

Stability of vacancy-oxygen complexes in bulk nickel: Atomistic and *ab initio* calculations



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ABSTRACT

This work is concerned with the interactions of multiple oxygen atoms with vacancy clusters V_m of size m in bulk nickel. The calculations were carried out using molecular statics, employing a reactive potential developed recently for the NiO system containing vacancies. In particular, segregation of oxygen inside a mono- and a divacancy are considered for the first time, to complete earlier work on the subject. Overall, we find strong attractive interactions between the oxygen atoms and the vacancy clusters. We argue that this leads to increasing dramatically the solubility of oxygen in nickel. Regarding the complexes V_mO_1 , the results indicate that atomic oxygen inside the vacancy clusters is more stable than at the conventional interstitial sites of the perfect Ni system. This stability is further enhanced as the size of the cavity increases. We have found that a monovacancy (V_1) and a divacancy (V_2) can trap up to 14 and 22 oxygen atoms, respectively. We have also carried out *ab initio* calculations, for the purposes of both comparison and validation of the potential used in the current work. We find a very good qualitative agreement between the *ab initio* results and the predictions obtained from the reactive potential. Both agree well with the experimentally observed facts establishing the influence of point defects on the oxidation processes observed in nickel and its alloys.

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1. Introduction

The study of phenomena related to oxidation and corrosion of materials, of widespread industrial use, has been the focus of a large number of investigations, experimental as well as theoretical. Thanks to their high resistance to oxidation and corrosion, nickel-based alloys have been widely used in a number of technological applications, such as aeronautics and energy production [1,2]. Resistance to oxidation of these alloys, especially at high temperatures, is ensured by the protective quality of the covering oxide layers. However, under real conditions of usage and with time, many effects can influence the durability of the structures. In particular, intergranular corrosion takes place due to condensation of species in solution as well as vacancies at grain boundaries. Thus an optimization of the materials is sought after by working out their microstructure and chemical composition, but also through the fabrication procedures, or treatment of the surfaces in order

to control the desired properties of the oxide layers (adherence, compactness, conductivity...). Though the limited lifetime due to oxidation is generally associated with the properties of the protective layers (inoxidability for instance), growth modes of the layers give rise to modifications in the underlying substrate: we mention for instance a depletion of alloy elements, which can impact the mechanical behavior of the affected region, or introduction of defects leading to a premature damage to the structure. For the latter scenario, experimental studies conducted on these types of alloys [3,4] have found evidence of an accelerated oxidation process. The hypothesis put forth by the workers to explain this phenomenon rests on an increased diffusion of oxygen inside the alloy, this being driven by a strong interaction between oxygen and vacancies. These are the vacancies present initially in the alloy, and also the ones injected during the oxidation process. According to these workers, this effect can be explained by a physical process that can be summarized through the following steps:

1. Preferential formation of vacancy clusters (isolated or in the form of microcavities) at grain boundaries.
2. Capture of the solute oxygen atoms, in the alloy, by the vacancies.

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3. Capture of vacancies at the microcavities- these grow as a result- and freeing of oxygen atoms in the cavity.
4. When the oxygen partial pressure in the cavity reaches a threshold corresponding to the equilibrium pressure of Ni/NiO, a process of oxidation, starting from the cavities, sets in and propagates along the grain boundaries. This leads to formation of an oxide seed deep inside the metal.

Along the lines of the first two stages, *ab initio* [5,6] as well as molecular statics [7] studies have pointed to a strong stability of vacancy clusters, as well as a strong interaction between a monovacancy or a divacancy and an oxygen in solution inside Ni. Recently, other *ab initio* [8] and molecular dynamics [9] studies yielded an interaction energy between an oxygen and a monovacancy of the orders of 1.26 eV and 1.12 eV, respectively. Experimentally, several studies on the diffusion of oxygen in nickel are available in the literature. Depending on the experimental approaches used, these studies exhibit a large dispersion in values found for the activation energies. These are in the range of 0.93–4.30 eV [10–14].

As concerns interactions between vacancy clusters and oxygen (vacancy-oxygen complexes), to our knowledge, apart from the works of Refs. [5,6], no other theoretical study has been reported in the literature. In the works of Megchiche [5] and Mijoule et al. [6] a strong interaction between a divacancy and an oxygen was uncovered. In this work we complete and extend these studies to the interaction of an oxygen atom with larger vacancy clusters by considering the trivacancy cluster, but also to the interaction of multiple oxygen atoms with a mono- and a divacancy. Indeed, with the aim to shed some light on the process described above (stage 2), and especially to find out how many oxygen atoms can be trapped at the vacancy cluster, we chose to study the stability of several oxygen atoms inside and in the vicinity of the cavities.

This work aims to address two important questions: (a) does oxygen prefer to be in the vicinity of cavities or in solution in the host away from the cavities, and accordingly what is the trapping capacity of a given vacancy cluster? (b) does the reactive potential ReaxFF used yield results sufficiently close to the *ab initio* ones, to make it useful in large scale simulations that are otherwise inaccessible to first principles calculations?.

