

Effect of manganese on grain boundary segregation of sulfur in iron

S.B. Gesari, M.E. Pronsato, A. Juan *

Departamento de Física, Universidad Nacional del Sur, Av. Alem 1253, 8000 Bahía Blanca, Argentina

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Abstract

The ASED-MO theory was used to study the electronic effects of S and the S–Mn couple upon the chemical embrittlement of Fe grain boundaries. The results obtained for S alone in a model of grain boundary (GB) are consistent with its observed behavior as a chemical embrittling agent. It was found that the total energy of the cluster decreases when the S atom is located at the GB. When S segregate at the Fe GB containing Mn, the embrittlement process was modified. The crystal orbital overlap population (COOP) curves gives a measure of Fe–Fe bond weakening due to the segregated atoms at the GB. Our calculations show that Mn behaves as a weak embrittler on the Fe GB. The Fe–Mn bonds were strengthened, while Fe–Fe bonds of the capped trigonal prism of the GB (CTP) were weakened. On the other hand, when S segregate at the Mn/Fe cluster, some metallic bonds were resistant to chemical embrittlement.

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1. Introduction

Modern primary and secondary steel making practices can reduce the level of impurities to a very low level, but usually a residual impurity remains. One of the trace elements that is present during the steel making process and is generally undesirable is sulphur. The presence of free sulphur in a steel product is detrimental to its properties [1,2]. Modern steel making processes and selection of raw materials means that the levels of sulphur present in a steel should be very low. Any remaining sulphur can be removed through the use of alloying additions of manganese which reacts with the sulphur to form MnS [3].

While experimental research [4] has been performed on the effect of Mn on the sulphur segregation to the Fe GB, the microscopic reasons of the role played by the Mn additions and the S–Mn interactions has not been well understood. In a theoretical work, Zhong et al. [5] showed that manganese on its own will embrittler iron, and further that Mn facilitates phosphorus embrittlement in the GB by strengthening in-plane P–Mn interaction, at the expense of cohesion across the boundary. Yang et al. [6], based on first principles calculations,

also found that substitutional Mn is a direct embrittler for the fcc Fe GB.

In this paper we present calculations for Mn as an alloying element on a bcc Fe GB and the effects on the segregated S, using qualitative electronic structure calculations in the framework of the atom superposition and electron delocalization molecular orbital (ASED-MO) theory. Calculations were performed using an Fe₁₇₆ cluster to simulate the $\Sigma = 5$ 36.9° [1 0 0] {0 1 3} symmetrical tilt GB structure. The structure was relaxed and the most stable positions for the S atom at the GB core were determined. An analysis of the orbital population helped us to determine the effects of the segregants on the cohesion of the GB.

2. Cluster model

The $\Sigma 5$ (0 1 3) GB was formed by two atomic blocks (each of eight (0 1 3) layers) with one block rotated 36.9° relative to the other around the $\langle 1 0 0 \rangle$ axis (see Fig. 1a). Then, a substitutional alloying A was put at the center of the GB core. In Fig. 2 we can see the (0 1 3) GB plane with Fe₁₇₆ substituted by Mn. When a solid solution is formed and the size difference between atoms is small, the component that is dissolved is located in a substitutional site [7]. In this case, the energy difference between the cluster with an Mn atom located in the bulk and that with a Mn atom at the GB result to be of 1.04 eV in favor to the last option.

* Corresponding author. Tel.: +54 291 4888218; fax: +54 291 4595142.

E-mail address: cajuan@criba.edu.ar (A. Juan).

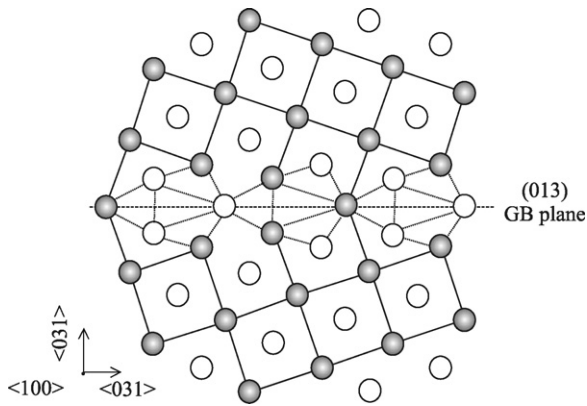


Fig. 1. Relaxed structure of (0 1 3) symmetrical tilt [1 0 0] grain boundary seen in projection along the [1 0 0] tilt axis. Three structural units are identified, each comprising a capped trigonal prisms (CTP).

