Comparison of Ab-initio Solute-Boundary Binding Energies and Experimental Recrystallization Data in Austenite for Solute Nb and Other Elements

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Niobium is a critical alloying element in modern steels, which is usually employed at microalloy concentrations in the hundredths of mass percent. Since its incorporation into industrial steels in 1958, Nb has enabled the development of the important class of high strength low alloy steels through its ability to limit prior austenite grain size and recrystallization. One of the mechanisms by which Nb is believed to limit grain growth is through solute drag on austenite grain boundaries. This study presents the first direct calculations of the binding energy for solute Nb at austenite grain boundaries, along with binding energies for additional important alloying elements in steel for which experimental data are available. The binding energies are then compared to select data sets for austenite recrystallization from the literature. The strong correlation between the calculated energies and the experimentally measured effects of the alloying elements confirms that the origin of the significant solute drag effect of Nb is the strong binding energy between solute Nb and austenite grain boundaries.

KEY WORDS: niobium; density functional theory; solute drag; simulation.

1. Introduction

Niobium is a critical alloying addition in modern high strength steels, employed at “microalloy” concentrations in the hundredths of mass percent. Nb was first incorporated into industrial heats of steel in 19581) and has since been studied extensively.2–12) Many of the studies have focused on the effects of Nb as a precipitate strengthening addition,2–3) but it is also known to have significant solute drag effects.3–11) The suppression of austenite recrystallization in particular has enabled the important class of HSLA (high strength low-alloy) steels. Nb is known to segregate to both austenite and ferrite grain boundaries4) as a result of a binding energy between the grain boundary and Nb.4–6) This energy has been investigated for ferrite both experimentally4,5) and computationally.6) Maruyama et al. calculated the segregation energy of solute Nb to /uni03B1 (ferrite) grain boundaries from measurements of the excess Nb at grain boundaries and found a segregation energy of 38 kJ/mol.5) Jin et al. used density functional theory calculations to determine the solute segregation energy for Nb, and other elements, for a symmetric Σ5 (013) grain boundary and reported an average interaction energy of 39 kJ/mol.6) Felfer et al. observed Nb enrichment at prior austenite grain boundaries (PAGBs) using atom probe tomography,4) and reported that the Nb concentration at PAGBs was approximately two and a half times greater than at ferrite grain boundaries (0.25 atoms nm$^{-2}$ for PAGBs as opposed to 0.1 atoms nm$^{-2}$ for ferrite-ferrite grain boundaries). This strong segregation energy of Nb to grain boundaries in low alloy steels is believed to be responsible for the effects of solute Nb on the microstructural development of these steels.

Solute Nb is particularly well known for its ability to delay recrystallization.3,7–10) It has been suggested that solute Nb is more effective at delaying dynamic recrystallization than Nb precipitates, whereas Nb precipitates are more effective at delaying static recrystallization than solute Nb.3) Additionally, the relative importance of solute Nb and Nb precipitates depends on the driving force for grain boundary motion and the Nb content of the steel.7) Through these combined effects, Nb is the most powerful element available for the retardation of recrystallization.8) Nb also serves to stabilize the austenite-ferrite interface through the solute-boundary binding energy of Nb.11) This sometimes translates to a decrease in the austenite-ferrite transformation temperature which can be greater than 100°C,4) although Nb can also increase the rate of transformation from unrecrystallized austenite.11)

Thermodynamics provides a fundamental understanding of driving forces for material processes. The Nb effects discussed above are assumed to arise from a thermodynamic interaction between solute Nb atoms and the grain boundary. To verify this interaction, it would be of inter-
est to examine the behavior of individual Nb atoms on the boundary. Unfortunately, this is not feasible with current experimental techniques. However, through the use of atomistic modeling, it is possible to predict the properties of individual atoms. For the industrially significant effects of Nb discussed above, an important property of interest is the solute-boundary binding energy. This energy can now be calculated directly using density functional theory simulations by observing the energy change in the system when a solute is placed at a boundary site relative to a site in the bulk. Previous studies have noted that certain sites on grain boundaries attract solutes while other sites on boundaries repel them. Of the sites that attract solutes, certain sites, identified as preferential solute sites, have a consistent atomic arrangement (morphology) which displays a greater solute-boundary binding energy than any other boundary sites. A study of the period four and five transition metal elements as individual solutes in austenite at these unique sites is performed in order to determine the maximum solute-boundary binding energies of the transition metals to austenite grain boundaries. These energies are then compared to available literature related to the effects of the solutes in austenite. Comparison of the results for different solutes sheds light on the thermodynamic origin of the unique properties that Nb has been found to have in the production of modern steels.