2. Computational details

The atomistic simulations were carried out at 0 K using molecular statics as implemented in the LAMMPS code [15]. The conjugate gradients method was used to perform relaxation of the atomic positions. We used a cubic simulation box of lateral size varying from four to twenty lattice parameters. This corresponds to the number of atoms in the box varying from 256 to 32000, respectively. Given that the initial tests showed no notable variation in the results when the box size was greater than four lattice parameters, we continued the rest of the calculations using a box size of 20 lattice parameters, which corresponds to 32,000 atoms. In all cases periodic boundary conditions were enforced in all three directions of space. The interatomic forces were derived from the reactive force field ReaxFF developed by Zou et al. [9]. This potential has been optimized to describe perfect bulk NiO, as well as bulk NiO containing vacancies. Indeed, as reported in [9] and as has been confirmed by a series of our own calculations on bulk Ni, Ni surfaces, and NiO, this potential yields results in very good agreement with those available in the literature, both experimental and theoretical.

2.1. Stability of vacancy clusters V_m

Each vacancy cluster of size m can have many different conformations. In order to compare their relative stability, we computed

the formation energy $\epsilon_{V_m}^f$ and the binding energy $\epsilon_{V_m}^b$ per vacancy for each conformation. These two quantities are evaluated as follows:

$$\epsilon_{V_m}^f = \frac{1}{m} \left[E_{tot}^{(N-m) \times Ni} - \frac{N-m}{N} E_{tot}^{N \times Ni} \right], \quad (1)$$

$$\epsilon_{V_m}^b = \epsilon_{V_m}^f - \epsilon_{V_1}^f, \quad (2)$$

where $E_{tot}^{N \times Ni}$ and $E_{tot}^{(N-m) \times Ni}$ are the total energies of the supercell containing N and $(N-m)$ nickel atoms, respectively. $\epsilon_{V_1}^f$ is the formation energy of a single vacancy. For each cluster size we consider the three most stable configurations, as shown in Fig. 1.

2.2. Interaction energy of an oxygen atom with a vacancy cluster V_m

To determine the interaction energies between an oxygen and a vacancy cluster, we need first to compute the energies required to put an oxygen in solution inside Ni. These are the energies needed to put an oxygen at the interstitial, octahedral and tetrahedral sites ($\epsilon_{ins-int}^O$). These energies are obtained as follows:

$$\epsilon_{ins-int}^O = E_{tot}^{N \times Ni+O} - \left[E_{tot}^{N \times Ni} + \frac{1}{2} E_{tot}^{O_2} \right] \quad (3)$$

where $E_{tot}^{N \times Ni}$ is the total energy of the supercell containing N nickel atoms, and $E_{tot}^{N \times Ni+O}$ is the total energy of the supercell containing an oxygen atom at an interstitial position. $E_{tot}^{O_2}$ represents the total energy of an oxygen molecule in vacuum.

The interaction energy between an oxygen and a vacancy cluster V_m of size m is obtained from the following expression

$$\epsilon_{V_m-O}^b = \underbrace{\left[E_{tot}^{(N-m) \times Ni+O} - E_{tot}^{(N-m) \times Ni} \right]}_{O \text{ inside } V_m \text{ cluster}} - \underbrace{\left[E_{tot}^{N \times Ni+O} - E_{tot}^{N \times Ni} \right]}_{O \text{ at interstitial site}}, \quad (4)$$

where $E_{tot}^{(N-m) \times Ni+O}$ and $E_{tot}^{(N-m) \times Ni}$ are the total energies of a supercell containing a vacancy cluster of size m with and without an oxygen inside the cavity, respectively. The interaction energy $\epsilon_{V_m-O}^b$ can be viewed as representing the energy gained or lost in the process of moving an oxygen initially in solution at an interstitial site, far from the vacancy cluster, to inside the vacancy cluster of size m .

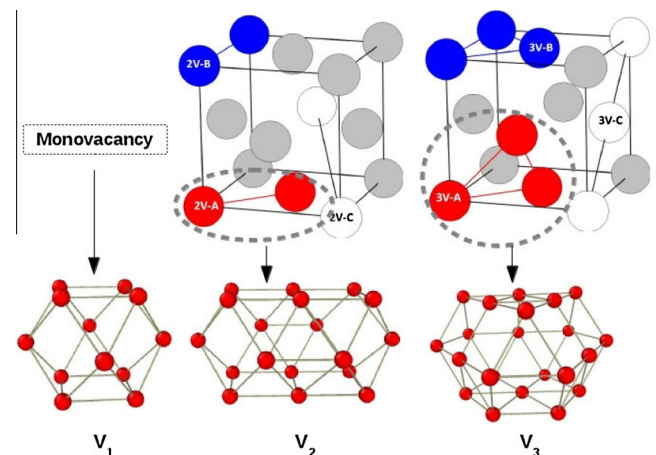


Fig. 1. Schematic view of the three considered configurations for each of the clusters of 1, 2, and 3 vacancies. The geometric form of the cavities created by the most stable cluster are presented.

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