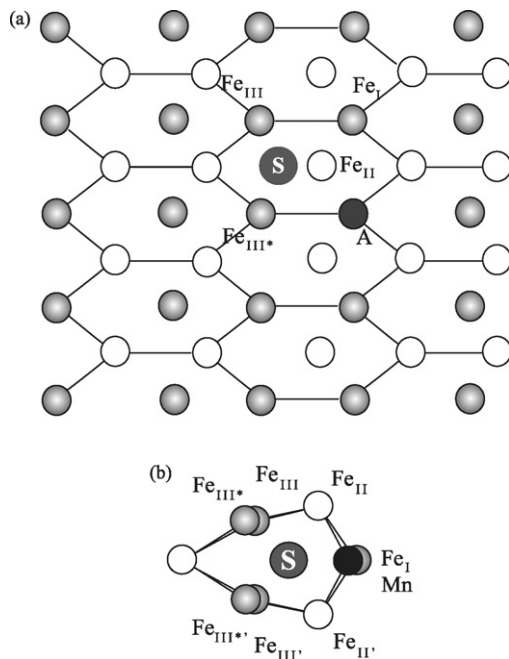


Fig. 2. (a) (0 1 3) GB plane, A: Fe or Mn atom; (b) side view for the CTP with a substitutional Mn atom and S interstitial atom.

The structure was relaxed by minimizing the energy as a function of the vertical interplanar distances for the clean Fe cluster, the Mn/Fe cluster and that with a S atom located in the center of a capped trigonal prism (CTP). The structures within the (0 1 3) planes were kept unchanged, maintaining the in-plane symmetry [8]. Secondly, the S–Mn distance was also optimized. The minimum energy was found for a S–Mn bond length of 2.36 Å, in good accordance with the literature [9,10]. The minimum total energy for the clusters S/Fe, Mn/Fe and S + Mn/Fe is –10.61, –10.30 and –10.45 eV, respectively.

3. Results and discussion

Table 1 shows the electronic densities and the net charge for the pure Fe, Mn/Fe and S + Mn/Fe clusters. In general, Mn drain charge from the nearest neighbor Fe atoms. If we compare

Table 1

Electron densities and net charges for the Fe, Mn/Fe and S + Mn/Fe clusters

| Cluster | Atom | Electron density | | | | Charge |
|-----------|-------------------|------------------|--------|--------|--------|---------|
| | | Total | s | p | d | |
| Fe | Fe _I | 6.8967 | 0.6941 | 0.2511 | 5.9515 | 1.1035 |
| | Fe _{II} | 6.6705 | 0.6981 | 0.2500 | 5.7224 | 1.3294 |
| | Fe _{III} | 6.9537 | 0.7001 | 0.2544 | 5.9992 | 1.0461 |
| Mn/Fe | Mn | 10.3251 | 0.8349 | 0.9683 | 8.5219 | –3.3251 |
| | Fe _I | 6.8157 | 0.6558 | 0.2294 | 5.9305 | 1.1844 |
| | Fe _{II} | 6.5431 | 0.6567 | 0.2412 | 5.6452 | 1.4568 |
| | Fe _{III} | 6.8882 | 0.6689 | 0.2363 | 5.9840 | 1.1117 |
| S + Mn/Fe | S | 5.5957 | 1.4781 | 4.1176 | 0 | 0.4042 |
| | Mn | 10.1155 | 0.7641 | 0.8822 | 8.4692 | –3.1155 |
| | Fe _I | 6.5474 | 0.5909 | 0.1821 | 5.7744 | 1.4526 |
| | Fe _{II} | 6.2872 | 0.5398 | 0.2403 | 5.5071 | 1.7127 |
| | Fe _{III} | 6.4574 | 0.5693 | 0.2194 | 5.6687 | 1.5427 |

the change of the charge in pure Fe and Mn/Fe clusters for the nearest neighbor to A (Fe or Mn), that is for Fe_{II}, is 0.127 (1.3294 versus 1.4568) with a Fe_{II}–A distance of 2.29 Å. Chen et al. [11] reported a change of 0.09 for the same GB with and without Mn, with a Fe–Mn distance of 2.68 Å. A similar effect was observed for Fe_I and Fe_{III}. This tendency for Fe atoms to lose charge is increased with S.

Fig. 3a shows the projected density of states (DOS) for the Fe_I atom interacting with Mn. The narrow band of states below the Fe d band belong to Mn based orbitals interacting mainly with Fe s and p orbitals (peaks at –13.9 and –12.8 eV). The addition of S introduces new states (peaks at –22.0, –15.1 and –12.5 eV, see Fig. 3b).