2. Procedure

Density functional theory (DFT) simulations of grain boundaries are capable of converging accurate grain boundary energies when considering periodic boundary conditions, which necessitates the use of coincident site lattice (CSL) boundaries. CSL boundaries are boundaries in which some proportion of the lattice sites between the two grains are identical and are identified by a sigma number (e.g., for example) where the number is the inverse of the number of sites common to the two grains. Thus, in a CSL grain boundary, one fifth of the lattice sites are common to the two grains. The interaction energy of a solute with the boundary can then be found by comparing the energy of the system with a solute at the boundary to the energy of the system with the solute in the bulk at a distance where it does not interact with the boundary.

Solute-boundary binding energies were determined for Nb and some additional solutes (Ti, V, Mn, and Mo) chosen based upon their importance in steel and availability of experimental data in the literature. The energies were calculated for the preferential solute sites (where maximum binding energies are found) in three pure tilt [001] type austenite grain boundaries: a 45° symmetric \( \Sigma 5 \), an 18.43° asymmetric \( \Sigma 7 \), and a 45° symmetric \( \Sigma 13 \). The average of the calculated binding energies at these sites weighted by the expected existence ratio of \( \Sigma 5 \), \( \Sigma 7 \), and \( \Sigma 13 \) grain boundaries in a low texture fcc metal (as determined by Pan and Adams) is referred to later in this paper as the solute-boundary "binding energy".

The Vienna \textit{ab-initio} Simulation Package (VASP) version 5.2.12 was used to run the DFT simulations with projector augmented wave (PAW) pseudopotentials, and a PBE functional by considering the difference in the system energy between a non-interacting grain boundary and a solute atom in the bulk and a boundary with a solute atom at given sites on the grain boundary. The k-point mesh varied based on the size of the boundary as follows: symmetric \( \Sigma 5 \) with a mesh of 4 2 5, 144 atoms, and 7.8×30×7 Å, asymmetric \( \Sigma 7 \) with a mesh of 3 2 5, 240 atoms, and 14×30×7 Å, and a symmetric \( \Sigma 13 \) with a mesh of 3 2 5, 236 atoms, and 12.7×30×7 Å. K-point convergence testing verified an energy convergence with increasing k-point meshes of 0.02 eV for the \( \Sigma 5 \) and \( \Sigma 13 \) boundaries and 0.05 eV for the \( \Sigma 7 \) boundary. The lowest k-point mesh to produce energetic convergence was used for computational efficiency. Solute-boundary binding energy convergence with respect to boundary size was found to stabilize for solute-solute separations of 7Å or greater and so simulations were run with a separation of 7Å in the z direction, one coincident site unit cell dimension in the x direction, and sufficient distance in the y direction to ensure that all boundaries in the system are non-interacting and that bulk properties are recovered in each grain. Simulation cell size was kept as small as possible to limit the computational expense of the calculations.

The possibility that magnetic effects could play a significant role in mediating solute boundary binding energies was evaluated following Klaver et al., who proposed that the magnetic ground state of an austenitic system might be determined by running multiple simulations of the same system with different starting magnetic configurations. If these simulations converge to the same final configuration, then that configuration can be assumed to be a true magnetic ground state. This procedure was followed with each of the grain boundaries investigated but, for each, different initial configurations led to different final configurations. The lack of convergence is not unexpected as the magnetic configuration of austenite is known to be highly complex, even in the presence of simple defects. Some studies have imposed an antiferromagnetic structure for austenite at fcc/bcc phase boundaries assuming that the moment on the austenite grain would align with that on the ferrite grain. However, at an austenite grain boundary, there is no known magnetic orientation to reference and a self-consistent orientation has proven difficult to identify, so any choice of magnetic orientation would be arbitrary. Additionally, as the phenomenon of interest to this investigation for the most part occurs at temperatures above the Currie temperature, the magnetic state in these materials persists only for short times. It should be noted that simulations without spin polarization have produced meaningful results in the past. Yang et al. studied the effects of 3 d transition metals on austenite grain boundary cohesion and determined that the effect of bonding anisotropy caused by a solute atom in the grain boundary was important in determining the effect of a solute on grain boundary cohesion in a non-magnetic system. Jiang and Carter studied the solution enthalpy and solute diffusion of interstitial carbon in both BCC and FCC Fe. They assumed a ferromagnetic state of the FCC Fe, but noted that this was unrealistic for bulk FCC Fe. Accordingly, this study treats the boundaries as non-magnetic.

The computed solute-boundary binding energies were compared to experimental datasets from the literature to determine the ability of the simulations to predict the behavior of solutes in real materials. These comparisons were then
analyzed to provide insight into niobium’s influence on the behavior of austenite in modern steels.

