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Effects of Segregation on Grain-Boundary Cohesion: A Density-Functional Cluster Model of Boron and Sulfur in Nickel

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Impurity-dopant effects on grain-boundary cohesion have been studied in a first-principles local spin-density atomic-cluster model of octahedral hole sites in nickel. Rigorous calculations of the total energy and gradient forces on the host atoms show that boron (an enhancer of cohesion) *increases* the maximum sustainable restoring force in the cluster, and sulfur (an embrittler) *decreases* the value of this force, consistent with observed segregation behaviors of these atoms.

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Impurities and dopants present in bulk concentrations of only a few hundred parts per million often lead to dramatic effects on the mechanical properties of solids.[1] The phenomenon of segregation of solute atoms to grain boundaries often evidences strong microchemical effects on the cohesion between grains. Classically based treatments of the thermodynamics of segregation[2] have traditionally served as the basis for control of segregation behavior and optimization of materials properties. With the increased demands on mechanical properties in new technologies and the refinement of microalloying design strategies,[3] the element of control becomes increasingly important. The solution of metallurgical problems for advanced materials requires an understanding of grain-boundary–segregation microchemical effects at the atomistic level.

Treatment of segregation phenomena at the quantum level has been limited by the complexity of grain-boundary structures and the necessity for highly accurate binding energies to address problems of interest. The low symmetry of these systems suggests use of an atomic-cluster model in which only the impurity atom and a limited number of grain-boundary atoms are explicitly treated. Using this type of model, Briant and Messmer[4,5] carried out a series of multiple-scattering calculations to identify impurity effects on the metal-metal bond density. This approach has also been used by Eberhart, Latanision, and Johnson[6] to investigate the role of impurity-impurity interactions and the bond directionality factor in embrittlement. Other researchers have adopted a semiempirical basis[7,8] to treat these problems. These works have stimulated much interest in achieving an atomistic-level understanding of grain-boundary microchemistry. However, charge-density shifts alone are not sufficient to determine energetics, and semiempirical approaches impose some important system characteristics on the energy functional *a priori.*

In the present study, we take a different first-principles approach to the understanding of segregation effects on grain-boundary cohesion. Using the density-functional formalism in the local spin-density approximation[9] (LSDA) and a self-consistent all-electron augmented Gaussian-orbital technique,[10] we have carried out rigorous calculations of the electronic structure, total energy, and restoring forces in atomic cluster grain-boundary–impurity models with only the atomic numbers of the components as input.

The field of forces on the nuclei in the cluster was calculated by direct evaluation of the gradient of the total energy E (with respect to nuclear coordinates), allowing for implicit orbital site dependence.[11] The x component of the gradient force on the pth nucleus F_x^p is defined in Hartree atomic units by

$$F_x^p \equiv -\frac{\partial E}{\partial X_p} = \int \rho(\mathbf{r}) \frac{\partial}{\partial X_p} \left(\frac{Z_p}{|\mathbf{r}-\mathbf{R}_p|} \right) d\mathbf{r} - \sum_{q(\neq p)} \frac{\partial}{\partial X_p} \left(\frac{Z_p Z_q}{|\mathbf{R}_p - \mathbf{R}_q|} \right) - 2\sum_i f_i \int \frac{\partial \psi_i(\mathbf{r})}{\partial X_p} H(\mathbf{r}) \psi_i(\mathbf{r}) d\mathbf{r},$$

where the $\psi_i(\mathbf{r})$ are self-consistent solutions (with occupation numbers f_i) to the one-electron wave equation with Hamiltonian $H(\mathbf{r})$, $\rho(\mathbf{r})$ the density generated from these orbitals, and Z_i the nuclear charge of the atom at location $\mathbf{R}_i$.

The octahedron was selected as a "generic" grain-boundary cluster (Fig. 1), since it frequently occurs as one of the void coordination polyhedra defining open, probable sites of impurity bonding at grain-boundary interfaces in computer simulation calculations.[12] A cluster model forms a reasonable approach for a study of the role of localized bonding in impurity effects at grain boundaries, based on the similarities between real metal-cluster complexes and analogous surface systems,[13] as well as the successful use of such models in chemisorption studies.[14] The cluster approach is justifiable for the present study in that *relative* effects of the two different segregants are of primary interest rather than the actual magnitudes of particular quantities for each.

