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THE EFFECT OF IMPURITY ELEMENTS ON CHEMICAL BONDING AT GRAIN BOUNDARIES

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Abstract. Impurity elements, which have very low bulk concentrations in metals, often segregate to grain boundaries where their concentrations can be greatly enriched. As a result of this segregation, the grain boundaries are often weakened so that they become preferred paths for brittle fracture. This paper presents the results of fully quantum mechanical cluster calculations which have been applied to this problem. The particular system which we have considered is the embrittlement of nickel by sulfur. Our results will show that embrittling elements are electronegative with respect to their host metal, and draw charge off of the host metal onto themselves. As a result of this charge transfer, there is less charge available to participate in metal-metal bonds and they are weakened. It is the weakening of these bonds that leads to embrittlement. The results further show that, although the qualitative model for embrittlement is independent of the cluster geometry, the degree of charge transfer and hence the amount of weakening of the metal-metal bonds does depend on geometry. Therefore, grain boundary embrittlement is not strictly a function of concentration of the impurity but of the structure as well.
concentrations at the grain boundary of 1 to 5 atomic per cent.

The metallurgical interest in grain boundary segregation arises from the fact that this difference in composition often exerts a great influence on the properties of the material. For example, impurity segregation to grain boundaries can make the boundaries particularly favored paths for fracture (1-11) or corrosion (12-16). Segregation can also retard grain boundary motion (17-18) and thus affect the various stages of recrystallization. Furthermore, segregation can modify precipitation reactions that occur at grain boundaries (19) and can also change the atomic structure of the grain boundary (6).

Of all of these metallurgical problems, perhaps the one that has received the most extensive experimental study has been intergranular fracture. It has been well demonstrated that intergranular fracture is associated with a brittle, low energy fracture process, and in the absence of an aggressive environment it is always produced by segregation of certain deleterious elements to the grain boundaries. As a result of experiments which have employed Auger electron spectroscopy, many of these harmful elements have been identified and some of them are listed in Table I. It has also been found that some segregated elements can counteract embrittlement and they are also listed in Table I.

Certainly, identification of these elements has been a great step forward in understanding this problem. However, the question has still remained as to why these elements cause the boundaries to be weakened. Undoubtedly, they must in some way weaken the chemical bonds at the grain boundaries, but the question one would like to answer is how this weakening comes about. In this paper we will describe results of fully quantum mechanical cluster calculations which address this question. We will specifically consider the embrittlement of nickel by sulfur. We will show that sulfur is electronegative with respect to nickel and that it draws charge off of the nickel atoms around it onto itself. Consequently, less charge is available to participate in metal-metal bonds and these bonds will be weakened. It is the weakening of these bonds that leads to embrittlement. Our results also show that grain boundary geometry may affect the degree of embrittlement, but qualitatively the electronic embrittlement mechanism is independent of the atomic arrangement.

2. Method. The computational method used for these calculations was the self-consistent-field X-α scattered-wave molecular orbital method. This method was developed by Slater (20) and Johnson (21) and has been very successfully applied to problems involving transition metals (22-24). One of the primary features of the X-α scattered-wave method is that it is a cluster method. One considers only a finite number of atoms in a fixed geometry and calculates their molecular orbitals. From these calculations one can then obtain such information as the molecular orbital energy levels, contour plots of the orbitals which correspond to these levels, and contour plots of the charge density.

For the problem being considered here, a cluster method is ideal because the grain boundary is a defect structure. The problem then remains to choose a cluster geometry that is similar to the local atomic arrangement at a grain boundary. Recent work (25-26) has shown that the structure of grain boundaries can be described as a series of interlocking clusters which are distorted versions of the Bernal polyhedra (27). These polyhedra provide cluster geometries which can be used in these calculations. In this paper we have used four of
$M = \text{Metal Atom}$
$I = \text{Impurity}$

Figure 1: The Bernal polyhedra used in these calculations. (a) The tetrahedron, (b) the tetragonal dodecahedron, (c) the capped trigonal prism, and (d) the Archimedian antiprism.
these polyhedra for our cluster geometries. These include the tetrahedron, the tetragonal dodecahedron, the capped trigonal prism, and the Archimedean antiprism. These clusters are shown in figures la, lb, lc, and ld, respectively.