3. Results and Discussion

Table 1 shows the calculated solute-boundary binding energy for each solute tested at each of the three preferential solute sites identified in or adjacent to the boundary plane for the four boundaries investigated. Figure 1 shows the atomic structure of the grain boundaries investigated and the site(s) at each boundary where binding energies were determined. Each site can be seen to be in the same location on a “filled kite” which is a common boundary structure found in multiple materials systems. The filled kite is identified by the characteristic organization of six atoms in a kite formation with a single atom in the center. It can be seen in the Table that the Nb boundary interaction energy is the greatest of all the solutes simulated at each of the sites and in terms of the overall average, and thus solute Nb would be expected to have a more significant impact on austenite grain boundary properties in steels than any other element modeled. These energies are compared below to the experimentally determined effects that solutes have on austenite recrystallization which is assumed to be dependent upon the thermodynamic interaction of solutes with the boundary.

Because of considerable industrial interest in recrystallization of austenite, there are some relevant experimental datasets associated with solute drag effects.9,10 Since recrystallization occurs at austenite-austenite interfaces, these solute effects should be applicable to both recrystallization and grain coarsening since, on a very short length scale, the interface between a recrystallized and un-recrystallized grain and the interface between two grains undergoing grain coarsening are similar. To determine the potential correlation between the calculated binding energy and the empirical activation energy constants, the results from the simulations in this work were compared to multiple recrystallization data sets from the literature for solute effects on both static9 and dynamic10 recrystallization.

Static recrystallization refers to recrystallization that occurs during isothermal holding without active deformation being applied to the material. Figure 2 shows empirically determined activation energies for static recrystallization reported by Medina and Mancilla, plotted against the binding energy calculated here. The data are well approximated by a linear fit ($r^2 = 0.957$) which indicates that the binding energy effectively predicts the trends associated with the measured static recrystallization activation energies.

![Fig. 1](image1.png)

**Fig. 1.** The structure of the symmetric Σ5 (a), asymmetric Σ7 (b), and symmetric Σ13 (c) grain boundaries used in the VASP simulations. The lines trace out the shape of the filled kite and the circled atoms are the preferential solute sites where the solute-boundary binding energy was calculated.

![Table 1](image2.png)

**Table 1.** Solute-Boundary Binding Energies (eV).

| Solute | Symmetric Σ5 | Asymmetric Σ7 | Symmetric Σ13 | Weighted Average |
|--------|--------------|---------------|---------------|-----------------|
| Ti     | −1.07        | −0.82         | −1.14         | −1.00           |
| V      | −0.56        | −0.35         | −0.65         | −0.51           |
| Mn     | −0.08        | 0.00          | −0.13         | −0.06           |
| Nb     | −1.61        | −1.32         | −1.70         | −1.53           |
| Mo     | −1.08        | −0.82         | −1.20         | −1.02           |

![Fig. 2](image3.png)

**Fig. 2.** The linear relationship between the empirical activation energies for static recrystallization (AESR) determined by Medina and Mancilla, and the binding energy (BE) for various solutes at austenite grain boundaries.

![Fig. 3](image4.png)

**Fig. 3.** The exponential relationship between the solute retardation parameter (SRP) for dynamic recrystallization determined by Akben et al. and the calculated binding energy (BE) for various solutes at austenite grain boundaries.
Dynamic recrystallization refers to recrystallization that occurs while the material is undergoing deformation. Figure 3 shows empirical solute retardation parameters for dynamic recrystallization determined by Akben et al.\textsuperscript{(10)} plotted against the binding energy. The solute retardation parameter is defined as:

\[
SRP = \log \left( \frac{t_x}{t_{ref}} \right) \times 0.1 \times \text{at.}\% x \quad \ldots \ldots \ldots \ldots \ldots \ldots (1)
\]

Where \(x\) is the solute, \(t_x\) is the time for the onset of recrystallization in the presence of the solute at a concentration defined by the atomic percent (at.%), and \(t_{ref}\) is a reference time for the base material. Unlike static recrystallization, the regression requires an exponential relationship between the solute retardation parameter for dynamic recrystallization and the calculated binding energy which provides an \(r^2\) value of 0.987. The origin of the exponential relationship between the binding energy and the SRP is not yet understood. The SRP is not an activation energy; instead, it is based upon time to the onset of recrystallization, making the expected form of the relationship between the binding energy and the SRP more difficult to determine. Nevertheless, the strong correlation between the binding energy and the SRP confirms that the computed binding energy serves as an accurate predictor of industrially significant material properties.

4. Summary

Simulations in this work have confirmed the assumption that the thermodynamic interaction of solutes with grain boundaries is responsible for the stronger influence of Nb, relative to several other important alloying elements in steel, on austenite microstructural evolution. This study provides the first direct calculation of Nb-austenite grain boundary binding energies and demonstrates that these energies can be directly related to experimentally observed behavior of solutes in real steels. In austenite, solute Nb has long been known to play a significant role in recrystallization and grain growth, and the results in this work confirm that there is strong thermodynamic interaction of Nb atoms with austenite grain boundaries. The strong solute-boundary binding energies provide an explanation for the observed solute drag behavior.

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