additionally, the models in [37,38] are limited to open systems, and are therefore less relevant for, e.g., fine-grained or nanocrystalline alloys, which must be treated as closed systems because segregation may appreciably change the concentration of solute remaining in the bulk.

It is our purpose in this study to develop a model capable of describing both equilibrium and non-equilibrium segregation-induced changes in grain boundary cohesion using readily

available materials parameters as inputs. Our developments are in the spirit of Lejcek's works above, but can be applied for fast and slow fracture conditions, include a consideration of the solubility limit and second phase precipitation, and are generalizable to capture both open and closed systems. The model is intentionally built under the same thermodynamic framework as previous models for the thermodynamics of polycrystals to enable a unified description of segregation-induced reductions in both grain boundary energies and grain boundary cohesion. Such a unified description should facilitate the design of nanocrystalline alloys which exhibit reduced grain growth and are not embrittled by segregation. We also use the model to systematically screen almost 2000 binary pairs from the periodic table, to provide guidance for future alloy development.

## 2. Quasichemical bond breaking model

We begin by adapting the definition of  $E_{\text{GBC}}$  from Eq. (1) to represent the difference in internal energy of the crystal in the presence of a grain boundary versus the internal energy of the crystal with the same atomic configuration, but with two free surfaces replacing the grain boundary:

$$E_{\text{GBC}} = E_{\text{surfaces}} - E_{\text{grain boundary}} \quad (4)$$

This quantity represents the work that must be provided by an external agent to create a free surface at a grain boundary, neglecting plastic deformation. The cohesive energy of a pure material, A, is then described by Eq. (1). The change in cohesion upon alloying,  $\Delta E_{\text{GBC}}$ , is given by the difference between the cohesive energies in the alloyed and the unalloyed states:

$$\Delta E_{\text{GBC}} = E_{\text{GBC}}^{\text{alloy}} - E_{\text{GBC}}^{\text{pure}} \quad (5)$$

Ignoring irreversible processes, a positive  $\Delta E_{\text{GBC}}$  represents a net increase in the thermodynamic resistance to decohesion, while a negative  $\Delta E_{\text{GBC}}$  represents a tendency for embrittlement [17].

Inspired by the success of Guttmann and Seah's models [21,30] in predicting temper embrittlement via use of interaction parameters, we propose a model for  $\Delta E_{\text{GBC}}$  of a binary alloy which employs interaction parameters appropriate to the bulk, surface, and intergranular regions of an alloy. Such a formulation is analogous to that used in several previous treatments of nanocrystalline stability [39–44], but has not previously been used to examine free surface effects or embrittlement. We hope that this formulation may be used to provide a unified description of embrittlement and thermal stability. We specifically consider the "regular nanocrystalline solution" model, which is a regular solution model based on nearest neighbor interactions in a polycrystalline structure [20], for which the internal energy is given as:

$$E_{\text{solution}}^{\text{gb}} = \sum_{r=\text{gb,b,t}} N_r^{\text{AA}} E_r^{\text{AA}} + N_r^{\text{BB}} E_r^{\text{BB}} + N_r^{\text{AB}} E_r^{\text{AB}} \quad (6)$$

Here  $E_r^{\text{XY}}$  represents a pairwise bonding energy between atoms of species X and Y in the region r and  $N_r^{\text{XY}}$  represents the total number of bonds between atoms of X and Y in region r. The regions, r, are captured by the subscripts gb, b, and t, corresponding to grain boundary, bulk, and transitional regions, respectively. The regions are permitted to have distinct bonding energies, i.e.  $E_{\text{gb}}^{\text{AA}} \neq E_{\text{b}}^{\text{AA}}$ , and distinct compositions. The energies of the transitional bonds are assumed to be the same as those of the bulk bonds in this work.

The internal energy of a solution containing a surface can be similarly defined:

$$E_{\text{solution}}^{\text{s}} = \sum_{r=\text{s,b,t}} N_r^{\text{AA}} E_r^{\text{AA}} + N_r^{\text{BB}} E_r^{\text{BB}} + N_r^{\text{AB}} E_r^{\text{AB}} \quad (7)$$

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