3. Results. As can be seen from Table I, sulfur is a strong embrittler of nickel, and boron counteracts this embrittlement. Furthermore, it has been shown that the beneficial effects of boron are not a result of site competition with the sulfur (10). Therefore, to begin our consideration of why certain elements cause grain boundary embrittlement, we consider these two extreme cases. The clusters which we will examine are the tetrahedra Ni$_4$S and Ni$_4$B. For each of these calculations the nickel atoms have been placed at the vertices of the tetrahedron and the impurity atom in the center.

Figure 2 shows the orbital energy levels for these two clusters. In both Ni$_4$S and Ni$_4$B there is a group of closely spaced orbitals near -5 to -6 eV. These energy levels correspond to orbitals which are almost entirely located on the metal atoms. However, in both cases there are four orbitals (1a*, 1a', 1t', and 1t*) which have energies well below the others. It is these orbitals which describe the metal impurity bond and we wish to consider them in some detail.

Figure 3 shows equi-valued contour plots for the four orbitals. The plane of these plots is the shaded plane in figure la. If we compare these plots orbital by orbital we see that there are definite but consistent differences between the two clusters. For any given orbital there is clearly more content on the nickel atoms in Ni$_4$B than in Ni$_4$S. Since these plots must reflect the location of charge in a given orbital, this result means that charge is drawn off the nickel atoms onto the sulfur, whereas in the cluster containing boron this charge transfer does not occur. In Ni$_4$S these orbitals are largely concentrated on the sulfur and are drawn rather tightly around it, having little content in the region between the nickel and sulfur. In Ni$_4$B the orbitals do have some content on the boron but they are not pulled in as tightly and there is considerable content in the region between the boron and the nickel atoms. Therefore, it would appear that the bond between the sulfur and the nickel atoms is heteropolar with charge concentrated on the sulfur whereas the bond between the boron and the nickel atoms is homopolar with charge shared between them.

Based on these results we can suggest the following mechanism for embrittlement. Sulfur, which embrittles nickel, is electronegative with respect to nickel in that it draws charge off of the nickel atoms around it onto itself. As a result of this charge transfer, there will be less charge available to participate in the nickel-nickel bonds and they will be weakened. The weakening of these bonds will lead to the observed embrittlement. In contrast, a cohesive enhancer such as boron in nickel is not electronegative with respect to the host metal and forms a rather homopolar bond with it. Consequently, charge will not be drawn out of the metal-metal bonds and they will not be weakened. The homopolar bond formed between this type of impurity and the metal will provide an additional increment of bonding at the grain boundary.

Clearly, to test these ideas we should examine larger clusters where we can directly observe the effect of an embrittling element on the metal-metal bonds. Therefore, we have performed calculations on the eight atom tetragonal dodecahedron (figure lb), the nine atom...
TABLE I

GRAIN BOUNDARY EMBRITTLLERS AND COHESIVE ENHANCERS OF TRANSITION METALS

(References to Work in Parentheses)

<table>
<thead>
<tr>
<th>Transition Metal</th>
<th>Grain Boundary Embrittler</th>
<th>Cohesive Enhancer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>Te(1), Bi(2)</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>S(3), N(4), Sn(5), Te(6), Se(7)</td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>P(8)</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>O(9)</td>
<td>C(9)</td>
</tr>
<tr>
<td>Ni</td>
<td>S(10, 11)</td>
<td>B(10)</td>
</tr>
</tbody>
</table>

Figure 2: The orbital energy levels for (a) Ni₄S and (b) Ni₄B.
Figure 3: Contour plots of the four molecular orbitals that contribute to the metal-impurity bond. (a) Ni$_4$S and (b) Ni$_4$B.
capped trigonal prism (figure 1c) and the ten atom Archimedian antiprism (figure 1d). In all cases we have first performed calculations for the cluster with nickel atoms at the vertices of the polyhedron and no embrittling atom present in cluster. We have then repeated the calculation, again with the nickel atoms at the vertices but also with a sulfur atom in the center of the cluster.