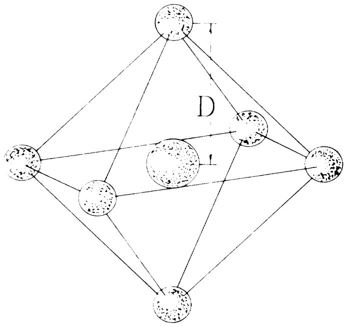

FIG. 1. Octahedral cluster with interstitial impurity atom at center and host atoms a distance D away.

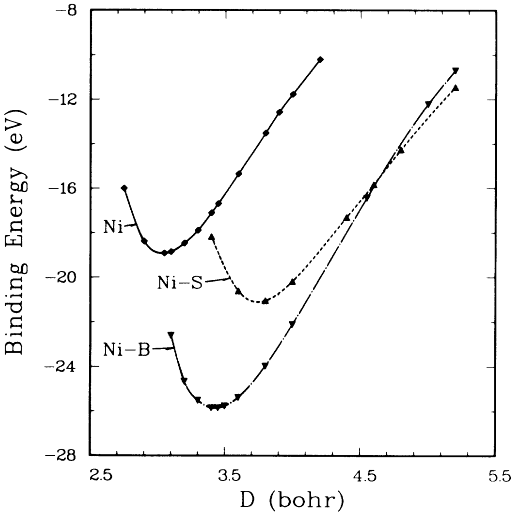

FIG. 2. Binding-energy variation with cluster radius D, the distance from the origin (impurity site) to one of the Ni atoms of the host octahedral cluster, for pure Ni and clusters containing boron (Ni-B) and sulfur (Ni-S). Symbols denote calculated values.

The effect of segregation on the host-cluster cohesive properties was studied by our treating the pure cluster as a reference system, incorporating various impurities in the octahedral interstice (see Fig. 1), solving the LSDA equations, evaluating the total energy, and allowing the cluster to relax according to the gradient forces on the atoms. Boron and sulfur were chosen as segregants since they produce strongly contrasting effects in Ni and Ni-based alloys. Sulfur causes grain-boundary embrittlement[15] in Ni, while boron is effective in reducing intergranular embrittlement of Ni.[16] Effects of boron are of particular interest since boron additions produce remarkable grain-boundary strengthening in $L1_2$ nickel aluminides.[17]

The principal result of these calculations is that the differences in energetics found for B and S binding in Ni are consistent with observed differences in their effects on cohesion. Boron and sulfur are found to produce very different quantitative effects on the restoring forces in the model grain-boundary cluster that correlate with their roles displayed in Ni as cohesion enhancer (B) and embrittler (S). The binding-energy dependence on the effective radius of the cluster, D (Fig. 1), is shown for the bare host Ni cluster and the clusters containing interstitial B and S in Fig. 2. The binding energy is defined as the difference in total energy of the cluster and the sum of component atom energies at infinite separation. The Ni curve displays an energy minimum (binding energy E_0) at $D = D_0$, defining the bare Ni-cluster ground state and reference for describing the energetics of impurity bonding.

Boron binds in the Ni host much more strongly (7.0 eV) than sulfur (2.2 eV) and produces less expansion of the host cluster (12%) than does sulfur (23%). This difference in binding energies is a consequence of the larger Ni-host strain energy (5.0 eV) to accommodate S compared with B (2.0 eV). The direct chemical bond energies for B and S with prestrained host clusters are 9.0 and 7.2 eV, respectively. This strain-energy factor explains the rapid rise of the Ni-S energy in Fig. 2 as D decreases to D_0. Whereas Ni-B is stable relative to the bulk host ($E < E_0$) over a broad distribution of hole sites ($2.9 < D < 4.3$ in atomic units), Ni-S is unstable except in a range only half as broad, centered about the fully relaxed cluster ($D = 3.8$ bohrs). For hole sizes $D \approx D_0$ (representing bulk interstitial coordination) boron is stably bound (3.0 eV), whereas S is unstable by over 14.4 eV. This represents a large repulsion on S and a strong driving force for S in the bulk to occupy substitutional sites or to segregate to open volumes. The segregation properties displayed in Fig. 2 are consistent with the observed tendency for S to segregate strongly to more open regions such as cavities, grain boundaries, and free surfaces.[18] While experimental results for boron segregation behavior in pure Ni are not available, B has been reported[19] to display unusual behavior in segregating more strongly to grain boundaries than to free surfaces in the Ni-based alloy, Ni_3Al. This unusual behavior is consistent with the Ni-B results in Fig. 2, which clearly show that B prefers binding at smaller hole sites, as occur at grain boundaries.

