Journal of Nuclear Materials 475 (2016) 140–148

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

First-principles study of interactions between substitutional solutes in bcc iron

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ARTICLE INFO

Article history:
Received 29 November 2015
Received in revised form
15 March 2016
Accepted 7 April 2016
Available online 9 April 2016

Keywords:
Iron
Substitutional defects
Interactions
Ab initio calculations

ABSTRACT

Using density functional theory based calculations, employing the locally self-consistent Green's function method and the projected augmented wave method, we develop a database of solute–solute interactions in dilute alloys of bcc Fe. Interactions within the first three coordination shells are computed for the ferromagnetic state as well as for the paramagnetic (disordered local moment) state of the iron matrix. The contribution of lattice relaxations to the defect interaction energy is investigated in the ferromagnetic state. Implications of the obtained results for modeling the phenomena of point defect clustering and phase precipitation in bcc Fe-based alloys and steel are discussed.

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1. Introduction

Alloying is an important instrument of materials development which provides an efficient way to control their structural state and properties [1]. Alloying additions play a crucial role in iron-based alloys and steel exerting a significant effect on their physical and chemical properties, phase stability and kinetics of phase transformations. For example, in low carbon pipeline steels microalloying by Ti, Nb, and V provides not only dispersion strengthening, but also a refinement of the grain structure (due to the suppression of recrystallization) beneficial for the mechanical properties [2]. The additions of Ni, Mn, and Cr (combined with alloying by Mo, Al, Ti, and Cu) are used to improve the strength and plasticity of maraging steels for automotive applications [3–5]. However, the precipitation can result in extra hardening and embrittlement in over-aged alloys; this process is greatly accelerated under irradiation in reactor pressure vessel steels [6].

Effective interactions of point defects are necessary input data for a systematic analysis of the structure, stability, and formation kinetics of various point defect arrangements that can then evolve into precipitates of metastable or stable phases in the alloy matrix. The knowledge of solute–solute as well as solute–vacancy interactions, which control the above mentioned processes in the bcc (α-Fe) matrix, is therefore of practical value as it enables us to predict the microstructure evolution and the mechanical behavior of these alloys. Also, it enables assessments of radiation damage effects, offering new insight into the origin of temperature- and dose-dependent response of ferritic and ferritic-martensitic steels to irradiation, a problem of pivotal significance for nuclear energy applications [20,21]. For example, the thermal stability of late blooming phases in reactor pressure vessel steels is under discussion [7,22,23].

Unfortunately, solute–solute interaction energies cannot be directly measured in an experiment. They can be evaluated, by means of thermodynamic models, from the phase diagrams or short-range order measurements [8]. Experimental data on the solute–solute interactions in iron are scarce [9–13], and typically the data are not available simultaneously for the temperature ranges above and below the Curie temperature [14] in which the interactions are expected to be quite different [15].

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http://dx.doi.org/10.1016/j.jnucmat.2016.04.013
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The so-called CALculation of PHAse Diagrams (CALPHAD) method [16] of thermodynamic modeling, which is based on the empirical data and the laws of equilibrium thermodynamics, is widely used to predict phase equilibria in multicomponent systems. As has been shown, the CALPHAD method has certain limitations due to the requirement of a high degree of extrapolation in the metastable phase regions. Combining this method with *ab initio* calculations based on the electron (spin) density functional theory (DFT) [17,18] allows one to overcome some limitations of the thermodynamic approach [19] and provides a reliable basis for developing new alloys.

Ab initio calculations allow for straightforward computations of the solute–solute interactions in the fully ordered ferromagnetic state [24,25], which are of interest for modeling the radiation damage in reactor pressure vessel steel [6,26]. At the same time, technologically important temperatures for steel production are typically close to the Curie point T_C where the magnetic structure is neither completely disordered nor fully ordered. As found in Refs. [14,27], the solute–solute interactions are very sensitive to the degree of magnetic order in Fe-based alloys. Hence, the state of magnetic order in the alloy may play a significant role in such processes as the decomposition [28,29] and ordering [31–33] of the solid solution.

Ab initio calculated solute–solute and solute–vacancy interactions are available for most of the binary Fe–X alloys (see, for example, Refs. [24,27,28]). At the same time, there are few theoretical studies of ternary or multicomponent systems [29,34–39], in spite of their direct practical relevance. While in binary alloys of Fe with 3*d* elements only Cu and Zn solutes show a tendency to clustering, the addition of *s*-*p* or 4*d* elements may result in the formation of a number of compounds including sulphide, phosphide, and intermetallic phases.

In this work, we use DFT-based methods to perform a systematic investigation of the interactions among the most important substitutional alloying elements and impurities in steel. Namely, we consider Al, Si, P, S, Ti, V, Cr, Mn, Co, Ni, Cu, Zr, Nb, Mo, and W (in the order of increasing the atomic number) and also vacancies in bcc iron, as well as all pair combinations of these point defects.