In a previous work, we have calculated the binding energy for S at the GB [8]. We found that the S segregates strongly at the GB in α -Fe as determined experimentally by Grabke [1]. The addition of S decreases the Fe–Fe orbital populations (OP) while a sort of Fe–S bond is developed (see Table 2). If we

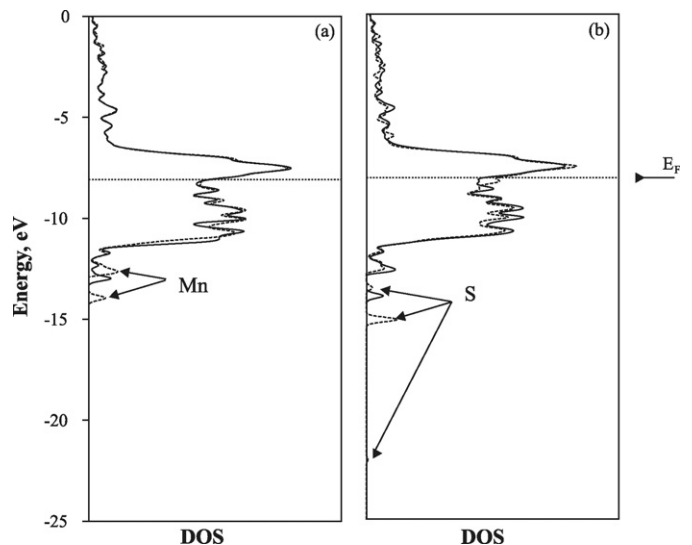


Fig. 3. Partial DOS for Fe_I: (a) in the Fe and Mn/Fe clusters, with solid and dotted line, respectively; (b) in the Mn/Fe and S + Mn/Fe clusters, with solid and dotted line, respectively.

Table 2
Interatomic distances and the orbital populations for the Fe, Mn/Fe and S + Mn/Fe clusters

| Bond | Distance Å | OP | | | Distance Å | OP (S/Fe) |
|---|---------------|--------|---------|-------------|---------------|--------------|
| | | (Fe) | (Mn/Fe) | (S + Mn/Fe) | | |
| Fe _I –Fe _{II} | 2.29 | 0.3675 | 0.3374 | 0.2236 | 2.29 | 0.2571 |
| Fe _I –Fe _{III} | 2.91 | 0 | 0 | 0 | 2.91 | 0.0216 |
| Fe _{II} –Fe _{III} | 2.36 | 0.3194 | 0.2911 | 0.1459 | 2.36 | 0.1657 |
| Fe _{II} –Fe _{II} * | 2.86 | 0.0887 | 0.0746 | 0.0659 | 2.86 | 0.0789 |
| Fe _{III} *–Fe _{III} ' | 2.08 | 0.5278 | 0.4932 | 0.3696 | 2.09 | 0.3807 |
| A–Fe _I | 2.86 | 0.0793 | 0.1720 | 0.1015 | 2.86 | 0.0452 |
| A–Fe _{II} | 2.29 | 0.3678 | 0.3878 | 0.2211 | 2.29 | 0.2571 |
| A–Fe _{III} * | 2.91 | 0.0791 | 0.1670 | 0.0674 | 2.86 | 0.0216 |
| S–A | 2.36 | | 0.2875 | | 2.43 | 0.1189 |
| S–Fe _I | 2.36 | | 0.1227 | | 2.43 | 0.1189 |
| S–Fe _{II} | 1.83 | | 0.5107 | | 1.87 | 0.4974 |
| S–Fe _{III} | 1.96 | | 0.3828 | | 1.93 | 0.4377 |

A: substitutional atom (Fe or Mn).

compare the COOPs curves for the S–Fe_I* and S–Mn bond (see Fig. 4) and the OP values in Table 2, we can observe that the interaction is stronger when Fe_I* is substituted by Mn. In other words, the S–Mn interaction is stronger than the S–Fe interaction.

The OP for Mn–Fe increases (for example 0.1720 versus 0.0793 for Mn/Fe and clean Fe clusters, respectively), while the other Fe–Fe bonds of the CTP are weakened. Although Mn appears to increase somewhat the embrittling power of S (see the Fe–Fe OPs for S + Mn/Fe and S/Fe), this is in part compensated by its direct cohesion-enhancer effect at the GB. Some bonds like Mn–Fe_I and Mn–Fe_{III} for S + Mn/Fe cluster are stronger than that for S/Fe cluster (Fe_I*–Fe_I and Fe_I*–Fe_{III}). Moreover, the OP value for S–Mn is more than twice of that for S–Fe_I*.