There is a direct connection between the results shown in Fig. 2 and the phenomenon of sulfur embrittlement. From Fig. 2, sulfur is observed to bond most favorably at sites corresponding to large grain-boundary holes where preexisting strain among the Ni—Ni bonds is large (23%). Sulfur is forced to these sites (and open surfaces) by the large repulsion from interstitial regions and smaller hole sites. But these larger hole sites are regions of intrinsically weaker metal-metal bonding, compared with the perfect solid. Even though the direct host-S bond is rather strong, the additional strain accompanying S binding further weakens the metal-metal bonds at the grain-boundary site, thereby promoting fracture processes. Boron binds most stably at smaller host sites without characteristics that lead to decohesion.

Outstanding, however, is the question of the effect of these segregants on the cohesive *strength* of the grain-boundary–model host cluster. As a measure of "strength," it is reasonable to adopt the value of the maximum attainable restoring force that the cluster can exert in response to stretching the bonds by displacing the nickel atoms isotropically outward. This force was determined by calculation of the gradient forces, and intercomparison of results for the pure cluster and the clusters containing boron and sulfur provides a direct basis to address quantitatively the question of segregation effects on cohesive strength.

In Fig. 3, gradient forces in each cluster are plotted as the Ni—Ni bond length is changed (negative force values are attractive). Referenced to the pure-Ni restoring-force behavior, B and S produce strikingly different effects. In the region about each equilibrium point, the restoring force on a reference Ni atom displays a Hooke's-law linear dependence on D. As the hole size increases, anharmonic components grow rapidly (note that the onset of anharmonicity is most rapid for Ni-S). In each case, a maximum restoring force is reached, corresponding to the inflection point in the energy curve, beyond which the onset of structural instabilities occurs.[20] The segregant-host interactions reflected in the modifications of the host force curve are directly relevant to the understanding of the mechanism by which segregation affects grain-boundary cohesion.

A possible factor in intrinsic grain-boundary fragility which occurs in some metals and alloys is suggested by the occurrence of hole sites with metal-metal bonds stretched to the point of maximum attainable stress ($D \approx 3.5$ bohrs). Additional forces on such sites would disrupt the metal-metal bond. Consider now a boron atom added to a large Ni hole site (point *a*, Fig. 3). The system switches from the Ni to the Ni-B curve with a large reduction in stress (point *b*), it is clear from this curve that appreciably more expansion (16%) can be sustained before the new point of maximum stress is reached. This effect is suggestive of an enhancement in ductility. More significantly, the magnitude of the maximum attainable stress in Ni-B is 11% greater than in Ni alone. This quantitatively establishes that the Ni host cluster is stronger, even though the fully relaxed Ni—Ni bonds are expanded by 12% in the presence of boron. This is of obvious relevance to the cohesive enhancement effect reported for B dopants in alloys.[17] On the other hand, sulfur produces the opposite effect, evidenced by the large *reduction* in maximum sustainable stress (17%) shown for the Ni-S curve in Fig. 3. This weakening of the Ni host by S directly relates to the role of S as an embrittling impurity in Ni.

