Interaction of sulfur with impurities in bcc iron

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Abstract. In this work, the modeling of the sulfur interaction with substitutional impurities (Mn, P) and interstitial (C) has been carried out. All calculations were performed using the density functional theory in the WIEN2k software package. For the first two coordination spheres, there is a strong repulsion between carbon and sulfur, but in the third relative position, a slight attraction arises between the atoms. When sulfur interacts with manganese, attraction occurs only for the first coordination sphere, while the dissolution energy of both manganese and sulfur decreases. In the case of the S-P interaction, the binding energy is negative, and the dissolution energy of both sulfur and phosphorus decreases for all configurations, although the distance between phosphorus and sulfur increases. It can be assumed that the presence of phosphorus leads to the accumulation of sulfur in the material.

1. Introduction

Modern steelmaking methods can reduce impurities to very low levels, but residual impurities usually remain. A common feature of non-metallic impurities such as hydrogen, oxygen, sulfur, phosphorus, etc. in a metallic material is that even a small amount of them can greatly affect the various properties of the material. Despite the fact that the solubility limit of such impurities is small, there is a possibility that the impurities will be locally concentrated, for example, segregation at grain boundaries (GBs) may occur, leading to a sharp change in the mechanical properties of metals [1].

One of the undesirable elements that are present in the steelmaking process is sulfur. The presence of free sulfur in a steel product has a negative effect on its properties, and therefore its content is strictly controlled [2]. However, most steels contain a large number of impurity elements that significantly modify this effect. It is well known that the steel embrittlement containing sulfur impurities in the presence of manganese decreases [3]. The addition of carbon to the Fe-S alloy reduces the sulfur segregation at GBs due to competition from carbon, which also has a high surface activity [4]. The difference in fragility between S and P is not well understood. Induced embrittlement of iron by sulfur occurs even when the volume concentration of S is only a few tens of at. parts per million [4], while in the case of phosphorus, the volume concentration of P exceeds 900 at. parts per million [5].

In recent years, microscopic approaches based on the first principles (ab initio) of the electronic theory of metals have become increasingly important in solving the problem of embrittlement. Modern methods of the electronic theory of metals and numerical modeling based on the theory of the electron density functional [6] make it possible to overcome the known limitations of thermodynamic approaches [7] and provide a reliable basis for the development of new doping schemes.

Therefore, the purpose of this work was to clarify the microscopic reasons for the influence of manganese, carbon, and phosphorus impurities on the dissolution of sulfur in bcc iron.
2. The method of ab initio modeling

All calculations were performed in the software package WIEN2k [8] with a full-potential LAPW method using GGA-96 that provides high precision of results. Calculations were carried out with a Tornado complex of the Supercomputer Centre of the South Ural State University [9]. As a model system, we chose a ferromagnetic $3 \times 3 \times 3$ bcc iron supercell containing iron atoms. The equilibrium lattice parameter was 2.84 Å, which agrees well with the experimental values [10]. The $k$-space integrations were performed using 64 $k$-point mesh. The muffin-tin sphere radius $R_m$ equal to 2.00, 2.00 and 1.25 a.u. was used for iron atom, substitutional impurities (P, S, Mn) and carbon, respectively. The cut-off energy of 340 eV was chosen for all systems. The ions were relaxed such that the maximum component of the force on each ion was less than 0.01 eV/Å while the total energies were converged to within 0.01 meV. These parameters have been tested to ensure the convergence of total energy to less than 0.01 eV.

Dissolution energy of an interstitial (C) or substitutional (S, Mn, P) impurity was calculated using the formula

$$E_{di} = E(Fe_nX) - nE(Fe) - E(X),$$

(1)

where $E(Fe_nX)$ is the total energy of a system containing $n$ iron atoms and one impurity atom ($n=54$ for interstitial and $n=53$ for substitutional impurities), $E(Fe)$ and $E(X)$ are the energies of one Fe atom and one impurity atom, correspondingly.

The binding energy of phosphorus atom with an impurity atom $X$ ($X=Mn, P, C$) was calculated as

$$E_{bin} = [E(Fe_{n-m}XS) - E(Fe_{n-k}X)] - [E(Fe_{n-1}S) - E(Fe_n)],$$

(2)

where $E(Fe_{n-m}S)$ is the total energy of a system containing $n-1$ iron atom and one sulfur atom; $E(Fe_n)$ is the total energy of a system containing $n$ iron atoms; $E(Fe_{n-m}XS)$ is the total energy of a system containing $n-m$ iron atoms, one atom of impurity $X$ ($X=Mn, P, C$) and one sulfur atom; $E(Fe_{n-k}X)$ is the total energy of a system containing $n-k$ iron atoms and one atom of impurity $X$ ($m=1, k=0$ for systems with interstitial impurity $X$ and $m=2, k=1$ for systems with substitutional one). Equation (2) may be treated as the difference of phosphorus dissolution energy in pure iron and a system with impurity. The negative (positive) value of the binding energy of sulfur and an impurity atom means attraction (repulsion) between them.