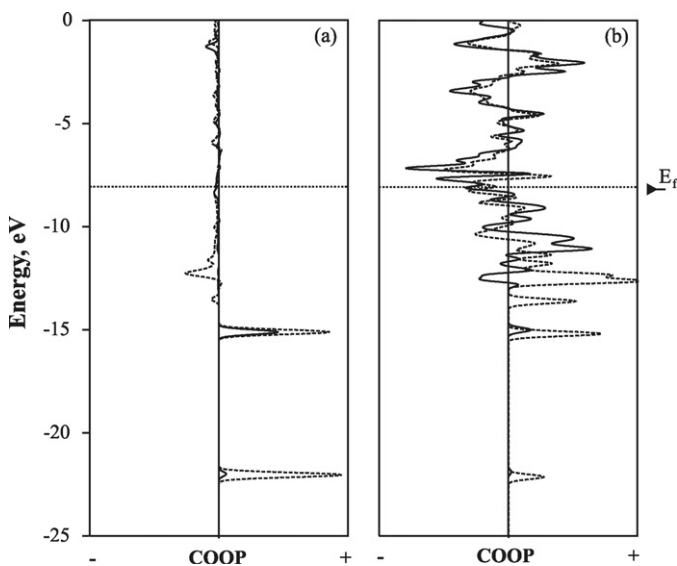


Fig. 4. COOPs curves for: (a) S–Fe_I*, OP: 0.1189 (solid line) in S/Fe cluster; S–Mn, OP: 0.2875 (dotted line) in S + Mn/Fe cluster; (b) Fe_I–Fe_I*, OP: 0.0452 (solid line) in S/Fe cluster; Fe_I–Mn, OP: 0.1015 (dotted line) in S + Mn/Fe cluster.

4. Conclusions

The ASED-MO theory was used to study the electronic effects of S and the S–Mn couple upon the chemical embrittlement of Fe grain boundaries. The results obtained for S alone in a model of grain boundary (GB) are consistent with its observed behavior as a chemical embrittler agent. It was found that the total energy of the cluster decreases when the S atom was at the GB. When S segregate at the Fe GB containing Mn the OP changes. Comparing the clean Mn/Fe with the clean Fe cluster we note that the Fe–Fe bonds of the CTP were weakened. Comparing the S + Mn/Fe with the S/Fe clusters we see that, although the Fe–Fe bond strengths are lower at the cluster containing Mn, the atoms that are connected to Mn form strong bonds. This last bonds are developed between atoms lying within the GB plane and the atoms responsible for the GB cohesion are those lying across the GB plane.

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Appendix A. Computational details

The calculations were carried out using the atom superposition and electron delocalization molecular orbital cluster method (ASED-MO) [12]. The ASED-MO is a semi-empirical method, which makes a reasonable prediction of molecular and electronic structures. This theory is based on a physical model of molecular and solid electronic charge density distribution functions, where by the latter is partitioned into a perfect following (with respect to the nucleus) atom part and an imperfect following bond charge part [12,13]. This method was described in a previous paper [8].

The total energy difference can be expressed as:

$$\Delta E_{\text{total}} = E(\text{Fe}_m\text{S}) - E(\text{Fe}_m) - E(\text{S}) + \sum E_{\text{repulsion}} \quad (1)$$

or

$$\Delta E_{\text{total}} = E(\text{Fe}_m\text{MnS}) - E(\text{Fe}_m\text{Mn}) - E(\text{S}) + \sum E_{\text{repulsion}} \quad (2)$$

where E is the electronic energy, m is the cluster size and S is the interstitial atom. The repulsion energy ($E_{\text{repulsion}}$) of nucleus B in the presence of a fixed atom A is calculated from:

$$E_{\text{repulsion}} = \frac{1}{2} \sum_A \sum_{B \neq A} E_{AB} \quad (3)$$

where E_{AB} is a pairwise electrostatic energy term. The summation is extended over all Fe–Fe, Fe–Mn, Fe–S and Mn–S pairs [12].

Throughout this paper, two conceptual tools: density of states (DOS) and crystal orbital overlap population (COOP)

curves were used to shed more light on the interactions computed with the YAHEMOP program [14]. The DOS curve is a plot of the number of orbitals per unit volume per unit energy. The COOP curve is a plot of the overlap population weighed DOS versus energy. Integration of the COOP curve up to the E_F gives the total overlap population of the bond specified. Looking at the COOP, we may analyze the extent to which specific states contribute to a bond between atoms or orbitals [15].

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