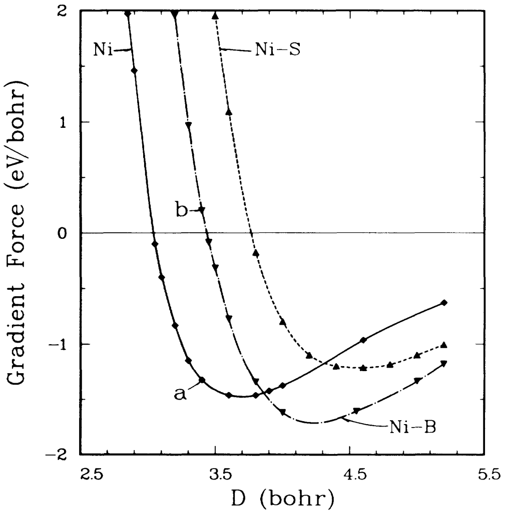

FIG. 3. Gradient force dependence on cluster radius, D, for pure octahedral nickel cluster (Ni) and clusters containing boron (Ni-B) and sulfur (Ni-S) in the octahedral interstice. Attractive forces on a reference nickel atom are negative and repulsive are positive.

Why do B and S show such different behavior as segregants? Analysis of the present results suggests a quantum basis. The valence orbitals of boron are particularly compact because of the absence of a large ion core, while those of sulfur are more extended (by several tenths of a bohr) because of their orthogonality to the Ne core. Thus, while both B and S form strong bonds with the Ni host atoms, energetically favorable bonding in the case of S requires large hole sites, while B prefers bond formation at smaller hole sites with less intrinsic strain. These results provide much of the basic information required to understand the fundamental microchemical mechanisms that determine the effects of segregation on grain-boundary cohesion. The metal-metal bond strength falls off rapidly at sites of S bonding, such that those sites cannot sustain much additional stress. On the other hand, the compact orbitals of B comprise strong direct bonds in smaller, intrinsically stronger sites without introducing much additional strain. The host atoms then can accommodate greater displacements before reaching the point of instability. This relates directly to enhancement of grain-boundary cohesion.

To be sure, numerous other factors must be included for a complete understanding of segregant effects on grain-boundary cohesion. The results of this study suggest that the local bonding component of the energetics and force field is strong enough to determine the differences in cohesion that segregants such as B and S produce at Ni grain boundaries.

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[1] C. L. Briant, *Metallurgical Aspects of Environmental Failures,* Materials Science Monographs No. 12 (Elsevier, New York, 1985).

[2] M. P. Seah, J. Phys. F **10**, 1043 (1980).

[3] C. T. Liu, in *High Temperature Alloys: Theory and Design,* edited by J. O. Stiegler (American Institute of Mining, Metrallurgical, and Petroleum Engineers, New York, 1984), p. 289.

[4] C. L. Briant and R. P. Messmer, Philos. Mag. B **42**, 569 (1980).

[5] R. P. Messmer and C. L. Briant, Acta Metall. **30**, 457 (1982).

[6] M. E. Eberhart, R. M. Latanision, and K. H. Johnson, Acta Metall. **33**, 1769 (1985).

[7] M. S. Daw and M. I. Baskes, Phys. Rev. Lett. **50**, 1285 (1983).

[8] M. Hashimoto, Y. Ishida, S. Wakayama, R. Yamamoto, M. Doyama, and T. Fujiwara, Acta Metall. **32**, 13 (1984).

[9] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[10] G. S. Painter and F. W. Averill, Phys. Rev. B **28**, 5536 (1983).

[11] F. W. Averill and G. S. Painter, Phys. Rev. B **32**, 2141 (1985).

[12] R. C. Pond, V. Vitek, and D. A. Smith, Acta Crystallogr., Sect. A **35**, 689 (1979).

[13] E. L. Muetterties and R. M. Wexler, Surv. Prog. Chem. **10**, 61 (1983).

[14] J. E. Müller and J. Harris, Phys. Rev. Lett. **53**, 2493 (1984).

[15] R. A. Mulford, Metall. Trans. A **14**, 865 (1983).

[16] Y. Ogino and T. Yamasaki, Metall. Trans. A **15**, 519 (1984).

[17] C. T. Liu, C. L. White, and J. A. Horton, Acta Metall. **33**, 213 (1985).

[18] M. P. Seah and C. Lea, Philos. Mag. **31**, 627 (1975).

[19] C. L. White, R. A. Padgett, C. T. Liu, and S. M. Yalisove, Scr. Metall. **18**, 1417 (1984).

[20] J. H. Rose, J. R. Smith, F. Guinea, and J. Ferrante, Phys. Rev. B **29**, 2963 (1984).