3. Results and discussion

To simulate pure sulfur, we were considered several configurations of this material. We were found that the alpha-S$_8$ modification has the lowest energy of the system. According to the experimental data, the parameters of this structure were the following: $a=10.4646$, $b=12.8660$, $c=24.4860$ Å, $\alpha=\beta=\gamma=90^\circ$ [11]. Since sulfur is located in the bcc lattice of iron, we were also considered the bcc structure of S. The optimal lattice parameter of this structure was found to be 3.16 Å. The volume of the Voronoi polyhedron per sulfur atom in these structures was 25.75 Å$^3$ and 15.78 Å$^3$, respectively. We were found that the dissolution energy of one sulfur atom relative to the modification energy alpha-S$_8$ equals 0.28 eV and relative to the energy of one sulfur atom with bcc structure equals -0.78 eV, the volume of the Voronoi polyhedron per one sulfur atom in the bcc iron lattice was 11.29 Å$^3$. The magnetic moment per iron atom was 2.24 $\mu_B$ (it decreases by 0.01 $\mu_B$ compared to the magnetic moment per iron atom of the bcc lattice without impurity, the magnetic moment of Fe in the first environment decreases to 2.19 $\mu_B$), and for a sulfur atom equals to 0.01 $\mu_B$, which is in agreement with other data (0.02 $\mu_B$ [12]).

When studying the interaction of sulfur with substitutional impurities (P, Mn) and carbon in the bcc lattice of iron, the first three environments for S were considered when the impurity atom gradually moves away from the sulfur atom. The carbon atom sequentially occupied octahedral positions 1’– 3’, and substitutional impurities (P and Mn) occupied positions 1-3 (Figure 1). For the Mn-S system, two structures were considered: when the magnetic moment on the manganese atom is parallel to the magnetic moment on the iron atoms (Mn$_{up}$) and antiparallel (Mn$_{dn}$). For each placement of the X-S pair, structural and volumetric system optimization was performed. Table 1 shows the magnetic
moments on the atoms of iron, impurity, and sulfur, as well as the distance between the X-S atoms and the volume of the Voronoi polyhedron per one impurity atom.

![Figure 1. X–S configurations in bcc iron. Carbon atom occupies octahedral sites 1’–3’. Substitutional impurity atoms (Mn and P) occupy positions 1-3, which correspond to the first three coordination spheres for sulfur.](image)

Table 1. Magnetic moments of iron atoms (average), impurity X (X = P, C, Mn), and sulfur in bcc iron (M(X)). The X–S distance is given in Å. The Voronoi polyhedron volume (V) per impurity atom is given in Å$^3$.

| X       | Site | M(Fe)$_n$ (µB) | M(S)$_n$ (µB) | M(X)$_n$ (µB) | X–S distance, Å | V(S), Å$^3$ | V(X), Å$^3$ |
|---------|------|----------------|---------------|---------------|-----------------|-------------|-------------|
| Mn$_{up}$ | 1    | 2.25           | 0.02          | 0.27          | 2.356           | 11.33       | 11.28       |
|         | 2    | 2.23           | 0.01          | 1.38          | 2.740           | 11.33       | 11.28       |
|         | 3    | 2.24           | 0.01          | 0.72          | 4.019           | 11.38       | 11.31       |
|         | 1    | 2.28           | 0.02          | -2.31         | 2.491           | 11.31       | 11.67       |
| Mn$_{dn}$ | 2    | 2.25           | -0.01         | -2.26         | 2.932           | 11.33       | 11.40       |
|         | 3    | 2.27           | 0.01          | -1.87         | 4.040           | 11.37       | 11.47       |
|         | 1    | 2.29           | 0.02          | -0.06         | 3.111           | 11.69       | 11.76       |
| P       | 2    | 2.27           | 0.03          | -0.06         | 3.325           | 11.34       | 11.27       |
|         | 3    | 2.22           | 0.01          | -0.07         | 3.947           | 11.36       | 11.26       |
|         | 1'   | 2.28           | -0.01         | -0.09         | 1.794           | 9.71        | 7.53        |
| C       | 2'   | 2.30           | -0.01         | -0.11         | 2.711           | 11.46       | 7.90        |
|         | 3'   | 2.27           | 0.02          | -0.10         | 3.401           | 11.74       | 6.97        |

From the data presented in Table 1, it can be seen that only in the case of interaction of sulfur with manganese for the Mn$_{up}$ system, the volume of the Voronoi polyhedron and the magnetic moment for sulfur change insignificantly. At the same time, the magnetic moment on the Mn atom changes greatly. For the Mn$_{dn}$ system, we have observed an increase in the distance between impurities, and as a consequence of the volume of the Voronoi polyhedron. According to [13], at a manganese concentration of less than 10% (in our case, about 2%), the magnetic moment strongly depends on the surrounding matrix and can vary significantly, which is what we observe. The interaction of phosphorus with sulfur leads to a significant increase in the distance between impurities in the first environment, and, as a consequence, the volume of the Voronoi polyhedron increases. It is for the interaction of sulfur and carbon that the magnetic moment of the sulfur atom in the first two environments changes from an initially positive value to a negative one. And with an increase in the S-C distance to 3.401 Å, the volume of the Voronov polyhedron for sulfur increases and the magnetic moment returns to a positive value.