In order to determine the effect of the presence of sulfur on the metal-metal bonds in the cluster we have examined the total valence charge density for each of these clusters. They are shown in figures 4, 5, and 6. Let us first consider the results for Ni₈ and Ni₈S shown in figures 4 a and b, respectively. The plane of these plots is such that it includes nickel atoms 1, 4, 7, and 8 in Ni₈ and these same nickel atoms plus the sulfur atom in Ni₈S. Particular attention should be paid in this figure to the darkened contour. In Ni₈ this contour clearly contributes to a bond between nickel atoms 1 and 7, 4 and 8, and 7 and 8. In Ni₈S this contour has been changed. It no longer contributes to a bond between atoms 1 and 7 and 4 and 8 and its contribution to a bond between atoms 7 and 8 has been greatly reduced. Instead it now contributes to a bond between the sulfur atom and nickel atoms 1 and 4. Therefore, we see that the same basic mechanism is holding in this larger cluster. When sulfur is added to the nickel cluster, it forms a strong heteropolar bond with the nickel atoms nearest to it. Charge is localized in this bond and is primarily centered on the sulfur atom. Less charge is then available to participate in the metal-metal bonds and they are weakened. This last fact is demonstrated by the change in the darkened contour in the figure.

The results for Ni₁₀ and Ni₁₀S, shown in figures 5 a and b, respectively, are quite similar to those for the eight atom cluster. The plane of these plots include nickel atoms 1, 2, 3, and 4 (see figure 1d for identification) in Ni₁₀ and these same atoms plus the sulfur atom in Ni₁₀S. In Ni₁₀ the darkened contour clearly contributes to a bond between atoms 1 and 3 and 2 and 3. However, when sulfur is added the contour is changed so that it no longer contributes to these bonds but to a bond between the sulfur atom and nickel atoms 1 and 2. The metal-metal bonds between atoms 1 and 3 and 2 and 3 are weakened. However, it would appear that the embrittling effect of sulfur may be less in this cluster because, although the contour is broken into two parts, the part enclosing only atom 3 is still practically touching that part surrounding the sulfur atom and nickel atoms 1 and 2. This result is in contrast to the clear separation observed in Ni₈S between that part of the contour surrounding nickel atoms 7 and 8 and that part surrounding nickel atoms 1 and 4.

Finally, we consider the results for Ni₁₂ and Ni₁₂S shown in figures 6 a and b, respectively. The plane of these plots is one which includes nickel atoms 1, 2, and 3 in both clusters. Contours on atom 4 are also observed but they are not in the plane of the plot. Although the change caused by adding sulfur is not nearly as great, close examination of these two figures reveals that the same mechanism is operative. Again we see that the darkened contour contributes to a bond between atoms 1 and 3 and 2 and 3 in Ni₁₂. In Ni₁₂S the contour is still continuous around all three nickel atoms, but between nickel atoms 1 and 3 and 2 and 3 it has been pulled in to form a tighter neck. This pulling in is a much milder form of the charge depletion which caused the complete break off of the contour observed in the eight and ten atom clusters. Therefore, the embrittling effect of sulfur is not as strong in this cluster, but the same qualitative effect of the addition of sulfur to a cluster of nickel atoms, i.e. less charge available to participate in nickel-nickel bonds, can still
Figure 4: Contour plots of the total valence charge density for (a) Ni$_8$ and (b) Ni$_8$S.

Figure 5: Contour plots of the total valence charge density for (a) Ni$_{10}$ and (b) Ni$_{10}$S.
Figure 6: Contour plots of the total valence charge density for 
(a) Ni_9 and (b) Ni_9S.

Figure 7: Contour plots of the total valence charge density for 
(a) Ni_10 and (b) Ni_10S. In these cluster nickel atoms 3 and 4 
have been brought in closer to the center of the cluster than 
they are in the clusters shown in Figure 5.
be observed.

4. Discussion. The results presented above have provided us with a general explanation of why certain impurity elements should cause grain boundary weakening. Those elements are electronegative with respect to their host metal and draw charge off of the metal onto themselves. There is then less charge available to participate in the metal-metal bonds and they are weakened. It is the weakening of these bonds that leads to grain boundary embrittlement. The results also show that the ease with which a grain boundary is embrittled will depend on its atomic structure. This result is quite consistent with experimental observations made in our laboratory which show that in an embrittled sample, even though one may achieve completely intergranular fracture, the amount of plastic tearing associated with individual grain boundaries can vary. This result is also consistent with our experimental observations that the boundaries most prone to fracture in a sample are not necessarily those with the highest concentration of segregant.

