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Influence of the "*surface effect*" on the segregation parameters of S in Fe(100): A multi-scale modelling and Auger Electron Spectroscopy study

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ABSTRACT

The article takes a new look at the process of atomic segregation by considering the influence of surface relaxation on the segregation parameters; the activation energy (Q), segregation energy (ΔG), interaction parameter (Ω) and the pre-exponential factor (D_0). Computational modelling, namely Density Functional Theory (DFT) and the Modified Darken Model (MDM) in conjunction with Auger Electron Spectroscopy (AES) was utilized to study the variation of the segregation parameters for S in the surface region of Fe(100). Results indicate a variation in each of the segregation parameters as a function of the atomic layer under consideration. Values of the segregation parameters varied more dramatically as the surface layer is approached, with atomic layer 2 having the largest deviations in comparison to the bulk values. This atomic layer had the highest Q value and formed the rate limiting step for the segregation of S towards the Fe(100) surface. It was found that the segregation process is influenced by two sets of segregation parameters, those of the surface region formed by atomic layer 2, and those in the bulk material. This article is the first to conduct a full scale investigation on the influence of surface relaxation on segregation and labelled it the "*surface effect*".

1. Introduction

Surface segregation is the surface enrichment of a material with one of the bulk species as it is exposed to elevated temperatures. The segregation of elements provides the researcher with information regarding the thermodynamic and kinetic properties of the system under study [1–3]. Valuable information from such studies has enabled the design of materials that are specific in use [4–6]. Metals have been a special field of interest due to their wide range of industrial applications [2,6,7]. Of specific interest to the study presented here is iron (Fe), a metal well known for its use in different alloys [8–10]. When Fe is used in alloys which are operated at elevated temperatures, S segregates towards the surface (free surface and grain boundaries) [11–15]. At the surface the increased concentration of the weaker S–S bonds results in a reduced strength of the material which eventually leads to grain boundary embrittlement [13,16,17]. This article does not attempt to investigate the influence of S segregation on the properties of the Fe(100) surface. Rather this binary component system is used to illustrate a new phenomenon namely the "*surface effect*".

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Various studies have been done on segregation and diffusion [1,2,8,13,14,18–24], but little is known about the influence of surface relaxation on the thermodynamic and kinetic parameters of segregation, namely the interaction parameter, Ω, the segregation energy, ΔG, the migration energy, E_m, and consequently the activation energy of diffusion, Q. These parameters are normally considered to be independent of the atomic layer in which the segregating atom resides. However, due to the surface relaxing, the crystal structure changes near the surface region. This relaxation of the surface, however small, and the resulting consequence on the thermodynamic and kinetic parameters of surface segregation was investigated in this study. Yuan et al. [25]. have conducted a study on the variation in segregation energy for each of the 3d metals in bcc Fe and found a layer dependence of the segregation energy. This dependence although different for each element was shown to extend to the fifth atomic layer of Fe(100). Similar to Yuan et al. [25], Gupta et al. [26] obtained results which showed a layer dependence on the segregation energy in Fe(100). The study presented here goes into more detail by considering all the parameters of segregation, namely: the segregation energy, activation energy, the interaction parameter and the pre-exponential factor to depend on the atomic layer in which the S impurity resides. Calculations performed by Density Functional Theory (DFT) delivered values for the segregation energy, activation energy and interaction parameter. Subsequent simulations were performed with the obtained segregation parameters inserted into the Modified Darken Model (MDM) [19] to predict the segregation profiles of S in Fe (100). Auger Electron Spectroscopy (AES) measurements were conducted and compared to the simulated segregation profile allowing the pre-exponential factors to be extracted. The findings show the importance of taking the *surface effect* into account when studying surface segregation.

2. Theory

It is well known that S diffuses in bcc Fe via a vacancy-mediated mechanism, that is S diffuses from one substitutional lattice site to a nearest neighbour vacancy site [27]. The total energy needed for S to diffuse, the activation energy of diffusion (Q), is the sum of the migration energy (E_m) and vacancy formation (E_{vac}) as described by equation (1) [20,21,28,29]

$$Q = E_m + E_{vac}. \tag{1}$$

The vacancy formation energy can be defined as the binding energy difference between an atom in any lattice site and an atom located on the surface layer. Terblans [20,21] first used this definition to calculate the bulk vacancy formation energy in Al and Cu single crystals respectively. Equation (2) provides the mathematical expression that was used in order to calculate the formation of a bulk vacancy, where E_B is the binding energy of a Fe atom on the surface layer and in the bulk respectively [20,21].

$$E_{vac} = E_B^{(Surf)} - E_B^{(Bulk)} \tag{2}$$

When considering the formation energy of a vacancy in each of the first 5 atomic layers then equation (2) becomes equation (3) with the superscript j indicating the atomic layer of interest.

$$E_{vac} = E_B^{(Surf)} - E_B^{(j)} \tag{3}$$

Differently stated, the vacancy formation energy is the total energy difference between the perfect crystal structure and that of the crystal containing a vacancy with the removed atom adsorbed onto the surface layer. Thus, the vacancy formation energy is the energy of the final state minus the energy of the initial state as stated by equation (4).

$$E_{vac} = E_{final} - E_{initial}. \tag{4}$$

The binding energy of a Fe atom in the bulk was calculated using equation (5) [30,31]

$$E_B^{(Bulk)} = \frac{E_{Fe} - NE_{FeAtom}}{N} \tag{5}$$

where E_{Fe} is the total energy of the $3 \times 3 \times 3$ supercell structure and E_{FeAtom} is the total energy of a single Fe atom in the gas phase. Using the binding energy of a bulk atom (equation (5)) and the respective vacancy formation energy of each atomic layer (equation (4)), the surface binding energy was calculated with the aid of equation (2). These values were then used to calculate the binding energy of a Fe atom in each of the atomic layers with the help of equation 6

$$E_B^{(j)} = E_B^{(Surf)} - E_{vac}. \tag{6}$$

Equations (4) and (6) were used to calculate the vacancy formation and binding energies of an Fe atom in each of the first 5 atomic layers of Fe(100).

The segregation of an impurity atom is defined as the migration of the impurity (S) from the bulk material towards the surface. Therefore, the segregation energy is considered as the energy difference between an atom bound in the bulk material