The energy characteristics of the interaction of X-S impurities are presented in Table 2. For a system with two impurities, the dissolution energy of each of them was estimated separately in order to evaluate their influence on each other using the following formula:

$$E_{d2}(Y) = E(Fe_{n-XY}) - E(Fe_{n-k}X) + kE(Fe) - E(Y)$$
Table 2. Dissolution energies $E_d$ of S and X in bcc Fe–S–X systems and S–X binding energies $E_{bin}$.

| Site | $E_d$(S), eV | $E_d$(X), eV | $E_{bin}$, eV |
|------|--------------|--------------|--------------|
| Mn_up | -0.83 | 0.10 | -0.05 (-0.16 [18]) |
| 2 | -0.76 | 0.18 | 0.02 (0.03 [18]) |
| 3 | -0.77 | 0.16 | 0.01 (0.05 [18]) |
| 1 | -0.99 | -0.09 | -0.21 (-0.16 [18]) |
| Mn_dn | -0.77 | 0.12 | 0.01 (0.03 [18]) |
| 2 | -0.77 | 0.13 | 0.01 (0.05 [18]) |
| 1 | -0.92 | -1.80 | -0.14 (-0.22 [18]) |
| P | -0.79 | -1.68 | -0.01 (-0.08 [18]) |
| 3 | -0.80 | -1.69 | -0.02 (0.05 [18]) |
| 1 | -0.43 | 1.15 | 0.35 |
| C | -0.41 | 1.17 | 0.37 |
| 3 | -0.79 | 0.79 | -0.01 |

The dissolution energies of impurities in the pure structure of bcc iron were equal: for carbon in octahedral position 0.85 eV (0.63–0.98 [14], 0.82 eV [15]); for phosphorus -1.66 eV (-1.62, -1.83, -1.71 eV [16]); for manganese 0.15 eV (0.16 eV [17]); for sulfur -0.78 eV.

Analyzing the energy characteristics of the interaction of sulfur with impurities, you can see the following:

1. When sulfur interacts with manganese in the first neighbor position, attraction is observed in both cases (Mn_up and Mn_dn), while the dissolution energy of both manganese and sulfur decreases, which indicates an increase in the solubility of sulfur and manganese in iron. It is in this position, on the manganese atom, that the minimum magnetic moment. It can be seen that, in the energy characteristics, a significant difference (~ 0.1 eV) between Mn_up and Mn_dn is observed only for the first environment; the antiparallel arrangement is energetically more favorable. The obtained binding energies are in good agreement with the theoretical work [18]. This circumstance may explain the formation of manganese sulfide, which lowers the red brittleness of steel caused by the precipitation of iron sulfide in intergranular boundaries.

2. The interaction of sulfur and phosphorus impurities is very curious. Despite the fact that the distance between phosphorus and sulfur in the first two coordination spheres is greater than in the case of C and Mn, the binding energy between them is large (-0.14 eV) and corresponds to attraction. In this case, the energy of solubility of both sulfur and phosphorus decreases for all configurations. It can be assumed that the presence of phosphorus leads to the accumulation of sulfur in the material.

3. In the case of the sulfur interaction with carbon for the first two neighborhoods, there is repulsion between these impurities and a significant increase in their dissolution energies. Whereas, in the third relative position, the magnetic moment of sulfur changes, and a slight attraction appears. Thus, carbon reduces the sulfur solubility, which is in agreement with experimental data on the competition between sulfur and carbon [4].

4. Conclusions

An ab initio simulation of the sulfur interaction with impurities of both substitution (Mn, P) and interstitial (C) in bcc iron was performed. The interaction between manganese and sulfur is strongest for the case of the nearest neighborhood and has the character of mutual attraction. It should be noted that the change in the orientation of the magnetic moment on the manganese atom is energetically more favorable only for the first environment. For sulfur and phosphorus impurities, attraction is observed in all three coordination spheres, which is very significant (-0.14 eV) for the first neighborhood. When a sulfur atom is adjacent to a carbon impurity in the first two coordination...
spheres, the magnetic moment $S$ changes sign, and as a consequence, repulsion is observed between the atoms. But already in the third coordination sphere, the magnetic moment on the sulfur atom returns to its value characteristic of pure iron, and the interaction practically disappears.

Carbon significantly increases the energy of sulfur dissolution, while phosphorus lowers it for all three configurations. Probably, phosphorus favors the dissolution of sulfur in iron, while carbon competes with it.

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