2. Method of calculations

Pair interaction energies of point defects (substitutional solutes as well as vacancies) in bcc iron were obtained by means of *ab initio* calculations employing a supercell geometry. The list of solute elements, to be considered as substitutional impurities in Fe, included 3*sp* elements from Al to S, 3*d* elements from Ti to Cu, 4*d* elements Zr, Nb, and Mo, a 5*d* element W, and also vacancies. The individual point defects and their pair combinations were considered in a 128-site ($4 \times 4 \times 4$) cubic supercell, with the two defects separated from each other by the distance of the *n*-th coordination shell radius, $n = 1, 2, 3$. If multisite interactions are not important, as we assume here, the pair effective interactions V_n for the *n*-th coordination shell (CS) can be determined in the dilute limit in the supercell total energy calculations as

$$V_n \equiv V_{pq;n} = E_{pq;n} + E_0 - E_p - E_q, \quad (1)$$

where the E terms on the right-hand side are the calculated total energies (all the supercells must be of the same size or their energies properly normalized). Subscript 0 denotes a supercell without defects, subscript p and q denote supercells containing single point defects p and q, respectively, while subscript $pq;n$ denotes a supercell containing two defects p and q at a distance of n-th CS radius relative to each other.

The total energies were computed within the generalized gradient approximation (GGA) [40] which correctly predicts the ferromagnetic bcc structure to be the ground state of iron and closely reproduces its equilibrium atomic volume [41]. The calculations employed two different electronic structure methods. First, similar to our previous studies of point defects in iron [14,43], we used the locally self-consistent Green's function (LSGF) method [42] to compute the chemical and magnetic contributions to the point defect interactions on a rigid bcc lattice. The use of atomic sphere approximation does not allow for any local relaxation around the point defects in the LSGF method calculations. This approach can be justified for the impurity atoms having a small size misfit with the matrix, so that the relaxation effects can be neglected [43]. To evaluate the local relaxation contribution, we calculated the interactions in the ferromagnetic state by using the projector augmented wave (PAW) method [51] as implemented in the Vienna *ab-initio* simulation package (VASP) [52].

In the LSGF calculations, each atom of the supercell, together with three coordination shells around it, was considered self-consistently as a local interaction zone (LIZ) embedded in the effective medium of the LSGF method. Green's function calculations were carried out using the orbital quantum number cutoff $l_{max} = 3$. The low-lying 3*s* valence states of P and S, as well as the semi-core 3*p* states of Ti and V, 4*p* states of Zr and Nb, were included in the valence panel. For that purpose, the depth of the contour for complex energy integration was increased, whenever necessary, in order to encircle the semi-core states and the valence states altogether. A $29 \times 29 \times 29$ Monkhorst-Pack mesh of *k*-points was used for Brillouin zone integration. Vacancies were modeled using empty spheres containing no nuclear charge. Equal Wigner-Seitz radii were used for the atomic and empty spheres. The contributions of non-spherical charge density moments to the electrostatic potential and energy were taken into account via the multipole-corrected atomic sphere approximation (ASA + M) [44,45].

The bcc-Fe matrix was considered in two different states of magnetic order, the case of a complete ferromagnetic (FM) order corresponding to $T = 0$ and that of a complete magnetic disorder, a paramagnetic (PM) state corresponding to $T \gg T_C$, where T_C is the Curie temperature. A comparison of these two limits enables us to predict how much (and in what direction) the solute–solute interactions may change as a result of magnetic disordering of the iron matrix. The magnetic disorder in the paramagnetic state was treated using the disordered local moment (DLM) model [46,47] based on the coherent potential approximation (CPA) [48]. In the FM calculations, all the magnetic moments on the host (Fe) atoms were initially set to be equal in length and direction; the magnetic moments on the impurity atoms were initially set to zero. All the moments were then allowed to relax completely during the self-consistency iterations. In the DLM calculations, each lattice site of the host was considered to be occupied 50% by Fe↑ (iron spin up) and 50% by Fe ↓(iron spin down) species. The magnetic moments on all the sites were given non-zero initial values and were then allowed to fully relax. A similar treatment was used for the impurity sites and even for the vacant sites. The effective alloy present at each lattice site of the supercell was treated within the CPA using an additional self-consistency loop.

In the PAW-VASP calculations, the same supercells (comprising 128 bcc lattice sites) were used as in the LSGF calculations. The plane wave basis was cut off at 350 eV. The Brillouin zone integrals were evaluated using a $4 \times 4 \times 4$ Monkhorst-Pack mesh of *k*-points. The defect interaction energies were computed at a fixed volume corresponding to the experimental room-temperature lattice parameter of pure iron, $a = 0.286$ nm [49,50]. Two series of PAW-VASP calculations were conducted: Every defect or defect pair was first considered on the undistorted bcc lattice, and then all the internal atomic coordinates for each supercell were relaxed

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