It is interesting to consider in more detail why sulfur has a less demonstrable embrittling effect on the nine atom capped trigonal prism than on the eight or ten atom clusters and also why the ten atom cluster appears to be slightly less embrittled by sulfur that the eight atom cluster. Several factors appear to contribute to these differences and they are all related to the spatial arrangement of atoms in the cluster. In \( \text{Ni}_8 \text{S} \) there are two distinct sets of atoms. Four of the atoms (numbers 1, 2, 3, and 4) are located near the sulfur and the other four are located at some distance from it. \( \text{Ni}_{10} \text{S} \) also has two distinct sets of atoms. Eight form the antiprism and are located near the sulfur while the two atoms that cap the antiprism are farther away. In \( \text{Ni}_9 \text{S} \) one set of six atoms forms the trigonal prism while three others form the caps. However, the arrangement of all nine atoms is such that they are all approximately equidistant from the sulfur. Therefore, as we proceed in the order \( \text{Ni}_9 \text{S}, \text{Ni}_{10} \text{S}, \) and \( \text{Ni}_{11} \text{S} \), the sulfur has an increasing number of nearest neighbors from which to draw charge. Therefore, one would expect less charge to be drawn off any one atom as this number increases which in turn means that the metal-metal bonds would be weakened less. This idea is quite consistent with the results. The second point concerns the difference between \( \text{Ni}_9 \text{S} \) and the other two clusters. In both \( \text{Ni}_{10} \text{S} \) and \( \text{Ni}_{11} \text{S} \) there are two sets of nickel atoms, one set near the sulfur atom and one set removed from it. In these clusters we can directly observe the effect of sulfur on the bonds between these two sets of atoms. In \( \text{Ni}_{11} \text{S} \), although we do have two sets of atoms, one is not distinctly farther away from the sulfur than the other. Therefore, any changes in metal-metal bonds caused by the charge transfer would primarily affect bonding between the nine atoms in this cluster and the next shell of neighbors. Finally, we have found that changes in the bond lengths in any given cluster can affect the results. Generally, as the cluster is contracted the embrittling effect of an element is decreased. This fact can be seen by comparing the results in figures 7 a and b with those in figures 5 a and b. Figures 7 a and b are plots for \( \text{Ni}_{10} \text{S} \) but in this case atoms 3 and 4 (see figure 1d for identification) have been brought in closer to the center of the cluster. When sulfur is added to this contracted \( \text{Ni}_{11} \text{S} \) cluster, the effect on the bonds between atoms 1 and 3 and 2 and 3 is much less. The only signs of weakening of these bonds are the small trapezoidal holes which form between the two pairs of atoms. These represent a decrease in charge in the bonds.
Previously reported results (28-29) have also shown that this model holds up well for systems other than sulfur in nickel. An examination of the embrittling systems listed in Table I shows that the embrittling elements tend to come from groups IV to VI in the periodic table and thus would generally be electronegative with respect to the embrittled metals. It would be tempting to try to correlate embrittling potency with values from an electronegativity scale such as Pauling's (30). However, our work (29) has shown that the Pauling scale, which was based on chemical data, is not always reliable for metallurgical problems such as this one and that naive use of such a scale could lead to erroneous conclusions.

Finally, we should point out the implications that our results have concerning the fracture path in the solid. Our model tells us that the fracture should occur by the breaking of metal-metal bonds. At first thought, this result might seem to imply that the fracture would occur at some distance from the boundary. However, it can easily be shown (31-32) that the crack can propagate within one atom layer of the center of the boundary and break only metal-metal bonds. Furthermore, the crack can cut back and forth across the center of the grain boundary by this same bond breaking mechanism.

5. Conclusions. The conclusions of this work are the following:

1. Impurity elements which cause embrittlement are electronegative with respect to the host metal atoms. They draw charge off of the surrounding atoms which leaves less charge available to participate in the metal-metal bonds.

2. The atomic arrangement at the boundary does not affect the general model for embrittlement. However, it does affect the amount of charge transfer and hence the degree of embrittlement. Therefore, certain arrangements of atoms at the grain boundaries would be more easily embrittled than others. Generally, an increase in the number of nearest neighbors around the impurity and a decrease in the lattice spacing tends to decrease the embrittling potency of the impurity.

6. Acknowledgments. This work was partially sponsored by the Office of Naval Research.

7. References.

DISCUSSION

P. CABANNE-BROUTY: You explain the embrittlement of nickel by sulfur; we observe that Cu-S and Ag-S high purity solid solutions are not brittle: could you explain the reason for this difference of behaviour between Ni on one hand and Cu and silver on the other hand?

C.L. BRIANT: Without performing calculations on the Cu-S and Ag-S system, I cannot explain your experimental observations. However, both experiment and theory have shown that the embrittling potency of an impurity element depends greatly on the transition metal that is being embrittled, (see reference 29). Therefore, one cannot extrapolate either experimental or theoretical results on Ni to these other metals and expect the same effects.

P. LESBATS: a) To begin some metallurgical comment, you told grain boundary brittleness is caused by impurity: we have experimental evidences that the grain boundaries can be brittle on pure b.c.c. metals. Concerning the role of phosphorous, even in steels, if they are very pure without sulfur or nitrogen, the embrittlement by phosphorous only is not very strong. Michel Biscondi will come back to these points in the last paper.

b) The X-α scattered wave technique is a very nice method. However I am wondering if in this case a cluster method is very appropriate because an isolated impurity generates a long range interaction which is important and which is not taken into account by such a method.

c) Are your calculations fully self-consistent, because the charge transfer is very sensitive to the degree of self consistency?
C.L. BRIANT: a) Dr. Biscondi's results are very interesting, but at this point it is very difficult for me to comment on them in any detail. b) The X-α scattered wave calculations seem to be quite appropriate for this type of problem. Examination of the literature will show its great success in problems of chemisorption and magnetism. In these problems one is also interested in a type of impurity interacting with a transition metal. Because of the excellent agreement between theory and experiment in these cases, it would appear that these should be no problem in applying the X-α scattered wave method to the problem of grain boundary embrittlement. The calculations are fully self-consistent.

M. AUCOUTURIER: Did you obtain results on "non electronegative" embrittlers like Gallium in Aluminium or Hydrogen in Iron or Nickel? Could it also be possible to show the influence of Hydrogen in Ni-S system?

C.L. BRIANT: We have only very recently begun to examine the effect of Ga on Al, but our preliminary results would suggest that an electronegativity argument might still hold. We have examined H in Ni and found very little change transfer. This result suggests that the mechanism for hydrogen embrittlement is different from that of the other embrittling elements.

V. VITEK: a) How much are the results affected by the symmetry and "free surfaces" of the clusters? Perhaps you get similar effects of charge redistribution if asymmetric clusters are used. b) If this is not so and electronegativity is the principal reason for charge redistribution then the effect is independent upon whether the impurity is in the grain boundary or not and the grain boundary effect is simply that it is a region of higher concentration of impurities. c) However, in boundaries a large variety of clusters and their orientations exist and thus it seems that, in average, the same number of stronger and weaker bonds will be formed.

C.L. BRIANT: a) In the text we have presented results for a number of different cluster geometries and, as pointed out there, we always see the same qualitative effects, i.e., the embrittling impurity draws charge off of the metal atoms and weakens the metal-metal bonds. We
further showed that the degree of charge transfer would depend on the number of nearest neighbours that the impurity atom has at the grain boundary. Any asymmetry of the cluster would be reflected in this manner. Asymmetry alone would not cause a charge redistribution in pure Ni clusters of the type seen here.

b) I believe that you are correct in assuming that one of the major functions of the grain boundaries is to concentrate impurity atoms. It also impedes dislocation motion which allows a stress to be built up there.

c) Our calculations would suggest that embrittling elements would cause the formation of both strong and weak bonds at the grain boundaries. It is the presence of the weak bonds and the fact that a crack can propagate along the boundaries by breaking only these weak bonds that causes embrittlement. This final point is illustrated in some details in reference 31.

L. HOBBS:
One of the things that one learns from studying defect aggregation, including impurities, is that atomic arrangements in defect aggregates often mimic those found in compounds of the elements involved. With the exception of the capped trigonal prism configuration of Ni$_3$S, which alone resembles the atom configurations in the NiAs structure of NiS or FeS, your cluster configurations appear rather arbitrary. In fact, the Ni$_9$S configuration predicts the least embrittlement on your model.

C.L. BRIANT:
These clusters were chosen because they should represent the arrangement of atoms at the grain boundaries. Although certainly a segregated atom will affect the arrangement of metal atoms around it, it seems unlikely that the atomic arrangement at all grain boundaries would take on a gallium arsenide (Ni$_3$S$_2$) structure. We did see the smallest effect for Ni$_2$S and the reasons for this are discussed in the text.